The Chemistry of Cyanates and Their Thio Derivatives
Edited by Saul Patai
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The chemistry of cyanates and their thio derivatives

Part 1

Edited by
SAUL PATAI
The Hebrew University, Jerusalem

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Foreword

The present volume, "The Chemistry of Cyanates and their Thio Derivatives" includes material on cyanates, isocyanates, thiocyanates and isothiocyanates as well as on isocyanate dihalides and on selenocyanates and related compounds. The volume is organized on the same general lines as the other volumes of "The Chemistry of Functional Groups" series, and which are described in the "Preface to the Series" appearing on the following pages.

For once, all the chapters included in the original plan of the volume materialized. Hence omissions, if any, this time are solely the responsibility of the Editor.

The chapters have been commissioned for this volume in the Spring of 1974, and were mostly delivered between March and August 1975. In most cases the literature coverage of the chapters is therefore roughly up to the Spring of 1975.

Jerusalem, June 1976 SAUL PATAI

The Chemistry of Functional Groups Preface to the series

The series 'The Chemistry of Functional Groups' is planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. For instance, the volume *The Chemistry of the Ether Linkage* deals with reactions in which the C—O—C group is involved, as well as with the effects of the C—O—C group on the reactions of alkyl or aryl groups connected to the ether oxygen. It is the purpose of the volume to give a complete coverage of all properties and reactions of ethers in as far as these depend on the presence of the ether group but the primary subject matter is not the whole molecule, but the C—O—C functional group.

A further restriction in the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews. Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors is asked *not* to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced post-graduate level.

With these restrictions, it is realized that no plan can be devised for a volume that would give a *complete* coverage of the subject with *no* overlap between chapters, while at the same time preserving the readability of the text. The Editor set himself the goal of attaining *reasonable* coverage with *moderate* overlap, with a minimum of cross-references between the chapters of each volume. In this manner, sufficient freedom is given to each author to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter dealing with the general and theoretical aspects of the group.

(b) One or more chapters dealing with the formation of the functional group in question, either from groups present in the molecule, or by introducing the new group directly or indirectly.

(c) Chapters describing the characterization and characteristics of the functional groups, i.e., a chapter dealing with qualitative and quantitative methods of determination including chemical and physical methods, ultraviolet, infrared, nuclear magnetic resonance and mass spectra: a chapter dealing with activating and directive effects exerted by the group and/or a chapter on the basicity, acidity or complex-forming ability of the group (if applicable).

(d) Chapters on the reactions, transformations and rearrangements which the functional group can undergo, either alone or in conjunction with other reagents.

(e) Special topics which do not fit any of the above sections, such as photochemistry, radiation chemistry, biochemical formations and reactions. Depending on the nature of each functional group treated, these special topics may include short monographs on related functional groups on which no separate volume is planned (e.g. a chapter on 'Thioketones' is included in the volume *The Chemistry of the Carbonyl Group*, and a chapter on 'Ketenes' is included in the volume *The Chemistry of Alkenes*). In other cases, certain compounds, though containing only the functional group of the title, may have special features so as to be best treated in a separate chapter, as e.g. 'Polyethers' in *The Chemistry of the Ether Linkage*, or 'Tetraaminoethylenes' in *The Chemistry of the Amino Group*.

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, it was decided to publish certain volumes in several parts, without giving consideration to the originally planned logical order of the chapters. If after the appearance of the originally planned parts of a volume it is found that either owing to non-delivery of chapters, or to new developments in the subject, sufficient material has accumulated for publication of a supplementary volume, containing material on related functional groups, this will be done as soon as possible.

The overall plan of the volumes in the series 'The Chemistry of Functional Groups' includes the titles listed below:

The Chemistry of Alkenes (two volumes)
The Chemistry of the Carbonyl Group (two volumes)
The Chemistry of the Ether Linkage
The Chemistry of the Amino Group
The Chemistry of the Nitro and Nitroso Groups (two parts)
The Chemistry of Carboxylic Acids and Esters
The Chemistry of the Carbon–Nitrogen Double Bond
The Chemistry of the Cyano Group
The Chemistry of Amides
The Chemistry of the Hydroxyl Group (two parts)
The Chemistry of the Azido Group
The Chemistry of Acyl Halides
The Chemistry of the Carbon–Halogen Bond (two parts)
The Chemistry of Quinonoid Compounds (two parts)
The Chemistry of the Thiol Group (two parts)
The Chemistry of Amidines and Imidates
The Chemistry of the Hydrazo, Azo and Azoxy Groups (two parts)
The Chemistry of Cyanates and their Thio Derivatives (two parts)
Supplement A: The Chemistry of Double-Bonded Functional Groups (two parts)

Titles in press:
The Chemistry of the Diazonium and Diazo Groups
The Chemistry of the Carbon–Carbon Triple Bond
Supplement B: The Chemistry of Acid Derivatives

Future volumes planned include:
The Chemistry of Cumulenes and Heterocumulenes
The Chemistry of Organometallic Compounds
The Chemistry of Sulphur-containing Compounds
Supplement C: The Chemistry of Triple-Bonded Functional Groups
Supplement D: The Chemistry of Halides and Pseudo-halides
Supplement E: The Chemistry of $-NH_2$, $-OH$, and $-SH$ Groups and their Derivatives

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editor.

The publication of this series would never have started, let alone continued, without the support of many persons. First and foremost among these is Dr. Arnold Weissberger, whose reassurance and trust

encouraged me to tackle this task, and who continues to help and advise me. The efficient and patient cooperation of several staff-members of the Publisher also rendered me invaluable aid (but unfortunately their code of ethics does not allow me to thank them by name). Many of my friends and colleagues in Israel and overseas helped me in the solution of various major and minor matters, and my thanks are due to all of them, especially to Professor Z. Rappoport. Carrying out such a long-range project would be quite impossible without the non-professional but none the less essential participation and partnership of my wife.

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SAUL PATAI

Contents

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CHAPTER 1

Electronic structure of the cyanato and thiocyanato groups—ground state and excited states†

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I. INTRODUCTION

There are several ways in which one might treat the electronic structures of such functionals as the cyanato and thiocyanato groups. One might, for example, compile lists of experimental and computational data; or one might focus on discussions of high quality *ab initio* wavefunctions, such as those of McLean for the NCS^- ion[1]. Both of these approaches have merit. However, we have chosen a more limiting path. We will select and discuss those experimental techniques which bear on the general question of electronic structure, and we will utilize the information which these techniques provide in order to present a 'status report' on the electronic structure of some simple cyanates and thiocyanates (i.e., the anions NCO^- and NCS^-, some of their covalent and ionic metal salts, and their methyl and phenyl derivatives).

The theoretical framework will consist of a molecular orbital (MO) approach and will reduce, on occasion, to such a simple, but fundamental, level as Walsh's rules[2]. That is not to say that we will evade all *ab initio* results, forget about any configuration interaction effects, neglect σ–π in-orbital mixings, etc.—indeed, we will not. Our intent is to remain simple, but when the proper interpretation of the phenomenon at hand demands theoretical complexity, we will not hesitate to use it.

The types of experimental data which we deem relevant to electronic properties include:

(i) Gas-phase structures as determined by electron diffraction and microwave spectroscopy. This information provides the minima of the total molecular energies with respect to the geometric coordinates.

(ii) ESCA (Electron Spectroscopy for Chemical Analysis) chemical shifts. Such data can be used to obtain atomic charges for an atom when the atom is part of a molecule.

(iii) Ultraviolet photoelectron spectra (PES). These spectra provide easy access to approximate valence MO energies.

(iv) X-ray emission spectra. The intensities of the individual bands in these spectra contain information on the shapes of valence molecular orbitals.

(v) Ultraviolet and visible absorption and emission spectroscopy. These techniques generate the set of excited state properties for valence as well as for Rydberg excitations (i.e., for $V \leftarrow N$ as well as $R \leftarrow N$ excited configurations).

The choices (i)–(v), not surprisingly, represent our own personal interests. We will endeavour to present a unified interpretation of these diverse experimental techniques, and to bring them to bear on the subject of the electronic structure of the cyanates and thiocyanates. We fear, however, that the principal result of our discussion will be the conclusion that a great deal of experimental work is still required even for these simple molecules enumerated above.

II. GROUND STATE PROPERTIES

A. *Anions*

1. Molecular orbitals and geometry

Triatomic ABC species are linear (e.g., the 16 electron molecules, CO_2, N_3^-, NO_2^+), bent (e.g., the 18 electron molecules, NO_2^-, O_3) or linear (e.g., the 22 electron molecules, I_3^-, XeF_2). Geometry seems to depend on the number of valence electrons. NCO^- and NCS^- contain 16 valence electrons and are isoelectronic with the linear species CO_2, CS_2, N_2O, NO_2^+, $HgCl_2$, N_3^-,

CN_2^{2-}, etc. and, as expected, they are also linear. The rationale for this simple behaviour was given by Walsh[2] in 1953.

Walsh's conclusions were based on the dependence of one-electron (or MO) energies on the bond angle, $\measuredangle ABC$. This dependence, in turn, was elaborated using arguments which, for their time (i.e., 1953), were necessarily intuitive. We are in a somewhat better situation nowadays: MO computations provide precisely the sort of information which Walsh had either to intuit or to derive using qualitative ideas. Therefore, rather than proceed through an extensive and sometimes unconvincing series of qualitative and semiquantitative arguments, we simply present the results of a representative semi-empirical MO calculation[3,4] for NCS^- in Figure 1. Figure 1 is similar to that of Walsh[2] and will be used to illustrate his arguments.

The most important feature of Figure 1 is the angular dependence of the 1π, 2π and 3π MO energies. The 2π MO is the highest occupied MO of ground state NCS^-. The degeneracy of this MO is split and both of the resulting non-degenerate MO's exhibit a decrease of binding energy as $\measuredangle SCN$ is decreased from the linear 180° case. A similar behaviour is also characteristic of the 1π MO. The net result is that the sum of electronic MO energies, as defined by $E \equiv \sum_{\mu} n_\mu \varepsilon_\mu$ where ε_μ is the energy of the μth MO and n_μ is its electron occupancy, exhibits a minimum at $\measuredangle NCS = 180°$. For example, we find $E(180°) - E(180°) = -1{\cdot}6\,eV = -37\,kcal/mol$, and we conclude that the ground state of NCS^- is linear. This prediction is confirmed by X-ray diffraction studies[5] and infrared investigations[6].

At least one of the excited electronic states produced by the one-electron MO excitation $2\pi \rightarrow 3\pi$ is expected to be non-linear. The electron configuration of one such state is depicted on the right hand side of Figure 1 and is more precisely represented as $\ldots(2a'')^2(6a')(7a')$; $^{1,3}A'$. The bent geometry of this particular excited state is a consequence of the considerably increased binding energy of the $3\pi(7a')$MO which occurs for $\measuredangle NCS < 180°$. This conclusion, which is also based on the angular dependence of E, is founded on arguments identical to those which are used to deduce a bent geometry for ABC molecules with 18 valence electrons and the electron configuration $\ldots(6a')^2(7a')^2$; $^1A'$. The spectroscopic consequences of a transition between two states, one of which is linear and the other bent, are interesting and will be discussed in Section IV.

Two further comments concerning Figure 1 are in order:

(i) This diagram differs slightly from that given by Walsh[2] for the symmetric triatomic ABA case. The differences occur in the behaviour of the 2σ, 3σ and 4σ MO's. These differences do not adversely affect the

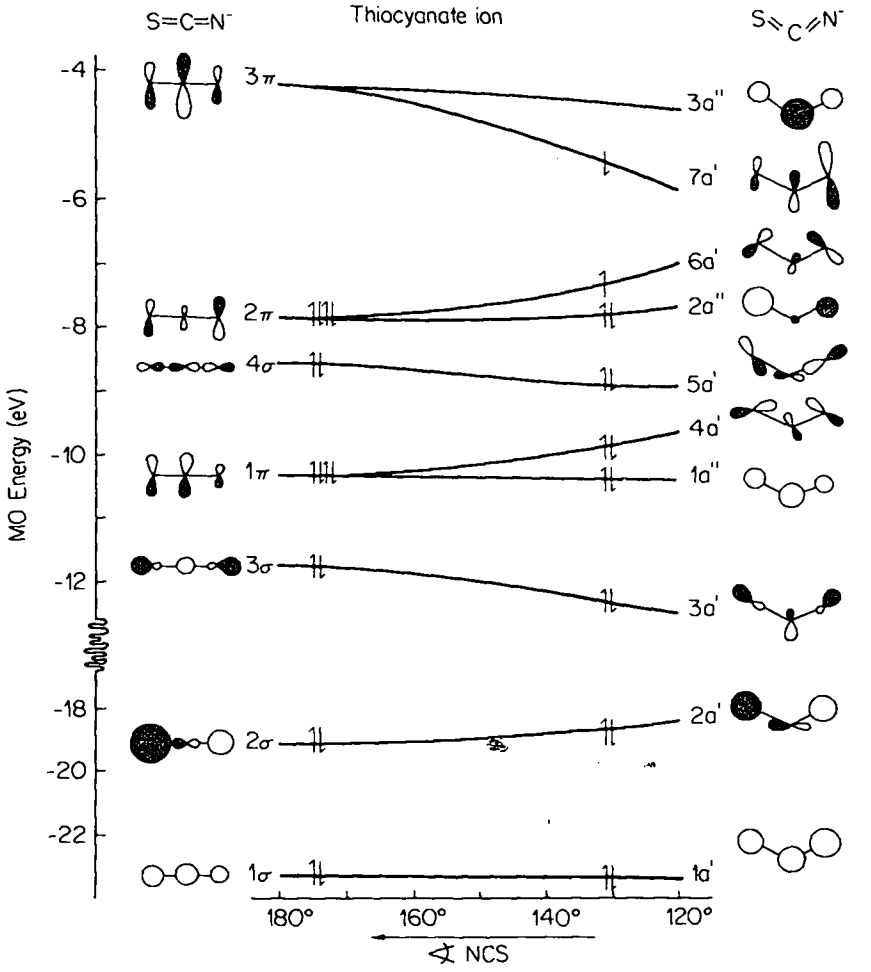

FIGURE 1. Walsh-type diagram for NCS^-.

quality of our deductions. Furthermore, they originate in the use of hybridization arguments by Walsh[2], arguments which are replaced here by concepts such as orbital interactions and electron redistributions among centres of differing electronegativities.

(ii) Arguments based on a sum of MO energies, E, have no theoretical foundation and, indeed, are expected to be wrong. The correct energy, and the one which should be used, is the total energy

$$\mathscr{E} = \sum_{\mu} n_{\mu}\varepsilon_{\mu}^{SCF} - \sum_{\mu}\sum_{\nu}(2J_{\mu\nu} - K_{\mu\nu}) + \sum_{A<B}\sum \frac{Z_A Z_B}{R_{AB}} \qquad (1)$$

where $J_{\mu\nu}$ is a Coulomb integral; $K_{\mu\nu}$ is an exchange integral; the summations μ and ν proceed over occupied MO's only, and the last term accounts for nuclear–nuclear repulsions. Fortunately, the computations of Peyerimhoff and Buenker[7] on N_3^- and O_3 provide some experimental justification for the use of $E^{SCF} = \sum_{\mu} n_\mu \varepsilon_\mu^{SCF}$ and, by extrapolation, for $E \equiv \sum_{\mu} n_\mu \varepsilon_\mu$, where ε_μ are non-SCF MO energies. Peyerimhoff and Buenker performed high quality *ab initio* SCF computations for various geometries of N_3^- and O_3. They then computed $\mathscr{E} - E^{SCF}$ and showed that this difference for any one angle of bend was essentially constant for all angles of bend. Thus, the changes $\Delta\mathscr{E}$ which occur upon bending are more or less equivalent to the corresponding changes in ΔE^{SCF}. Therefore, at least in the two entities studied (i.e., azide ion and ozone), the Walsh 'sum of orbital energies' is justified.

2. Shapes and energies of valence orbitals: X-ray emission spectra

Although a fairly large number of semi-empirical[8–17] and *ab initio*[1,18–20] MO SCF calculations for NCO and NCS compounds are available, some doubt as to the correct MO shapes and MO energies remains. Fortunately, provided one is willing to accept a few approximations, these types of information can be obtained experimentally.

One of these approximations is embodied in Koopmans' theorem[21]

$$IE_\mu = -\varepsilon_\mu^{SCF} \tag{2}$$

which allows us to equate the μth-ionization potential with the energy of the μth topmost filled molecular orbital. It is well to stress that 'orbital energies' are not physical observables, except in a one-electron system. Consequently, any implication of such observability must involve many suppositions. In the case of Koopmans' theorem, these approximations consist of a neglect of both relaxation and correlation effects. The neglect of relaxation effects implies that the electrons of the molecule do not readjust upon ionization (i.e., that the increase of positive potential caused by the removal of one electron will not produce any effects on the motions of the remaining electrons). This approximation is also known as the 'frozen core' approximation. The neglect of correlation effects implies that the error caused by the use of Hartree–Fock SCF computational procedures is equal in both the molecule and the cation and that it cancels when we subtract the HF–SCF energy of one from the other. Both of these approximations are quite severe and it is hardly surprising that Koopmans' theorem often fails.

Two different ionization events are illustrated in Figure 2. Ionization of a core electron, (A) → (B), is best achieved by X-ray irradiation. This technique, unfortunately, has been christened ESCA—which is an acronym for Electron Spectroscopy for Chemical Analysis—although its impact is much wider[22,23]. The ionization of a valence electron, (A) → (C), is also achieved by photoionization, usually by irradiation with the He I resonance line at 21·21 eV. This technique is termed Photoelectron Spectroscopy[24,25]

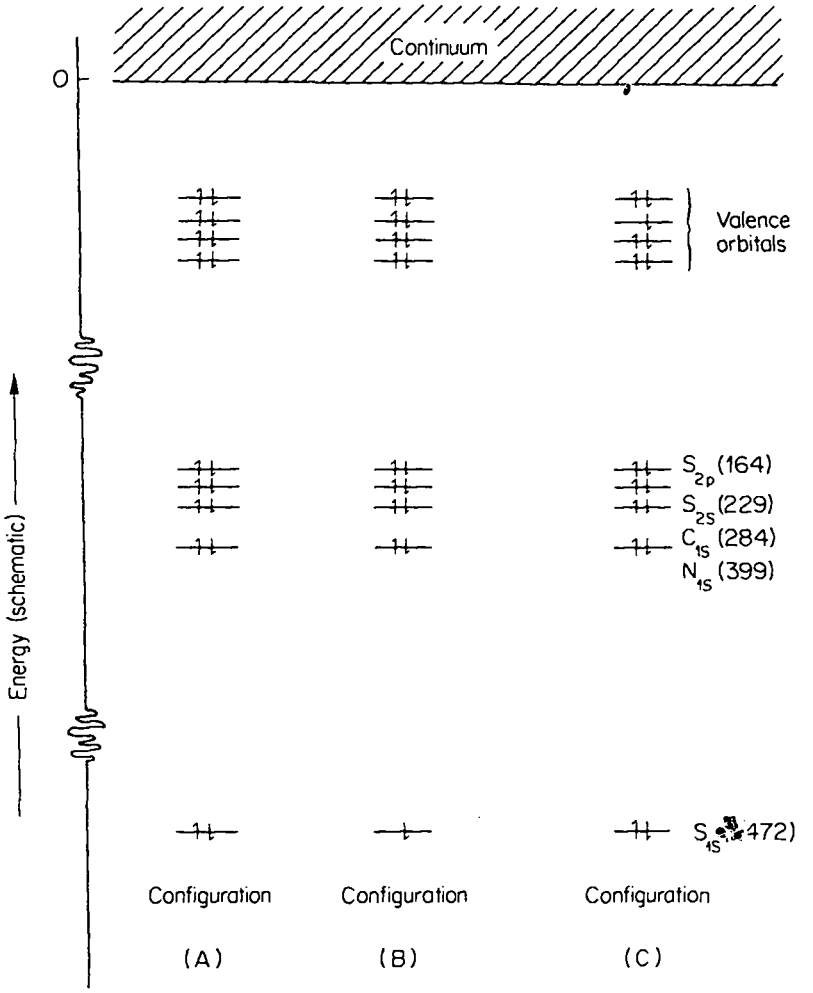

FIGURE 2. Configurations describing (A), a closed-shell ground state; (B), a 1s hole state, and (C), some valence hole state. The energies of the core orbitals are approximate and taken from Reference 22.

or PES. The removal of an electron from the topmost filled orbital of A is referred to as the 'first ionization energy'. The energy difference between states (C) and (A) represents a 'second ionization energy' which, contrary to the use in atomic spectroscopy, *does not* refer to the removal of an additional electron.

The highly excited state (B) may decay into state (C) by emission of light which, because of the high energies involved, will usually lie in the X-ray region. The observation of X-ray emission dictates a dipole-allowed process. Since the 1s hole is very localized and 'atom-like', the atomic selection rules, $s \rightarrow p$, $s \not\rightarrow s$, $s \not\rightarrow d$, etc., will be valid. If we now invoke a second approximation, namely the LCAO expansion for the valence MO's

$$\varphi_\mu = \sum_k c_{k\mu}\chi_k \tag{3}$$

the intensity of an X-ray emission band in SCN^- will be given by[26]

$$\mathcal{I}_\mu \propto \sum_{k \in S_{3p}} |c_{k\mu}|^2 \tag{4}$$

where the summation runs over all three sulphur 3p atomic orbitals. The quality of this proportionality has been demonstrated by Manne and coworkers[26,27]. The success they obtained allows us to use X-ray intensities as probes into the shapes of valence molecular orbitals.

It is also clear from Figure 2 that the energy differences between X-ray emission bands and the energy differences between photoelectron bands should be exactly equal—the final states, after all, are the same in both techniques. Unfortunately, X-ray emission and valence ionization data for solids are scarce. Hence, our discussion will centre around the analysis of a typical example, one taken from Karlsson and Manne[26].

The experimental sulphur Kβ emission spectrum of a thiocyanate salt is shown in Figure 3. The Kβ emission refers to the transition (B) → (C) shown in Figure 2. Arrayed above the experimental curve are the calculated spectral intensity distributions as obtained by different computational schemes. All calculations obtain some kind of agreement except the most simple, non-iterative Extended Hückel Molecular Orbital Theory (EHMO) which is known to perform poorly on ionic, polar compounds. 'Best' agreement is obtained with the *ab initio* SCF wavefunctions of McLean and Yoshimine[1].

The first prominent peak is very intense and refers to a final state which is the ground state of the NCS radical (i.e., a hole occurs in the 2π MO). The high intensity of this band is caused by a high sulphur 3p amplitude in the highest energy occupied 2π MO of NCS^-. The next band, which occurs some 3.2 eV to lower transition energies, is assigned to two final states, both

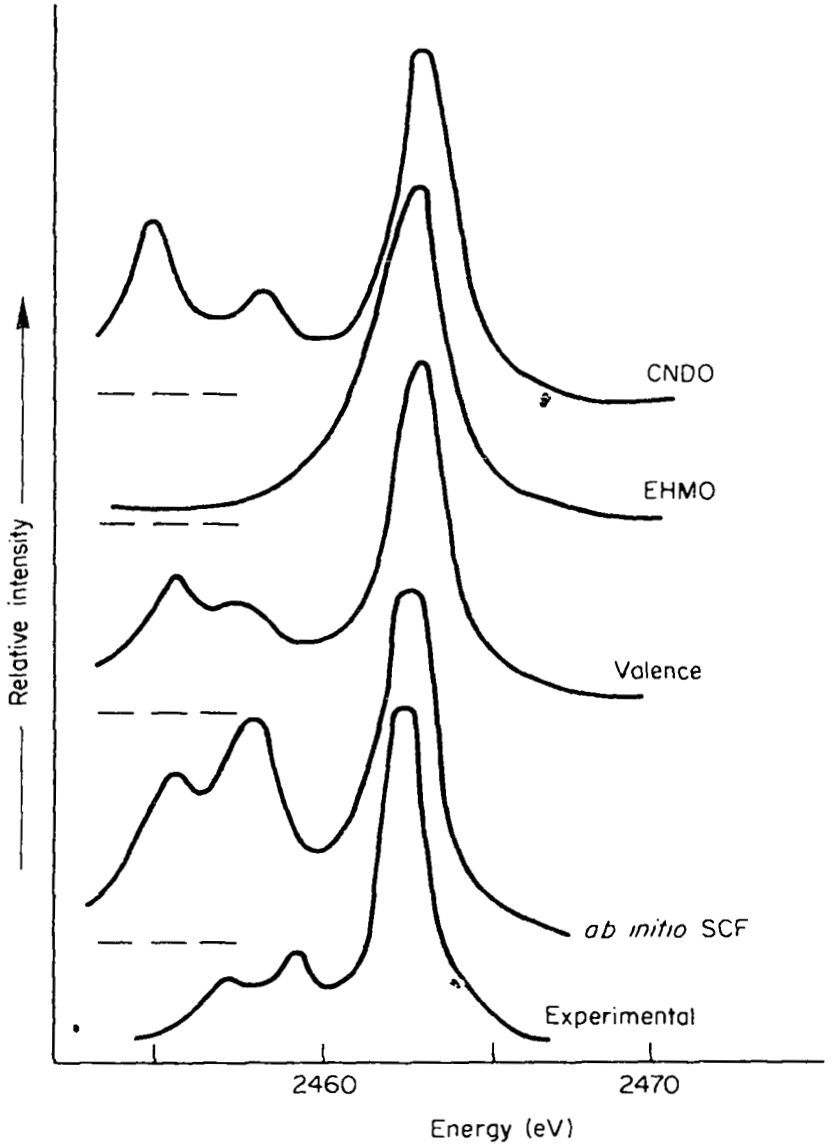

FIGURE 3. Experimental and calculated sulphur Kβ emission spectrum of NCS^-. (Reproduced, with permission, from Reference 26).

excited, of the NCS radical. In one of these, the hole is in the 1π MO; in the other, it is in the 4σ MO. The shape of this second band suggests that the 1π

and 4σ MO's contain similar S_{3p} amplitudes and that these are considerably smaller than the S_{3p} amplitude in the 2π MO. Some additional S_{3p} character is found in a band which is 5.5 eV below the main peak. This third peak refers to an excited state of the NCS radical in which the hole is resident in the 3σ MO. The calculated intensities, $\mathcal{I}_\mu$(calc.), are collected in Table 1.

The energy differences which occur in the X-ray emission spectrum of NCS^- are equal to the electronic excitation energies, ΔE(electronic), of the radical NCS. The analysis of the optical spectrum[28] of the radical NCS has produced a ground state assignment of $(4\sigma)^2(1\pi)^4(2\pi)^3$; $X^2\Pi$. The two lowest-energy excited states of the radical occur at 3·23 and 3·32 eV and have been assigned[28] as $\ldots(4\sigma)^2(1\pi)^3(2\pi)^4$; $A^2\Pi$ and $\ldots(4\sigma)^1(1\pi)^4(2\pi)^4$; $B^2\Sigma^+$, respectively. These assignments are in excellent agreement with the X-ray emission spectrum of NCS^- and its interpretation[26].

Hartree–Fock energies for NCS^- are available[1] and are also included in Table 1. The differences between the MO energies of NCS^-, $\Delta\varepsilon^{SCF}$, should correspond to the X-ray emission energy differences, ΔE(X-ray), and to the electronic excitation energies, ΔE(electronic), of the NCS radical; both of these latter quantities, as discussed above, should also be identical. The equality ΔE(X-ray) ≈ ΔE(electronic) has been established for the NCS radical. However, since the data base for this molecule is not very extensive and since the data base for other polyatomic molecules is equally sparse, it is well to insert a caveat. The X-ray data probably refer to a geometry of the NCS radical which has minimum energy for the 1s hole state, whereas the electronic data—insofar as we use adiabatic energies—are energy differences taken for the geometries of minimum energy of the initial and final states, respectively. There is no reason why these geometries should be identical and, hence, we should expect instances where the correlation of ΔE(X-ray) and ΔE(electronic) data is poor. The Hartree–Fock MO energies, on the other hand, refer to the geometry of ground state NCS^-. Apart from the approximation implicit in the use of equation (1), it is also clear that the ground state geometry of NCS^- might be considerably different from that for either of the two different hole states discussed above. Consequently, one should not be surprised to find deviations between calculated and experimental values, and even between experimental values obtained by different measurement techniques.

The energies $\Delta\varepsilon^{SCF}$ for the NCO^- ion[1] and the energies ΔE(electronic) for the NCO radical[29] are also included in Table 1. Both sets of data predict that the 4σ MO should lie between the 1π and 2π MO's. The corresponding data for NCS^-/NCS suggest that the 4σ MO is subjacent to the 1π MO, and contradict the predictions made in Figure 1.

TABLE 1. Data pertinent to the electronic structure of NCO^- and NCS^-
(all energy units are eV; intensity units, $\mathcal{I}_\mu$, are relative)

Anion	MO; φ_μ	2π	1π	4σ	3σ	2σ	1σ	Reference
NCS^-	ε_μ^{SCF}	−3·06	−7·58	−8·32	−10·26	−21·29	−25·86	1
	$\Delta\varepsilon^{SCF}$	0	−4·52	−5·26	−7·20	−17·23	−22·80	
	ΔE(electronic)	0	3·23	3·32	—	—	—	28
	ΔE(X-ray)	0	←	−3·2 →	−5·5	—	—	26
	$\mathcal{I}_\mu$(calc.)	0·49	0·19	0·11	0·17	0·03	0·01	26
NCO^-	ε_μ^{SCF}	−3·67	10·00	−7·96	−12·77	−24·65	−32·23	1
	$\Delta\varepsilon^{SCF}$	0	6·33	4·29	9·10	20·98	28·56	
	ΔE(electronic)	0	3·94	2·82	—	—	—	26

3. Charge distributions and ESCA chemical shifts

Core ionization energies, as determined by the ESCA technique, have been found to depend on the chemical nature of the sample[22,23]. The main effect is readily understood: One need only remember that it is more difficult to remove an electron from a region with positive charge than from one with a negative charge. In line with this, many correlations with valence charge densities have been established for inner shell ionization energies.

The two most common correlative equations are[21,22]:

$$IE(X_{1s}) = K_1 + K_2 q_X \tag{5}$$

$$IE(X_{1s}) = K_3 + K_4 q_X + \sum_{A \neq X} \frac{q_A}{r_{AX}} \tag{6}$$

where $IE(X_{1s})$ is the ESCA value for ionization of a 1s electron from atom X; q_X is the charge on atom X; K_1, K_2, K_3 and K_4 are constants and r_{AX} is the distance between atoms A and X. Equation (6), which originates in the 'point charge potential' model, reduces to equation (5) if the last term of equation (6) is somehow incorporable into the first two terms. Unfortunately, it turns out that the last term in equation (6) is as important as the second. As a result, while ESCA chemical shifts can provide a means to test calculated valence charge densities, it is best to do so correlatively. One may attempt to use equation (5) by working with a series of molecules which are related in such a way that the term $\sum_{A \neq X} q_A/r_{AX}$ is either roughly constant or roughly subsumable within the other two.

Another problem enters when one attempts to compare the values of q_X obtained by ESCA with values of q_X obtained from MO calculations. The manner in which the charge in a bond is partitioned between the two bonded atoms is not unique and may well depend on the choice of partitioning criterion[30]. As a result, the translation of the 'experimental' q_X values into 'theoretical' q_X values could be invalid.

ESCA core ionization potentials for cyanates and thiocyanates are collected in Table 2. These data have been correlated[31,32] with each other and with numerous other nitrogen-containing compounds using equation (5). All of the data of Table 2[31–35] refer to the anions NCO^- and NCS^-. Therefore, it is surprising that ionization energies recorded by different workers are so different. For example, the N_{1s} ionization energy of NCS^- varies by $\sim 4{\cdot}5$ eV. Part of this variation may be associated with changes in the Madelung potential produced by the different cations, and part of it may be caused by calibration difficulties.

TABLE 2. Core ionization energies (eV) for cyanates and thiocyanates and calculated atomic (valence) charges

Molecule	M = NCO⁻			M = NCS⁻			Reference
	N_{1s}	C_{1s}	O_{1s}	N_{1s}	C_{1s}	S_{2p}	
$[\varphi_4As]M$	397·0	291·2	532	396·6	291·3	161·8	33
KM	398·3	—	—	—	—	—	31
KM	398·3	—	—	398·5	—	—	32
$[(\varphi_3p)_2N]M$	400·5	—	—	400·2	—	—	34
CuM	—	—	—	401·0	287·0	165·9	35
q_X	−0·50	−0·05	−0·45	—	—	—	18
q_X	−0·64	0·13	−0·49	−0·47	0·03	−0·55	19

In any event, the data do show that the N_{1s} and C_{1s} ionization energies are equal in NCO^- and NCS^-. Thus, by equation (5), one concludes that the atom charges in NCO^- are identical to those in NCS^-. This conclusion, while not quite obvious from *ab initio* results[1,19] is in rather good agreement with the atom charges obtained by both CNDO/2 and EHMO computations[31,32].

Using equation (5), ESCA ionization potentials should correlate with any other physical property whose magnitude is determined by atom charges. Basch[36] has suggested that n.m.r. chemical shifts correlate with atom charges. And, indeed, the ^{13}C chemical shifts, measured relative to benzene, are small and similar for both cyanates and thiocyanates[37], in full accord with the equality of the C_{1s} ionization energies of Table 2. A linear relation between C_{1s} ionization potential and ^{13}C chemical shifts has also been established for many other compounds[38].

The ^{14}N chemical shifts for NCS^- and NCO^- differ considerably[39], although the calculated charge densities (Table 2) for the two nitrogen centres are very similar. Thus, one must conclude[33] that ^{14}N chemical shifts are not as sensitively dependent on atom charges (i.e., on the diamagnetic shielding) as they are on paramagnetic contributions. This conclusion is further substantiated by the results of π MO calculations[17].

B. Covalent Compounds

1. Geometrical structure

Once the cyanato or thiocyanato group is covalently bonded to another atom or radical R, $\measuredangle$ RNC is generally assumed and usually found to differ significantly from 180°. Some typical examples[40–43] are collected in Figure 4. Phenyl isocyanate and phenyl isothiocyanate are usually assumed to possess C_{2v} symmetry because *p*-diisothiocyanatobenzene has a zero dipole moment. This observation, however, merely proves the existence of a centre of symmetry and does not preclude a non-linear C—N=C=S arrange-

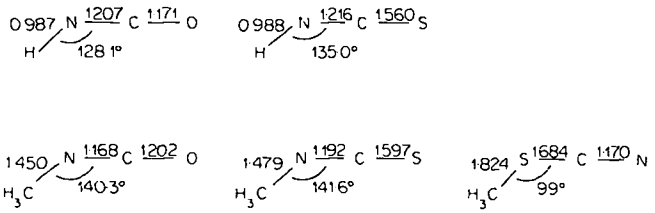

FIGURE 4. Gas-phase structures of isocyanic acid[40], isothiocyanic acid[41], methyl isocyanate[42], methyl isothiocyanate[42], and methyl thiocyanate[43].

ment. Thus, the actual preference for a C_{2v} symmetry for phenyl isocyanate and phenyl isothiocyanate derives from considerations of bond moments and MO arguments[44].

Some ambiguity exists for silyl isocyanate and silyl isothiocyanate. Microwave determinations[45,46] favour a C_{3v} symmetry with a linear

—SiNCX skeleton, whereas electron diffraction data have been in-

terpreted[47] on the basis of ∡ SiNC equal to 153° or 164°. This difference is of some importance to photoelectron spectroscopic results since a C_{3v} symmetry would result in some degeneracies and yield a possible simplification of the spectrum. On the other hand, one should keep two factors in mind:

(i) The different structures which have been proposed represent 'best fits' to experimental data of quite different natures.

(ii) The low-energy bending vibrations of the –NCO and –NCS groupings possess fairly large amplitudes. These amplitudes, if large enough, will make the concept of molecular geometry more diffuse than normally supposed.

Electron diffraction data for Cl—NCO suggest[48] a bent structure for which ∡ NCO = 171°. Although one might wonder whether semi-empirical schemes can predict structures to such a high accuracy, a bond angle of 176·1° has been calculated[8,49] by the CNDO/2 method[50]. The same workers, using the same semi-empirical MO approach, also predict non-linear N=C=O groups for a variety of other isocyanates[13].

Electron diffraction data[51,52] are available for a variety of isocyanate and isothiocyanate molecules, but will not be discussed here.

2. Energies and shapes of valence orbitals: Photoelectron and X-ray emission spectra

a. *Molecular orbitals.* Since the MO description has provided a consistent and unified interpretation of different spectroscopic results for the cyanato and thiocyanato anions, we will initiate our discussion of the covalently bonded NCO and NCS groups similarly. The results of a set of representative semi-empirical MO calculations[53] are given in Figure 5. The results of a minimal basis set, *ab initio*, self-consistent field calculation[18] for HNCO are also included in Figure 5 for completeness.

Comparison of Figures 1 and 5 reveals a close similarity between the MO's of NCO^- and HNCO. Because of the symmetry reduction,

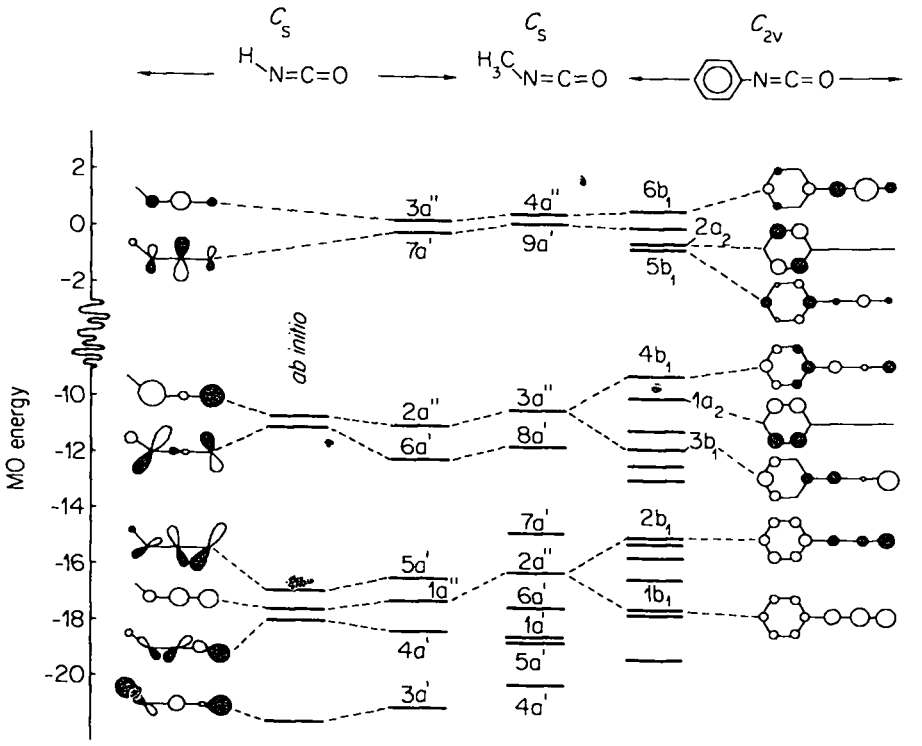

FIGURE 5. Molecular orbitals and orbital energies obtained from CNDO/s calculations for isocyanic acid, methyl isocyanate, and phenyl isocyanate. *Ab initio* results for HNCO are included for completeness.

$C_{\infty v} \rightarrow C_s$, all π-levels split into a' and a" components, the latter being antisymmetric with respect to the HNCO molecular plane. The 2π orbitals of NCO^- retain most of their original character in HNCO, whereas the a' component of the 1π MO, 5a', is heavily mixed with the NCO^- σ-bonding orbital, 4a'. The 3a' MO of HNCO can be characterized as a N—H bonding MO, although such a description is merely a rough approximation. The inner a' MO's of CH_3NCO are not shown in Figure 5 because of their experimental inaccessibility. The inner MO's of C_6H_5NCO are truncated for similar reasons. The good agreement with the minimal basis set, *ab initio*, SCF calculation[18] for HNCO lends some credibility to the CNDO/s results for methyl and phenyl isocyanate.

The replacement of hydrogen by the methyl group introduces relatively minor changes. The methyl group contributes three additional orbitals, all of which remain more or less local to the methyl group. Orbital energies are

generally higher in CH_3NCO than in HNCO, which is the normal effect of methyl substitution, and some 'crowdedness' arises between ~16 and 20 eV.

Molecular orbital 'crowdedness' is even more pronounced for phenyl isocyanate. Therefore, the only MO diagrams shown in Figure 5 for this molecule are for the π MO's. The NCO-group produces a splitting of the degenerate benzene π MO's, one of which, the a_2 MO, retains its original D_{6h} form in the C_{2v} point group assumed for phenyl isocyanate.

b. *Photoelectron spectra.* A representative set of photoelectron spectra[54] is collected in Figure 6. These spectra, plus the silyl isocyanate and silyl isothiocyanate spectra[55], are analysed in Table 3. With molecular orbital calculations (Figure 5) at hand, the assignments of these photoelectron spectra proceed quite readily.

The ionization energies relating to the 2a″ and 6a′ orbitals of the acids and the 3a″ and 8a′ orbitals of the methyl derivatives correspond to two well-separated structures in the photoelectron spectra in all cases except methyl isothiocyanate. The apparent degeneracy of the first two photoelectron bands of methyl isothiocyanate could suggest a linear C—N=C=S skeleton. Fortunately, there is little doubt as to the structure[42] (see Figure 4) and, consequently, the degeneracy must be accidental. Indeed, the width of this first photoelectron band of CH_3NCS is so large that it can accommodate substantial (i.e., more than 30°) deviations of the CNCS skeleton from linearity. Similar comments apply to the photoelectron spectra of certain silyl derivatives.

Despite the simple reflection of the MO diagram of Figure 5 in the photoelectron spectra of Figure 6, some ambiguity remains as to the number of ionization events in the 15·8 and 17·54 eV bands of HNCO and in the 13.31 and 15.12 eV bands of HNCS. The earlier investigators[54,55] placed two ionization events (π(5a′, 1a″)) into each of the 15·8/13·31 eV bands, respectively, whereas Kosmus and coworkers[56] prefer to switch the assignment so that two events (π(4a′, 1a″)) occur in each of the 17·54/15·12 eV bands. There is not much experimental support for either set of assignments. Vibrational fine structure is usually taken to indicate π-character and its presence favours the former assignment[54,55]. Furthermore, the supposition that the occurrence of the symmetrical NCO bending vibration is suggestive of a bent ground state[56] is erroneous—it merely points up the fact that the excited cationic state is more bent than the HNCO ground state.

The effects of methylation on the photoelectron spectrum are identical to those predicted by MO calculations: The ionization energies decrease and additional bands due to the CH_3 group appear in the 15–20 eV region. The

TABLE 3. Photoelectron spectroscopic ionization energies (eV)[55] and assignments[54,55]

HNCO	11·62/2a″	12·30/6a′	15·8/1π(5a′, 1a″)	17·54/4a′	19·24/3a′	
HNCS	9·94/2a″	10·3/6a′	13·31/1π(5a′, 1a″)	15·12/4a′		
CH_3NCO	10·67/3a″	11·20/8a′	14·7/2π(2a″, 7a′)	16·1/6a′	16·7/5a′, 1a″	18·0/4a′
CH_3NCS	9·37/3π(3a″, 8a′)		12·6/2π(2a″, 7a′)	14·6/6a′	15·6/5a′, 1a″	17·5/4a′
SiH_3NCO	11·10/1π(NCO)		13·1/σ(SiH_3)	15·7/π(NCO)	17·1/σ	
SiH_3NCS	9·54/π(NCS)		12·5/σ(SiH_3)	13·9/π(NCS)	14·7/σ	15·9/σ

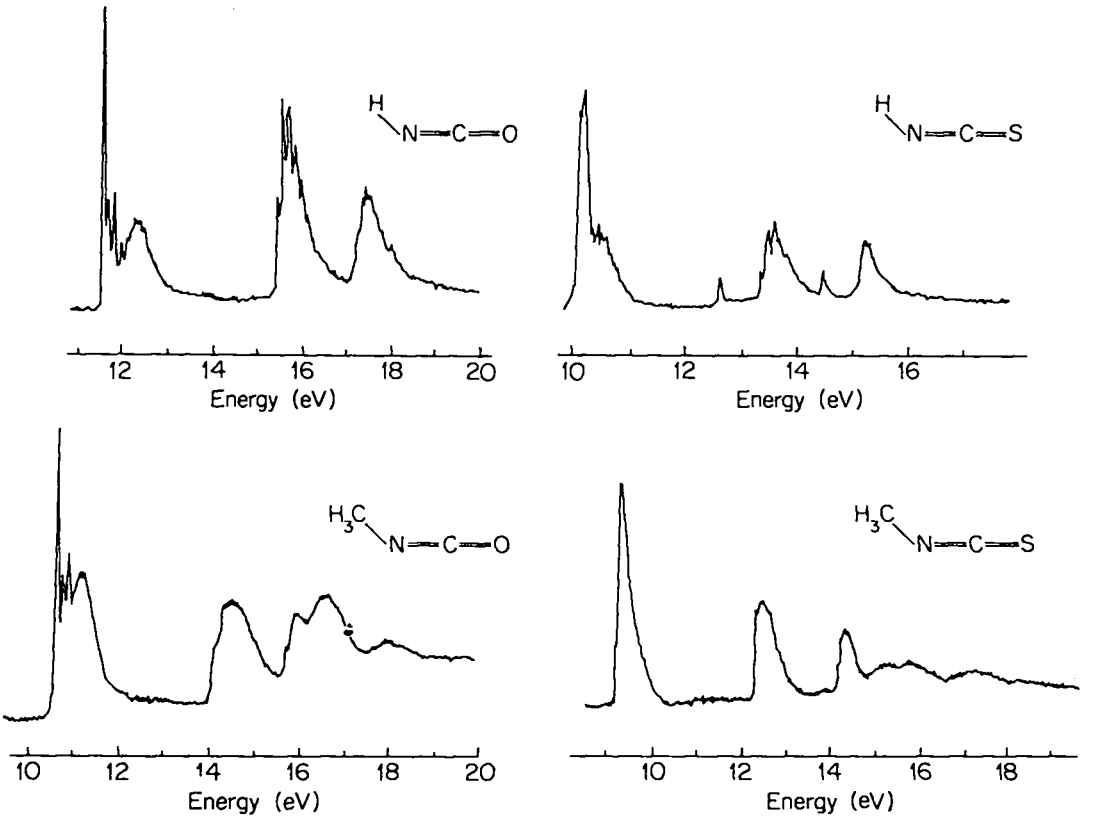

FIGURE 6. Photoelectron spectra of isocyanic acid, isothiocyanic acid, methyl isocyanate and methyl isothiocyanate. (Adapted from Figures 1, 2, 7 and 8 of Reference 54.)

increase of ionization energies which occurs upon replacing the methyl by the silyl group was supposed to constitute evidence for π-acceptor properties of the SiH_3 group (i.e., for d_π–p_π bonding)[55]. However, the photoelectron bands of the silyl compounds are quite broad and no real distinction can be made between a 'nearly' linear skeleton with ∡SiNC = 153° and near degeneracy of π-orbitals[47], or a linear structure with ∡SiNC = 180°[45] and exact degeneracy[55].

The photoelectron spectra of a number of other NCO and NCS compounds are known (i.e., CF_3HgNCO[57], H_3GeNCO[55], H_3GeNCS[55], $S(CN)_2$[58], CH_3SCN[59]. Of these, the R—S—CN spectra[58,59] are very similar to those of a cyano-substituted sulphide and, as a result, they are not appropriate in the present context.

c. *X-Ray emission spectra.* Unfortunately, sulphur Kβ X-ray emission spectra are scarce. Katahashi and Yabe[60] report two structures, which are separated by 5·2 and 4·9 eV, in the spectra of allyl and phenyl isothiocyanate, respectively. Although a detailed analysis is not available, the results clearly indicate the presence of a large sulphur 3p amplitude in the highest occupied MO's and a much smaller amplitude in those MO's which possess 4–6 eV higher binding energy. The Kβ X-ray emission spectrum of allyl isothiocyanate is shown in Figure 7.

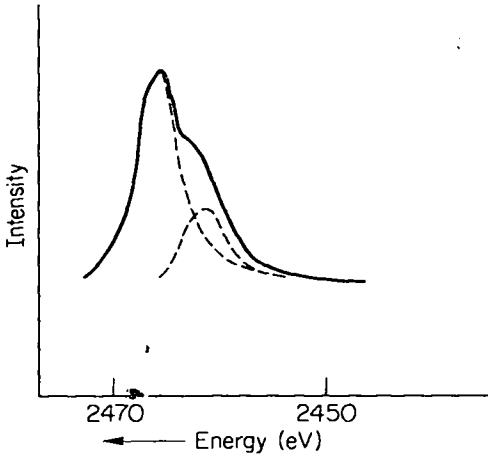

FIGURE 7. X-Ray emission spectrum of $CH_2{=}CHCH_2SCN$. (Adapted from Figure 4 of Reference 60.)

3. Valence electron distribution: ESCA chemical shifts

As already demonstrated in Section II.A.3, core ionization potentials are found to correlate fairly well with 'atomic charges'. It has been pointed out, in an ESCA investigation of NCO and NCS compounds[30], that an operator whose expectation value is an 'atomic charge' in a molecule does not exist. Such a concept, although useful, is fated to be a rough approximation and to depend on the actual recipe used in its numerical evaluation. For this there are several methods available: One method is based on a symmetrical orthogonalization of the atomic orbital basis set[61]; another involves a Mulliken population analysis[62], and, in computations involving non-atomic basis sets, the space must be subdivided into regions pertaining to each atom, and the charge obtained by integration over these individual regions[19]. All three methods involve the determination of the

electronic population on a nuclear centre; this, followed by subtraction of the core charge, yields the 'atomic' charge.

Unfortunately, even when based on rather precise wavefunctions, the two MO methods yield widely differing numbers. However, certain trends within a series of related molecules do seem to be reproduced rather readily by them. A set of illustrative data is given in Table 4. The use of semi-empirical MO functions, such as those of CNDO or INDO types, produces still different sets of atomic charges and, eventually, the whole process becomes futile.

TABLE 4. Calculated atomic charges[30]

	Carbon[a]		Nitrogen	
Molecule	Mulliken[b]	Löwdin[c]	Mulliken[b]	Löwdin[c]
$CH_3N\underline{C}O$	0·93	0·49	−0·63	−0·34
$CH_3N\underline{C}S$	0·25	0·08	−0·54	−0·23
$CH_3S\underline{C}N$	0·07	−0·12	−0·39	−0·18

[a] Data refer to underlined carbon atom.
[b] According to Mulliken[62].
[c] According to Löwdin[61].

The ESCA experimental data are collected in Table 5. Correlations with atomic charges, as processed according to equation (5), are rather poor regardless of the definition of 'atomic charge' used; on the other hand, fairly good correlations exist when all atomic charges are included in the manner specified by the point charge potential model of equation (6). Thus, in view of the large role played by neighbouring atoms, any derivation of atomic charges from ESCA data is simply too complex. Indeed, the only reasonably firm conclusion is that the anions NCS^- and NCO^- possess a more symmetrical charge distribution[19] than do the covalently bonded molecules[30].

C. Summary of Ground State Considerations

We have presented a simple unified description of the ground state electronic structure of cyanato and thiocyanato compounds. The MO description of the closed shell ground state is adequate to the task of accounting for geometries, photoelectron and ESCA spectra, and the X-ray

TABLE 5. ESCA core ionization energies (eV) in the solid (s) and gaseous (g) phase[30]

Molecule	C^a_{1s}	N_{1s}
$CH_3N\underline{C}O$	295·2(g)	406·1(g)
	284·5(s)	400·4(s)
$CH_3N\underline{C}S$	288·0(s)	400·4(s)
$CH_3S\underline{C}N$	293·6(g)	406·0(g)
	287·2(s)	399·7(s)

[a] Data refer to underlined carbon atom.

emission spectra and electronic absorption spectra of the photoionized cyanato and thiocyanato entities. The success achieved is directly attributable to Koopmans' theorem and to the MO concept (i.e., the supposition that each electron experiences only the *average* field produced by all the other electrons). The limitations of Koopmans' theorem and of the ground state MO description are well documented in the literature[63,64], as are also the difficulties associable with the concept of atom charges in a molecule[30]. Yet, despite these limitations, a high degree of interpretive success is feasible and has, we hope, been achieved here.

There remains hardly any doubt that the highest occupied MO in NCO^- and NCS^- is of π-symmetry, and that the next, whether σ or π, lies several electron volts to higher binding energies. These results also hold for covalently bonded NCO and NCS groups—although there is, of course, some slight splitting due to the lowering of symmetry. Indeed, the constituent ground state orbitals of the NCO and NCS groups can be recognized even in such complex molecules as phenyl isothiocyanate. Thus, it may be concluded that the cyanato and thiocyanato groups are true functional groups or, in a more spectroscopic language, true chromophores.

In a more jaundiced vein, there are a few other observations which we feel obliged to make. These are:

(i) There is a great need for much further *experimental* work. This work should include structure determinations of phenyl isocyanate and phenyl isothiocyanate; extensive photoelectron spectroscopic and ESCA investigations, and—with high preference—a systematic X-ray emission spectroscopic study of both salts and covalent compounds. These X-ray studies should include sulphur Kβ, carbon Kα, nitrogen Kα and oxygen Kα investigations at the highest attainable resolution.

(ii) No particular need exists for any further semi-empirical com-

putational works, unless they constitute an attempt to unify existing or, even better, new experimental data.

(iii) Approximate means for 'experimental' access to such quantities as orbital energies, LCAO coefficients, and even 'atom charges' in a molecule do exist. However, any effort to attain high precision (i.e., several significant figures) intrudes on the theoretical difficulties already discussed. In other words, while the MO ideology can ensure a close relatedness of experiment and theory, this relatedness is fated to remain inexact and, at a certain limit, to be ill-defined.

III. CONCERNING THE DIFFICULTIES INHERENT TO A DISCUSSION OF ELECTRONICALLY EXCITED STATES

Our discussion, so far, has been restricted to one single electronic state, the ground state (e.g., the $X^1\Sigma^+$ state of NCO^-). We must now intrude on the realm of excited states. When we do so, we run into certain difficulties. These are:

(i) There is obviously a very large number, in fact an infinity, of excited states. Thus, if the valence set of MO's consists of n filled and m virtual orbitals, all non-degenerate, Koopmans' theorem correctly predicts n ionization potentials. Similar reasoning leads to a prediction of at least $n \cdot m$ excited states. And, if we include Rydberg orbitals and take account of spin quantization, the number nm increases to infinity. This, however, is a technical difficulty(!): We can, if we so choose, attack these states one at a time and do as thorough a job on each one as we might on the ground state.

(ii) Experimental access to excited state studies is exceedingly difficult. Many of these states possess lifetimes which are shorter than 10^{-12} sec and this places them beyond the range of complex picosecond studies. Indeed, in most instances, it becomes immediately necessary to dispense with the whole panoply of techniques (n.m.r., e.s.r., ESCA, PES, electron diffraction, dipole measurement, etc.) which were so invaluable in specifying ground state characteristics. In fact, until quite recently, the study of excited states was more or less restricted to one technique, namely the technique used to generate them. Thus, in many instances, the only information available concerning excited states is their energies. This situation, fortunately, is changing.

(iii) The MO's of the ground state may not be used to construct excited electronic states. In other words, the 'frozen core' approximation is not valid for excited states. We will illustrate this statement by specific reference to HNCO. The Koopmans configurations of $HNCO^+$ are non-interacting

with respect to the cationic Hamiltonian. On the other hand, different excited configurations of HNCO can and will interact with respect to the neutral-molecule Hamiltonian. This interaction may be very severe and is known as Configuration Interaction (CI). In this sense, even if we freeze the whole valence set of orbitals, filled as well as virtual, we cannot, generally, retain an orbital picture for the excited states. Nevertheless, this is also a technical difficulty—technical in the sense that it may be possible to perform Hartree–Fock computations on the excited configuration and thus generate a new set of orbitals, one which provides as accurate a description of the excited state as the former set of Hartree–Fock orbitals did for the ground state. This, however, is a rather distasteful affair since it forces us to use different orbitals for different states.

(iv) The retention of an MO attitude for the description of excited states is not merely a technical difficulty, it is also fundamentally inadequate. We will illustrate: The spin-orbital excitation $\varphi_i\alpha \rightarrow \varphi_j\alpha$, where α denotes a $+\frac{1}{2}$ electron spin, does not produce a pure spin state (i.e., one which is an eigenfunction of the spin angular momentum operator, S^2). The resulting configuration, in other words, does not transform as an irreducible representation of the permutation group of all electrons. To obtain the appropriate transformation properties, one is irretrievably forced into a multiconfigurational description of the excited state. This leads to a total loss of spin-orbital identifications and, if spin-orbital coupling (*vide infra*) is large, to a complete loss of MO identifications.

As another example, consider a $\pi_i \rightarrow \pi_j$ excitation in NCO^-. This MO excitation is four-fold degenerate. In fact, since the maximum non-accidental degeneracy in $C_{\infty v}$ is twofold, this excitation produces three different excited 'states': Σ^+, Σ^- and Δ. We will construct symmetry adapted functions for these states in Section IV, and will see that they must be described as linear combinations of the four determinants which arise from the $\pi_i \rightarrow \pi_j$ MO excitation (i.e., $\pi_{ip} \rightarrow \pi_{jq}$ where $\{p, q\} = \{x, y\}$). In this instance, MO identifications are totally lost.

As a final example, consider singlet → triplet absorption intensities[65]. These are usually small and difficult to measure. The reverse process, phosphorescence or triplet → singlet emission, is somewhat less difficult to measure and, in fact, is a standard analytical technique. The observation of phosphorescence implies the presence of spin-orbital coupling effects and, also, the necessary argument to solidify the conclusions of the next to last paragraph above.

In summary, although ground state properties, especially ionization events and related phenomena, are easily understood using an orbital level

description, one is forced to abandon this single configurational description when one initiates a study of excited states. For reasons listed above, one will have to consider both *intra*- and *inter*configurational mixings in order to do no more than provide a qualitative account of experiment. Thus, the group theoretical discussions which, for the ground state, were so neatly summarized by a Walsh diagram such as Figure 1, must become more elaborate—although not necessarily more difficult—when we discuss excited states. This increase of complexity is not avoidable. Nevertheless, we will attempt, in the spirit of Section II, to be as simple and as fundamental as possible.

IV. EXCITED STATE PROPERTIES

A. Theoretical

Molecular orbital calculations, of both the EHMO and CNDO varieties, provide level schemes for NCO^- and NCS^- which are similar to that of Figure 1. In particular, the 4σ MO is usually predicted to lie between the 1π and 2π MO's. This conclusion also follows from the *ab initio* MO SCF calculations of McLean and Yoshimine[1] except that in NCS^- the 4σ MO is computed to lie subjacent to the 2π MO by $\sim 0{\cdot}75$ eV. These latter conclusions[1] agree with the results of the X-ray emission and the electronic spectroscopy of the radicals NCO and NCS, as given in Section II.A.2. In addition, all calculations predict that the lowest-energy unoccupied MO will be of π symmetry.

1. Spin and symmetry adaptation in the $\{p_0, p_1, p_{-1}\}$ basis

It is reasonable to expect that the lowest-energy excited electronic states of the anions will arise from the MO excitations $2\pi \rightarrow 3\pi$ and that these will be followed, at somewhat higher energies, by states deriving from the $4\sigma \rightarrow 3\pi$ and $1\pi \rightarrow 3\pi$ MO excitations. Any $\sigma \rightarrow \pi$ (or $\pi \rightarrow \sigma$) MO excitation produces two states, $^{(1,3)}\Pi$, which are separated by $2K_{\sigma\pi}$, where $K_{\sigma\pi}$ is an exchange integral given by $(\sigma(1)\pi(1)|\pi(2)\sigma(2))$. The $\pi \rightarrow \pi$ MO excitations, on the other hand, are quite complex: They give rise to six excited states, $^{(1,3)}\Sigma^+$, $^{(1,3)}\Sigma^-$, and $^{(1,3)}\Delta$. The energetic order of these excited states is not immediately obvious and must be determined. In order to do this, it is convenient to construct antisymmetrized state functions which are eigenfunctions of the angular momentum operators S_z, S^2 and $\mathscr{L}_z$, and which are also symmetry adapted (i.e., constitute bases for the irreducible representations Σ^+, Σ^- and Δ of the $C_{\infty v}$ point group).

It is better, at the outset, to redefine the set of valence p AO's so that they constitute eigenfunctions of l_z in the cylinder point group. The appropriate set is:

$$\begin{aligned} p_0 &= p_z \\ p_1 &= 1/\sqrt{2}(p_x + ip_y) \\ p_{-1} &= 1/\sqrt{2}(p_x - ip_y) \end{aligned} \tag{7}$$

These new AO's possess components of orbital angular momentum along the internuclear C_∞^ϕ axis (i.e., the z axis) of 0, $\hbar$ and $-\hbar$, respectively. In terms of these AO's, the set of pertinent MO's for the $2\pi \rightarrow 3\pi$ excitation of NCO^- is given by

$$\begin{aligned} 2\pi &\begin{cases} \varphi_1 = c_{1N}p_{1N} + c_{1C}p_{1C} + c_{1O}p_{1O} \\ \varphi_{-1} = c_{-1N}p_{-1N} + c_{-1C}p_{-1C} + c_{-1O}p_{-1O} \end{cases} \\ 3\pi &\begin{cases} \varphi_{1^*} = c_{1^*N}p_{1N} + c_{1^*C}p_{1C} + c_{1^*O}p_{1O} \\ \varphi_{-1^*} = c_{-1^*N}p_{-1N} + c_{-1^*C}p_{-1C} + c_{-1^*O}p_{-1O} \end{cases} \end{aligned} \tag{8}$$

where the coefficients c_{1A}, c_{-1A}, c_{1^*A} and c_{-1^*A} are taken from some type of MO computation; and where A = N denotes 'nitrogen', A = C denotes 'carbon', and A = O denotes oxygen.

a. *Spin adaptation.* The set of configuration wavefunctions for the one-electron $2\pi \rightarrow 3\pi$ MO excitation is given in Table 6. These wavefunctions, being of Slater determinantal type, are antisymmetrized and are eigenfunctions of S_z and $\mathscr{L}_z$. They are not, however, eigenfunctions of S^2, nor are they properly symmetry adapted. The generation of the eigenfunctions of S^2 is most conveniently performed using spin projection operators[66]. The results are given in Table 7.

b. *Symmetry adaptation.* The final step is symmetry adaptation and, for this purpose, the simplest set of operations of the $C_{\infty v}$ group which one may use is E, $\sigma_v(xz)$ and C_γ^ϕ. In terms of the effects on individual MO's, the results of these operators are:

$$\begin{aligned} E\varphi_1 &= \varphi_1; \qquad E\varphi_{-1} = \varphi_{-1} \\ \sigma_v\varphi_1 &= \varphi_{-1}; \qquad \sigma_v\varphi_{-1} = \varphi_1 \\ C_\infty^\phi\varphi_1 &= e^{-i\phi}\varphi_1; \qquad C_\infty^\phi\varphi_{-1} = e^{i\phi}\varphi_{-1} \end{aligned} \tag{9}$$

Straightforward, tandem application of equation (9) to the product wavefunctions of Table 6, as combined in Table 7, yields

$$\begin{aligned} \Sigma^+ &= 1/\sqrt{2}(\Psi'_1 + \Psi'_3) \qquad \Sigma^- = 1/\sqrt{2}(\Psi'_1 - \Psi'_3) \\ \Delta &= \{1/\sqrt{2}(\Psi'_2 + \Psi'_4); \qquad 1/\sqrt{2}(\Psi'_2 - \Psi'_4)\} \end{aligned} \tag{10}$$

TABLE 6. Eigenfunctions of S_z and $\mathscr{L}_z$ derived from the $2\pi \rightarrow 3\pi$ electronic excitation (the $\{p_0, p_1, p_{-1}\}$ basis)

(This table is to be read in the manner exemplified by $\Psi_8 = |\overset{+}{\varphi}_1(1)\overline{\varphi}_1(2)\overline{\varphi}_{-1}(3)\overline{\varphi}_{1^*}(4)|$. All wavefunctions are Slater determinants. All the functions Ψ_1 through Ψ_4 are orbitally (i.e., spatially) identical. Insofar as we ever work solely with the orbital parts, these four functions, therefore, may be labelled Ψ'_1.)

	Ψ_i	Electron 1	Electron 2	Electron 3	Electron 4	M_S	Λ
Ψ'_1	Ψ_1	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overset{+}{\varphi}_{-1}$	$\overset{+}{\varphi}_{-1^*}$	1	0
	Ψ_2	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1^*}$	0	0
	Ψ_3	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overline{\varphi}_{-1}$	$\overset{+}{\varphi}_{-1^*}$	0	0
	Ψ_4	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overline{\varphi}_{-1}$	$\overline{\varphi}_{-1^*}$	−1	0
Ψ'_2	Ψ_5	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overset{+}{\varphi}_{-1}$	$\overset{+}{\varphi}_{1^*}$	1	2
	Ψ_6	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{1^*}$	0	2
	Ψ_7	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overline{\varphi}_{-1}$	$\overset{+}{\varphi}_{1^*}$	0	2
	Ψ_8	$\overset{+}{\varphi}_1$	$\overline{\varphi}_1$	$\overline{\varphi}_{-1}$	$\overline{\varphi}_{1^*}$	−1	2
Ψ'_3	Ψ_9	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overset{+}{\varphi}_1$	$\overset{+}{\varphi}_{1^*}$	1	0
	Ψ_{10}	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overset{+}{\varphi}_1$	$\overline{\varphi}_{1^*}$	0	0
	Ψ_{11}	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overline{\varphi}_1$	$\overset{+}{\varphi}_{1^*}$	0	0
	Ψ_{12}	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overline{\varphi}_1$	$\overline{\varphi}_{1^*}$	−1	0
Ψ'_4	Ψ_{13}	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overset{+}{\varphi}_1$	$\overset{+}{\varphi}_{-1^*}$	1	|−2|
	Ψ_{14}	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overset{+}{\varphi}_1$	$\overline{\varphi}_{-1^*}$	0	|−2|
	Ψ_{15}	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overline{\varphi}_1$	$\overset{+}{\varphi}_{-1^*}$	0	|−2|
	Ψ_{16}	$\overset{+}{\varphi}_{-1}$	$\overline{\varphi}_{-1}$	$\overline{\varphi}_1$	$\overline{\varphi}_{-1^*}$	−1	|−2|

TABLE 7. Eigenfunctions of S_z and S^2

Eigenfunctions	M_S	S
$\Psi_1, \Psi_5, \Psi_9, \Psi_{13}$	1	1
$\Psi_2 + \Psi_3, \Psi_6 + \Psi_7, \Psi_{10} + \Psi_{11}, \Psi_{14} + \Psi_{15}$	0	1
$\Psi_4, \Psi_8, \Psi_{12}, \Psi_{16}$	−1	1
$\Psi_2 - \Psi_3, \Psi_6 - \Psi_7, \Psi_{10} - \Psi_{11}, \Psi_{14} - \Psi_{15}$	0	0

TABLE 8. State eigenfunctions for states which derive from the $2\pi \rightarrow 3\pi$ one-electron MO promotion (the $\{p_0, p_1, p_{-1}\}$ basis

$^{(2S+1)}\Gamma$	State eigenfunctions	S	M_S	Λ
$^1\Sigma^+$	$1/2(\Psi_2 - \Psi_3 + \Psi_{10} - \Psi_{11})$	0	0	0
$^3\Sigma^+$	$1/\sqrt{2}(\Psi_1 + \Psi_9)$	1	1	0
	$1/2(\Psi_2 + \Psi_3 + \Psi_{10} + \Psi_{11})$	1	0	0
	$1/\sqrt{2}(\Psi_4 + \Psi_{12})$	1	−1	0
$^1\Sigma^-$	$1/2(\Psi_2 - \Psi_3 - \Psi_{10} + \Psi_{11})$	0	0	0
$^3\Sigma^-$	$1/\sqrt{2}(\Psi_1 - \Psi_9)$	1	1	0
	$1/2(\Psi_2 + \Psi_3 - \Psi_{10} - \Psi_{11})$	1	0	0
	$1/\sqrt{2}(\Psi_4 - \Psi_{12})$	1	−1	0
$^1\Delta$	$1/2(\Psi_6 - \Psi_7 + \Psi_{14} - \Psi_{15})$; $1/2(\Psi_6 - \Psi_7 - \Psi_{14} + \Psi_{15})$	0	0	2
$^3\Delta$	$1/\sqrt{2}(\Psi_5 + \Psi_{13})$; $1/\sqrt{2}(\Psi_5 - \Psi_{13})$	1	1	2
	$1/2(\Psi_6 + \Psi_7 + \Psi_{14} + \Psi_{15})$; $1/2(\Psi_6 + \Psi_7 - \Psi_{14} - \Psi_{15})$	1	0	2
	$1/\sqrt{2}(\Psi_8 + \Psi_{16})$; $1/\sqrt{2}(\Psi_8 - \Psi_{16})$	1	−1	2

The set of final state wavefunctions—antisymmetrized, eigenfunctions of S^2, S_z and $\mathscr{L}_z$, and symmetry adapted—may now be written by inspection. They are given in Table 8.

The set of final state wavefunctions for the $\sigma \rightarrow \pi$ (or $\pi \rightarrow \sigma$) MO promotion may be obtained similarly, but with considerably less difficulty. Finally, the ground state wavefunction, of course, is simply

$$^1\Psi_0 = |\overset{+}{\varphi}_1 \overset{-}{\varphi}_1 \overset{+}{\varphi}_{-1} \overset{-}{\varphi}_{-1}| \tag{11}$$

and is of representation species Σ^+.

2. Spin and symmetry adaptation in the $\{p_x, p_y, p_z\}$ basis

Almost all quantum chemical calculations are done in the $\{p_x, p_y, p_z\}$ basis. Hence, while it is more convenient to work theoretically in a $\{p_0, p_1, p_{-1}\}$ basis, the pragmatic business of analysing the results of semi-empirical calculations makes it convenient to have spin and symmetry adapted functions available in the cartesian coordinate system. Since the means of generating such functions are no different than that described in Section IV.A.1, we present the results without comment.

The π-MO functions are obtained from equation (8) by replacing 1 by x, and -1 by y everywhere. The coefficient c may also be replaced by a in order to make clear the fact that the coefficients in both bases need not be the same. With the same replacements, we obtain a new Table 6 from which we must delete the rightmost (i.e., A) column. Table 7 remains unchanged but equation (10) now reads as follows:

$$\begin{aligned} \Sigma^+ &= 1/\sqrt{2}(\Psi'_1 + \Psi'_3) \\ \Sigma^- &= 1/\sqrt{2}(\Psi'_2 - \Psi'_4) \\ \Delta &= \{1/\sqrt{2}(\Psi'_1 - \Psi'_3); \quad 1/\sqrt{2}(\Psi'_2 + \Psi'_4)\} \end{aligned} \tag{10a}$$

This change in equation (10) yields the new Table 8, namely Table 8a, of adapted wavefunctions.

The interesting result that evolves directly from Table 8a is that the $^1\Sigma^+$, $^3\Sigma^+$, and one of each of the two components of the $^1\Delta$ and $^3\Delta$ states are composed of 'parallel' (denoted //) MO excitations. That is, these states, or components thereof, are generated by an excitation between the MO's which are parallel (e.g., $\pi_x \rightarrow \pi_{x^*}$ or $\pi_y \rightarrow \pi_{y^*}$). All other states are composed of 'perpendicular' (denoted $\perp$) MO excitations of type $\pi_x \rightarrow \pi_{y^*}$ or $\pi_y \rightarrow \pi_{x^*}$. It is these excitation characteristics that provide easiest access to the analysis of CNDO/s results. We shall use the results of Table 8a only when we engage in such analyses.

TABLE 8a. State eigenfunctions for states which derive from the $2\pi \rightarrow 3\pi$ one-electron MO promotion (the $\{p_x, p_y, p_z\}$ basis)

$^{(2S+1)}\Gamma$	State eigenfunctions	S	M_S	Λ	MO excitation type[a]
$^1\Sigma^+$	$1/2(\Psi_2 - \Psi_3 + \Psi_{10} - \Psi_{11})$	0	0	0	//
$^3\Sigma^+$	$1/\sqrt{2}(\Psi_1 + \Psi_9)$	1	1	0	//
	$1/2(\Psi_2 + \Psi_3 + \Psi_{10} + \Psi_{11})$	1	0	0	//
	$1/\sqrt{2}(\Psi_4 + \Psi_{12})$	1	−1	0	//
$^1\Sigma^-$	$1/2(\Psi_6 - \Psi_7 - \Psi_{14} + \Psi_{15})$	0	0	0	⊥
$^3\Sigma^-$	$1/\sqrt{2}(\Psi_5 - \Psi_{13})$	1	1	0	⊥
	$1/2(\Psi_6 + \Psi_7 - \Psi_{14} - \Psi_{15})$	1	0	0	⊥
	$1/\sqrt{2}(\Psi_8 - \Psi_{16})$	1	−1	0	⊥
$^1\Delta$	$1/2(\Psi_2 - \Psi_3 - \Psi_{10} + \Psi_{11})$	0	0	2	//
	$1/2(\Psi_6 - \Psi_7 + \Psi_{14} - \Psi_{15})$				⊥
$^3\Delta$	$1/\sqrt{2}(\Psi_1 - \Psi_9)$	1	1	2	//
	$1/\sqrt{2}(\Psi_5 + \Psi_{13})$				⊥
	$1/2(\Psi_2 + \Psi_3 - \Psi_{10} - \Psi_{11})$	1	0	2	//
	$1/2(\Psi_6 + \Psi_7 + \Psi_{14} + \Psi_{15})$				⊥
	$1/\sqrt{2}(\Psi_4 - \Psi_{12})$	1	−1	2	//
	$1/\sqrt{2}(\Psi_8 + \Psi_{16})$				⊥

[a] See text for explanation of symbols.

The ground state function, of course, is given by

$$^1\varphi_0 = |\overset{+}{\varphi_x}\overset{-}{\varphi_x}\overset{+}{\varphi_y}\overset{-}{\varphi_y}| \tag{11a}$$

3. Intraconfigurational splitting

Six states originate in the same $2\pi \rightarrow 3\pi$ orbital promotion (i.e., from the same primitive excited configuration $\ldots(2\pi)^3(3\pi)^1$). These states will not usually have the same energies despite the fact that they are configurationally similar. Their energy splitting is usually termed 'Intraconfigurational Splitting'.

The six states, being symmetry adapted, are non-interacting with respect to the non-relativistic Hamiltonian operator, $\mathscr{H}$. The energy of any of these states, for example the $^1\Sigma^-$ state, is given by a diagonal element of the

Hamiltonian matrix, which can be evaluated[65] using the wavefunctions of Table 8. The energy relative to the ground state, $X^1\Sigma^+(^1\Psi_0)$, is given by

$$\langle {}^1\Sigma^-|\mathscr{H}|{}^1\Sigma^-\rangle - \langle X^1\Sigma^+|\mathscr{H}|X^1\Sigma^+\rangle = E({}^1\Sigma^-) - E(X^1\Sigma^+)$$
$$= \varepsilon_{3\pi}^{SCF} - \varepsilon_{2\pi}^{SCF} + A + C \qquad (12)$$

where A and C are the two-electron integrals defined below (equation 14). This energy consists of the difference of the SCF orbital energies and two electron–electron interaction terms, A and C. Since the orbitals 3π and 2π are common to all states deriving from $2\pi \rightarrow 3\pi$ excitations, the difference in orbital energy will be the same for all these states. Similarly, it turns out that the A integral is present in all configurational energies. Consequently, the different states deriving from $2\pi \rightarrow 3\pi$ excitations will differ in their energies only by electron–electron interaction terms, namely B, C and D. This is exemplified for the $^1\Sigma^-$ and $^1\Delta$ states, for which

$$E({}^1\Sigma^-) - E({}^1\Delta) = C - 2D \qquad (13)$$

The energies of all states of the $2\pi \rightarrow 3\pi$ excitations are depicted in Figure 8; the two electron integrals, finally, are defined as

$$A = (\varphi_1(1)\varphi_1(1)|e^2/r_{12}|\varphi_{1*}(2)\varphi_{1*}(2))$$
$$= (11|1^*1^*) = J_{11^*}$$
$$B = (11^*|11^*) = K_{11^*}$$
$$C = (1\ -1|-1^*1^*)$$
$$D = (1\ -1^*|-1^*1) \qquad (14)$$

The integral A is large whereas the others (i.e., B, C and D) are expected to be relatively small. In the absence of more specific information, we simply assume that $A \gg B \simeq C \simeq D$, and it is on this basis that we have drawn Figure 8. All conclusions implicit in Figure 8, except one, are independent of actual computation of the integrals A, B, C and D. The one disputable conclusion relates to whether $^1\Delta$ is of higher or lower energy than the $^{(1,3)}\Sigma^+$ states (i.e., whether $D > \frac{1}{2}C$ or $D < \frac{1}{2}C$). For the moment, we will assume that $^1\Delta$ is the higher.

The $^{1,3}(\Sigma^+, \Sigma^-, \Delta)$ states which arise from the $1\pi \rightarrow 3\pi$ MO promotion are expected to lie at considerably higher energy (say, greater than 9 eV above the ground state) in both NCO^- and NCS^-. Hence, they are not expected to exhibit any observable spectroscopic consequences in the visible and near u.v. region.

The $^{(1,3)}\Pi$ states which arise from the $4\sigma \rightarrow 3\pi$ promotion may well lie somewhere in the vicinity of the $^1\Sigma^+$ excited state of Figure 8 for NCO^- but

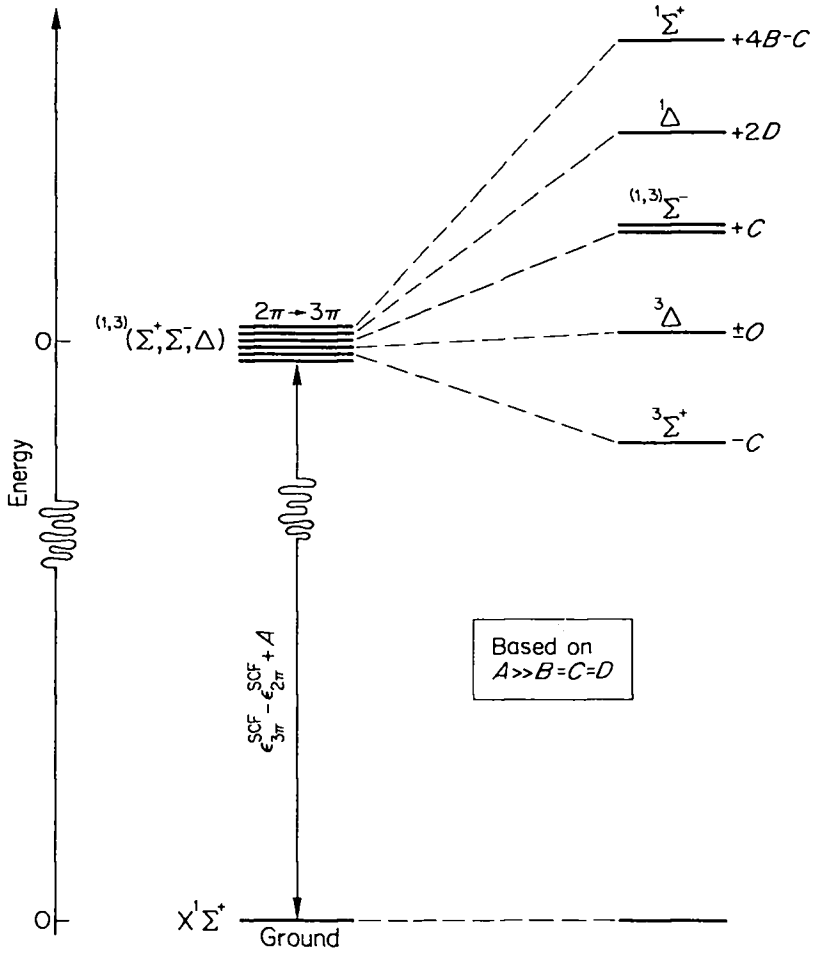

FIGURE 8. Intraconfigurational splitting (schematic) in the $\ldots(2\pi)^3(3\pi)^1$ configuration of a linear NCO^- or NCS^- anion.

not for NCS^-. Unfortunately, any further information on these states requires specific calculations. In any event, the $^{(1,3)}\Pi$ states split into two components, $^1\Pi$ and $^3\Pi$. The integral $K_{\sigma\pi}$ involves the repulsion of two overlap densities, $\sigma(i)\pi(i)$, and is very small because of the σ/π orthogonality (i.e., $\int \sigma(i)\pi(i)\,d\tau = 0$). A not unreasonable value for $K_{\sigma\pi}$ is $\sim 0{\cdot}5$ eV. Hence, the $^1\Pi - {}^3\Pi$ splitting should be of the order of 1 eV. In fact, in the CNDO/s approximation, both of these states, in the absence of configuration interaction, are exactly degenerate.

4. Interconfigurational splitting

This type of mixing, by contrast to that discussed in the previous section, Section IV.A.3, is concerned with the interaction of configurations which originate in different orbital promotions. Thus, the interaction of the two $^1\Delta$ states, one arising from the $2\pi \rightarrow 3\pi$ promotion and the other from the $1\pi \rightarrow 3\pi$ promotion, would fall in this category. This type of mixing is often termed CI. The configurations which mix must form bases for the same irreducible representation of the molecular point group (i.e., transform identically). As in the intraconfigurational case, this interaction is introduced by the electron–electron repulsion, $\sum_{i<j} 1/r_{ij}$.

Let us first consider the mixing of the two configurations of similar symmetry which arise from the $1\pi \rightarrow 3\pi$ and $2\pi \rightarrow 3\pi$ promotions. Based on the orbital energy difference $\varepsilon_{2\pi} - \varepsilon_{1\pi}$, as obtained either 'experimentally' from X-ray or u.v. data for the radicals or computationally from *ab initio* calculations (Table 1), all interacting states are expected to be separated by ~ 3 eV or more. Hence, relative to the off-diagonal matrix elements, which we estimate to be less than 0·5 eV, CI effects, while not negligible, will neither introduce any major alteration of the intraconfigurationally interacted energy level scheme of Figure 8 nor give rise to any new phenomenon.

The situation may be different for the $^{(1,3)}\pi$ configurations arising from $4\sigma \rightarrow 3\pi$, $3\sigma \rightarrow 3\pi$ and $2\pi \rightarrow 5\sigma$ promotions. By symmetry, these cannot mix with the Σ^+, Σ^- or Δ states resulting from the $2\pi \rightarrow 3\pi$ excitation. However, although the individual interactions of these three π states may be small, the overall effect may push one of them into the vicinity of the lowest excited $^1\Sigma^+$ state. Since the $^1\pi$ state is connected to the ground state by an electric dipole allowed transition, it is possible that these latter CI effects may be observationally germane.

5. Spin-orbit coupling

Spin-orbit coupling will be treated as another form of CI. In contrast to the other two types (See Sections IV.A.3 and 4), which only mix configurations of equal spin multiplicity, spin-orbital coupling mixes configurations of different spin multiplicity. It may also mix configurations which arise from the same or different MO excitations. The net effect of spin-orbit coupling is destruction of the 'goodness' of the spin quantum numbers.

Spin-orbit mixing is induced by the one-electron operator $\sum_i \mathscr{A} \vec{l}_i \cdot \vec{s}_i$ where $\vec{l}_i$ and $\vec{s}_i$ are orbital and spin angular momentum operators and $\mathscr{A}$ is

the spin orbit coupling parameter which, for molecules, can be quite complicated. Spin-orbit mixing will be very small in molecules such as NCO^- or NCS^- because they contain no heavy atoms. Despite this, the effects of this latter mixing, small though it be, gives rise to phenomena which cannot be otherwise interpreted. Therefore, we will have to devote some attention to it.

a. *(Λ, Σ)-Coupling*. A discussion of spin orbit mixing is best initiated at the group theoretical level using double group formalism[67] (i.e., in the $C^*_{\infty v}$ point group). The representation symbols of Figure 8 refer to orbital transformation properties, the transformation properties of the spin parts being neglected. The spin parts of the wavefunctions, not very surprisingly, transform as the rotation operators[65]. Hence, the total symmetry of the state functions, spin plus orbital, can be determined by taking direct products[67] of the rotation operator representations with the state orbital representations of Figure 8. The results of this procedure are illustrated in Figure 9.

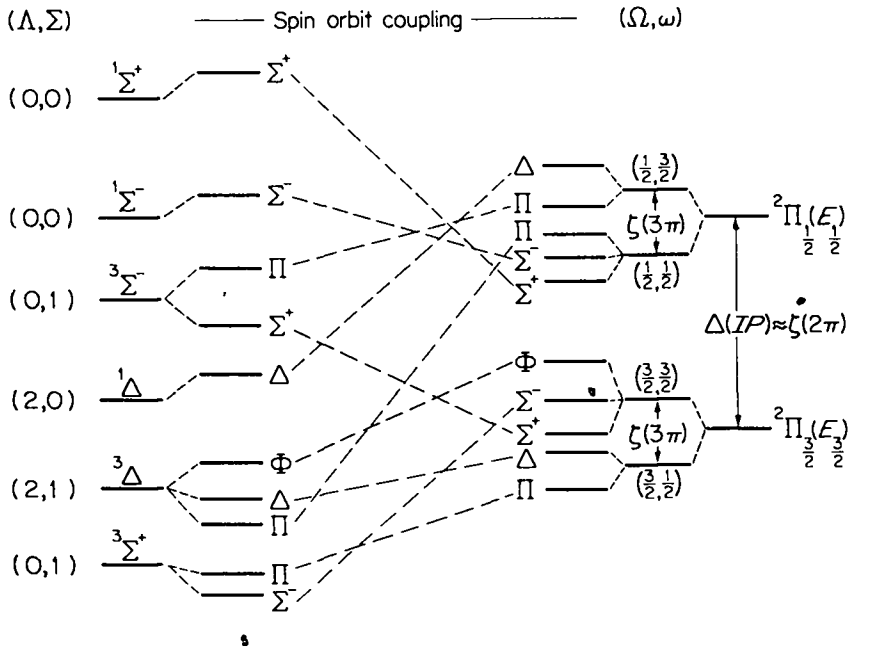

FIGURE 9. The progression from a Russell–Saunders or (Λ, Σ)-coupling limit (left hand side) to an (Ω, ω)-coupling limit (right hand side) for a linear molecule NCO^- or NCS^-. The split components of a given (Λ, Σ)- or (Ω, ω)-state are arbitrarily ordered upwards according to increasing component of angular momentum along the $C_{\infty v}$ axis of the molecule.

The effect of spin-orbital coupling is to destroy the 'goodness' of the quantum numbers Λ(atoms: L) and Σ(atoms: S) and to require their replacement by the total angular momentum quantum number Ω(atoms: J). It will, as a result, produce a splitting of triplet states in the manner shown in Figure 9. The resultant situation, known as (Λ, Σ)-coupling (atoms: L, S or Russell–Saunders), is shown on the left of Figure 9.

b. (Ω, ω)-*Coupling*. The ultimate in spin-orbit coupling is illustrated on the right hand side of Figure 9. The two lowest energy states of the radicals NCO and NCS (i.e., those which arise from the configuration $\ldots(2\pi)^3$) are shown on the extreme right and labelled using the formalism $^{(2S+1)}\Gamma_{\Omega}(\Gamma^*)$. The separation of these two states is also denoted Δ(IP) since it corresponds to the energy difference between the two lowest-energy ionization events in the photoelectron spectrum of the corresponding anion (i.e., NCO^- or NCS^-). This separation is also equal to the spin-orbital coupling parameter of the 2π hole state. This parameter can be approximated by the atomic spin-orbital coupling constant of the heaviest atom in the molecule (i.e., $\xi_{2p(O)}$ or $\xi_{3p(S)}$, respectively). Since these coupling constants are quite small, the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states are effectively degenerate for NCO and NCS (i.e., degenerate within the PES resolution capability for complex molecules).

We now imagine the addition of a single electron of 3π MO nature into the $\ldots(2\pi)^3$ core in such a way that the electrostatic 3π/core interactions are less than the spin-orbit interactions internal to either the core itself or to the (λ, σ)-interactions (atom: *l*, s-coupling) of the added electron. This type of interaction is known as (Ω, ω)- coupling (atoms: *J*, *j*-coupling).

c. *Intermediate coupling*. In the $C^*_{\infty v}$ point group, the states of a single electron in the 3π MO are denoted $E_{1/2}$ and $E_{3/2}$. The interaction of an electron in one of these states, say $E_{3/2}$, with the $^2\Pi_{3/2}$ core, which also forms a basis for $E_{3/2}$, gives, via the direct product, the states Δ, Σ^+ and Σ^- of $C^*_{\infty v}$. It is in this way that the right hand set of states of Figure 9 has been constructed. The connection of the (Λ, Σ) states on the left with the (Ω, ω) states on the right may now be completed by making use of the non-crossing rule. These connections provide a simple schematization of the effects of increasing spin-orbital coupling.

Spin-orbit interaction not only produces a splitting of the (Λ, Σ) states but also mixes different (Λ, Σ) states of the same double group species. The situation is similar regarding the electrostatic interaction in the (Ω, ω) limit. In this latter limit, the $1/r_{ij}$ terms of the Hamiltonian induce a splitting as well as a mixing of different (Ω, ω) states. Whether the (Λ, Σ) or the (Ω, ω) description is more applicable depends on the relative magnitude of the electrostatic and spin-orbit interactions. If they are of similar strength, one

is forced to work in the intermediate coupling scheme, where neither Λ and Σ nor Ω and ω are even good approximate quantum numbers.

It will be obvious from the experimental data (Section IV.C) that the (Λ, Σ) description is most appropriate for the systems of interest.

6. Bending of excited states

The linear ground state anion may bend to a C_s point group symmetry in some of its excited states. The rationale for this conclusion was broached in Section II.A.1. using Walsh's rules and was diagrammed in Figure 1 for the specific case of a state of $^1\Delta(C_{\infty v})$ parentage. A more concise set of

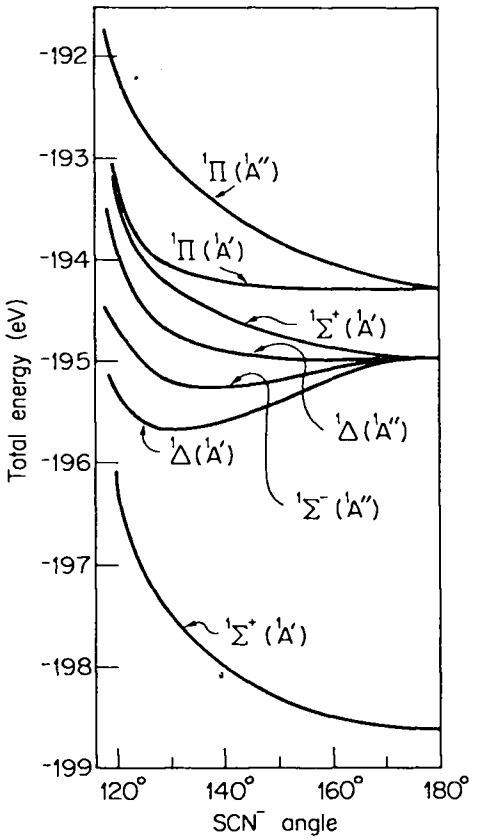

FIGURE 10. Total energies, $E = \sum_{\mu} n_{\mu}\varepsilon_{\mu}$, of various electron configurations of NCS^- as a function of $\measuredangle$ NCS. The eigenvalues ε_n are of an EHT nature.

conclusions is given in Figure 10 where the 'sum of orbital energies' for NCS^- is plotted as a function of $\measuredangle$ NCS. It is seen that the $^1A''$ state of $^1\Sigma^-$ parentage, the $^1A''$ state of $^1\Delta$ parentage and, possibly, the $^1A'$ state of $^1\Pi$ parentage are predicted to exhibit NCS bending. Since the EHMO approach does not distinguish between singlet and triplet states, the same set of predictions presumably obtains also for the triplet states.

The correlation of representations of $C_{\infty v}$ with those of the subgroup C_s is shown in Figure 11. Four main effects should be observed if bending occurs. These are:

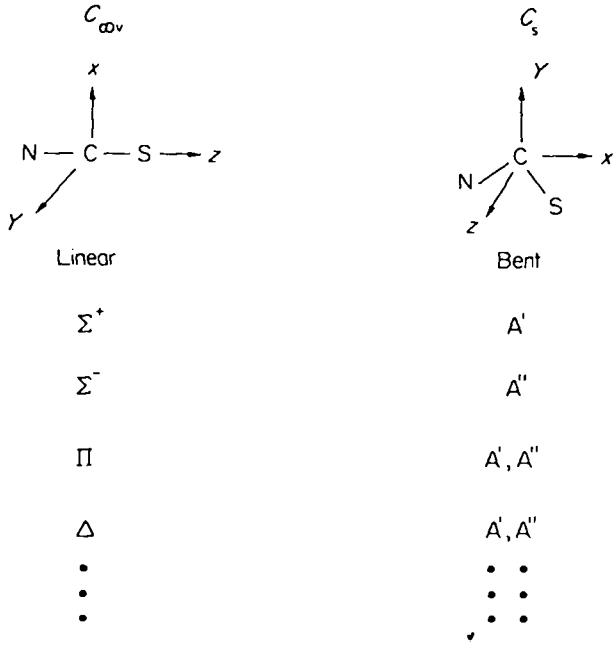

FIGURE 11. Correlation of representations between the point groups $C_{\infty v}$ and C_s.

(i) Transitions $^1M \leftarrow X^1\Sigma^+$, where $M = \Pi, \Delta, \Phi, \ldots$, will split into two transitions if the molecule is bent in the ^1M state.

(ii) Transitions which are forbidden in the linear molecule will become allowed in the non-linear case. The $^1\Delta \leftarrow X^1\Sigma^+$ transition, for example, splits into two transitions in C_s, $^1A'' \leftarrow X^1A'$ and $^1A' \leftarrow X^1A'$, both of them allowed.

(iii) If a given transition between linear and bent states is observed, it should consist of a long progression in the bending vibration, with considerable separation between vertical and adiabatic energies.

(iv) If a given transition between linear and bent states is observed in both emission and absorption, there should be a large Stokes shift between the vertical energies of the two radiative processes. If, on the other hand, both connecting states possess the same geometry and if the transition between them is allowed, the individual spectra should exhibit strong origin bands and the two origins, emission and absorption, should be coincident.

Linear polyatomic molecules of $C_{\infty v}$ type do not exhibit a Jahn–Teller effect. That is, the degenerate electronic states of these molecules do not split under the influence of a perturbation which is linear in the normal vibrational coordinates, Q_i. They may split, however, under the influence of a perturbation, Q_iQ_j, which is quadratic in the normal coordinates. Such splitting is known as the Renner effect[68]. Specifically, linear polyatomic molecules in degenerate electronic states may or may not distort by bending into more stable, non-degenerate states[69]. Thus, the $^1\Delta$ state may remain degenerate; may separate into two component states, both of which possess bent geometries which may or may not be identical; or may separate into two component states, one of which is bent and the other essentially linear[70]. The point of all of this is that the conclusions concerning bending or no-bending which are intrinsic to Figure 10 are in full accord with the spirit of the Renner effect.

7. Intensities of transitions

The only transitions of interest are those which terminate or initiate in the $X^1\Sigma^+$(ground) state. In the $C_{\infty v}$ point group, the only states which can combine radiatively with the ground state are $^1\Pi$ (x, y polarized) and $^1\Sigma^+$ (z polarized). If the molecule is bent in both combining states, all combinations with the ground state, namely $^1A' \leftrightarrow X^1A'$(ground) and $^1A'' \leftrightarrow X^1A'$(ground), are allowed. If the molecule is bent in only one of the combining states, the conclusions of the prior sentence still hold.

The numerical quantities which characterize the probability of a transition between two states are the molar decadic extinction coefficient ε, the oscillator strength f, and the lifetime of the upper state τ. The extinction coefficient is defined as

$$\varepsilon \equiv (1/cl)\log(I_0/I) \tag{15}$$

where c is the concentration in moles/litre, l is the absorbing path length and $\log(I_0/I)$ is the optical density. The oscillator strength is given by

$$f \equiv 4{\cdot}32 \times 10^{-9}\int \varepsilon(\bar{\nu})\,d\bar{\nu} \simeq 4{\cdot}32 \times 10^{-9}\varepsilon_{max}\bar{\nu}_{1/2} \tag{16}$$

where $\bar{\nu}$ is specified in cm^{-1} and $\bar{\nu}_{1/2}$ is the absorption half-band width. The radiative lifetime of the excited state may be obtained directly by decay studies combined with quantum yield measurements. It may also be obtained from absorption measurements by the relation

$$\tau = [0{\cdot}6632\,\bar{\nu}_e^2 f]^{-1} \tag{17}$$

where $\bar{\nu}_e$ is the energy of the emission maximum.

a. *Effects of matrix on transition intensities.* The molecules NCO^- or NCS^- may be studied readily only in solid or liquid phases. The charged nature of these entities induces considerable coupling with the matrix, liquid or solid, in which they are embedded. As a result, the distinction between solute and solvent vanishes and the NCS^- molecule is best considered to be NCS^- anion *plus* associated cations *plus* associated solvent molecules. In other words, the NCS^- ion may be quite a large polyatomic aggregate and must be treated in a 'large molecule' limit. By this we mean four things:

(i) The motions of the individual molecular components of the aggregate will contribute to any excitation/de-excitation event of the NCS^- ion and, as a result, the spectra will be expected to be diffuse.

(ii) These same motions will provide numerous individual pathways for non-radiative de-excitation of excited electronic states and, as a result, if the system emits any luminescence at all, it will do so only from the S_1 or T_1 (i.e., lowest energy excited singlet or triplet) states. This is known as Kasha's rule[71].

(iii) Because of these interactions, the spectra may vary considerably from matrix to matrix and may even exhibit transitions which depend for their existence on the presence of the matrix. A category of such transitions, known as 'Charge Transfer to Solvent' or CTTS transitions, has been discussed by Treinin[72].

(iv) Because of their large sizes, the Rydberg orbitals will sample the whole or part of the environment provided by the aggregate and will become energetically diffuse. This characteristic is embodied in a statement by Robin[73]: N–R transitions in condensed media will be either absent or, if present, will be very weak and diffuse.

b. *The relaxation of spin forbiddenness.* If we are to suppose, per the dictates of Figure 9, that the lowest-energy excited state of either NCO^- or NCS^- is of $^3\Sigma^+$ nature, we must conclude that the transition $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ is forbidden by electric dipole selection rules. In other words, this transition is spin-forbidden in the (Λ, Σ)-coupling limit. In the presence of some spin-orbital coupling, however, this state splits into two components, one of

which (Π) can combine radiatively with the ground state by normal electric dipole radiation. The other component, Σ^-, may not combine radiatively with the ground state, even in the (Ω, ω) limit, and, hence, will not be considered further.

In a group theoretic sense, the effect of spin-orbital coupling on the $^3\Sigma^+(\Pi)$ component is to mix into it small contaminations of $^3\Delta$, $^3\Sigma^-$ and $^1\Pi$. Since neither of the transitions $^3\Delta \leftrightarrow X^1\Sigma^+$ and $^3\Sigma^- \leftrightarrow X^1\Sigma^+$ carry any intensity, these contaminations, while real, do not contribute to the 'allowedness' of the $^3\Sigma^+ \leftarrow X^1\Sigma^+$ transition. However, the $^1\Pi$ state, which derives from the $4\sigma \rightarrow 3\pi$ MO promotion, remains Π in the double group and a slight contamination of this state in the nominal $^3\Sigma^+$ state can confer 'allowedness' on the nominal $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ transition simply because the process $^1\Pi \leftrightarrow X^1\Sigma^+$ is electric-dipole allowed. In this way, the $^1\Pi$ states may attain importance because of their significance to the intensity of the lowest energy $T_1 \leftrightarrow S_0$ absorption/emission properties of NCO^- and NCS^-.

The actual process of intensity conferral via spin-orbit interactions is complicated by the fact that nominal triplets may also mix into the $X^1\Sigma^+$ state and intensity may also be gained by this route. The totality of intensity conferring mixings is shown in Figure 12. Despite this complexity, it is

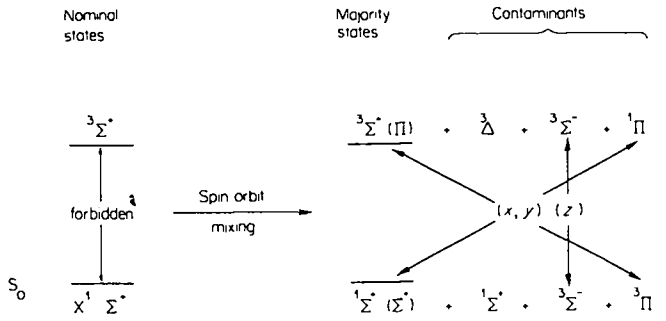

FIGURE 12. The process by which spin-orbit coupling confers intensity on a spin forbidden transition $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ of a linear NCO^- or NCS^- anion.

possible to draw a few straightforward conclusions without doing any computations whatsoever. These are:

(i) The coefficients of the contaminants which are admixed into the nominal states will be small. Hence, we may neglect the $^3\Sigma^- \leftrightarrow {}^3\Sigma^-$ z-polarized part since it is of 2nd order in these coefficients. Thus, the $S_0 \leftrightarrow T_1$ event will be (x, y) polarized.

(ii) The (x, y)-polarized components are stolen from allowed transitions which are of $\sigma \rightarrow \pi$ nature (i.e., $\perp$ in an MO excitation sense). All such events are usually of fairly low intensity. Hence, since that which may be 'stolen' is small, the 'stealing' cannot ever confer a massive 'allowedness' on the $T_1 \leftrightarrow S_0$ event. In other words, the $T_1 \rightarrow S_0$ event (i.e., phosphorescence) will have a rather long lifetime[65], $\tau_P \simeq 1$ sec.

(iii) We now note the one-electron nature of the individual components, $\mathscr{A}_i \vec{l}_i \cdot \vec{s}_i$, of the spin-orbit operator and the extra restrictions which this imposes on the contaminant states of Figure 12. Specifically, any nominal triplet state which mixes with the $X^1\Sigma^+$ state must be of the representation species listed in Figure 12 and, additionally, may differ from the configurations intrinsic to the nominal $X^1\Sigma^+$ state by no more than a single electron excitation or de-excitation. These considerations induce considerable simplification into the process of spin-orbital coupling computations.

B. Computational

1. Anions

The results of a CNDO/s-CI computation[53] for NCO^- are shown in Figure 13. Unfortunately, the CNDO approximation is rather drastic and, in the case of a very symmetric molecule such as NCO^-, it can lead to results which are not only wrong numerically but even wrong physically. For example, CNDO/s-CI intensities for the allowed $^1\Pi \leftarrow X^1\Sigma^+$ transitions are all arbitrarily set equal to zero because the transition in question is out-of-plane [i.e., $z \rightarrow (x, y)$] and transition moments of the type $(p|\vec{r}|q)$, where $(p, q) = (x, y, z)$, are taken to be zero unless $p = q$. Hence, the $^1\Pi \leftarrow X^1\Sigma^+$ intensities of Figure 13 were computed by methods outlined in McGlynn and coworkers[66]. The CNDO approximation also neglects exchange integrals of type $(zq|qz)$, $q \neq z$; consequently, all $^1\Pi$ states are computed to be degenerate with their configurationally related $^3\Pi$ states.

However, it is in the lower energy excited states that the CNDO approximations can lead to drastic discrepancies. The net effect of the approximation is to set the integrals C and D of equation (14) either to zero or very close to zero. As a result, the states $^1\Sigma^-$ and $^1\Delta$ are found to be more or less degenerate. Indeed, unless one pays close attention to the forms of the properly symmetry-adapted functions of Table 8a, one could even choose the wrong components for the $^1\Delta$ state. Furthermore, the same dilemma also occurs for the $^3\Sigma^-$ and $^3\Delta$ states and must be sorted out using the results of Table 8a.

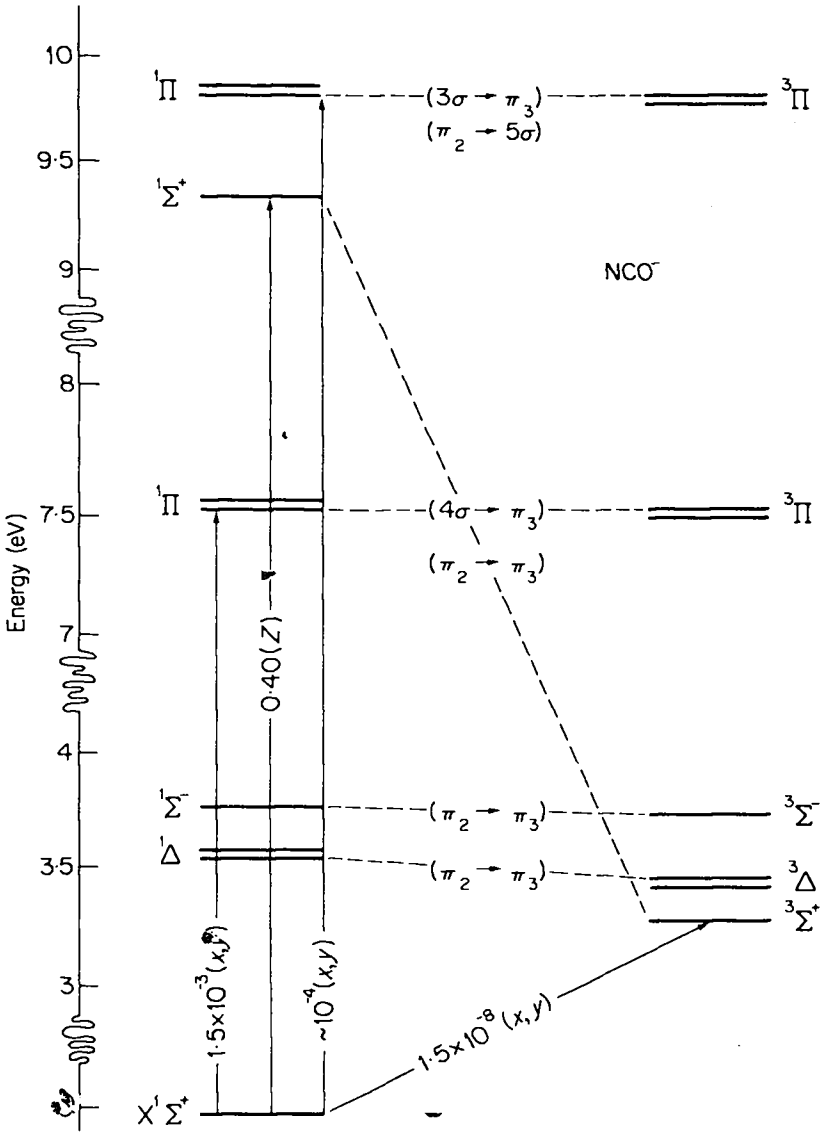

FIGURE 13. Energy levels and transition moments for the NCO^- anion. Energies were obtained from a CNDO/s-CI computation but were modified to take some account of electron repulsion integrals which are neglected in the CNDO approximation. Transition moments for the $^1\Pi \leftrightarrow X^1\Sigma^+$ and $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ transitions were evaluated as described in the text.

Inspection of the symmetry-adapted functions of Table 8a (in a $\{p_x, p_y, p_z\}$ basis) yields some interesting conclusions. The $^1\Sigma^+$, $^3\Sigma^+$, and one component of each of the (spatially) doubly degenerate $^1\Delta$ and $^3\Delta$ states are composed of parallel excitations (that is, excitations between two component MO's which are mutually parallel, $2\pi_x \rightarrow 3\pi_x$ or $2\pi_y \rightarrow 3\pi_y$). It is for this reason that the CNDO approximation provides a proper rendering of the large $^1\Sigma^+ - {}^3\Sigma^+$ splitting and a partial, but incomplete, rendering of the $^1\Delta - {}^3\Delta$ splitting.

The CNDO approximation sets many integrals to zero simply because they are small. As discussed, this can lead to serious error. On the other hand, it can also be turned to advantage. For example, based on the concept of parallel and perpendicular MO transition types discussed above and on the CNDO approximation, we can conclude that the pattern of intensities outlined in Table 9 will hold in any point group in which the given transitions are symmetry allowed. Thus, in the C_s point group, where transitions to the $^1A'$ and $^1A''$ components of the parent $^1\Delta$ state are both allowed, the $^1A' \leftarrow X^1A'$ transition will be the more intense. In fact this transition should be considerably more intense than transitions to either of the $^1A'$ or $^1A''$ components of the $^1\Pi$ state (to which transitions were allowed in $C_{\infty v}$).

TABLE 9. Transition intensities expected between states of $C_{\infty v}$ parentage in any molecular point group in which the transition in question becomes allowed

Transition	MO excitation type	Intensity
$^1\Sigma^- \leftarrow X^1\Sigma^+$	$\perp$	Weak
$^1\Delta(^1A') \leftarrow X^1\Sigma^+$	//	Strong
$^1\Delta(^1A'') \leftarrow X^1\Sigma^+$	$\perp$	Weak
$^1\Sigma^+ \leftarrow X^1\Sigma^+$	//	Strong
$^3\Sigma^+ \leftarrow X^1\Sigma^+$	//	Very weak[a]
$^1\Pi \leftarrow X^1\Sigma^+$	$\perp$	Weak

[a] Since this transition is // it may only obtain first-order intensity by 'stealing' from those $S_0 \rightarrow S_i$ and $T_1 \rightarrow T_j$ transitions which are of $\perp$ type. Since these types of transition are always weak, it follows that $S_0 \rightarrow T_j$ transitions of // type will always be considerably weaker ($\times 10^{-3}$ or so) than $S_0 \rightarrow T_j$ transitions of $\perp$ type[65].

The oscillator strength f of the $^3\Sigma^+ \rightarrow X^1\Sigma^+$ transition was computed by methods outlined by Vanquickenborne and coworkers[74]. This value of f corresponds to a phosphorescence lifetime of $\sim 0{\cdot}1$ sec.

2. Molecules

The molecules of interest belong to one of the C_{2v} or C_s point groups. Pertinent examples are phenyl isocyanate (probably C_{2v}), isocyanic acid (C_s) and methyl isocyanate (nearly C_s). The manner in which the electronic states of these compounds correlate with each other and with those of NCO^- is shown in Figure 14.

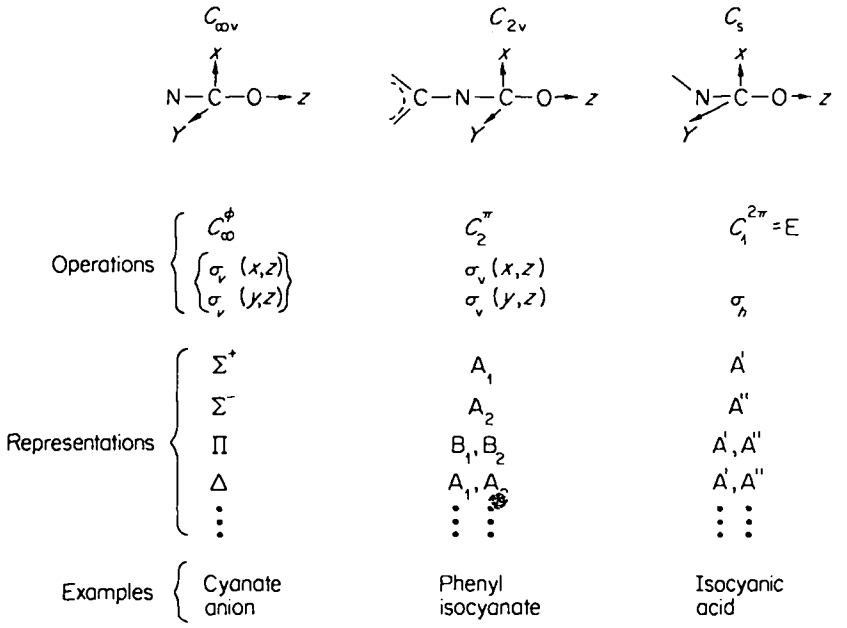

FIGURE 14. Correlation of representations between the point groups $C_{\infty v}$, C_{2v} and C_s.

a. *Isocyanic acid, HNCO.* The spectroscopic effects of adding a proton to NCO^- to form HNCO are numerous. They will be best appreciated by referring to the energy level diagram of Figure 15. The results contained in this Figure were obtained by CNDO/s-CI, spin-orbit coupling and transition dipole length computations.

(i) Degeneracies Π, Δ, Φ, etc. will split. The $^1\Delta$ state, for example, is computed to exhibit a split of ~ 1 eV in HNCO.

(ii) The 4σ bonding MO becomes more bonding and, consequently, the components of the $^1\Pi$ state move to considerably higher energy (i.e., by ~ 2 eV). It is now predicted to lie above the $^1\Sigma^+(^1A')$ state whereas in NCO^- the $^1\Pi$ state lies below the $^1\Sigma^+$ excited state.

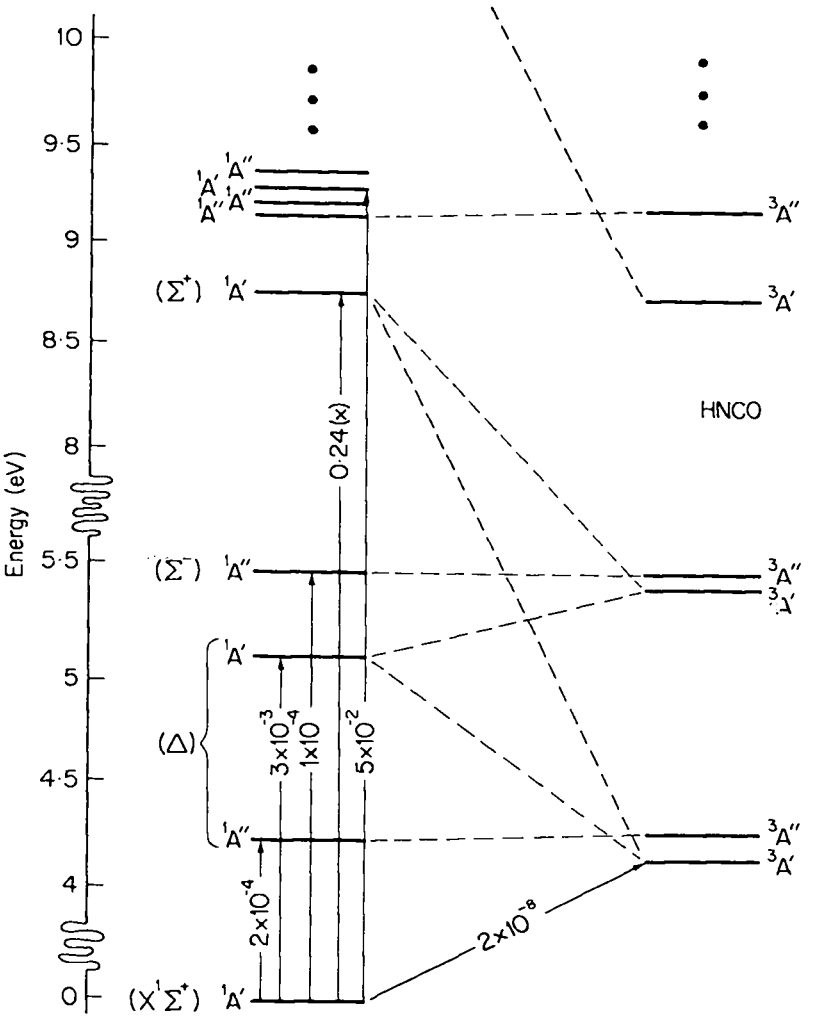

FIGURE 15. Energy levels and transition moments for the HNCO molecule. Energies were obtained from a CNDO/s–CI computation but were modified to take some account of electron repulsion integrals which are neglected in the CNDO approximation. Transition moments for the $^1\Pi \leftrightarrow X^1\Sigma^+$ and $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ transitions were evaluated as described in the text.

(iii) The lower energy excited states shift to higher energy presumably because of the electron acceptor properties of the attached proton. The higher energy $^1\Sigma^-(^1A')$ state moves to lower energy because of the increased CI in the lower-symmetry point group.

(iv) All transitions of $S_0 \rightarrow S_i$ type are now allowed. The intensity characteristics outlined in Table 9 apply generally. The intensity of the $S_0 \rightarrow T_1$ transition is, as expected, essentially unaltered.

(v) The question of bending of the NCO group in the excited states of HNCO has been investigated. The conclusions obtained are essentially identical to those of Figure 1 for NCS^- and Rabalais and coworkers[75] for the isoelectronic CO_2 molecule.

b. *Methyl isocyanate, CH_3NCO.* The computed energy level diagram of CH_3NCO is shown in Figure 16. The methyl group is a better electron donor than hydrogen and the energies of the lower excited states are all less than those of HNCO. The intensity of the $^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition of NCO^- is predicted to decrease in the order $CH_3NCO < HNCO < NCO^-$. This decrease is largely due to CI mixings in the point groups of lower symmetry.

Apart from these few differences, the energy level scheme is basically the same as that for HNCO.

c. *Phenyl isocyanate, C_6H_5NCO.* Computations on phenyl isocyanate indicate that the excited states of this molecule behave more like a substituted benzene than an arylated isocyanate (cf. Figure 5).

The lowest-energy singlet state is best classified as $^1\Gamma_{\pi\pi^*}$ (i.e., $n \rightarrow \pi^*$). This S_1 state is predicted to occur at 3·95 eV and to be charge transfer in nature. The $S_0 \rightarrow S_1$ transition is associated with a transfer of ~0·6 electron charge density of p_σ type from the NCO group to a π MO of the phenyl group.

The S_2 and S_3 states are best identified as ^1L_b and ^1L_a states, respectively. As such, the transitions to them, not surprisingly, are predicted to be weak and strong, respectively[76].

The lowest triplet state is predicted to be largely benzenoid and to be of ^3L_a type[76].

C. Experimental

1. Singlet–triplet absorption and emission

All theoretical approaches indicate the presence of two low-energy triplet states, $^3\Sigma^+$ and $^3\Delta$ (or a component of the latter), in all cyanates and thiocyanates, the phenyl derivative excepted. Of these, the transition to the $^3\Sigma^+$ state, $^3\Sigma^+ \leftarrow X^1\Sigma^+$, is predicted, by all computational avenues, to be of lower energy. A précis of the expected oscillator strengths and emission lifetimes for the two radiative processes, $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ and $^3\Delta \leftrightarrow X^1\Sigma^+$, is given in Table 10. The conclusions which follow from this Table are quite

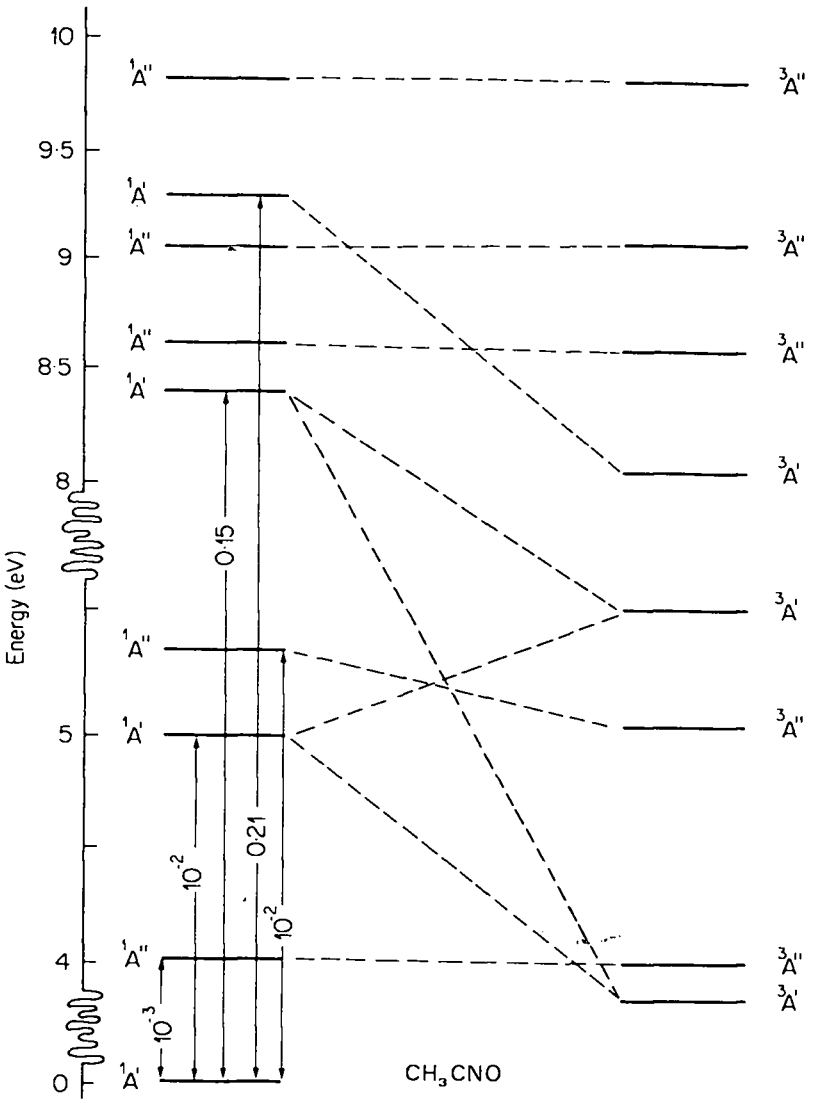

FIGURE 16. Energy levels and transition moments for the $CH_3N\dot{C}O$ molecule. Energies were obtained from a CNDO/s–CI computation but were modified to take some account of electron repulsion integrals which are neglected in the CNDO approximation. Transition moments for the $^1\Pi \leftrightarrow X^1\Sigma^+$ and $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ transitions were evaluated as described in the text.

straightforward: Oscillator strengths will lie in the range 1×10^{-8}–5×10^{-7} and will be approximately 30-times more intense for the $^3\Delta \leftrightarrow X^1\Sigma^+$ process than for the $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$ process.

TABLE 10. Calculated emissive lifetimes and oscillator strengths for two low-energy triplet ↔ singlet transitions in cyanates and thiocyanates[a]

Anion	State	Geometry (∢ NCA)	$f(\times 10^8)$	τ_P(sec)	Polarization
NCO^-	$^3\Sigma^+$	180°	1·5	$1{\cdot}3 \times 10^{-1}$	z
	$^3A'(^3\Delta)$	129°	1·8	$1{\cdot}1 \times 10^{-1}$	z
	$^3A''(^3\Delta)$	129°	48	$4{\cdot}4 \times 10^{-3}$	y
NCS^-	$^3\Sigma^+$	180°	18	$1{\cdot}1 \times 10^{-2}$	z

[a] These computational results are taken from References 77 and 78. The computations in the 2nd and 3rd rows refer to bent NCO^-. The computations of the 1st row for NCO^- (180°) are unaffected by bending for $180° \geq$ ∢NCO $\geq 129°$.

The lowest energy $T_1 \leftrightarrow S_0$ event in phenyl derivatives is best described as a process characteristic of the phenyl group with but little amplitude (~25%) on the NCO or NCS attachments. In the Platt notation, this transition is designated $^3L_a \leftrightarrow {}^1A$ and is computed[77] to have an emissive lifetime $\tau_P \simeq 5$ sec ($f \simeq 0{\cdot}04 \times 10^{-8}$). It is doubtful that a state of such low oscillator strength would be detectable in absorption studies.

The long wavelength absorption spectra of some cyanates are shown in Figure 17. Many of these exhibit a low intensity absorption band in the 300 nm region. The oscillator strengths of this weak absorption region are collected in Table 11 whence, by comparison with Table 10, it is clear that the intensities fall squarely in the range predicted for $^3\Delta \leftarrow X^1\Sigma^+$ and $^3\Sigma^+ \leftarrow X^1\Sigma^+$ transitions. It is also obvious that the agreement with the predictions is almost exact for a $^3\Delta(^3A'')$ assignment.

The 300 nm absorption region is assuredly of $T_i \leftarrow S_0$ nature. This conclusion follows for three reasons:

(i) In systems as complex as those of Figure 17, all $S_j \leftarrow S_0$ processes, regardless of how forbidden they might be in the isolated $C_{\infty v}$ NCO^- ion, can readily obtain intensity by vibronic means. In other words, deviations from Born–Oppenheimer conditions can readily induce absorption intensities of the order of $\varepsilon \simeq 100$ and will not usually allow ε to be less than unity for any $S_j \leftarrow S_0$ transition, regardless of how forbidden it might be. Thus, the extinction coefficients found in the 300 nm region are concluded to be too small for identification as an $S_j \leftarrow S_0$ transition, forbidden or otherwise.

(ii) The intensities of the 300 nm transition exhibit a 'heavy atom' effect. Lead, for example, is a system in which spin-orbital coupling effects are extremely large. Consequently, when the lead cation associates with NCO^- and the electrons disperse over the whole of the $Pb(NCO)_2$ complex, the

TABLE 11. Experimental data for lowest energy absorption and emission processes, $^3\Sigma^+ \leftrightarrow X^1\Sigma^+$, in cyanates[77,79] and thiocyanates[78]

System	Absorption λ_{max}(nm)	Absorption $f \times 10^7$	Absorption τ_P(sec)	Phosphorescence λ_{max}(nm)	Phosphorescence τ_P(sec)
NaOCN	300	1·3	$1·0 \times 10^{-2}$	406	$2·1 \times 10^{-1}$
KOCN	300	1·2	$1·1 \times 10^{-2}$	425	$3·7 \times 10^{-1}$
$Cd(NCO)_2$	295	9·5	$1·4 \times 10^{-3}$	425	$10^{-1} - 10^{-2}$
$Hg(NCO)_2$	285	9·8	$1·4 \times 10^{-3}$	460	3×10^{-2}
$Pb(NCO)_2$	300	95	$1·4 \times 10^{-4}$	490	7×10^{-3}
HNCO	—	—	—	430	—
CH_3NCO	—	—	—	418	2·05
C_6H_5NCO	—	—	—	387	3·15
KSCN	>300	<0·2	$<3 \times 10^{-1}$	440	$3·1 \times 10^{-1}$
$Zn(NCS)_2$	350	16	$2·5 \times 10^{-3}$	460	$4·4 \times 10^{-1}$
$Cd(NCS)_2$	320	~2·0	3×10^{-2}	450	$3·9 \times 10^{-1}$
AgNCS	—	—	—	400, 550	6×10^{-3}
$Pb(NCS)_2$	—	—	—	~450	5×10^{-3}

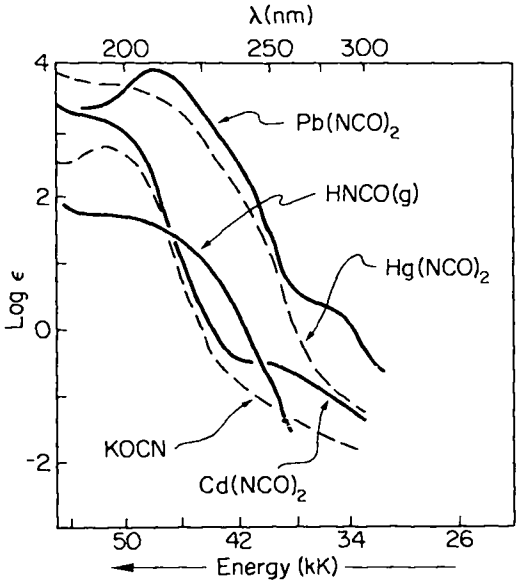

FIGURE 17. Low-energy electronic absorption spectra of some cyanates. This figure is adapted from Figure 1 of Rabalais, McDonald, and McGlynn[79]. One kiloKayser, 1 kK, equals $1000\,cm^{-1}$.

large spin orbital coupling on the Pb centre will relax the forbiddenness of all $T_i \leftrightarrow S_0$ processes and increase their absorption probabilities. Effects of this sort are very well-known and are used as diagnostics of spin intercombination events[65] and, even in analytical chemistry, as a means of enhancing the sensitivity of phosphorimetric techniques[80,81]. Such effects are particularly evident not only in cyanates but also in thiocyanates and have been developed into a viable theory of colour in all post-transition metal salts[82].

(iii) Most of these compounds exhibit a $T_1 \rightarrow S_0$ phosphorescence. Data on this phosphorescence are also collected in Table 11. The observed lifetimes, while generally longer than those computed from the absorption data are in excellent agreement with the spin-orbit coupling computations for the $^3\Sigma^+ \rightarrow X^1\Sigma^+$ transition.

Phosphorescence and phosphorescence excitation spectra for a variety of cyanates are shown in Figures 18 and 19. Since the phosphorimetric technique is beset with difficulties attributable to the presence of impurities, it is well to emphasize that the observed phosphorescences are intrinsic to the NCO moiety. The evidence for the intrinsic nature derives from the commonality of the luminescence (i.e., it is found in all salts as well as in HNCO and alkyl isocyanates) and from the vibrational progression in the symmetrical NCO^- stretching mode which is observed[77] in the luminescence of NaOCN.

The phosphorescence spectra of Figures 18 and 19 and the $T_j \leftarrow S_0$ absorption regions of Figure 17 exhibit Stokes shifts which, in some instances, are of the order of 1·2 eV. This is a rather large Stokes shift for two events presumed to be related as $T_1 \rightarrow S_0$ and $T_1 \leftarrow S_0$, respectively. The situation can be salvaged by assuming that the $T_1(^3\Sigma^+)$ state is bent whereas the $S_0(X^1\Sigma^+)$ state is linear, and that emission and absorption processes initiate in states of different geometry. Unfortunately, were this so, the phosphorescence event in NaOCN would be expected to be very much broader than it actually is, and to exhibit a long progression in the vibrational bending mode, which it does not. In view of these discrepancies, it seems better to assume that the $^3\Delta(^3A'') \leftarrow X^1\Sigma^+$ absorption event (i.e., the $T_2 \leftarrow S_0$ event) is responsible for the 300 nm absorption band of Figure 17. Certainly, this identification yields better accord between experimental and calculated absorption intensities than does the $^3\Sigma^+ \leftarrow X^1\Sigma^+$ assignment. It also rationalizes the diffuse nature of the 300 nm absorption band: The $^3\Delta$ state should split into two components by bending and one of these, the $^3A''$ state, should carry much of the intensity resident in the $T_2 \leftarrow S_0$ transition.

The $^3\Sigma^+$ state must now be located somewhere in the 300–400 nm region.

The weak intensity of the $^3\Sigma^+ \leftarrow X^1\Sigma^+$ transition (~ 30 times less than that of the $^3\Delta \leftarrow X^1\Sigma^+$) will make it difficult to observe. This assignment rationalizes the large Stokes shift: The 1·2 eV shift corresponds to an energy

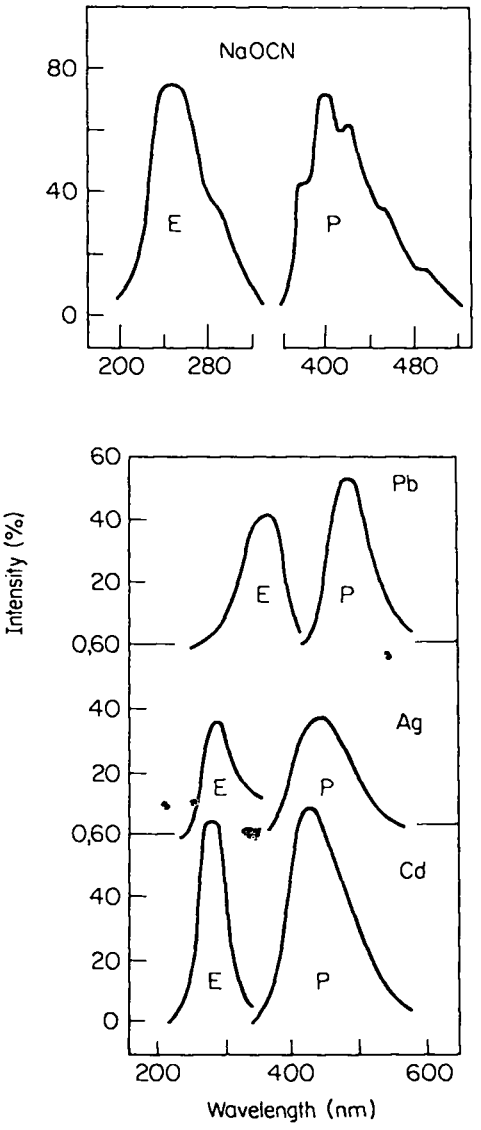

FIGURE 18. Phosphorescence (P), $T_1 \rightarrow S_0$, and phosphorescence excitation spectra (E) for a variety of ionic and covalent cyanate salts. This figure is adapted from Figures 1 and 2 of Rabalais, McDonald, and McGlynn[77].

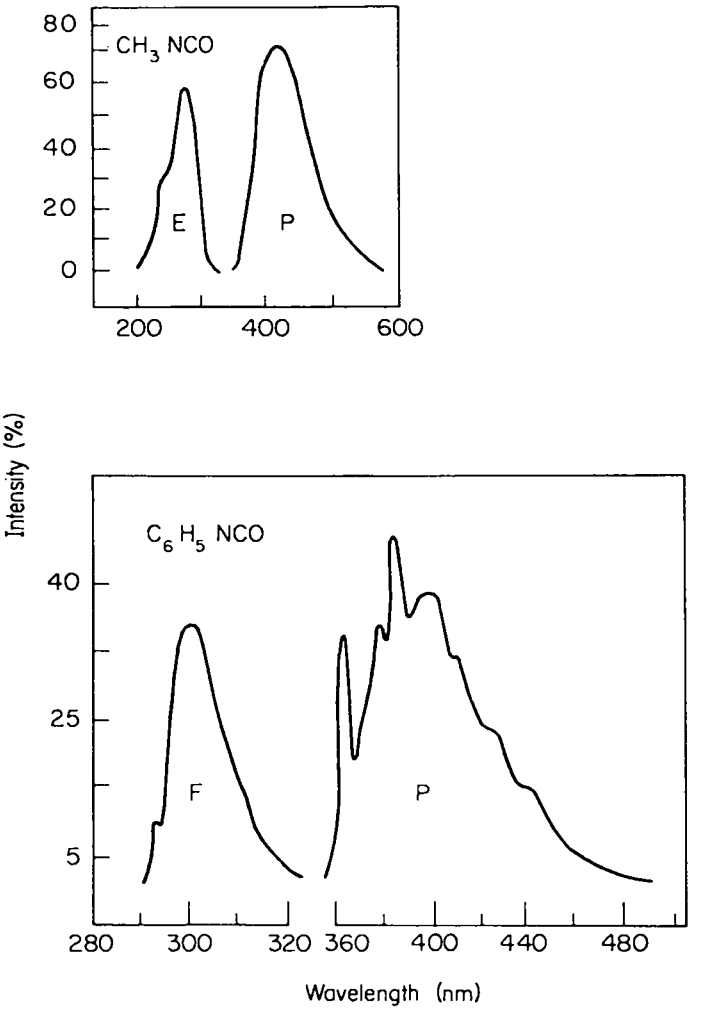

FIGURE 19. Phosphorescence (P), $T_1 \rightarrow S_0$, phosphorescence excitation (E), and fluorescence (F), $S_1 \rightarrow S_0$, spectra for CH_3NCO and C_6H_5NCO. This figure is adapted from Figures 3 and 4 of Rabalais, McDonald and McGlynn[77].

difference between $^3\Delta$ and $^3\Sigma^+$ states and, hence, is of no concern. It also rationalizes the discrepancy between lifetimes measured by phosphorimetric techniques and those estimated from the absorption data (Table 11).

Phenyl isocyanate (Figure 19) emits both fluorescence and phosphorescence. The emission spectra typify those of a substituted benzenic entity. The fluorescence is a standard benzenic $^1L_b \rightarrow {}^1A$ process and the phos-

phorescence is a standard $^3L_a \rightarrow {}^1A$ process. The lifetime of the phosphorescence, 3·15 sec, is typical for $^3L_a \rightarrow {}^1A$ processes and much of the observed vibrational activity occurs in modes internal to the phenyl moiety. However, some vibrational activity in modes internal to the NCO attachment is also observed, indicating a mixing of excited states of the two moieties, phenyl and NCO. Nevertheless, the ^3L_a attribution remains the best assignment.

No discussion of the parent $^3\Sigma^-$ state of any cyanate or thiocyanate has been given. The $^3\Sigma^-$ state is degenerate with the $^1\Sigma^-$ state in $C_{\infty v}$ and it is not expected that $^3\Sigma^- \leftarrow X^1\Sigma^+$ processes will be observable: They cannot compete with the more probable $^1\Sigma^- \leftarrow X^1\Sigma^+$ absorption processes which will occur in the same, or closely similar, energy region.

A synopsis of triplet state assignments is given in Figure 20, where also are shown the absorption/emission events upon which these assignments are based. A considerable body of data concerning thiocyanates is available[78] and has been used to construct the rightmost level scheme of Figure 20.

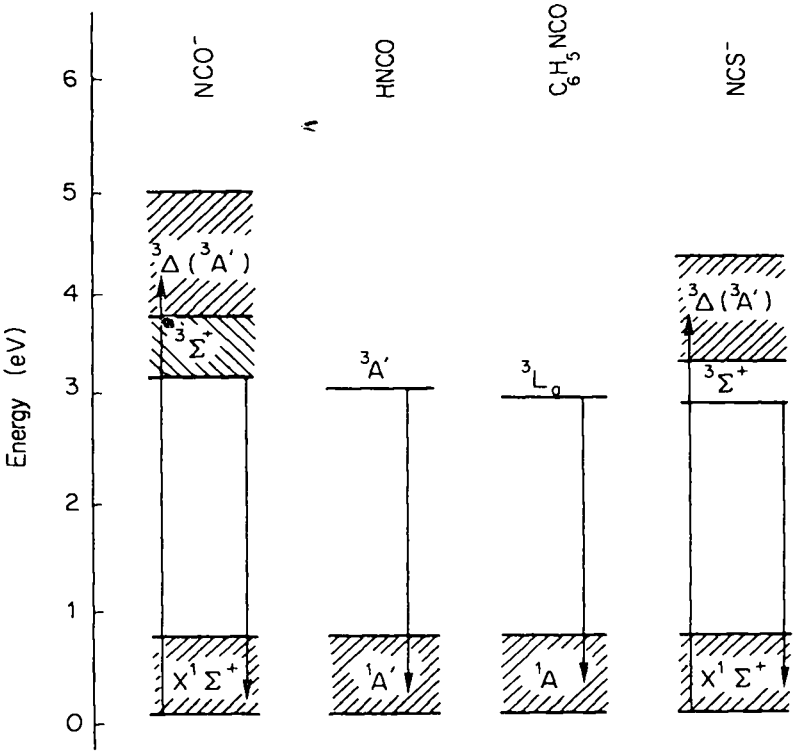

FIGURE 20. Triplet state assignments in cyanates and thiocyanates.

The 280–220 nm absorption region has been investigated by Dixon and Kirby[83] in HNCO and DNCO, and by Woo and Liu[84] in alkyl isocyanates. Dixon and Kirby observed long series of weak vibrational members in the NCO bending mode initiating in origins at 2813 and 2624 Å, respectively. They concluded that the excited state was planar but severely bent, $119° \leq \measuredangle \text{NCO} \leq 129°$, with a double minimum, one in the *trans* and one in the *cis* configuration. The transition was assigned as $^1A'' \leftarrow X^1A'$ on the basis of the out-of-plane polarization of the transition moment. However, in view of the low extinction coefficient, $10^{-2} \geq \varepsilon \geq 10^{-3}$, Rabalais and coworkers[79] prefer a $^3A' \leftarrow X^1A'$ assignment. It is difficult to say which one of these two assignments is correct.

2. Singlet excited states

The u.v. absorption spectra of some cyanates are given in Figure 17. The v.u.v. absorption spectra of NCO^- and C_2H_5NCO are shown in Figure 21; that of HNCO is given in Figure 22. These spectra constitute almost all the data available for the $S_j \leftarrow S_0$ transitions of cyanates. This scarcity of

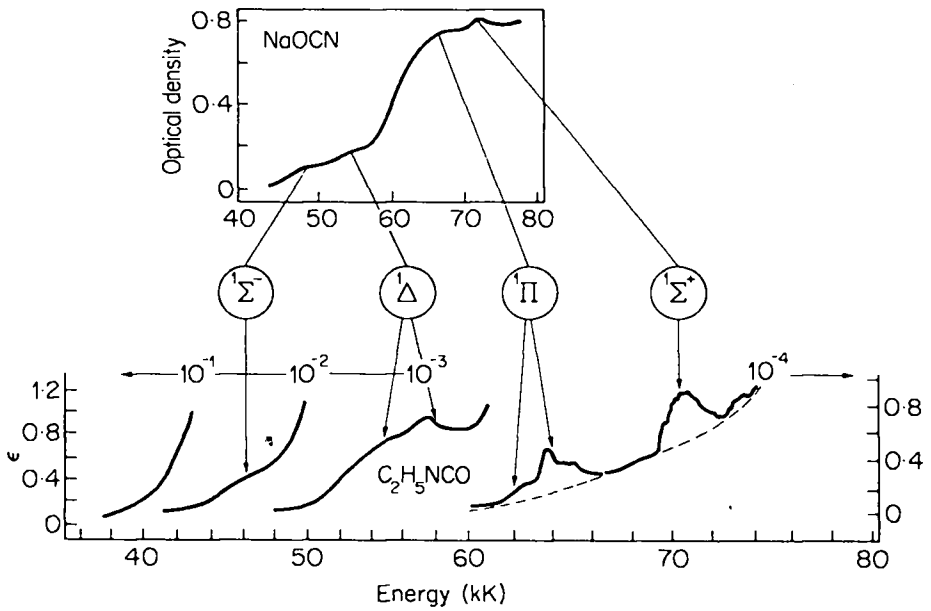

FIGURE 21. Absorption spectra of a thin film of NaOCN and of gaseous C_2H_5NCO. These spectra are adapted from Figures 2 and 3 of Rabalais, McDonald and McGlynn[79]. One kiloKayser, 1 kK, equals 1000 cm^{-1}.

spectra would be tolerable if each spectrum was of high quality. Unfortunately, this is not the case. These spectra, for reasons we will now discuss, are all inadequate in one way or another.

The spectrum of the NCO^- ion is that of a thin film of NaOCN. The supposition that one may treat the NCO^- ion as being in a $C_{\infty v}$ environment is certainly wrong. The correct point group is determined by the symmetry of the site at which the anion is located in the thin film, and this is not known. In addition, since this is a solid state spectrum, it may exhibit optical transitions which cannot occur in the gas phase (i.e., exciton and defect spectra) and it may not exhibit certain optical transitions which do occur in the gas phase (i.e., Rydberg transitions). Hence, the specification of a $C_{\infty v}$ symmetry for NCO^- and the blithe statement that this spectrum refers to an isolated NCO^- entity are assumptions.

The gas phase spectrum of C_2H_5NCO (Figure 21) probably refers to a C_1 and not a C_s species. In addition, the quality of this spectrum is poor. The rising background absorption, as shown by the dashed line, is a sure indicator of poor spectrometric photon throughput and, hence, poor resolution. Finally, the absence of absorption bands which might, with some assurance, be assigned as Rydberg transitions is disturbing. This spectrum requires remeasurement and it should be supplemented, at least, by those of CH_3NCO and SiH_3NCO. Hence, the specification of C_s symmetry for the gaseous molecule and the assertion that the spectrum of Figure 21 represents a 'real' spectrum of C_2H_5NCO are assumptions.

The spectrum of HNCO (Figure 22), though apparently of good quality for $\lambda \leq 160$ nm, is unsatisfactory for $170 \leq \lambda < 200$ nm. The low-intensity transitions which should lie at $\lambda > 170$ nm, the $^1\Sigma^- \leftarrow X^1\Sigma^+$ and $^1\Delta \leftarrow X^1\Sigma^+$ analogues in the C_s point group, have not been observed. This spectrum was not measured at adequately high HNCO pressures and the $\lambda > 170$ nm region has not been scanned at appropriate optical density. This spectrum should also be re-measured.

The molecular point groups of these molecules are $C_{\infty v}(NCO^-)$, $C_s(HNCO)$ and 'primitive' $C_s(C_2H_5NCO)$. The correlation table between states of $C_{\infty v}$ and C_s species is given in Figure 11. The electric dipole allowedness and forbiddenness properties of the various $S_j \leftarrow S_0$ transition are catalogued in Table 12.

a. *Intravalence (or $V \leftarrow N$) transitions.* With the above reservations in mind, we now proceed to interpret the spectra. The arguments follow those of Rabalais and coworkers[79], and this source should be consulted for details.

One may now use Table 12 in order to make distinction between the various transition types. The process is straightforward.

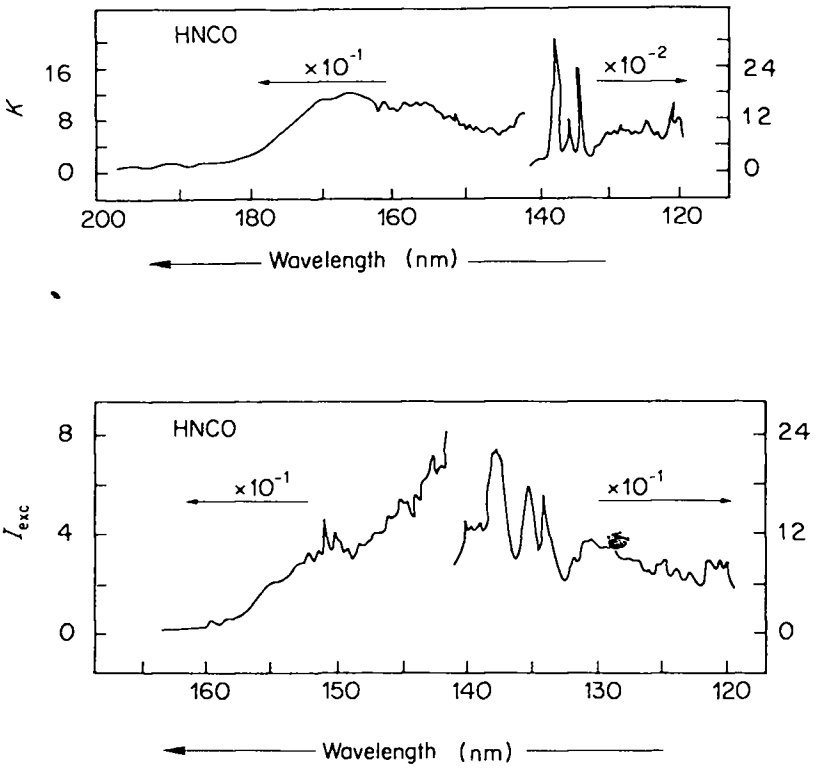

FIGURE 22. Absorption spectrum (top) of gaseous HNCO and excitation spectrum (bottom) of the $A^2\Sigma$ fluorescence of the NCO radical. Apart from intensity variations, both spectra are identical. The absorption coefficient, k, is defined as $k = (1/pl)\log I/I_0$ where p is pressure in atm. This figure is adapted from Figures 1 and 4 of Okabe[85].

TABLE 12. Allowedness (a) or forbiddenness (f) of $S_j \leftrightarrow S_0$ transitions in $C_{\infty v}$ and C_s point groups and the manner in which they correlate

$S_j(C_{\infty v})$	f/a	$S_j(C_s)$	f/a	Number of transitions
$^1\Sigma^-$	f	$^1A''$	a	1
$^1\Delta$	f	$^1A'$, $^1A''$	a, a	2
$^1\Sigma^+$	a	$^1A'$	a	1
$^1\Pi$	a	$^1A'$, $^1A''$	a, a	2

For example, of the two allowed $S_j \leftarrow S_0$ transitions in the $C_{\infty v}$ point group, the $^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition, being of // MO excitation type, should be more intense than the $^1\Pi \leftarrow X^1\Sigma^+$ transition, which is of $\perp$ MO excitation type. Furthermore, the former transition should not split whereas the latter should split into two non-degenerate components in C_s. Distinction between the two forbidden $^1\Sigma^- \leftarrow X^1\Sigma^+$ and $^1\Delta \leftarrow X^1\Sigma^+$ transitions of the linear molecule can be predicated upon observing the splitting of the latter by reducing the symmetry.

The assignments of Figure 21 were made using arguments such as the above. These assignments, and the data used in making them, are given in Table 13. It is clear that the assignments of Figure 21 and Table 13 are based on a large number of questionable inferences. Some of these are:

(i) It was assumed that the spectra of Figure 21 were totally of intravalence (V ← N) nature. While this is probably true for the thin film, it may be wishful thinking to suppose that it is also true for the gaseous sample.

(ii) The transition which is identified as $^1\Sigma^- \leftarrow X^1\Sigma^+$ has $\varepsilon \simeq 650$ in NCO^- and $\varepsilon \simeq 60$ litre mol^{-1} cm^{-1} in C_2H_5NCO. While the latter value of ε is in line for a forbidden $S_j \leftarrow S_0$ event, the former does seem to be a bit large. Thus, the assertions that both transitions are related, and that both are electric dipole forbidden, have little basis in fact.

(iii) The 8·43 eV absorption band of NaOCN is assigned as $^1\Pi \leftarrow X^1\Sigma^+$. The evidence for this assignment consists of the apparent allowedness of the 8·43 eV band ($\varepsilon = 5310$) and the supposition that it splits into two bands in C_2H_5NCO, 7·80 eV ($\varepsilon = 2200$) and 7·93 eV ($\varepsilon = 4800$ litre mol^{-1} cm^{-1}). The only type of transition which can exhibit such behaviour is a $^1\Pi \leftarrow X^1\Sigma^+$ transition—hence, the assignment. The defects in this assignment are two-fold: Firstly, the $^1\Pi \leftarrow X^1\Sigma^+$ transition is $\perp$, in the MO promotion sense which was used to construct Table 9, and the observed intensities appear somewhat large for such an assignment; and, secondly, the $^1\Pi \leftarrow X^1\Sigma^+$ transition is predicted (see Figures 15 and 16) to lie at higher energies than the $^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition.

(iv) Objections similar to those of items (ii) and (iii) may be raised with respect to all assignments of Figure 21.

The data base for the thiocyanates is virtually non-existent. It consists of a number of solution spectra which have been reported by McDonald and collaborators[78] and the gas phase spectrum of HNCS (Figure 23) which is taken from the same source. Assignments are cited in Figure 23 for the two bands of HNCS. These assignments are based on arguments given by McDonald and coworkers[78]. They are unconvincing.

TABLE 13. Experimental data and assignments for the singlet electronic states of NCO^- and CH_3CH_2NCO

	Linear $NCO^-(C_{\infty v})$					$CH_3CH_2NCO(C_s)$					
Configuration	State	Energy (eV)	ε_{max}	Oscillator strength	Polarization	State	Energy (eV)	ε_{max}	Oscillator strength	Polarization	NCO angle
$\ldots(2\pi)^4$	$^1\Sigma^+$	0·0	—	—	—	$^1A'$	0·0	—	—	—	Linear
$\ldots(2\pi)^3(3\pi)$	$^1\Sigma^-$	6·36	650	$2{\cdot}25 \times 10^{-2}$	f	$^1A''$	5·95	60	$2{\cdot}07 \times 10^{-3}$	z	Bent
$\ldots(2\pi)^3(3\pi)$	$^1\Delta$	6·92	$1{\cdot}19 \times 10^3$	$4{\cdot}11 \times 10^{-2}$	f	$^1A''$	6·82	680	$2{\cdot}35 \times 10^{-2}$	z	Bent
						$^1A'$	7·13	870	$3{\cdot}00 \times 10^{-2}$	x,y	Linear
$\ldots(4\sigma)^1(2\pi)^4(3\pi)$	$^1\Pi$	8·43	$5{\cdot}31 \times 10^3$	$1{\cdot}83 \times 10^{-1}$	x,y	$^1A''$	7·80	$2{\cdot}2 \times 10^3$	$7{\cdot}60 \times 10^{-2}$	z	Bent
						$^1A'$	7·93	$4{\cdot}8 \times 10^2$	$1{\cdot}66 \times 10^{-1}$	x,y	Linear
$\ldots(2\pi)^3(3\pi)$	$^1\Sigma^+$	9·17	$5{\cdot}74 \times 10^3$	$1{\cdot}98 \times 10^{-1}$	z	$^1A'$	8·77	$8{\cdot}8 \times 10^3$	$3{\cdot}04 \times 10^{-1}$	x,y	Linear

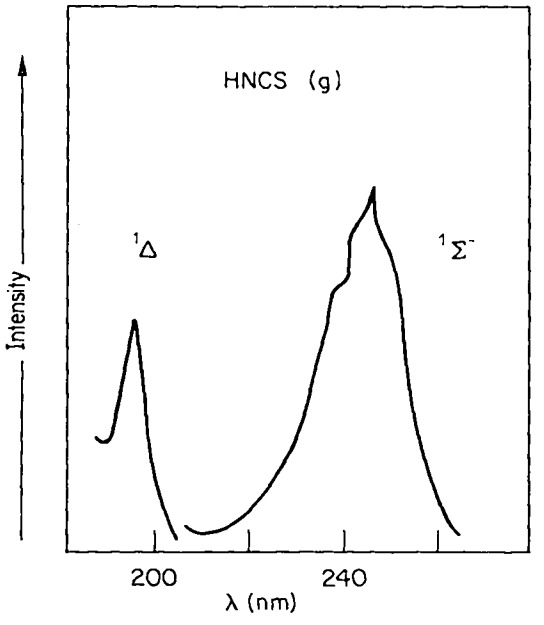

FIGURE 23. The gas phase absorption spectrum of HNCS. Excited state assignments ($C_{\infty v}$ representations) are given. This spectrum is adapted from Figure 2 of McDonald, Scherr and McGlynn[78].

The intravalence assignments for all spectra are collected in Figure 24. These assignments are in general agreement with the computational results collected in Figures 13, 15 and 16.

b. *Extravalence (Rydberg or R ← N) transitions.* Rydberg transitions are of valence → extravalence excitation nature. In NCO^-, for example, the lowest-energy Rydberg excitation, in an MO sense, would be designated $2\pi \rightarrow 3s$, whereas in NCS^- it would be designated $2\pi \rightarrow 4s$. The Rydberg spectroscopy of polyatomic molecules has been reviewed by Robin[86] who has induced considerable order in an area which previously, for the chemist anyway, had been a *terra incognita*. As a result of Robin's synthesis, we now have available a large number of simple empirical rules which enable us, given the set of molecular ionization potentials, to predict the energy of the various Rydberg absorption bands.

The first of these rules relates to an occurrence criterion for Rydbergs. For example, if the PES band for the $X^1\Sigma^+ \rightarrow {}^2\Pi_{1/2,3/2}$ ionization event of NCO^- is sharp (i.e., not diffuse), then the $X^1\Sigma^+ \rightarrow 3s$, $X^1\Sigma^+ \rightarrow 3p$, $X^1\Sigma^+ \rightarrow 4s$, etc. transitions should be expected to be sharp also. Sharpness implies a concentration of oscillator strength in a small wavelength interval

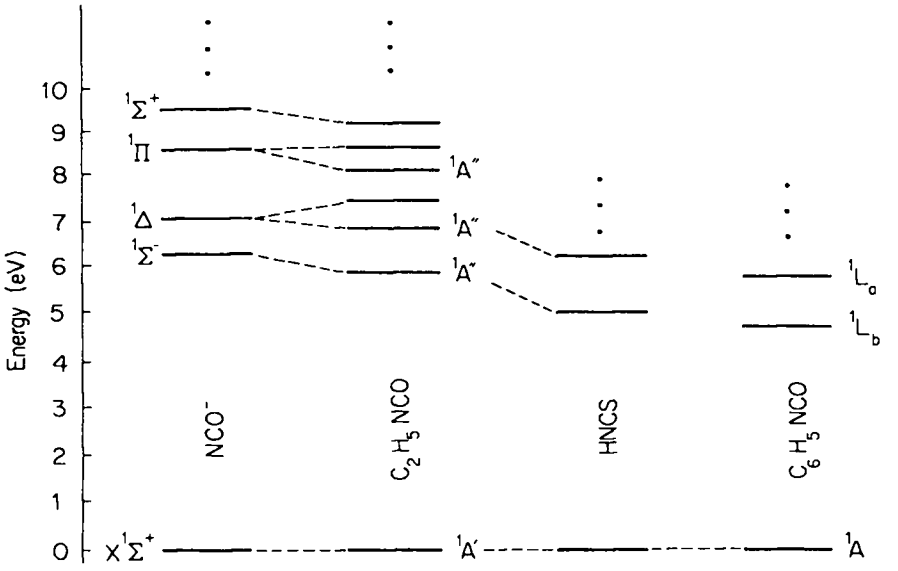

FIGURE 24. Experimental energy level diagrams, with tentative assignments, for NCO^-, C_2H_5NCO, HNCS and C_6H_5NCO.

and, hence, the ability of otherwise moderately intense transitions to insinuate their peaks above the background of intravalence absorptivity. The rationale for this inference, very simply put, is that the $^2\Pi_{1/2,3/2}$ state of NCO^- is the terminal excitation event in the progressive set of excitations $2\pi \rightarrow 3s$, $2\pi \rightarrow 4s$, $2\pi \rightarrow 5s$, ... Since an electron is removed from a 2π MO in all cases and inserted either into the continuum (i.e., the ionization event) or into an ns non-bonding orbital (i.e., the Rydberg event), the band shapes should be similar for both the Rydberg and the ionization processes.

The second rule is also an occurrence criterion. It states that Rydberg orbitals, being large and diffuse, are exceedingly sensitive to environment. Thus, a sharp Rydberg transition of gaseous NCO^- becomes rapidly diffused and submerges into background when NCO^- is inserted into a solution, solid or liquid. In doing so, the Rydberg transition may be said to 'disappear'. In the same vein, we may view the attached alkyl group of C_2H_5NCO as a solvent in which the NCO group is embedded. Hence, when the alkyl group gets large enough it may diminish the chances of observing Rydberg transitions.

The third rule relates to the energy of the R $\leftarrow$ N event. It is assumed that the Rydberg equation holds and that the energy of the R $\leftarrow$ N transition is given by

$$h\nu = IP - R/(n + \delta)^2 \qquad (18)$$

TABLE 14. Energies of Rydberg transitions (kK) predicted by the Rydberg equation (equation 18)
[1 kK = 1 kiloKayser = 1000 cm^{-1}]

HNCO	IP_1 = 11·62 eV			HNCO	IP_2 = 12·30 eV		
N → nl	$l = 0$	$l = 1$	$l = 2$	N → nl	$l = 0$	$l = 1$	$l = 2$
N → 3l	65·5	73·9	79·0	N → 3l	71·0	79·4	—
N → 4l	80·8	83·5	—	N → 4l	86·2	—	—
N → 5l	86·0	—	—	N → 5l	—	—	—
CH_3NCO	IP_1 = 10·67 eV			CH_3NCO	IP_2 = 11·2 eV		
N → nl	$l = 0$	$l = 1$	$l = 2$	N → nl	$l = 0$	$l = 1$	$l = 2$
N → 3l	57·9	66·3	71·4	N → 3l	62·2	70·5	75·6
N → 4l	73·2	75·9	77·8	N → 4l	77·4	80·1	—
N → 5l	78·5	79·7	—	N → 5l	—	—	—
N → 6l	81·0	—	—	N → 6l	—	—	—
C_2H_5NCO	IP_1 = 10·36 eV			C_2H_5NCO	IP_2 = 10·9 eV		
N → nl	$l = 0$	$l = 1$	$l = 2$	N → nl	$l = 0$	$l = 1$	$l = 2$
N → 3l	55·4	63·8	68·9	N → 3l	59·7	68·5	73·1
N → 4l	71·7	73·4	75·3	N → 4l	74·9	77·6	—
N → 5l	76·0	76·8	—	N → 5l	—	—	—
N → 6l	78·5	—	—	N → 6l	—	—	—

where IP is the ionization energy of the ionic state in which the Rydberg series terminates (at $n = \infty$); n is the principal quantum number of the Rydberg orbital; R is the Rydberg constant; and δ is the quantum defect which describes the extent to which the system of interest departs from hydrogen-like behaviour. The term value of the Rydberg transition is defined as

$$T = IP - h\nu = R/(n + \delta)^2 \tag{19}$$

The gist of the Robin synthesis[86] is that he has been able, on the basis of a large amount of correlative work, to formulate simple rules for the term value, T. Unfortunately, these rules are of little help in the present instance and we must have recourse to equations (18) and (19).

Based on the criteria of the three preceding paragraphs, one expects that HNCO and CH_3NCO will exhibit Rydberg spectra. All one need do is refer to the photoelectron spectra of these molecules given in Figure 6. It is apparent that the lowest-energy ionization event, IP_1, is fairly sharp and intense in both spectra. Unfortunately, the photoelectron spectrum of C_2H_5NCO is not available. However, if we assume that the effect of adding another methyl group to CH_3NCO is to reduce both IP_1 and IP_2 of CH_3NCO by $\sim$0·3 eV, we can use equation (18) to predict the approximate energies of the various R $\leftarrow$ N transitions of C_2H_5NCO. These predictions for HNCO, CH_3NCO and C_2H_5NCO are given in Table 14.

Inspection of Figure 22 indicates the presence of a number of transitions which might be of Rydberg nature. These are tabulated in Table 15 where they are also identified with respect to the nl indices. A similar comparison for C_2H_5NCO is also given in Table 15. It is apparent that the R $\leftarrow$ N assignments provide a facile interpretation of much of the HNCO and C_2H_5NCO spectra. This set of Rydberg assignments for C_2H_5NCO suggests that many of the intravalence assignments of Figure 21 ought to be considered further.

In sum, if the assignments of Table 15 are correct, the need to designate the 7·13 eV band of C_2H_5NCO as $^1A'(^1\Delta) \leftarrow X^1A'(^1\Sigma^+)$ disappears. The $^1A'(^1\Pi) \leftarrow X^1A'(^1\Sigma^+)$ and $^1A''(^1\Pi) \leftarrow X^1A'(^1\Sigma^+)$ assignments for the 7·80 and 7·93 eV bands, respectively, also become superfluous. This latter superfluity eliminates an obvious discrepancy between experiment and calculation: Calculations for CH_3NCO, as previously noted, do not predict any $^1\Pi$ state to be subjacent to the $^1\Sigma^+$ excited state. Finally, the $^1A'(^1\Sigma^+) \leftarrow X^1A'$ assignment at 8·77 eV is no longer unique since the $4s(IP_1) \leftarrow$ N assignment is equally good.

TABLE 15. A comparison of predicted R ← N transition energies with absorption band energies

HNCO (Figure 22)			C_2H_5NCO (Figure 21)		
R ← N Energy (kK)[a]			R ← N Energy (kK)[a]		
Exptl.	Calc. (equation 18)	$nl(IP_j)$	Exptl.	Calc. (equation 18)	
66·0	65·5	$3s(IP_1)$	57·0	55·4	$3s(IP_1)$
71·4	71·0	$3s(IP_2)$	62·0	62·2	$3s(IP_2)$
72·0, 72·7, 73·2, 74·7	73·9	$3p(IP_1)$	63·7, 64·2, 65·0	63·8	$3p(IP_1)$
77·0	79·0	$3d(IP_1)$			
80·6	80·8	$4s(IP_1)$	70·6	71·7	$4s(IP_1)$
82·6, 83·8	83·5	$4p(IP_1)$	73·0	73·4	$4p(IP_1)$

[a] 1 kK = 1 kiloKayser = 1000 cm^{-1}.

This speculative Rydberg analysis demands a re-evaluation of the intravalence assignments of the previous Section. It also demands an experimental re-evaluation of the valence and/or Rydberg character of each absorption event prior to any attempt at assigning it.

D. Charge Transfer to Solvent (CTTS) Transitions

Treinin and coworkers[72,87] have reported electronic absorption bands of thiocyanate, selenocyanate, and tellurocyanate ions in various solvents; these absorption bands exhibit molar extinction coefficients $\varepsilon \sim 3 \times 10^3$. It was concluded that these transitions, which occur in the range 220–240 nm in NCS^- solutions, correspond to a 'charge transfer to solvent' electronic transition. In view of the observation of a similar but very much less intense absorption band in the gas-phase spectrum of HNCS, the 220–240 nm absorption band may well be assigned as a $^1\Sigma^- \leftarrow X^1\Sigma^+$ transition of the linear NCS^- ion. Since the $^1\Sigma^+$ ground state and the $^1\Sigma^+$ excited state of NCS^- are both polar states, it follows that the corresponding transition energies and intensities should exhibit considerable solvation effects.

According to EHMO calculations, the charge densities appropriate to the NCS^- ground state are S: −0·31; C: −0·22; and N: −0·47. Those appropriate to the $\ldots(2\pi)^3(3\pi)^1$ configuration are S: −0·05; C: −0·61; and N: −0·35 for the linear NCS^- ion. Thus the $2\pi \rightarrow 3\pi$ excitation possesses considerable charge-transfer character. Furthermore, the excited state shows more asymmetry of charge than does the ground state. In view of this, one expects the lowest-energy $S_1 \leftarrow S_0$ transition to decrease in energy in polar solvents. This attitude explains some, but not all, of the observations upon which the CTTS postulate is based.

E. *Summary of Excited State Considerations*

It seems obvious that our knowledge of excited states of cyanates and thiocyanates is in an exceedingly poor state of repair. In order to be more specific, we enumerate:

(i) The intravalence (N → V) assignments for the cyanates overlap to a considerable degree with the extravalence (N → R) assignments (Section IV.C.2.a and b). Both sets of assignments cannot be simultaneously correct. The determination of the proper assignments demands the redetermination of vacuum ultraviolet (v.u.v.) spectra of HNCO, C_2H_5NCO and NaOCN; the determination of v.u.v. spectra of CH_3NCO and SiH_3NCO; and the use of independent assignment criteria such as are provided by Stark effect studies and magnetic circular dichroism measurements.

(ii) No v.u.v. spectra of any thiocyanates appear to be available. These, of course, should be measured.

(iii) The tellurocyanates and selenocyanates, if their spectra were available, could settle the question of N → R or N → V assignments in the cyanates[88].

(iv) The behaviour of the energy levels $^{(1,3)}\Sigma^+$, $^{(1,3)}\Sigma^-$ and $^{(1,3)}\Delta$ must be studied as a function of the parameters A, B, C, D, ξ_{np} and $\xi_{(n+1)p}$ (see Figures 8 and 9). Such studies would lead to predictions[89] about the spectra of cyanates, thiocyanates, tellurocyanates and selenocyanates which might help in making definitive assignments for all of them.

(v) The luminescence studies are qualitative and require reinvestigation in order to establish the intrinsic nature of the luminescence, its polarization, and its dependence on matrix.

(vi) The study of solvent effects on transition energies, intensities and polarizations must be extended in order to confirm or negate the CTTS concept.

Despite the deficiencies implied in items (i)–(vi), a number of definitive statements can be made. These are:

(vii) Cyanates and thiocyanates emit phosphorescence of $T_1 \rightarrow S_0$ nature. This phosphorescence is assigned as $^3\Sigma^+ \rightarrow X^1\Sigma^+$. The $^3\Sigma^+$ state may be characterized by a bent NCO or NCS group.

(viii) Non-aryl cyanates and thiocyanates do not emit fluorescence of $S_1 \rightarrow S_0$ nature. It is probable that the density of states at the S_1 level is so high that $S_1 \rightarrow S_0$ emission cannot compete with the energy degradative events $S_1 \rightsquigarrow S_0$ or $S_1 \rightsquigarrow T_1$.

(ix) The lower-energy $S_j \leftarrow S_0$ absorption region is dominated by the $^1\Delta \leftarrow X^1\Sigma^+$ and $^1\Sigma^- \leftarrow X^1\Sigma^+$ transitions (or their analogues in point groups of lower symmetry). Many, if not all, of these lower energy S_j states are characterized by a bent NCO or NCS grouping. The resulting spectra, as expected, are diffuse.

(x) The higher-energy $S_j \leftarrow S_0$ absorption region is dominated by $^1\Sigma^+ \leftarrow X^1\Sigma^+$ (or its analogue in point groups of lower symmetry) and $R \leftarrow N$ transitions. The possible occurrence of $^1\Pi \leftarrow X^1\Sigma^+$ transitions (or analogues) in this region is debatable.

(xi) Theory and computation are in much better repair than is experiment. It is in the realm of experiment that the greatest amount of work is required.

V. CONCLUSION

The results of this work are summarized in Sections II.C. and IV.E. and will not be elaborated further. It is worth noting, however, that our knowledge of the ground state far surpasses that for any excited state. This, of course, is a general state of affairs, the reasons for which are given in Section III.

The discussions of this work have much broader implications than mere reference to cyanates and thiocyanates. The discussions bear on the spectroscopy of all linear molecules which contain 16 valence electrons. In other words, the assignments of excited states and the characteristic properties of these and the ground state for cyanates and thiocyanates must fit smoothly within the context of all linear functionals, molecules, and ions with 16 valence electrons. An attempt at such a fitting is available[77].

The authors are indebted to a number of persons. David Dougherty (LSU) performed the majority of the computations which are reported, and Anne Wahlborg deserves credit for inducing order in a manuscript in which, initially, there was none.

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 2

Structural chemistry of the cyanates and their thio derivatives

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I. INTRODUCTION

In this chapter, an attempt will be made to survey the geometrical and conformational information that is available on the cyanate (**1a**) and isocyanate (**1b**) groups and on the thiocyanate (**2a**) and isothiocyanate

(**2b**) groups. Some data will also be presented on selenium analogues. The group NCE (E = O, or S) is called cyanate (thiocyanate) or isocyanate (isothiocyanate) depending on whether it is bonded to the remainder of the molecule through E or through N. Information obtained by studies on the gas phase and on the crystalline phase will be presented on molecules containing these groups. Unfortunately very few molecules containing these groups have been studied *both* in the gas phase and in the crystal, so a detailed comparison of dimensions obtained on the same molecule in the two phases is not possible. The preponderance of microwave and electron

R—OCN	R—NCO
(1a)	(1b)
R—SCN	R—NCS
(2a)	(2b)

diffraction studies are on small molecules where the cyanate or thiocyanate group is a major portion of the structure, whereas the X-ray studies that have been reported are largely concerned with thiocyanates and often with molecules that contain more than one sulphur or selenium atom. A great many metal complexes of the pseudohalide cyanate (isocyanate) or thiocyanate (isothiocyanate) group have been studied by X-ray diffraction. No attempt will be made to give a comprehensive coverage of the metal complexes as there are a number of recent reviews and the subject is inappropriate for detailed coverage in a book basically designed for a readership drawn from organic chemists.

More members of the isocyanate and isothiocyanate classes of compound have been studied in the vapour phase for the purposes of structural elucidation than of any other class. Those members of the isocyanate and isothiocyanate classes whose molecular structures have been determined by either electron diffraction or microwave spectroscopy are listed in Table 1 where the experimental technique used is also indicated.

With modern experimental techniques and large computers, it is now possible to achieve uncertainties in the parameters determined that are smaller than the differences between the values for the same parameters that are determined by different physical techniques. These latter differences arise due to the different physical meaning attached to what is actually measured.

The present discussion starts with a very brief survey of the types of molecular geometrical information that can be obtained by electron diffraction and microwave spectroscopy and of the types of internuclear

TABLE 1. Isocyanates and isothiocyanates for which vapour-phase molecular geometries have been elucidated

Isocyanates			Isothiocyanates		
Compound	Technique[a]	Reference	Compound	Technique[a]	Reference
HNCO	MW	1	HNCS	MW	2, 3
CH_3NCO	MW	4	CH_3NCS	MW	4
	ED	5		ED	5
NCNCO	MW	6			
C_6H_5NCO	MW	7			
SiH_3NCO	MW	8	SiH_3NCS	MW	10
	ED	9		ED	9
$(CH_3)_3SiNCO$	ED	11	$(CH_3)_3SiNCS$	ED	11
$Si(NCO)_4$	ED	12			
$ClSi(NCO)_3$	ED	13			
$Cl_2Si(NCO)_2$	ED	13			
Cl_3SiNCO	ED	13			
F_3SiNCO	ED	14			
GeH_3NCO	ED	15			
F_2PNCO	ED	16	F_2PNCS	ED	16
$Cl_2(O)PNCO$	ED	17			
ClNCO	MW	18, 19			
	ED	20			

[a] Techniques: MW—microwave spectroscopy,
ED—electron diffraction.

distance parameters that appear most often in the original papers and in some of our Tables. Then the structural results on isocyanates and isothiocyanates will be reviewed and, in conclusion, structural data on two thiocyanates will be mentioned.

Completeness has not really been attempted, but rather we wanted to provide a general picture of the state of vapour-phase molecular structure determinations in these classes of compounds. Nevertheless, since vapour phase studies are a quite well-defined, although not very wide, area and also because of the importance of these very simple molecules, we attempted a nearly complete coverage. It may also be noted that most of the references are of quite recent origin, providing witness to a renewed and intensive interest towards the structural—and, accordingly, bonding—properties of simple isocyanates and isothiocyanates.

It is anticipated that experimental studies in this area will be continued and that more and more experimental data will contribute to an extension

of our knowledge about chemical bonding in isocyanates and related compounds. We have not attempted to draw too far-reaching conclusions from the available data at this time but rather we have tried to systematize them and in so doing we hope to have facilitated further development in this area. As an aid to systematization, we have also included information concerning the types of representation of the geometrical parameters from the original papers. Such information is becoming increasingly important.

Some comment should also be made concerning the uncertainties reported for the structural parameters. In all cases the values from the original papers are given although their meaning may vary considerably. Accordingly, if further use of the structural parameters is intended, particularly if effects whose magnitude is comparable with the experimental error are to be examined, it will be necessary to consult the original papers for more detailed information.

In the section on X-ray diffraction studies, most of the analyses on cyanates, isocyanates, thiocyanates, isothiocyanates, and selenium analogues that are covalently bonded to non-metals will be examined. In many of these cases, the X-ray diffraction studies were carried out 15–25 years ago; they were based on intensity data measured on film, and sometimes intensities from only one or two reciprocal lattice zones were used in the refinement. Accordingly, while the gross structural details are usually correct, no definite evidence for molecular dimensions can be drawn. An attempt will be made to provide a reasonably critical discussion of the analyses that are available.

The crystallographic R-factor, which is defined as $\sum \| F_{obs} | - | F_{calc} \| / \sum | F_{obs} |$, has been traditionally used as indicator of the agreement between the observed and calculated structure factors and, somewhat indirectly, as a measure of the quality of the analysis. While there are other measures of the quality of the analysis or refinement, e.g. the size of the estimated standard deviations for the structural parameters, the value for the standard deviation of an observation of unit weight, or the 'goodness of fit'[21], and the internal consistency of bond lengths that should be chemically equivalent, some of which are definitely superior to the R-factor, the R-factor remains a widely-quoted and fairly useful measure of the level of reliability of the analysis. With photographic data, R-factors less than 0·13–1·14 indicate fairly well-refined structures, while R-factors of about 0·20 imply either that the measured intensities are quite inaccurate or that there is something significantly wrong with the structural model, although probably not to the extent that the overall molecular structure is incorrect. When the reflection data are measured by counters, usually on an automatic diffractometer, R-factors below 0·05 can be obtained in careful

work. However, some of the crystal structures to be described in the following section are based on intensity data collected from only one or two zero-level nets of the reciprocal lattice. Data from such a net can give information on only two of the fractional atomic coordinates. In such cases, a low R-factor can be quite misleading. It can imply a good level of refinement, yet as only two coordinates for the atomic positions can be obtained from such a projection, great uncertainties remain as to the three-dimensional structure. Serious obscurities in the atomic resolution can also arise due to 'overlap' of atoms along the direction of projection.

The estimated standard deviations that are quoted in an X-ray diffraction paper usually are obtained from the elements of the inverse matrix of the normal equations relating the atomic parameters in the least squares procedures. For a discussion of these procedures, see Reference 21. However, such estimated standard deviations are based on an assumption that the errors in the data follow a normal distribution, i.e., that they are random errors. Unfortunately, there are several sources of systematic error in X-ray intensity measurements, some of which can be quite difficult to correct exactly. In the case of data collected by film, errors often arise due to variations in the response of the X-ray film, the difficulty of measuring integrated intensities particularly when the intensity of the reflection was distributed in different shapes at different parts of the film, and because of the problems of scaling the films of different nets together. While the advent of automatic diffractometers employing counters has removed many of these problems, errors can also arise due to the difficulty of treating such corrections that arise from absorption or extinction of the scattered X-ray beams. Many of the effects of these types of errors would not be reflected in the value of the R-factor or in the estimated standard deviations that would be obtained from the least-squares refinement.

Another type of complication that can arise, particularly when dealing with a small linear or near-linear group such as isothiocyanate, concerns an artificial shortening of the bond length that is measured in the diffraction experiment due to the type of thermal vibration that the group undergoes in the crystal. The electron density at a particular point that is measured in the diffraction experiment will be a time average of the density at that point in all the unit cells. If the group is vibrating in a direction perpendicular to its extended length, and pivoting or 'riding' on the inner atom, then the electron density will appear smeared out as shown in Figure 1. However, when the density is averaged along the axis of the linear group, the maximum will appear closer to the pivot point than the actual atomic position. If the group 'rides' precisely on an inner atom, and if the thermal

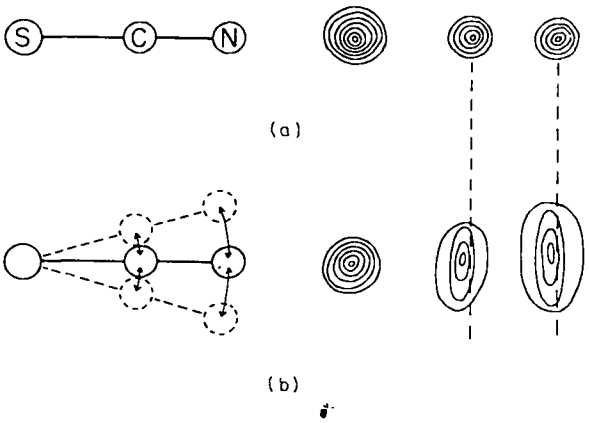


FIGURE 1. Diagram showing the effect of 'riding' motion on a linear group, (a) no thermal vibration, (b) thermal vibration normal to the length of the group, showing that the mean electron density is displaced toward the pivot point.

parameters are well defined, a fairly good correction can be made[21]. However, such motion is often coupled with some other type of vibrational motion and it is difficult to carry out an accurate correction. One should therefore be aware of the probability that 'uncorrected' measurements of bond lengths in linear groups such as cyanate or thiocyanate may well be artificially short in an X-ray diffraction experiment.

Finally, while the molecular dimensions obtained in an X-ray diffraction experiment conducted under optimum conditions (good crystals, good data collection facilities, and adequate computing facilities) should be quite accurate, e.g. ~0·005 Å for a C–C (or C–N) bond, it should be kept in mind that the molecules in the crystal are in a high state of aggregation, are almost always required by the nature of crystals and their symmetry to adopt a uniform conformation, and that intermolecular interactions can play a more important role in determining the molecular conformation than they would in the gas phase or in solution.

II. EXPERIMENTAL INFORMATION ON THE GEOMETRY OF MOLECULES IN THE GAS PHASE

Of the various aspects of molecular structure, those dealing with the *geometry* of molecules will be stressed in the following discussion. The geometry of molecules can be dealt with on two levels. One level is a qualitative characterization of the atom connectivity and the overall shape and symmetry of the molecule. The other level is more quantitative

and involves the determination of the precise relative spatial positions of the atoms in a molecule. These results are often described in terms of the bond lengths, bond angles, and the angles of internal rotation in the molecule. The variations of such geometrical parameters, especially when considered in series of related compounds, may reveal important information concerning chemical bonding. However, in gas-phase studies, the quantitative determination of molecular parameters cannot be carried out without a knowledge of the first level, as will be demonstrated by the studies to be discussed in this chapter.

The experimental data obtained in the vapour phase are particularly important because only here can a molecule really be considered to be unperturbed by the presence of others and so the structure found in the vapour phase should be determined exclusively by intramolecular forces. There are cases where substantial differences have been recorded between the structures determined in the crystal by X-ray diffraction and in the vapour phase by electron diffraction or microwave spectroscopy[22].

An unambiguous description of the molecular geometry would be that of the equilibrium geometry, which would represent the geometry of a hypothetically motionless structure corresponding to the minimum of the potential energy function. Molecules, however, are not rigid bodies and the distances between constituent atoms are considerably influenced by molecular vibrations and rotations. The influence of the intramolecular motion appears in different ways depending on the exact nature of the physical techniques used to determine the geometrical parameters. Such effects are particularly important for molecules that undergo large amplitude motion.

The two principal techniques for determining the molecular geometry in the vapour phase are electron diffraction and rotational spectroscopy [(for further reading and references see, for example,[23–25])]. The internuclear distances obtained directly from a least-squares analysis of the electron diffraction intensities are the so-called r_a effective parameters. The r_a distance is rigorously equal to the $r_g(1)$ distance that corresponds to the position of the centre of gravity of the $P(r)/r$ distribution function where $P_{ij}(r)\,dr$ expresses the probability that an r_{ij} distance is between r and $r + dr$. The r_g [or often $r_g(0)$] distance corresponds to the position of the centre of gravity of the $P(r)$ function, or, in other words, r_g is the average value of the internuclear distance. To a good approximation

$$r_g = r_a + l^2/r_a.$$

In the above expression, l^2 is the mean square amplitude of vibration also obtainable from the electron diffraction experimental data. It should be

noted that the electron diffraction intensities are obtained as averages from the molecules distributed among the vibrational states.

The average internuclear distance (r_g) can be expressed in terms of the equilibrium internuclear distance (r_e) in the following way:

$$r_g = r_e + \delta r + \langle \Delta z \rangle + \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2r_e} + \ldots$$

This relationship refers to a Cartesian coordinate system whose z-axis coincides with the equilibrium internuclear axis and whose origin is at the equilibrium position of one of the two atoms. The term δr is the centrifugal stretching and Δx, Δy, and Δz are the differences of the displacements of the atoms in the directions of the three Cartesian axes. The quantity $\langle \Delta z \rangle$ vanishes in case of harmonic vibrations, while the mean square perpendicular amplitudes are finite even if there are only harmonic vibrations.

Furthermore, the average internuclear distance (r_g) is not the same as the distances (r_α and r_α^0) between the average positions of the atomic nuclei. When there is thermal equilibrium at a given temperature T, the distance between the average positions of the atomic nuclei (r_α) is related to the equilibrium internuclear distance (r_e) by

$$r_\alpha = r_e + \langle \Delta z \rangle.$$

In the ground vibrational state, the distance between the average positions of the atomic nuclei (r_α^0) is related to r_e by

$$r_\alpha^0 = r_e + \langle \Delta z \rangle_0.$$

The distances r_α and r_α^0 differ from r_e only on account of anharmonicity. The r_α and r_α^0 distances can be obtained from the r_g distance by applying harmonic corrections.

In summary, as regards electron diffraction studies, care has to be taken to distinguish among the following types of distances:

r_a—the effective distance
r_g—the average value of the internuclear distance
r_e—the equilibrium internuclear distance
r_α—the distance between the average positions of the nuclei

Microwave spectroscopy (producing pure rotational spectra) is the other principal technique for the determination of molecular geometry in the vapour phase. Up to three rotational constants can be obtained from the rotational spectrum of a given isotopic species yielding three independent pieces of data. However, the geometry of other than the

very simplest molecules is determined by a larger number of independent parameters. In such cases, additional data from the rotational spectra of isotopically-substituted species can be utilized. Such a procedure is possible because the equilibrium internuclear distances are unchanged by the isotopic substitution, while there is usually an appreciable change in the atomic masses, leading to differences in the moments of inertia. The method, however, is complicated by the fact that the ground state structure is somewhat different from the equilibrium structure because of the zero-point vibrations. Since the molecular vibrations are also dependent on mass, the influence of the zero-point vibrations will be somewhat different for various isotopically substituted species.

The internuclear distance which is obtained from the rotational spectrum, or rather from the effective rotational constants as isotopic substitution is utilized, is an effective parameter and is called r_0 (it usually corresponds to the ground vibrational state). This effective r_0 parameter will be somewhat dependent on the particular choice of isotopic substitutions performed. Such difficulties are clearly brought out in those cases where it is possible to investigate more than the minimum number of isotopically-substituted species (cf., for example, the studies on CH_3SCN as compared by Dreizler and coworkers[26]).

If the isotopic substitution is performed consistently in turn for each atom in the molecule, and the so-called substitution coordinates for each atom are obtained, it is possible to calculate the r_s substitution structure. This structure approximates well the equilibrium structure although it has no well-defined physical meaning.

As neither the effective (r_0) nor the substitution (r_s) structures have well-defined physical meanings, they cannot be used to make rigorous and precise comparisons with results obtained by other techniques, particularly when subtle effects are sought. Fortunately, it is possible to obtain the parameters corresponding to the distances between average nuclear positions from the rotational spectroscopic data as well as from electron diffraction data. However, the complicated correction procedures cannot be applied directly to the internuclear distance parameters (the end-product of the investigation) but only to the rotational constants (which are obtained at an intermediate stage). The average structures, with well-defined physical meaning, can be obtained from the average rotational constants which are obtained by applying harmonic corrections to the effective rotational constants. The r_z internuclear distances derived in this way from the microwave spectroscopic data are essentially identical to the r_α^0 internuclear distances obtainable from the electron diffraction analysis.

Several kinds of internuclear distance parameters have already been listed and many more can be found in the literature. The question then arises: What is the best representation of the molecular geometry? The best and the most unambiguous representation would be the equilibrium geometry. However, with one or two exceptions, it is not attainable. Among the other representations, the structures characterized by the average nuclear positions are most useful. The great merits of such structures are their definite physical significance and their experimental attainability.

The average value of the internuclear distance, r_g, is the most convenient way to characterize the average length of a chemical bond. This parameter has no clear meaning, however, in the case of distances between non-bonded atoms because of the effects of the perpendicular vibration of the atoms. Thus, e.g., in a linear symmetric triatomic molecule the r_g distance between the two non-bonded atoms may be smaller than the sum of the bond distances. This effect is called *shrinkage* and was first observed by Bastiansen and coworkers (see details in Cyvin[27]). The shrinkage effect may conceal important features of the molecular geometry of cyanates, isocyanates and related substances if there are considerable perpendicular vibrations in the three-membered chain N=C=E (E = O or S) or in the four-membered chain X—N=C=E, where X is the atom adjacent to the isocyanate group. Because of shrinkage effects, lower symmetries may be observed in the molecular configurations obtained from electron diffraction data than would have been expected for the equilibrium structure.

III. STRUCTURAL VARIATIONS IN THE ISOCYANATE AND ISOTHIOCYANATE GROUPS IN THE GAS PHASE

The bond distances r(N=C) and r(C=O) determined in the gas phase in isocyanates as well as r(N=C) and r(C=S) in isothiocyanates are compiled in Tables 2 and 3, respectively.

It is seen that with the exception of the electron diffraction data on the two methyl compounds[5], the lengths of the N=C bonds in isocyanates are larger than, or are equal to, within the stated uncertainties, those in isothiocyanates. The earlier microwave spectroscopic investigation[4] on CH_3NCO and CH_3NCS assumed values for these bond distances. Unfortunately, since the lengths of the N=C and C=O bonds are almost equal, particularly strong correlations appear in the electron diffraction analysis between these distances and also between these distances and the

TABLE 2. The distances for the N=C and C=O bonds as determined in the gas phase for molecules containing the isocyanate group

Compound	r(N=C) (Å)	r(C=O) (Å)	Comment	Reference
HNCO	1·207 ± 0·01	1·171 ± 0·01	r_0 parameters	1
CH_3NCO	1·168 ± 0·005	1·202 ± 0·005	r_a parameters	5
SiH_3NCO	1·216 ± 0·009, 1·200 ± 0·005	1·164 ± 0·008 Å, 1·180 (assumed)	Using different assumptions	9
	1·150	1·179	r_0 (N=C), r_s (C=O)	8
$(CH_3)_3SiNCO$	1·20 ± 0·01	1·18 ± 0·01	r_g parameters	11
F_3SiNCO	1·190 (assumed)	1·168 ± 0·025	r_a parameters	14
Cl_3SiNCO	1·219 ± 0·007	1·139 ± 0·008		13
$Cl_2Si(NCO)_2$	1·217 ± 0·005	1·146 ± 0·005	Probably r_a parameters	13
$ClSi(NCO)_3$	1·213 ± 0·005	1·144 ± 0·005		13
$Si(NCO)_4$	1·209 ± 0·002	1·165 ± 0·002	r_a parameters	12
GeH_3NCO	1·190 ± 0·007	1·182 ± 0·007	r_a parameters	15
F_2PNCO	1·256 ± 0·006	1·165 ± 0·006	r_a parameters	16
$Cl_2(O)PNCO$	1·161 ± 0·015	1·221 ± 0·015	Probably r_a parameters	17
ClNCO	1·228	1·174	Utilizing electron diffraction and microwave spectroscopic[18] data	20
	1·226 ± 0·005	1·162 ± 0·005	r_s parameters	19

TABLE 3. The distances for the N=C and C=S bonds as determined in the gas phase for molecules containing the isothiocyanate group

Compound	r(N=C) (Å)	r(C=S) (Å)	Comment	Reference
HNCS	1·216 ± 0·002	1·561 ± 0·002	r_s (C=S), $r_{s'}$(N=C)	2
CH_3NCS	1·192 ± 0·006	1·597 ± 0·005	r_a parameters	5
SiH_3NCS	1·197 ± 0·007	1·563 ± 0·006	r_a parameters	
	1·211 ± 0·010	1·560 (assumed)	r_s (N=C)	10
$(CH_3)_3SiNCS$	1·18 ± 0·01	1·56 ± 0·01	r_g parameters	11
F_2PNCS	1·221 ± 0·006	1·553	r_a parameters	16

associated mean amplitudes of vibration. Thus, for example, the parameters l(N=C) and l(C=O) had to be fixed in the least-squares refinement of the molecular parameters in methyl isocyanate[5].† A closer look at the correlation matrix for the parameters of CH_3NCO reveals that the strongest correlation ($|\rho| = 0{\cdot}864$) appears between r(N=C) and r(C=O). Because of the inherent uncertainties in these data, any discussion, based on these results, of the bond distance variations in terms of the bonding properties may be somewhat suspect.

Another kind of structural variation that would be of interest to examine is the effect on the lengths of the N=C bonds as various substituents are attached to the isocyanate or isothiocyanate group. Unfortunately, however, no pattern of correlation can readily be noted on the basis of the available data (see Tables 2 and 3).

A comparison of the lengths of the N=C and C=O bonds in isocyanates shows that, in most cases r(N=C) appears to be larger than r(C=O). Of the two exceptions, *viz.*, CH_3NCO and $Cl_2(O)PNCO$, the case of methyl isocyanate has been discussed above in some detail.

The question of linearity or non-linearity of the N=C=O and N=C=S chains is of considerable interest. In the great majority of the studies it was stated explicitly that linearity of the N=C=O chain was assumed, while in other cases it is only implied but was nevertheless used. Only in very few cases was the N—C—O or N—C—S angle determined or even examined in detail. Of these, two examples will now be discussed. Thus, for the molecule SiH_3NCS, the linearity of the whole

† The assumed values were very reasonable. (It is unfortunate that due to a probable misprint they appear 10-times larger in Table 2 of Reference 5 than they should be. This error adds somewhat to the slight confusion encountered in reading this paper[5] due to the reporting of the distance and amplitude parameters in pm units.)

Si—N=C=S chain was established from the accurate symmetric top behaviour deduced from the microwave spectra[10]. In the case of ClNCO, non-linearity of N—C—O was determined both from the electron diffraction[20] and microwave spectroscopic[19] data (see Figure 2). It appears that the possibility of non-linearity should always be considered in the experimental determinations of the geometry of the N=C=O or N=C=S groups. Several electron diffraction studies indicated some slight (usually within 0·01 Å) shrinkage effects for the N...E distances in the N=C=E chains (E = O or S). It may not be possible, however, to distinguish between linear and nearly-linear structures on the basis of the electron diffraction data alone.

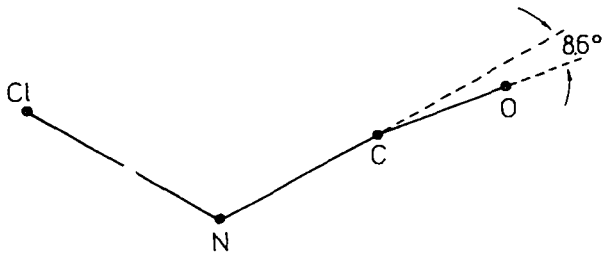


FIGURE 2. The molecule of ClNCO showing the non-linearity of the NCO group.

Throughout the literature dealing with the structural properties of isocyanates and isothiocyanates resonance structures are often presented for the NCE (E = O or S) groups to account for linearity. On the other hand, Rode and associates have recently applied semiempirical molecular orbital methods[28–31] and *ab initio* calculations[32] and found the N=C=O groups to be non-linear in a series of simple isocyanate derivatives.

IV. STRUCTURAL VARIATIONS INVOLVING THE ATOM ADJACENT TO THE ISOCYANATE (OR ISOTHIOCYANATE) GROUP

One of the most interesting geometrical parameters relating to the isocyanates and isothiocyanates is the X—N=C bond angle when X is the atom attached to the nitrogen of the isocyanate or isothiocyanate. The experimentally determined values are compiled in Table 4. It is seen that these bond angles range from linear or near-linear to 120°.

There is also a striking and apparently significant difference between the bond angles in SiH_3NCO and SiH_3NCS as determined by microwave

TABLE 4. Bond angles ∠X—N=C and X–N bond distances in isocyanates and isothiocyanates (vapour-phase data)

Compound	∠X—N=C (deg)[a]	r(X–N) (Å)[b]	Reference
HNCO	128·1 ± 0·5	0·987 ± 0·01	1
HNCS	135·0 ± 0·2	0·989 ± 0·003	3
CH_3NCO	140·0		
	140·3 ± 0·3	1·450 ± 0·004	5
CH_3NCS	147·5		4
	141·6 ± 0·4	1·479 ± 0·008	5
NCNCO	140·0	1·283	6
C_6H_5NCO	140·6	1·370	7
SiH_3NCO	linear	1·699	8
	152·2 ± 1·2	1·703 ± 0·004	9
SiH_3NCS	linear	1·714 ± 0·010	8
	163·8 ± 2·6	1·704 ± 0·006	9
$(CH_3)_3SiNCO$	150 ± 3	1·76 ± 0·02	11
$(CH_3)_3SiNCS$	154 ± 2	1·78 ± 0·02	11
$Si(NCO)_4$	146·4	1·688 ± 0·003	12
$ClSi(NCO)_3$	145 ± 2	1·684 ± 0·003	13
$Cl_2Si(NCO)_2$	136 ± 1	1·687 ± 0·004	13
Cl_3SiNCO	138·0 ± 0·4	1·646 ± 0·008	13
F_3SiNCO	160·7 ± 1·2	1·648 ± 0·010	14
GeH_3NCO	141·3 ± 0·3	1·831 ± 0·004	15
F_2PNCO	130·6 ± 0·8	1·683 ± 0·006	16
F_2PNCS	140·5 ± 0·7	1·686 ± 0·007	16
$Cl_2(O)PNCO$	120 ± 1·5	1·684 ± 0·010	17
ClNCO	118·8 ± 0·5	1·705 ± 0·005	19

[a] The electron diffraction bond angles usually correspond to the r_a or r_g internuclear distances.

[b] Usually the same parameter types as those in Tables 2 or 3.

spectroscopy and by electron diffraction. Because of these differences or apparent differences and also because of the importance of the influence of intramolecular motion on the geometrical parameters determined by spectroscopic and diffraction techniques, the physical significance of the parameters will be discussed briefly before considering the data from a more chemical or structural viewpoint.

The interpretations of the vibrational spectra for Cl_3SiNCO and Cl_3SiNCS[33], and for $Si(NCO)_4$[34] and $Si(NCS)_4$[35,36] were based on molecular models possessing C_{3v} and T_d symmetry, respectively. Such models imply linear Si—N=C=E skeletons. Such a geometry differs substantially from that given by the available electron diffraction results, as detailed in Table 4.

The microwave spectroscopic results establishing a linear Si—N=C=O(S) skeleton in $SiH_3NCO(S)$[8,10] can be considered unambiguous since they were derived from rotational spectra characteristic of symmetric top molecules. On the other hand, the low-frequency, large-amplitude bending motion of these molecules may produce large enough shrinkage effects that could account for the apparent non-linear Si—N=C angles found by electron diffraction, as was pointed out by Glidewell and collaborators[9]. Earlier, Cyvin and coworkers[37] had examined in detail the interdependence of the lowest bending frequency (ν_{10}) and the quantities measured in an electron diffraction experiment, notably the shrinkage effect (δ). These authors compared the observed and calculated shrinkages δ(Si ... C) and δ(Si ... O, S). Their results are illustrated in Table 5, which is reproduced from their paper. It should be noted that these calculations of shrinkage were carried out using the harmonic approximation[27] which breaks down if the vibrations are appreciably anharmonic. Nevertheless, such calculations may provide useful, even though very tentative, information regarding the interpretation of the apparent parameters for ∠X—N=C obtained by electron diffraction and they will also be valuable for further spectroscopic studies in the low frequency region. The plots of δ(Si ... C) and δ(Si ... S) vs. ν_{10} are shown in Figure 3 in order to illustrate how steeply the sensitivity of the shrinkage increases

TABLE 5. Observed and calculated shrinkages. $SiH_3NCO(S)$ after Cyvin and coworkers[37]

	SiH_3NCO[a]		
	δ(Si ... C) (Å)	δ(Si ... O) (Å)	ν_{10} (cm^{-1}) assumed
Experimental	0·084 ± 0·004	0·121 ± 0·005	
Calculated	0·403	0·574	30
	0·103	0·149	60
	0·059	0·086	80
	SiH_3NCS[b]		
	δ(Si ... C) (Å)	δ(Si ... S) (Å)	ν_{10} (cm^{-1}) assumed
Experimental	0·028 ± 0·004	0·042 ± 0·007	
Calculated	0·102	0·161	54
	0·033	0·052	100
	0·017	0·027	150

[a] At 0 °C
[b] At 25 °C

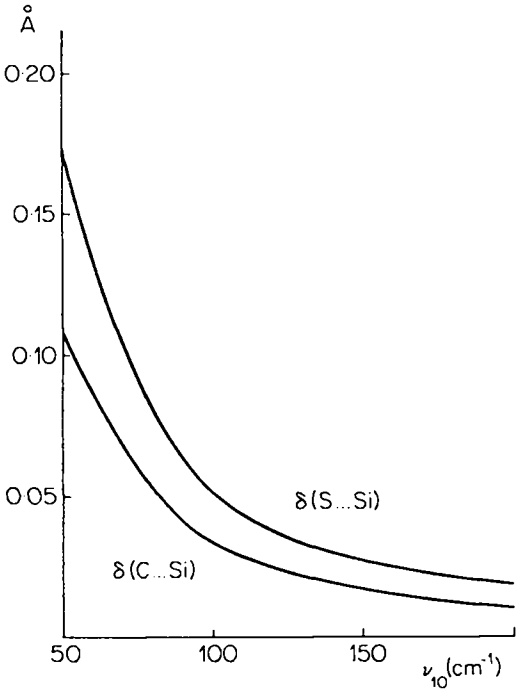


FIGURE 3. A plot of δ(C ... Si) and δ(S ... Si) against the ν_{10} bending frequency.

with lower values of the ν_{10} bending frequency. Thus, for lowest bending frequencies below 100 cm^{-1}, the effect becomes extremely large.

By analogy with carbon suboxide for which similar analyses have been reported[38], Glidewell and coworkers[9] evaluated the probability $P(\alpha)\,d\alpha$ that the molecule is bent at nitrogen by an angle

$$\alpha = \pi - \angle\text{Si—N=C}$$

(in radians). They used the following classical expression:

$$P(\alpha) = N \sin\alpha \exp\left[-\frac{V(\alpha)}{RT}\right],$$

where N is a normalizing factor and $V(\alpha)$ is the bending potential function. Various $V(\alpha)$ bending potential functions have been tested by examination of the radial distribution in the region that is assigned to the Si ... O(S) distance, and with the assumption that the Si ... N and N ... O(S) distances remain unchanged during the bending motion.

The anharmonic functions tested for SiH_3NCS did not yield a better

agreement than the harmonic potential. On the other hand, in the case of SiH_3NCO a mixed harmonic–quartic function that had a minimum at $\angle Si-N-C = 159°$ (cf. the experimental values in Table 4) and a barrier of 20 cm^{-1} at $\angle Si-N-C = 180°$ provided a much better fit than the harmonic potentials tested. After performing this analysis, Glidewell and coworkers[9] concluded: '... we consider that the Si—N=C=E group in most of the substituted silicon pseudohalides studied by electron diffraction is in fact linear in the equilibrium configuration or has at most a very small barrier to linearity.' Unfortunately, it still does not seem to be possible on the basis of available experimental data either to confirm or to discard the above statement.

In the cases of F_2PNCO and F_2PNCS the bond angles obtained directly from the electron diffraction (r_a) distances did not correspond to bond angles with well-defined physical meaning. In these examples, the bending vibrations had an effect similar to that described for $SiH_3NCO(S)$, but of lesser magnitude. To correct the electron diffraction results, Rankin and Cyvin[16] postulated the values of 105 cm^{-1} and 81 cm^{-1} for the bending modes in F_2PNCO and F_2PNCS, respectively, on the basis of the vibrational spectroscopic data. The appropriateness of these values was indicated by the apparent good agreement between the experimental and calculated shrinkage effects. Using the perpendicular amplitude correction terms, an approximate r_α structure was obtained and the r_α internuclear distances gave rise to the following P—N=C bond angles:

$$F_2PNCO \quad \angle_\alpha P-N-C = 134{\cdot}8°$$

$$F_2PNCS \quad \angle_\alpha P-N-C = 144{\cdot}0°,$$

i.e. the effect of the bending vibration lowered the apparent bond angles at nitrogen (see Table 4) only by about 4°.

Evidence from both spectroscopic[39] and electron diffraction[15] studies indicates a non-linear Ge—N=C=O skeleton in GeH_3NCO similar to that encountered in the phosphorus derivatives discussed above.

It is difficult to notice any systematic trends among the X—N=C bond angles. The linearity of the Si—N=C=E skeletons, or at least the very large Si—N=C bond angles, are usually associated with the p_π–d_π character of the bonding involving the available 3d orbitals of silicon (see, e.g., References 9, 10, 16 and 40).

Similar bonding properties could be expected for the phosphorus and germanium derivatives, where, however, considerably bent structures have been determined unambiguously. The particularly small X—N=C angles in $Cl_2(O)PNCO$ and ClNCO (see Table 4) are also surprising.

Even the C—N=C angles in CH_3NCO and CH_3NCS are definitely larger.

A somewhat more definite correlation emerges between the variations of the ∠X—N=C and r(X—N) parameters. As the values of the X—N=C bond angles decrease, the double bond character of the X–N bonds also seems to decrease. This loss of double bond character is demonstrated by the relative lengthening of these bonds compared to what would be expected from the Schomaker–Stevenson equation[41], cf. Table 6. It would be interesting to compare the lengths of the X–N bonds

TABLE 6. Comparison of observed and calculated[a] X–N bond distances

X	r(X—N) (Å) obs.	calc.	(calc.–obs.)
Si	1·65–1·71[b]	1·82	0·17–0·11
P	1·685	1·76	0·07
Cl	1·69–1·70	1·69	0·0

[a] Using the Schomaker–Stevenson equation[41]

$$r(X—N) = r_X + r_N - c|\chi_X - \chi_N|,$$

with $c = 0{\cdot}04$[42] and the values of covalent radii r_X and r_N and electronegatives χ_X and χ_N taken from Pauling[43].

[b] The values of r(Si—N) in $(CH_3)_3SiNCO$ (or S) were not considered in these comparisons.

for a given X atom with changing ligand electronegativities. Unfortunately, no characteristic pattern emerges, although some variations for the silicon derivatives indicate a shortening with increasing ligand electronegativity in agreement with what would be expected. The Si–N bonds in the trimethylsilyl derivatives seem to be particularly long. However, they could not be determined very accurately because of large correlations with the parameters for the Si–C bonds, which would occupy similar positions in the radial distributions. Kimura and coworkers also have drawn attention to the great variability of the Si–N bond distances in isocyanates and isothiocyanates[11]

V. CONFORMATIONS OF MOLECULES IN THE GAS PHASE

The X—N=C=O(S) molecules or skeletons have been shown to be planar, for example Figure 4. In many of these molecules, coplanarity is an automatic consequence of linear NCO and NCS groups. The benzene

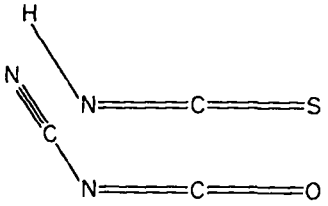


FIGURE 4. Coplanar arrangements for isothiocyanates and isocyanates.

ring and the N=C=O chain were described as coplanar in phenyl isocyanate on the basis of a microwave analysis (Figure 5). In methyl derivatives some observations (cited in Reference 38 of Reference 16)

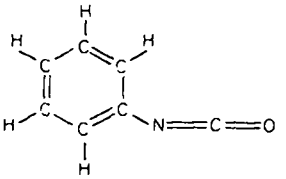


FIGURE 5. Coplanar arrangement for phenyl isocyanate.

have indicated a tendency for the pseudohalide group to eclipse one of the hydrogen atoms. This was thought to be the result of repulsion from the lone pair of electrons on nitrogen. In fact the angle of rotation could not be definitely determined from the electron diffraction data but an eclipsed conformation was preferred[5] (Figure 6). In the work cited[5] the

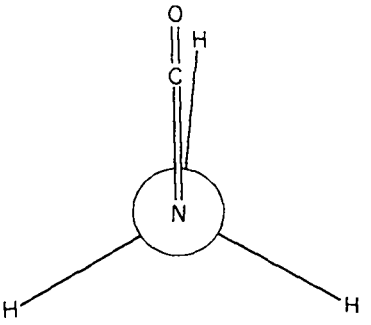


FIGURE 6. Eclipsed form of methyl isocyanate looking along $N-C(CH_3)$ axis.

zero twist angle was defined for the form in which one hydrogen atom eclipses the N=C=E group, and therefore is completely staggered with respect to the nitrogen lone pair. In our description the relative orientation of the C–H bonds and the N=C=E chain is considered. According to the microwave spectroscopic data, the barrier to internal rotation in methyl isocyanate is 83 ± 15 cal/mol[4]. On the other hand, an almost-staggered conformation with a twist angle of 54 ± 6° was found for methyl isothiocyanate[5] (Figure 7) with a 304 ± 50 cal/mol barrier to

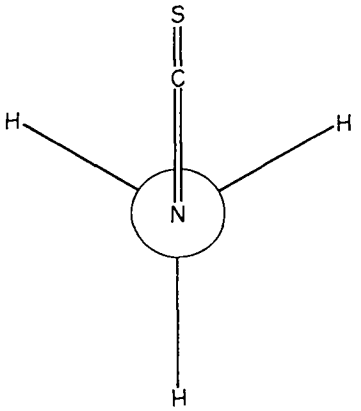


FIGURE 7. Staggered form for methyl isothiocyanate.

internal rotation[4]. There was also an attempt to refine the angle of tilt between the threefold symmetry axis of the methyl group and the carbon–nitrogen bond in the plane of the CNCE skeleton. However, the threefold axes and the C–N bonds were found to coincide within experimental uncertainties for both CH_3NCO and CH_3NCS[5].

With linear Si—N=C=E chains, i.e., C_{3v} symmetry, all conformations are equivalent by symmetry for the molecules, SiH_3NCO or SiH_3NCS (Figure 8).

The far-infrared spectroscopic studies on *t*-butyl isocyanate and isothiocyanate, $(CH_3)_3CNCE$(E = O, S) by Durig and coworkers[44] revealed that both molecules exhibit C_s symmetry with barriers to rotation around the C–N bond of 0·3 and 1·3 kcal/mol, respectively. Similar structures were determined from the electron diffraction data on $(CH_3)_3$-SiNCE (E = O, S)[11] (Figure 9).

The electron diffraction data for trifluorosilyl isocyanate, F_3SiNCO, were consistent with a model in which the following two assumptions were made: that the threefold symmetry axis of the trifluorosilyl group

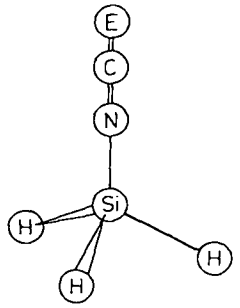


FIGURE 8. The molecule of SiH_3NCE (E = O or S) showing the C_{3v} molecular symmetry.

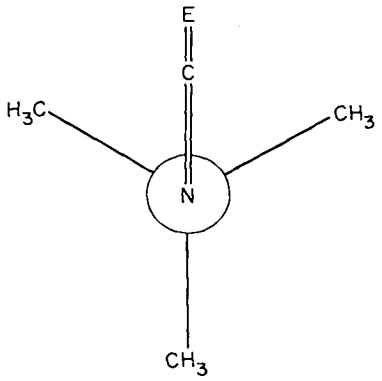


FIGURE 9. C_s symmetry conformation for trimethylsilyl isocyanate and isothiocyanate.

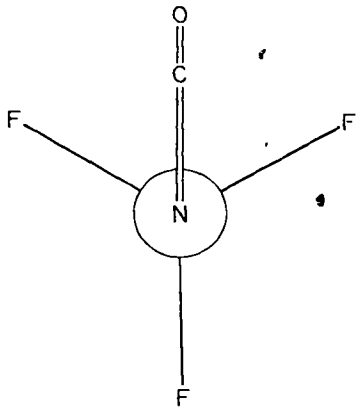


FIGURE 10. Conformation of F_3SiNCO viewed along the N–Si bond.

coincided with the Si–N bond and that the conformation is staggered with one fluorine atom in the plane of the Si—N=C=O chain[14] (Figure 10). For the analogous chlorine derivative, Cl_3SiNCO, however, neither the staggered nor the eclipsed conformation (Figure 11) (both with C_s sym-

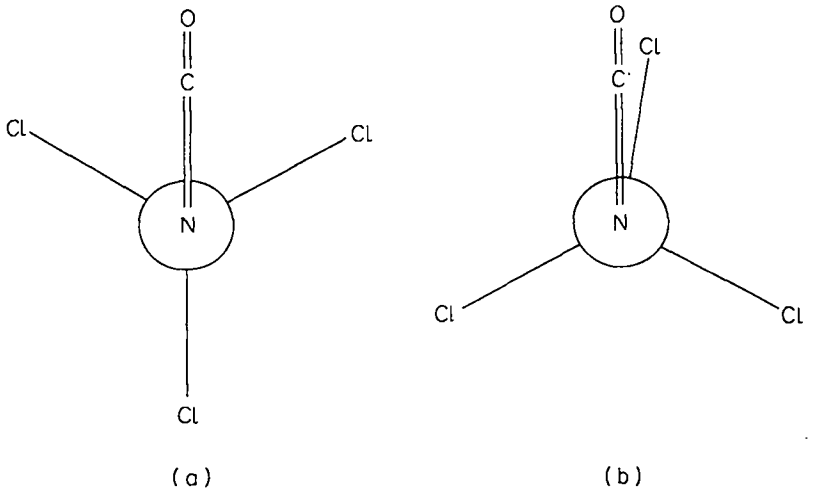


FIGURE 11. Staggered (a) and eclipsed (b) conformations for Cl_3SiNCO.

metry) gave satisfactory agreement with the experimental data[13]. Accordingly, Hilderbrandt and Bauer[13] eventually introduced two further parameters in an attempt to reach a better agreement. One such parameter was the angle of rotation (ϕ) of the NCO group relative to the

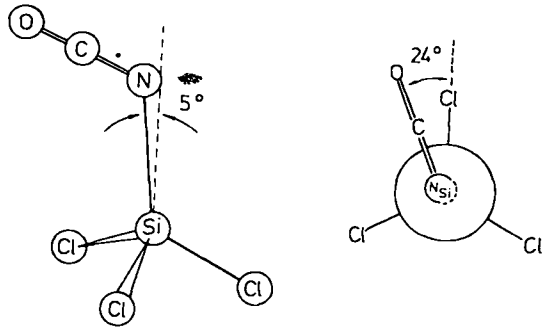


FIGURE 12. Views of the molecule of Cl_3SiNCO showing the angle of tilt between the Si–N bond and the C_3 symmetry axis of the $SiCl_3$ group and the torsion angle between the NCO group and one of the Cl atoms when viewed along the N–Si bond. This figure was modelled after one presented by Hilderbrandt and Bauer[13].

Cl_3Si group around the silicon–nitrogen bond (with $\phi = 0°$ for the eclipsed form) and the other parameter was the tilt between the threefold symmetry axis of the trichlorosilyl group and the Si–N bond. The best agreement was obtained for a model in which $\phi = 24 \pm 4°$ and the tilt angle was $5 \pm 1°$ as illustrated by Figure 12.

Similarly, the experimental electron diffraction data for $Cl_2Si(NCO)_2$ could be better approximated with a C_2 symmetry model than with a C_{2v} symmetry model. Both of these possible models are shown in Figure 13 with side views and projections along the twofold axes[13].

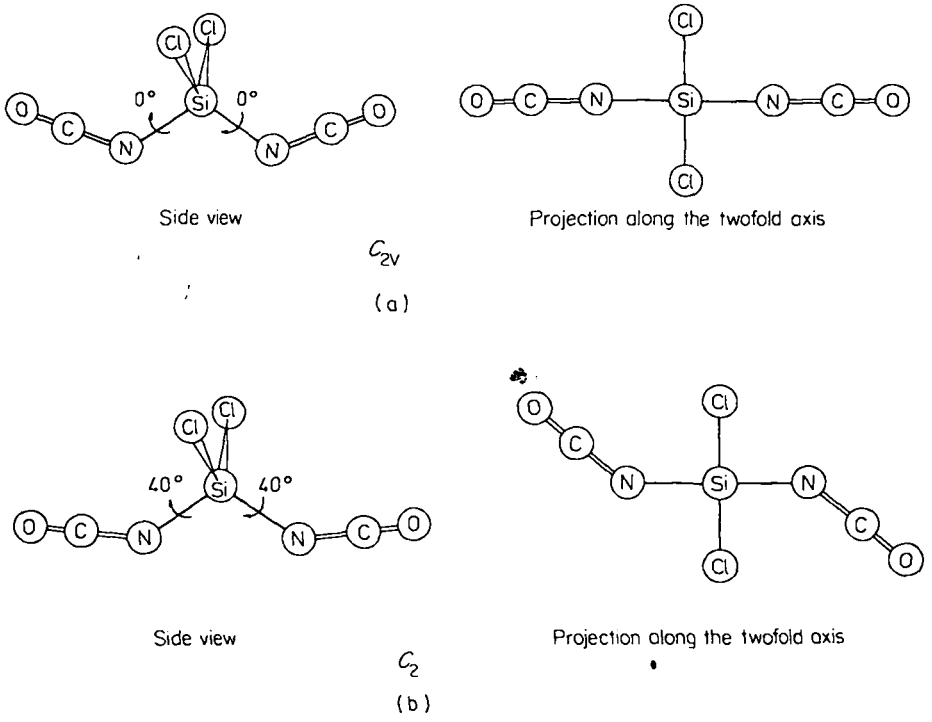


FIGURE 13. Two possible models for the $Cl_2Si(NCO)_2$ molecule: (a) a C_{2v} model seen from two orientations; (b) a C_2 model seen from two orientations. This figure was modelled after one presented by Hilderbrandt and Bauer[13].

A study on $ClSi(NCO)_3$ was carried out simultaneously and resulted in a C_3 conformation as shown by its projection along the threefold symmetry axis in Figure 14 rather than the C_{3v} model to which it is related by rotations of 85·5° around the Si–N bonds[13].

The vibrational spectra of Cl_3SiNCO as well as Cl_3SiNCS were inter-

preted in terms of a C_{3v} model[33]. For $ClSi(NCO)_3$ the difficulty of distinguishing between C_{3v} and C_s models was stressed.

The vibrational spectra of $Si(NCO)_4$ and $Si(NCS)_4$ were interpreted in terms of T_d symmetry[34–36]. Assuming a tetrahedral arrangement of the nitrogen atoms in the electron diffraction study of Hjortaas[12], the best agreement was produced with models in which the NCO groups were freely rotating around the Si–N bonds.

Various disagreements between the spectroscopic and electron diffraction results for silyl isocyanates clearly demonstrate the difficulties of interpreting and reconciling data from different physical techniques, and the great importance of molecular motion in discussing molecular geometry.

There are very few data on the conformation of germyl isocyanate. The vibrational spectra were assigned on the basis of a pseudo symmetric top model with $C_{3v} \simeq C_s$ symmetry[39] and the electron diffraction structural analysis appears to have been performed with the assumption of a staggered conformation[15].

For difluorophosphino isocyanate and isothiocyanate, F_2PNCO and F_2PNCS, the electron diffraction structural analyses have been performed

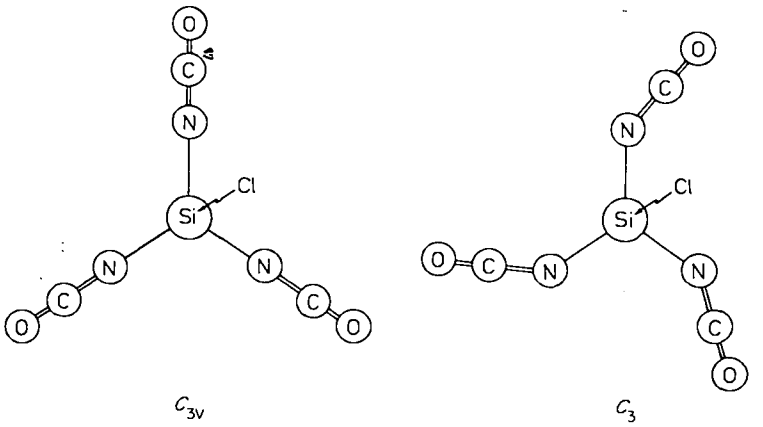


FIGURE 14. Two possible conformations for the molecule of $ClSi(NCO)_3$: one has C_{3v} symmetry while the other has C_3 symmetry. This figure was modelled after one presented by Hilderbrandt and Bauer[13].

by Rankin and Cyvin[16] constraining the NCE group to the *anti* position with respect to the bisector of the F—P—F angle (C_s symmetry) and later allowing rotation around the phosphorus–nitrogen bond. Various models have been tested some with fixed dihedral angles and others with

free or slightly restricted rotation. The molecular model is shown in Figure 15. The best agreement with experimental data was obtained with a dihedral angle of 14° for both compounds. Refinement schemes were also

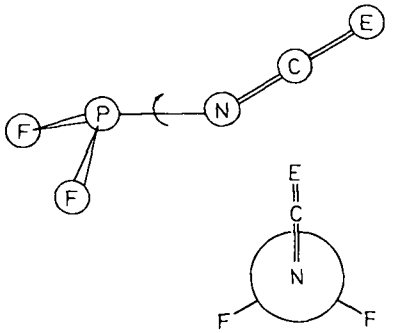


FIGURE 15. A view of the molecular model for F_2PNCE (E = O or S) one looking normal to the plane of the PNCE group and the other looking along the N–P bond.

constructed in which the internuclear distances that are different in the C_s symmetry model were treated as independent parameters. Such an approach may prove to be very useful in a case where the molecule undergoes large amplitude motion. Such motion will result in considerable shrinkage effects and therefore even the bond distances may be strongly influenced if geometrical constraints are applied. In the absence of reliable spectroscopic data for the torsional frequencies, it may not be possible to distinguish between a model with C_s symmetry with the N=C=E groups in *anti* positions to the PF_2 bisectors but with large amplitude torsional motion around the P–N bond, and a model in which there is some deviation from this symmetry and a somewhat smaller amplitude of torsional motion.

The determination of the molecular conformation of $Cl_2(O)PNCO$ was particularly difficult because of very strong correlation between the dihedral angle (ϕ) and the bond angle P—N=C[17]. The most probable structure turned out to be the one in which the P=O bond is in an *anti* position with respect to the N=C=O chain ($\phi = 0°$). However, as the method of gradient was applied for the radial distributions, two other minima were obtained. The corresponding dihedral angles and bond angles are listed below:

$$\phi = 0° \quad \text{and} \quad \angle P{-}N{=}C = 120°$$

$$\phi = 90° \quad \text{and} \quad \angle P{-}N{=}C = 126°$$

$$\phi = 160° \quad \text{and} \quad \angle P{-}N{=}C = 125°$$

The molecular conformations are illustrated by the projections along the P–N bond (Figure 16). Because it gave the best agreement with experimental data, the conformation with $\phi = 0°$ is considered to prevail at least in the vapour phase, although it is not possible to rule out the presence of other conformers[45].

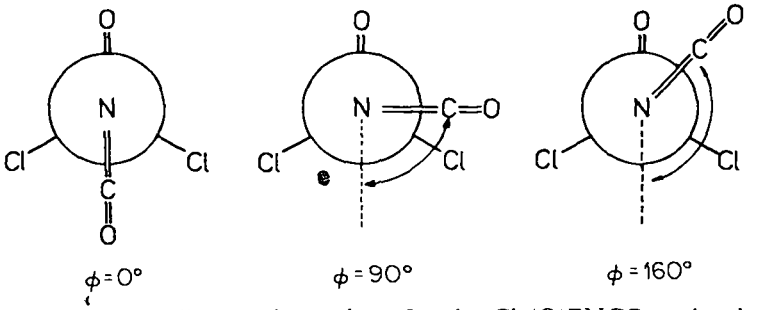


FIGURE 16. Some possible conformations for the $Cl_2(O)PNCO$ molecule looking along the N–P bond with different torsion angles.

VI. GEOMETRICAL VARIATIONS IN THE REST OF THE MOLECULE AS OBSERVED IN THE GAS PHASE

The structural variations in the rest of the molecule may reveal the influence of a functional group such as isocyanate or isothiocyanate. While variations in chemical behaviour can be most directly correlated with change in electronic structure, it is possible that some conclusions might also be drawn on the basis of geometrical changes. In the following discussion we have restricted ourselves to a comparison of selected features in some related molecules.

While it would be of interest to compare the lengths of the cyanide bonds in the molecules of N=C—N=O and N=C—N=C=O, the length determined for the former molecule (1·170 Å[46]) was assumed in the study of the latter[6]. This bond distance is somewhat larger than those determined in cyanogen azide (1·155 ± 0·002 Å) and azodicarbonitrile (1·151 ± 0·001 Å) both by electron diffraction[47]. However, it should be noted that in the two latter compounds, Almenningen and collaborators have observed non-linear N=C—N and N=N=N chains in terms of r_a average structures[47].

No discussion of the benzene ring structure in C_6H_5NCO is relevant since values for the dimensions were assumed and were utilized for this part of the molecule in the microwave spectroscopic investigation of the structure[7].

The electron diffraction study of trimethylazidosilane, $(CH_3)_3SiN_3$, by Dakkouri and Oberhammer[48] revealed only C_1 symmetry. These authors found a value of 1·854 ± 0·003 Å for r_a (Si–C) as compared to a value for r_g(Si–C) of 1·89 ± 0·01 Å in $(CH_3)_3SiNCO$[11]. Because of the low symmetry, all the bond angles around the silicon atom in $(CH_3)_3SiN_3$ were found to be different. However, the values for these bond angles are not relevant for our present discussion since the bond angles at silicon were not reported in the determination of $(CH_3)_3SiNCO$. The molecular conformation of $(CH_3)_3SiNCO$ is such that there is a rotation of 36·2 ± 4·9° from the form with the N–C and Si–C bonds eclipsed[48].

There are considerable geometric data for molecules with silicon–chlorine bond(s). Some of the Si–Cl bond lengths and Cl—Si—Cl bond angles are compiled in Table 7. The most noteworthy feature of these

TABLE 7. The lengths of the Si–Cl bonds and the values of the Cl—Si—Cl bond angles in a series of molecules

	r(Si—Cl) (Å)	∠Cl—Si—Cl	Reference
$SiCl_4$	2·019 ± 0·003	Tetrahedral	49
$HSiCl_3$	2·021 ± 0·002		50
$(CH_3)_2NSiCl_3$	2·023 ± 0·005	107·6 ± 0·4°	51
H_3SiCl	2·0479 ± 0·0007	—	52
$[(CH_3)_2N]_3SiCl$	2·082 ± 0·006	—	53
Cl_3SiNCO	2·015 ± 0·005	109·5°[a]	13
$Cl_2Si(NCO)_2$	2·024 ± 0·005	107·7 ± 0·6°	13
$ClSi(NCO)_3$	2·020 ± 0·009	—	13

[a] The angle Z—Si—Cl is given as 109·5 ± 0·2° in Reference 13, where Z corresponds to the threefold axis of the $SiCl_3$ group.

dimensions is the constancy of the Si–Cl bond distances in the isocyanate derivatives and their close similarity to those in tetrachlorosilane. For some other substituents larger deviations are seen and these deviations seem to be sensitive to the number of substituents considered.

A remarkable lack of variation can be observed in the structures of the fluorophosphine derivatives, data for which are compiled in Table 8. Even those changes in the phosphorus bond angles that can be noted may not be significant because of the very strong correlation between the ∠F—P—F and ∠F—P—N angles in the electron diffraction analysis[16].

For the dichlorophosphinyl compounds (see in Table 9) again some substantial differences may be concealed by the relatively large experimental errors and in any case no detailed discussion seems to be justified.

All in all the lack of large structural changes that can be correlated with

TABLE 8. Geometrical parameters of some fluorophosphine derivatives

	r(P—F) (Å)	∠F—P—F	∠F—P—N	Reference
PF_3	1·570 ± 0·001	97·8 ± 0·2°	—	54
F_2PCN	1·568 ± 0·003	97·9 ± 0·3°	—	55
F_2PNCO	1·565 ± 0·003	97·9 ± 0·8°	99·5 ± 0·7°	16
F_2PNCS	1·567 ± 0·003	99·4 ± 0·9°	97·7 ± 0·8°	16

the presence of the isocyanate, or for that matter of the isothiocyanate, group suggest that no strong influences are exercised by these groups on the rest of the molecule.

VII. TWO THIOCYANATES IN THE GAS PHASE

The bond lengths and bond angles characterizing the geometry of the CSCN skeleton in the two thiocyanates, CH_3SCN and CH_3CH_2SCN, as determined by microwave spectroscopy are presented in Table 10. For methyl thiocyanate a complete r_s structure was determined while only r_0 values were given for the ethyl derivative since only one isotopic species was investigated for this compound. The geometrical parameters are seen to be very similar for the two compounds.

TABLE 10. Bond lengths and bond angles in two thiocyanate molecules

	CH_3SCN[26]	CH_3CH_2SCN[61]
r(C—S) (Å)	1·824 ± 0·002	1·820
r(S=C) (Å)	1·684 ± 0·003	1·690
r(C≡N) (Å)	1·170 ± 0·002	1·160
∠C—S—C	99°2′ ± 5′	101·0°

Only the conformation that has the CH_3 and C≡N groups in a *gauche* orientation about the C–S bond was identified from the microwave spectrum[61] of ethyl thiocyanate. Because of a strong correlation between the C—S—C bond angle and the dihedral angle shown in Figure 17, the values determined for these parameters have large uncertainties. Since no lines originating from the *anti* conformer were assigned, Bjørseth and Marstokk[61] concluded that the *gauche* form should be at least 0·8 kcal mol^{-1} more stable than the *anti* form. A recent extensive vibrational spectroscopic study[62] showed that only the *gauche* form was present in the solid, liquid and vapour phases, a result that was at variance with earlier observations[63]. The determination of the force field of ethyl thiocyanate based on the *gauche* form was recently communicated[64].

TABLE 9. Geometrical parameters of some dichlorophosphinyl derivatives

	r(P—Cl) (Å)	r(P=O) (Å)	∠Cl—P—Cl	r(P—N) (Å)	Reference
$POCl_3$	1·993 ± 0·003	1·449 ± 0·005	103·3 ± 0·2°	—	56
	1·989 ± 0·002	1·455 ± 0·005		—	57
$Cl_2(O)PN(CH_3)_2$	2·033 ± 0·008	1·47 ± 0·02	102 ± 1°	1·67 ± 0·04	58
$Cl_2(O)PNCO$	2·006 ± 0·005	1·455 ± 0·010	103·9°[a]	1·684 ± 0·010	17
$Cl_2(O)PCH_3$	2·032 ± 0·009	1·448 ± 0·005	101·8°[a]	—	59
$Cl_2(O)PC_6H_5$	2·025 ± 0·005	1·47 ± 0·01	102 ± 2°	—	60

[a] Calculated from other bond angles that were used as independent parameters in the structural analysis; uncertainties not given.

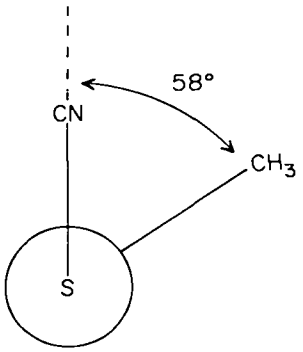


FIGURE 17. Torsion angle between the CH_3 and CN group in ethyl thiocyanate viewed along the S–C bond.

VIII. CRYSTAL STRUCTURE DATA ON COVALENT CYANATES AND ISOCYANATES

The only single crystal X-ray structure analysis on a cyanate or isocyanate group covalently bound to an 'organic' moiety seems to be that on the parent isocyanic acid, itself, HNCO[65]. Even in this instance, the use of the term 'organic' is rather arbitrary.

On the basis of powder photographs, von Dohlen and Carpenter[65] concluded that there were two crystalline modifications of isocyanic acid. The transition temperature between the two forms was not determined exactly but was believed to be in the neighbourhood of $-100\,°C$. The structure of the low temperature form was not determined; the high temperature form is orthorhombic and the space group is either *Pnma* or $Pn2_1a$. The X-ray analysis was carried out assuming the former possibility, which, as there are four molecules in the unit cell, requires the molecule to have C_s crystallographic symmetry if the structure is ordered. The results of the analysis showed that the positions of the carbon, nitrogen, and oxygen atoms lay on or very close to the plane $y = 1/4$ and therefore conformed to the symmetry requirements for the space group *Pnma;* however, the hydrogen atom could not be located. As the intensity data were collected by photographic methods, the failure to locate the hydrogen atom is not terribly surprising.

The bond lengths and angles found in the study are listed in Table 11, together with the dimensions found in the gas phase by microwave spectroscopy[1] and by electron diffraction[66]. The errors quoted in the X-ray study were estimated both from the least squares results and from Fourier results[21]. Within the limits of error quoted from the X-ray study, the N–C and C–O bond lengths are in good agreement. Von Dohlen and

TABLE 11. Dimensions found in isocyanic acid

	H—N(Å)	N—C(Å)	C—O(Å)	H—N—C (deg)	N—C—O (deg)
X-ray study[a]	—[b]	1·183(20)	1·184(20)	—[b]	179(1)
Microwave study[c]	0·987(10)	1·207(10)	1·171(10)		—[d]
Electron diffraction study[e]	1·01[f]	1·19(3)	1·19(3)	—[g]	—[h]

[a] Reference 65.
[b] The hydrogen atom was not determined in the X-ray study.
[c] Reference 1.
[d] The N—C—O angle was assumed to be linear.
[e] Reference 66.
[f] Estimated distance.
[g] The hydrogen atom was not located.
[h] The intensities were consistent with a linear N—C—O group.

Carpenter[65] also concluded that the deviation of the N—C—O angle from linearity was not significant.

Three possible models were considered in the analysis: (a) that the space group is *Pnma* and the molecules are ordered in the crystal; (b) that the space group is *Pnma* but the hydrogen atoms are disordered above and below the mirror plane, and (c) that the true space group is $Pn2_1a$ and the heavy atoms conform fairly closely to the *Pnma* space group symmetry. The ordered arrangement in *Pnma* was apparently rejected on the basis of an unfavourable hydrogen bonding arrangement. If the hydrogen atom lay within the plane $y = 1/4$, there would be an N—H···O hydrogen bond with an N···O distance of 3·19 Å and C—N···O and N···O—C angles of 157·3° and 162·9°. This arrangement was considered unlikely because the C—N···O angle would imply a near-linear C—N—H angle, which would not be in agreement with the value found in the microwave study[1]. Attempts to construct models in the $Pn2_1a$ space group did not give an improved fit to the observed data. The assumption of the space group *Pnma*, but with the inclusion of the hydrogen atom in a disordered arrangement above and below the mirror plane, gave a somewhat better fit to the observed data. Such an arrangement would imply an N—H···N hydrogen bond with an N···N distance of 3·07 Å and a C—N···N angle of 102·6°, which would correspond to a C—N—H valency angle close to that found in the vapour phase[1]. The crystal would then consist of a series of zig-zag chains of HNCO molecules, held together with N—H···N hydrogen bonds, running along the *b*-crystallographic axis (Figure 18).

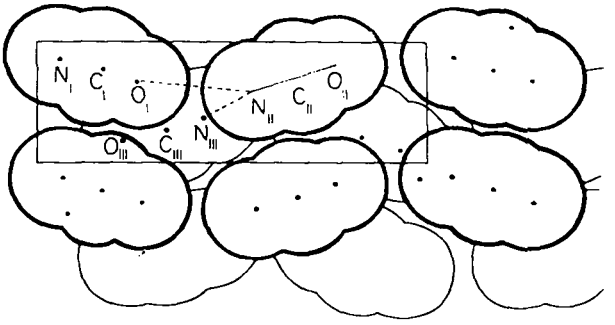
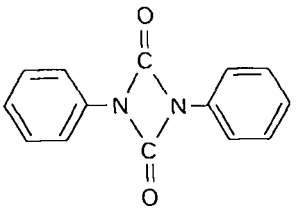


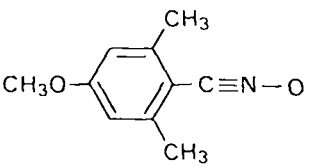
FIGURE 18. The crystal structure of the high-temperature form of HNCO viewed down the *b*-axis. Atoms are drawn with van der Waals radii. The heavy-outlined molecules lie at $y = 1/4$, the lightly-outlined molecules at $y = -1/4$. [After von Dohlen and Carpenter, *Acta Crystallogr.*, **8**, 646 (1955).]

Herzberg and Reid[67] noted a large shift in the N–H stretching frequency upon going from the vapour (3531 cm^{-1}) to the crystal (3133 cm^{-1} at $-196\,^{\circ}C$) and interpreted the change as being due to a strong hydrogen bond in the solid. However, von Dohlen and Carpenter[65] recognized that the data of Herzberg and Reid referred to the low temperature form. Von Dohlen and Carpenter studied the N–H stretching frequency in the higher temperature solid and found that the frequency was not shifted so much (3400 cm^{-1} at $-89\,^{\circ}C$), and interpreted the results as indicating a weaker hydrogen bond in the higher temperature form than in the low temperature form. They indicated that these spectroscopic results are consistent with an N—H···N hydrogen bond in the high temperature form and an N—H···O hydrogen bond in the low temperature form.

Two crystal structures that are somewhat related to the structures of cyanates and isocyanates are those of the phenyl isocyanate dimer (**3**)[68] and of 4-methoxy-2,6-dimethylbenzonitrile-*N*-oxide (**4**)[69].



(**3**)



(**4**)

When phenyl isocyanate is treated with pyridine and the product crystallized from benzene, crystals of a dimeric species are obtained that have been shown by X-ray analysis[68] to correspond to the centrosym-

metric dimer (3) formed by ring formation between the C–N multiple bonds. In the crystal, the dimer has a central four-membered ring with non-equivalent C–N bonds of 1·42(1_4) and 1·49(1_4) Å and an exocyclic C–O bond of 1·15(1_4) Å.

A preliminary report on the study of the nitrile *N*-oxide, containing the group C—N—O, 4-methoxy-2,6-dimethylbenzonitrile-*N*-oxide (4), has been published[69]. This group is very nearly linear, but has the sequence of the carbon and nitrogen atoms interchanged from that found in isocyanates. The C–N and N–O bond lengths in the C—N—O group are 1·147(8) and 1·249(8) Å, and the C(ring)—C—N and C—N—O angles are 173·8(6) and 178·3(6)°. The C—N—O group lies effectively in the plane of the phenyl ring. The structure of the parent acid, fulminic acid (HCNO), has been shown to be linear on the basis of a microwave study in the gas phase[70]. The H–N, N–C, and C–O bond lengths in this latter study were 1·027(1), 1·161(15), and 1·207(15) Å.

IX. CRYSTAL STRUCTURE DATA ON COVALENT THIOCYANATES AND ISOTHIOCYANATES

The crystal structures of several molecules that contain the thiocyanate group in a covalently bonded form have been solved. Some of the structures that have been determined more reliably are listed in Table 12. In addition the structure of *p*-thiocyanatoaniline has been determined on the basis of projection data, although no very reliable bond length or angle data can be taken from the study[76]. (*Note Added in Proof*: A new report on this structure based on a complete reinvestigation has just appeared [I. V. Isakov, E. E. Rider, and Z. V. Zvonkova, *Cryst. Str. Commun.*, **5**, 95 (1976)]. In this report, the S–C and C–N distances were 1·704(4) and 1·132(5) Å, respectively, while the S—C—N and C(ring) —S—C angles were 178·4(3) and 99·9(2)°, respectively. In contrast to the statements in the earlier report[76], the thiocyanate group lies significantly from the plane of the phenyl ring with S, C, and N lying −0·051, 1·550, and 2·610 Å, respectively, from that plane. There do not appear to be any hydrogen bonds involving the amino group in the structure. The packing of the molecules is shown in Figure 19.)

Values for the C–S bond lengths in the covalently-bonded thiocyanates listed in Table 12 range from 1·63(1) to 1·736(15) Å; the most reliable determination is probably that of 1·677(9) Å for the length in methylene dithiocyanate ($CH_2(SCN)_2$)[71]. There are insufficient data and evidence to reach any judgment as to whether the C–S length varies with the nature of the atom attached to sulphur. However, the longer C–S bonds that are found in the structure of sulphur dicyanide[75] may arise from the rather smaller valency angle at sulphur in this compound. The C–N bond

TABLE 12. Molecular dimensions in some covalently-bound thiocyanate groups

Compound	Crystallographic molecular symmetry	S—C (Å)	C—N (Å)	S—C—N (deg)	C—S—X[a] (deg)	Torsion angle[b] C—S—X—Y (deg)	Reference
$CH_2(SCN)_2$[c]	C_2	1·677(9)	1·194(12)	176·4(1·0)	98·2(4)	71	71
$(CH_2SCN)_2$	C_i	1·63(1)	1·18(2)	172·3(1·3)[d]	99·4(7)	78	72
$S(SCN)_2$[c]	C_s	1·69[e]	1·21	180	99	87	73
$Se(SCN)_2$[f]	C_s	1·69[e]	1·13	178·8	104	79	74
$S(CN)_2$	C_1	1·736(15) 1·718(18)	1·118(21) 1·134(23)	177·5(1·3) 176·4(1·7)	95·6(8)	—	75

[a] Atom X refers to the atom covalently bonded to sulphur.

[b] Atom Y refers to atom covalently bonded to atom X. The torsion angle C—S—X—Y is the angle that the C—S bond makes with the X—Y bond, when projected along the S–X bond. The sign of the torsion angle is neglected in this compilation.

[c] The two S—C—N groups in the molecule are related to each other by crystallographic symmetry.

[d] The authors[72] say that the deviation from linearity may not be significant.

[e] No estimated standard deviations were given in the paper.

[f] Very limited data available for this analysis.

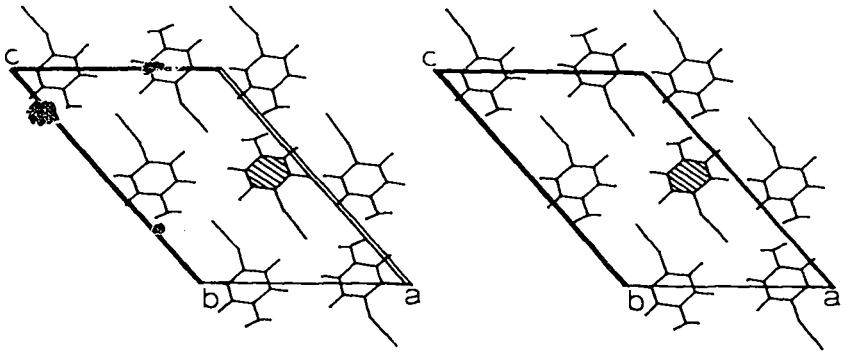


FIGURE 19. Stereoscopic view of the packing of *p*-thiocyanatoaniline in the crystal. This figure was drawn from the very recently published results (see note added in proof on p. 101) and differs considerably from that based on the results given earlier in Reference 76. The reference molecule is shaded. The shortest non-hydrogen intermolecular contact is 3·253 Å between N(amino) and N(thiocyanato) in the molecule at x, $2\frac{1}{2} - y$, $1/2 + z$, but the corresponding H···N(thiocyanato) distance is 2·49 Å.

lengths vary from 1·118(21) to 1·194(12) Å. One might anticipate that some of the variety in C–N bond lengths in thiocyanates may result from artifacts due to the type of thermal motion encountered in the crystal, as was discussed in Section I. While the relatively low accuracy of many of the crystal structure determinations must be recognized, there is no evidence that there are significant differences between the bond lengths for the thiocyanate group as determined in the crystal by X-ray structure analysis and in the gas phase by microwave spectroscopy. The molecule of sulphur dicyanide is one of the few molecules discussed in this chapter that has been studied in both the gas phase (by microwave spectra[77] and by electron diffraction[78]) and in the crystal (by X-ray diffraction[75]). A comparison of the geometric data is shown in Table 13. The most detailed

TABLE 13. Comparison of geometrical parameters for the molecule of sulphur dicyanide, $S(CN)_2$

Method	C—S(Å)	C—N(Å)	C—S—C (deg)	N—C—S (deg)	Reference
X-ray diffraction	1·73(2)	1·12(2)	95·6(8)	177(1)	75
Microwave spectroscopy	1·701(2)	1·157(2)	98·37(17)	—[a]	77
Electron diffraction	1·65(1)	1·19(1)	101(1)	—[b]	78

[a] In the text of Reference 77, it is stated that the N—C—S angle deviates from linearity by 5°.

[b] No information on the linearity of the N—C—S group was given.

studies are those using microwave spectroscopy and X-ray diffraction and they reveal no significant differences in the dimensions.

There are also no clear cut answers to the question as to whether the thiocyanate group is strictly linear or not. In ethylene dithiocyanate, the S—C—N angle was found to be 172.3(1·3°), yet Bringeland and Foss concluded that 'the deviation from linearity of the thiocyanate group is probably not significant'[72]. In describing their analysis of methylene dithiocyanate, Konnert and Britton[71] concluded that their value for the S—C—N angle of 176·4(1·0)° was possibly real. They pointed out that the deviations from linearity of the S—C—N groups were away from the methylene carbon atoms. In the structure of sulphur dithiocyanate, the S—C—N angle was 180°; however, no standard deviations were given in the paper.

The C—S—X angles, where X is the atom covalently bonded to sulphur, lie in a fairly narrow range, particularly if the value of 104° found in the structure of selenium dithiocyanate is given low weight in the comparisons; the other values lie in the range 95·6(8) to 99·4(7)°. The torsion angles made by the thiocyanate group around the S–X bond with an X–Y bond (Figure 20) will be described under each structure.

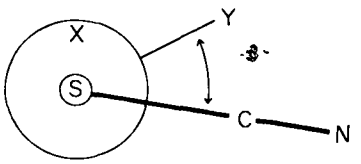


FIGURE 20. Torsion angle made by the thiocyanate group with the X–Y bond when viewed along the S–X bond. Atom X is the atom covalently bonded to sulphur, while atom Y is covalently bonded to atom X.

A stereoscopic view of the molecule of $CH_2(SCN)_2$ is shown in Figure 21. The molecule has C_2 molecular symmetry with the SCN groups taking up a *trans* arrangement. The (NC)S–C(S) torsion angle is 71°. A view of the molecular packing is shown in Figure 22. Konnert and Britton[71] have pointed out that there are similarities in the crystalline environment around sulphur and selenium in several of the thiocyanate and selenocyanate structures. They have pointed out that in $S(SCN)_2$[73] about the two crystallographically-independent sulphur atoms, in $Se(SCN)_2$[74] about both selenium and sulphur, in $Se(SeCN)_2$[74] about the two crystallographically-independent selenium atoms, about the one crystallographically-distinct sulphur in $(CH_2SCN)_2$[72], and about the one sulphur in $S(CN)_2$[75], there is a tendency for two nitrogen atoms from other thiocyanate or

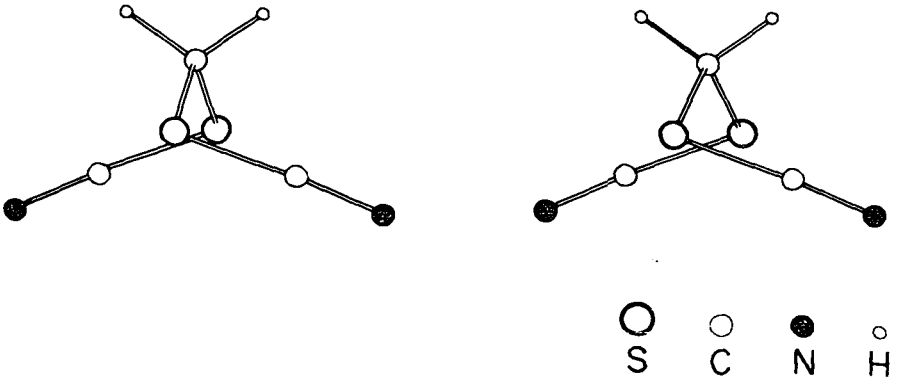


FIGURE 21. Stereoscopic view of a single molecule of methylene dithiocyanate. Drawn by us from the coordinates from Reference 71.

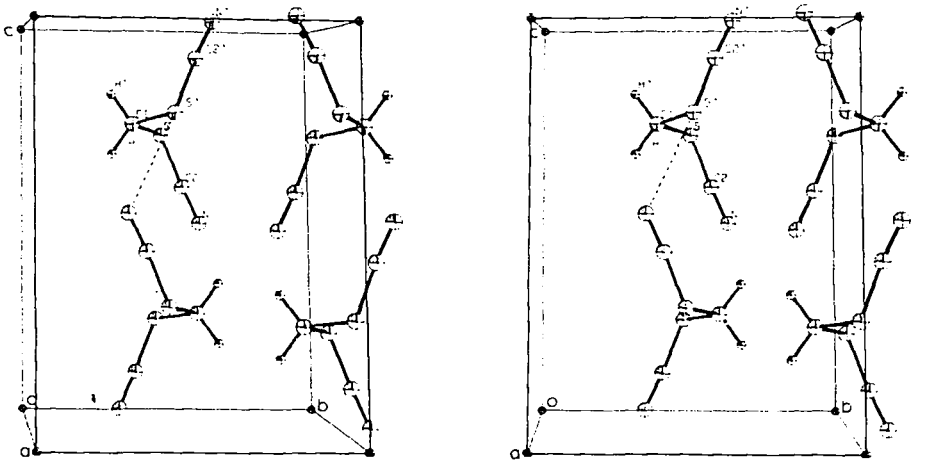


FIGURE 22. Stereoscopic view of the molecular packing in the crystal for methylene dithiocyanate. Drawn by us from the coordinates presented in Reference 71. The intermolecular interaction between sulphur and the nitrogen of a thiocyanate group is shown by a discontinuous line.

selenocyanate groups to approach an approximate square planar arrangement (Figure 23). The non-bonded S···N distances range from 2·95 to 3·39 Å (sum of the van der Waals radii is 3·35 Å, if one takes the value of 1·85 Å given by Pauling[80]; see however, Reference 81), while the Se···N distances lie between 2·98 and 3·25 Å (sum of van der Waals radii is 3·5 Å[80]). Not only is the square arrangement of substituents quite common, but the nitrogen atoms tend to lie close to the plane defined by the sulphur

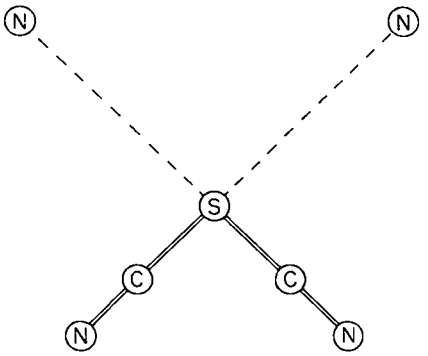


FIGURE 23. Approximately square–planar arrangement shown around the central sulphur or selenium atom with two covalently-bound carbon atoms and two approaching non-bonded nitrogen atoms.

(or selenium) atom and its two covalently-bonded neighbours. A diagrammatic representation of many of these arrangements is shown in Figure 24. In methylene dithiocyanate, however, only one such interaction was present with an S···N distance of 3·17 Å. Many of the analogous compounds, such as $Se(SCN)_2$, $S(SCN)_2$, and $Se(SeCN)_2$ adopt C_s symmetry in the crystal, possibly on account of the tendency to form two of these intermolecular interactions. It was suggested by Konnert and Britton[71] that, in $CH_2(SCN)_2$, the stability gained by a second intermolecular S···N interaction was insufficient to pull the molecule into the presumed less stable (for an isolated molecule) C_s conformation. However, in the crystal of $CH_2(SCN)_2$, the one nitrogen atom that interacts with sulphur does so from one of the positions expected for a square–planar type of arrangement.

A stereoscopic view of the molecule of $Se(SCN)_2$[74] is shown in Figure 25. The molecule has C_s symmetry in the crystal. The (NC)S–Se(S) torsion angle is 79°. A stereoscopic view of the packing is shown in Figure 26. Both the selenium and sulphur atoms in this molecule participate in Se···N and S···N intermolecular interactions with square–planar types of arrangement. The crystal of $S(SCN)_2$ is isostructural with that of $Se(SCN)_2$. The (NC)S–S(S) torsion angle is 87°.

A stereoscopic view of ethylene dithiocyanate $(CH_2SCN)_2$[72] is shown in Figure 27. The molecule has C_i symmetry in the crystal with the thiocyanate groups pointing in a direction normal to the plane of the four central atoms. The (NC)S–C(C) torsion angle is 78°. A view of the packing is shown in Figure 28. There are S···N intermolecular interactions.

There has been considerable confusion regarding the crystallography

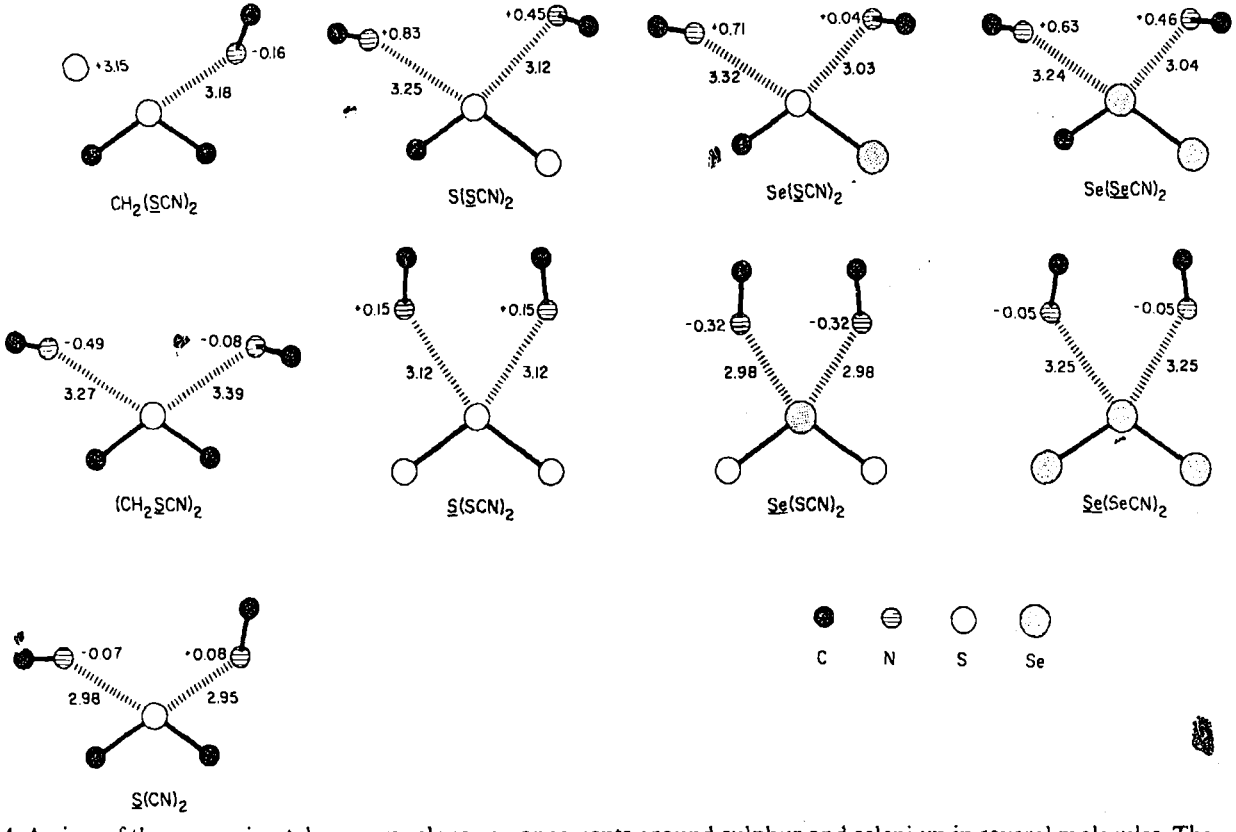


FIGURE 24. A view of the approximately square-planar arrangements around sulphur and selenium in several molecules. The central atom in the arrangement depicted is underlined. The intermolecular interactions are shown by shaded lines with the distance in Å marked beside the line. The distance of the atom from the plane of the central atom and its two covalent neighbours is also given. This Figure is modelled after one presented by Konnert and Britton[71].

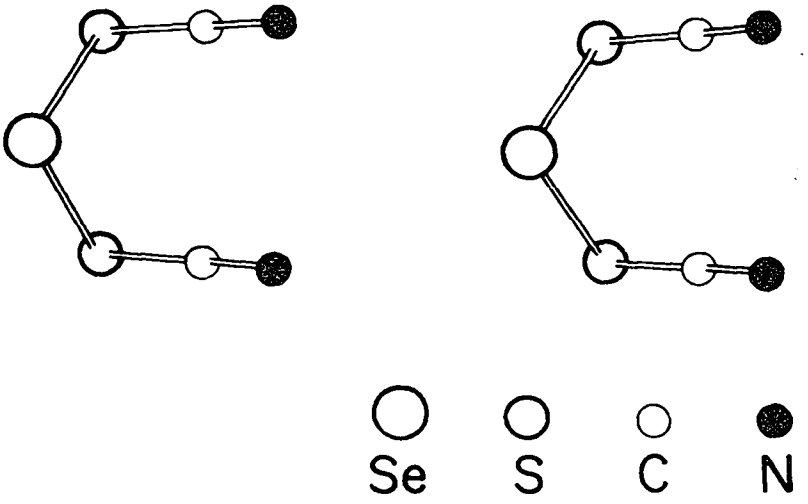


FIGURE 25. Stereoscopic view of a single molecule of $Se(SCN)_2$. Drawn by us from the coordinates presented in Reference 74.

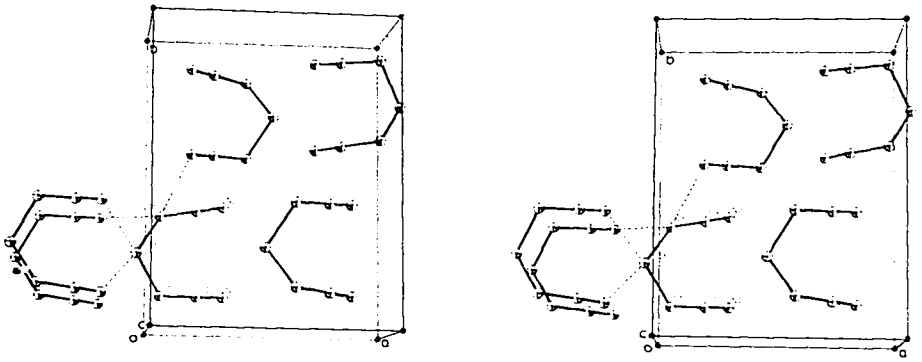


FIGURE 26. Stereoscopic view of the packing in the crystal of $Se(SCN)_2$. Drawn by us from the coordinates presented in Reference 74. The approximately square planar arrangements of intermolecular interactions with nitrogen atoms around both nitrogen atoms around the sulphur atom is shown by discontinuous lines.

of $S(CN)_2$. First, Fehér, Hirschfeld, and Linke[82] reported that the crystals were orthorhombic, $a = 10{\cdot}80$, $b = 12{\cdot}70$, and $c = 5{\cdot}310$ Å, that the space group was $P2_12_12_1$ and that there were four molecules in the unit cell. Then Hazell[83], in studying the structure of $Se(CN)_2$, observed that $S(CN)_2$ was isomorphous with $Se(CN)_2$. He reported cell data of $a = 8{\cdot}60$, $b = 6{\cdot}85$, and $c = 12{\cdot}80$ Å and that the space group was *Cmca*. Emerson[75]

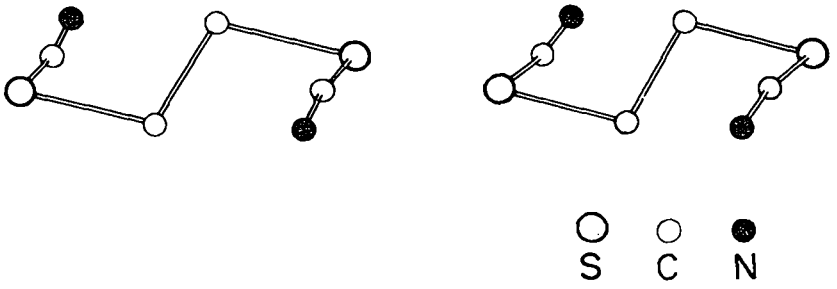


FIGURE 27. Stereoscopic view of a single molecule of ethylene dithiocyanate. Drawn by us from the coordinates in Reference 72.

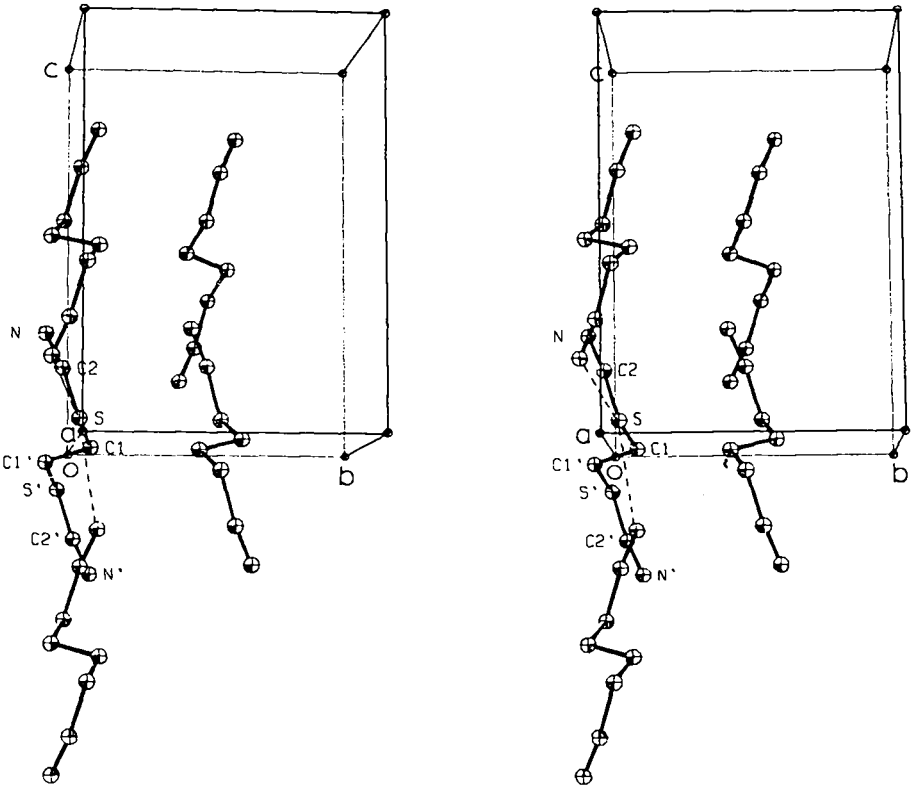


FIGURE 28. Stereoscopic view of the molecular packing in the crystal of ethylene dithiocyanate. Drawn by us from the coordinates presented in Reference 72. The approximately square–planar arrangement of intermolecular interactions with nitrogen atoms around the sulphur atom is shown by discontinuous lines.

found effectively the same cell dimensions for $S(CN)_2$ as had Hazell, but he concluded that the space group was *Pbca*. He also showed that the results obtained by Fehér and coworkers could arise if the crystal was rotating about the [011] direction and an incomplete examination of the diffraction spectra had been undertaken. Emerson carried out a structure analysis on $S(CN)_2$ and refined the model to an *R*-factor of 0·106. In attempting to reconcile the differences between Hazell's results and his own, Emerson observed that the sulphur atom positions in $S(CN)_2$ (i.e., excluding the rest of the structure) approximate *Cmca* symmetry and such an effect would be enhanced in the isomorphous selenium compound. Hazell[84] now indicates that the two compounds are probably isomorphous and that the space group he reported for $Se(CN)_2$ and in which he refined the structure, is probably incorrect. Hence, the true space group for both compounds is probably *Pbca*.

Recently, we have been made aware (through correspondence with Dr A. C. Hazell) of some additional X-ray structural work on the molecules of $S(CN)_2$ and $Se(CN)_2$. Linke and Lemmer[85–87] have reported analyses for $S(CN)_2$ and $Se(CN)_2$ based on projection data. They assigned the space group *Pbca* for both compounds. In the case of $S(CN)_2$, their results appear less reasonable than those of Emerson[75]; for example, Linke and Lemmer report S–C lengths of 1·87 and 2·07 Å, whereas Emerson found 1·736 and 1·718 Å.

The thiocyanate ion has been studied in the crystal structures of KSCN[88] and NH_4SCN[89], although the latter analysis suffered from a lack of data and a relatively low level of refinement. In the KSCN complex, the structure is clearly ionic with the shortest $K^+ \cdots S$ and $K^+ \cdots N$ distances being 3·27 and 2·97 Å, respectively. The thiocyanate ion is essentially linear with the N—C—S angle being 178·3(1·2)°; the S–C and C–N bond lengths are 1·69(1) and 1·15(1) Å, respectively. These dimensions do not differ significantly from those collected in Table 12 for molecules containing covalent isocyanate groups.

Finally, dimensions have been obtained by X-ray methods on covalently bound *iso*thiocyanate groups in a trimeric phosphonitrilic isocyanate (**5**)[90], on tetra-*B*-isothiocyanatotetra-*N*-*t*-butylborazocine (**6**)[91], and on two isothiocyanate derivatives of boron hydrides, 6-isothiocyanatodecaborane (**7**)[92] and ammonia-isothiocyanatoborane (**8**)[93]. The geometric dimensions of the isothiocyanate group in these molecules are given in Table 14.

A stereoscopic view of the trimeric phosphonitrilic isothiocyanate is shown in Figure 29. This molecule does show considerable variation in the P—N—C angle, with values ranging from 135(2) to 165(2)°. In the

TABLE 14. Bond lengths and angles in some covalently-bound isothiocyanate groups.

	C—S(Å)	N—C(Å)	N—C—S (deg)	X—N—C (deg)	Reference
$[NP(NCS)_2]_3$[a]					
Ligand 1	1·51(2)	1·19(3)	178(2)	156(1)	90
2	1·60(3)	1·11(3)	173(3)	152(2)	90
3	1·61(3)	1·09(4)	172(2)	149(2)	90
4	1·60(3)	1·08(3)	174(2)	156(2)	90
5	1·61(3)	1·13(3)	176(1)	135(2)	90
6	1·58(2)	1·12(3)	176(1)	165(2)	90
$[(CH_3)_3C \cdot NB \cdot NCS]_4$[b]	1·560(8)	1·172(10)	177·3(7)	176·4(8)	91
$6\text{-}B_{10}H_{13}NCS$[c]	1·581(4)	1·149(5)	178·1(6)	171·0(6)	92
	1·534(11)	1·170(13)	179·8(1·0)	173·2(1·0)	92
$NH_3 \cdot BH_2 \cdot NCS$	1·627(6)	1·137(8)	179·2(5)	177·5(6)	93

[a] There was no crystallographic symmetry in this molecule.

[b] There was crystallographic $\bar{4}$ symmetry in this molecule and thus only one independent NCS group.

[c] In the case of 6-isothiocyanatodecaborane, there were two crystallographic forms; the low temperature form is given first, then the room temperature form. In the case of the room temperature form, the dimensions for the isothiocyanate groups were calculated by us from the coordinates presented in Reference 92.

case of the other molecules listed in Table 14, the B—N—C angles all lie in the range 171–178°. However, great variability in X—N—C angle is also a feature of many of the simple isocyanates and isothiocyanates studied in the vapour phase (Table 4).

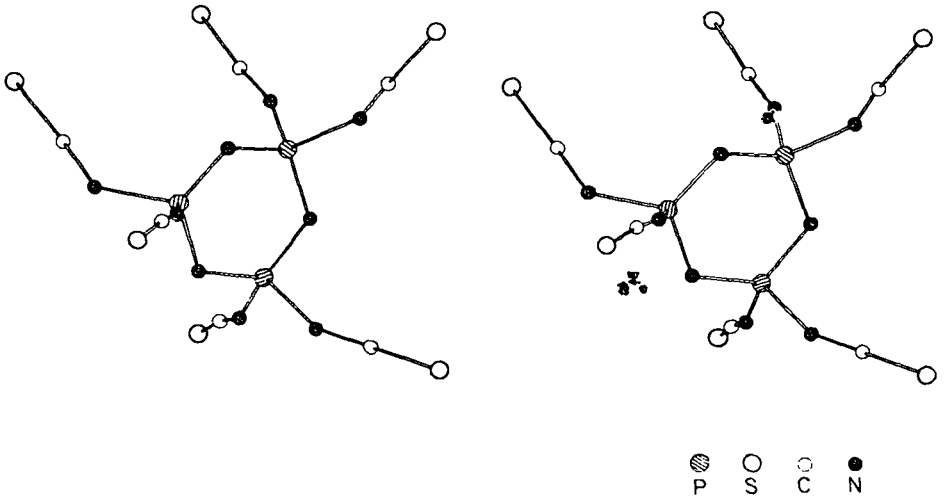
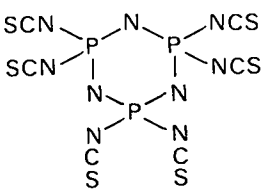


FIGURE 29. A stereoscopic view of a single molecule of the trimeric phosphonitrilic isothiocyanate. Drawn by us from the coordinates presented in Reference 90.



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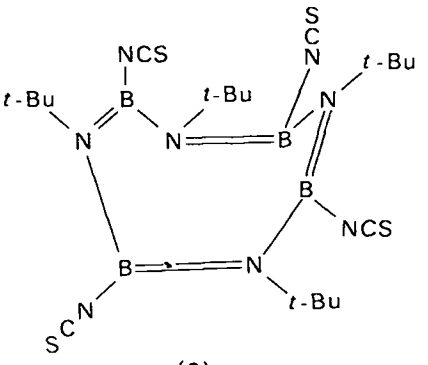

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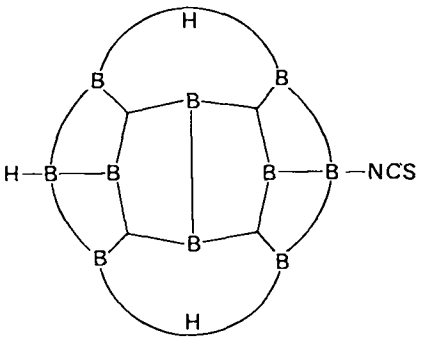

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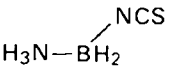


(8)

In the borazocine derivative (**6**)[91] and 6-isothiocyanatodecaborane (**7**)[92], B–N(CS) lengths of 1·431(11) and 1·435(6) Å were found and attributed to multiple bonding between the isothiocyanate group and the borazocine or boron hydride framework. In the case of **6**, such bonding was cited as a reason for the near linear B—N—C angle[91]. In the ammonia-isothiocyanatoborane (**8**), the B–N distance was 1·534(8) Å and no significant multiple bonding (other than hyperconjugation) could be invoked. It was pointed out by Kendall and Lipscomb[93] that in **8**, the C–S bond was somewhat longer and the N–C bond somewhat shorter than in the other molecules. Such features would be consistent with a contribution from a structure such as **9** for the ammonia-isothiocyanatoborane. The crystal of **8**

$$H_3N{\bullet}BH_2-\overset{+}{N}\equiv C-S^-$$

(**9**)

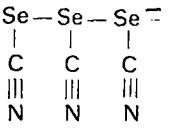
contains weak N—H···S (isothiocyanate) hydrogen bonds, a feature that would tend to stabilize a partially dipolar structure such as **9**. The H···S distance involved in the hydrogen bond is 2·62 Å; there may also be some

additional weaker N—H···S hydrogen bonds with H···S lengths of 2·89 Å.

Inspection of Table 14 does show some variations in N–C and C–S lengths which may be attributed to varying extents of bonding with the remainder of the molecule. It also suggests that, in general, the C–S bond lengths in isothiocyanates (1·51–1·63 Å) are shorter than those typically found (~1·68 Å) in the thiocyanate group (Table 12). However, it is possible that in some cases the terminal C–S bonds in the isothiocyanates are shortened artificially due to thermal motion. Comparison with the vapour phase data (Table 3) suggests pretty good agreement for the C–S bonds, although many of the N–C bonds appear shorter in the X-ray studies.

X. CRYSTAL STRUCTURE DATA ON SELENOCYANATES AND RELATED COMPOUNDS

The crystal structures of several compounds containing the SeCN group have been studied. The geometric dimensions for most of the compounds are listed in Table 15. Several of the compounds listed[95,96,97] contain the triselenocyanate anion $(SeCN)_3^-$ (**10**). There is also one example of the single selenocyanate anion[98].



(10)

There is general agreement that the Se–C bond length lies in the range 1·77–1·86 Å, with most values being in the 1·81–1·83 Å range. These values are in quite good agreement with the central C–Se bond length [1·802(11) Å] found in the molecule of **11**[99] and the terminal C–Se bonds 1·81(3) and 1·86(3) Å, found in 6a-selenaselenophthene (**12**)[100], all of which can be considered to have a large amount of double bond character. There is a somewhat greater range in the C–N bond lengths, although the value of 1·05 Å for $Se(SeCN)_2$ must be considered unreliable; otherwise the range is from 1·11 to 1·22 Å. The Se—C—N group approaches linearity in most of these molecules, with the exception of the $Se(SeCN)_2$ molecule where a value of 164° was quoted. However, this analysis was based on projection data only and must therefore be considered of low reliability. The authors state that 'the deviation from linearity... may, partly at least, be due to experimental errors'[94]. The C—Se—X angle lies in the

TABLE 15. Geometric data for several molecules containing the SeCN group

Compound	Crystallographic symmetry[a]	Se—C (Å)	C—N (Å)	Se—C—N (deg)	C—Se—X (deg)	C—Se—X—Y Torsion angle[b]	Reference
$Se(SeCN)_2$	C_s	1·83[c]	1·05	164	95	86	94
$K(SeCN)_3 \cdot \frac{1}{2}H_2O$	C_1	1·86(3)	1·11(4)	178·3(2·5)	96·3(8)	58	95
		1·83(3)[d]	1·12(4)	178·6(2·0)	94·1(8)	60[f]	
		1·82(3)	1·13(4)	179·2(2·5)	87·8(7)[e]		
					88·3(7)		
$Rb(SeCN)_3 \cdot \frac{1}{2}H_2O$	C_s[g]	1·81(2)	1·17(3)	178·4(1·7)	95·3(8)	67	96
		1·82(4)	1·16(5)	179·3(3·0)	88·6(1·5)[h]		
$C_s(SeCN)_3$	C_2	1·838(18)	1·156(27)	176·7(1·4)	95·5(6)		97
		1·772(24)	1·222(31)	180·0[i]	89·2(1)[h]		
KSeCN	C_1	1·829(25)	1·117(26)	178·8(2·5)	—[j]	—	98

[a] Refers to moiety containing Se atom or atoms.

[b] Atom X refers to the atom covalently bonded to Se; atom Y to an atom covalently bonded to atom X. The torsion angle C—Se—X—Y is the angle that the C–Se bond makes with the X–Y bond, when projected along the Se–X bond. The sign of the torsion angle is neglected in the compilation.

[c] No estimated standard deviations were given in the original paper[94].

[d] The first two Se–C lengths refer to the terminal Se–C bonds in the structure, the last one to the central Se–C bond.

[e] This refers to the central Se atom, so there are two C—Se—X angles.

[f] This refers to the central Se atom, so there are two C—Se—X—Y torsion angles where X = Se, Y = C.

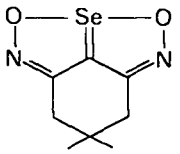
[g] The crystallographic mirror plane passes through the central Se—C—N group and relates the two other SeCN groups.

[h] The two central C—Se—Se bond angles are equal by symmetry.

[i] Linear by crystallographic symmetry.

[j] Not applicable.

range 87·8 to 96·3°. The external C—Se—Se angles (94–96°) in the triselenocyanate anion seem to be consistently larger than the internal C—Se—Se angles (88–89°). The former values seem to be in better agreement with those found in the $Se(SeCN)_2$ molecule[94].



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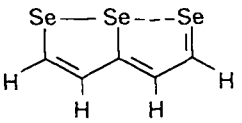


(12)

A stereoscopic view of the molecule of $Se(SeCN)_2$[94] is shown in Figure 30. This structure was determined on the basis of three projections of two-dimensional data and thus cannot be considered to be highly accurate by present-day standards, although the main features are undoubtedly clearly demonstrated. The molecule has C_s symmetry in the crystal and adopts a *cis* arrangement about the central selenium atom. As mentioned previously, the reported non-linearity, 164°, of the Se—C—N group must be treated with caution. The crystals of $S(SCN)_2$[73], $Se(SCN)_2$[74] and $Se(SeCN)_2$[94] appear to be isostructural. The cell dimensions reported for the three crystals are listed in Table 16 and the structures obtained appear quite similar. All the selenium atoms in the molecule of $Se(SeCN)_2$ participate in intermolecular Se···N interactions as described in the

TABLE 16. Cell data reported for $S(SCN)_2$, $Se(SCN)_2$ and $Se(SeCN)_2$[a]

	a(Å)	*b*(Å)	*c*(Å)	Reference
$S(SCN)_2$	10·14	12·82	4·35	73
$Se(SCN)_2$	9·87	13·03	4·44	74
$Se(SeCN)_2$	10·07	13·35	4·48	94

[a] The space group is *Pnma*.

previous section. These are indicated by dashed lines in Figure 31, which is a stereoscopic view of the molecular packing. The C—Se—Se—Se torsion angle is 86°.

The potassium[95], rubidium[96], and caesium[97] salts of the triselenocyanate anion (**10**) have all been the subject of an X-ray analysis. While all three studies were based on photographic data, the work has been carefully carried out and the structures fully refined.

In the potassium salt, no crystallographic symmetry was imposed

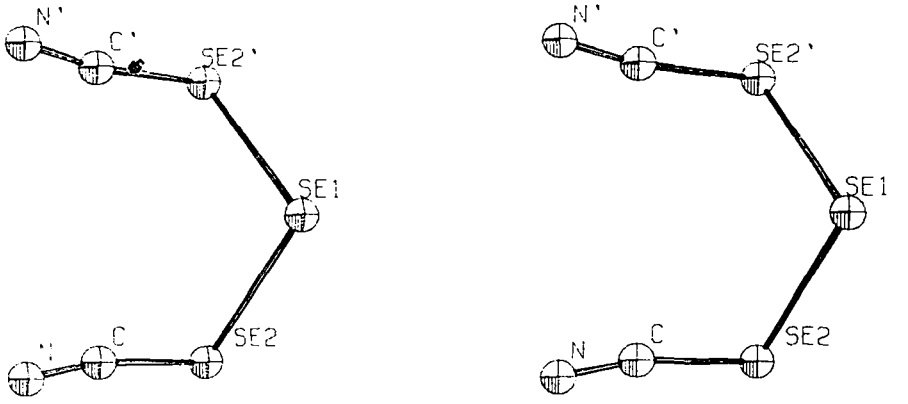


FIGURE 30. A stereoscopic view of a single molecule of $Se(SeCN)_2$. This picture was drawn by us from the coordinates presented in Reference 94.

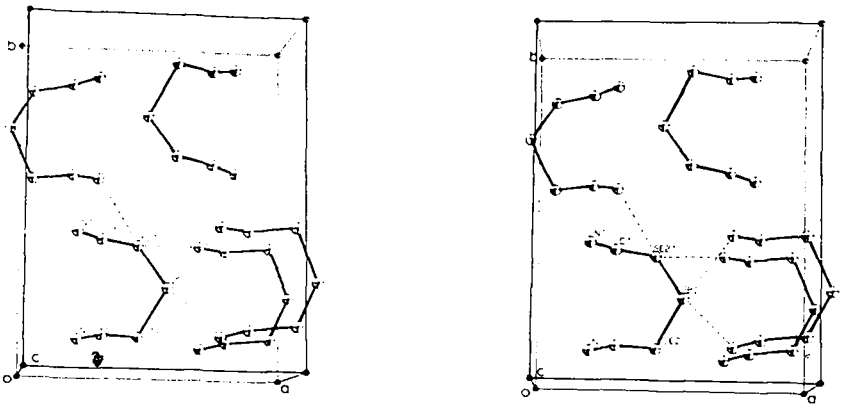


FIGURE 31. A stereoscopic view of the packing in the crystal of $Se(SeCN)_2$. The picture was drawn by us from the coordinates presented in Reference 94. The approximately square-planar arrangement of Se---N intermolecular interactions is shown by a discontinuous line.

on the anion, although it approaches C_s symmetry (Figure 32). The C—Se—Se—C torsion angles in the two 'halves' of the molecule are 58° and 60°. A stereoscopic view of the molecular packing is shown in Figure 33. This shows that there are short Se···Se contacts between the effectively linear groups of Se—Se—Se atoms, reminiscent of the types often found in the thiathiophthene structures[101]. Some of these contacts are as much as 0·5 Å less than twice the van der Waals radius for selenium[80]. A short Se···Se contact of 3·467 Å that involves two of the central selenium atoms

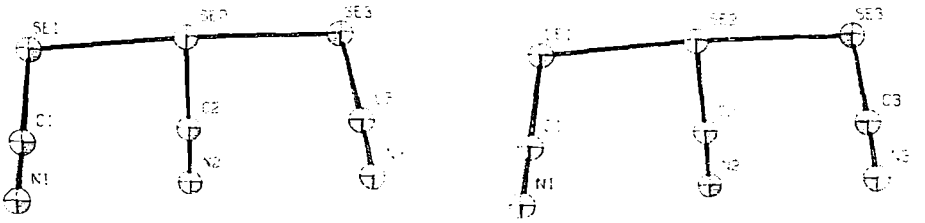


FIGURE 32. Stereoscopic view of the triselenocyanate anion in the structure of $K(SeCN)_3 \cdot 1/2H_2O$. The picture was drawn by us from the coordinates presented in Reference 95.

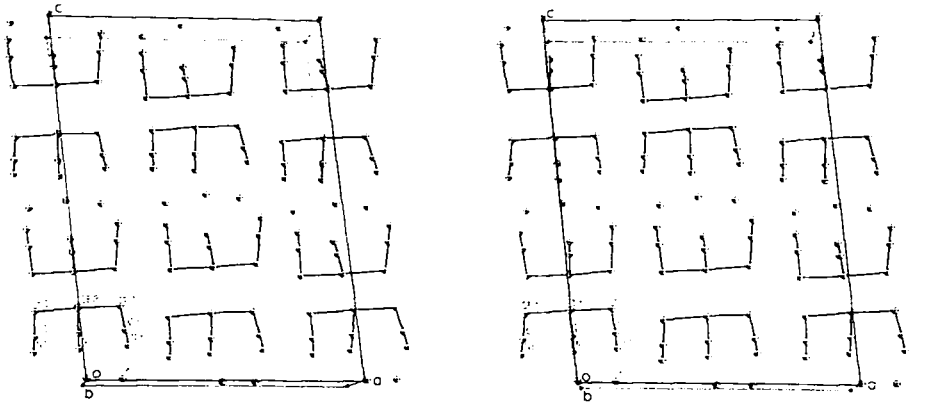


FIGURE 33. Stereoscopic view of the packing in the crystal of $K(SeCN)_3 \cdot 1/2H_2O$. This picture was drawn by us from the coordinates presented in Reference 95. The non-standard F2 setting used in Reference 95 was retained for this drawing.

lies close to the plane of the three covalently-bonded atoms (Se, Se, and C) and may represent a significant interaction with square-planar geometry[95]; see also the previous section. The two terminal selenium atoms are also involved in short Se···Se contacts. The nitrogen atoms, along with the water molecule, are involved in the coordination sphere of the K^+ ion.

The conformation of the triselenocyanate anion in the rubidium salt[96] is similar to that found in the potassium salt, although in this case the C_s symmetry is imposed by the crystal. The C—Se—Se—C torsion angle is 67°. A view of the crystal packing is shown in Figure 34. Despite the difference in the space groups and imposed symmetry, there are quite close similarities in the crystal packing and interactions. There are also

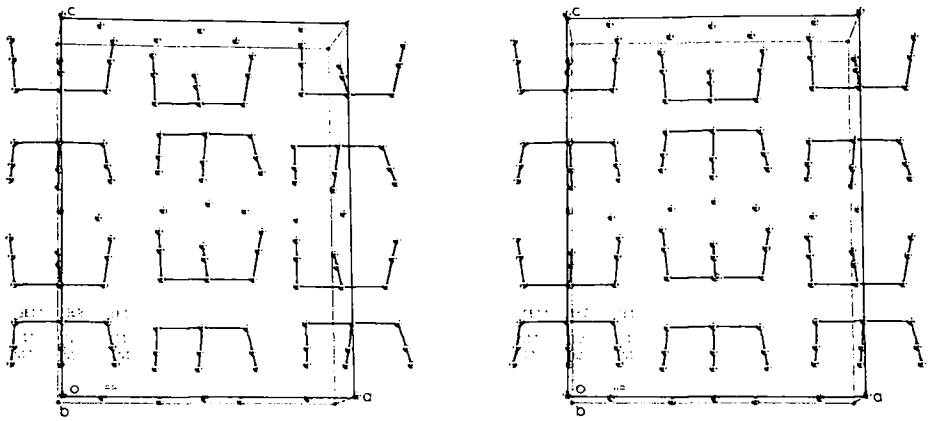


FIGURE 34. Stereoscopic view of the packing in the crystal of $Rb(SeCN)_3 \cdot 1/2H_2O$. The picture was drawn by us from the coordinates presented in Reference 96.

close Se···Se intermolecular contacts in the rubidium salt, the shortest being 3·516 Å.

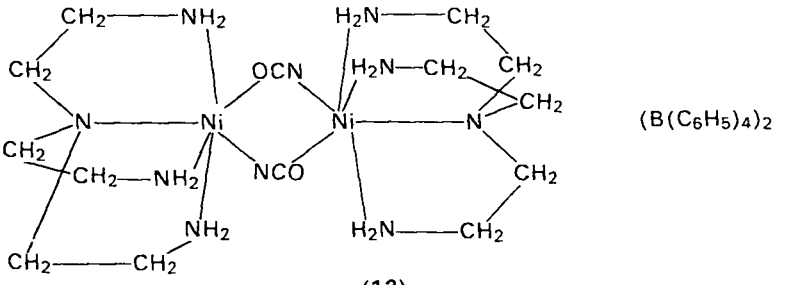
The dimensions of the triselenocyanate anion in the caesium salt[97] are similar to those in the potassium and rubidium salts, but in the Cs^+ salt, the anion has C_2-crystallographic symmetry. The coordinates were not published in Reference 97, so we cannot include a stereoscopic view. However, the C—Se—Se—C torsion angle is close to 43·9° and the anion must be more extended than in the other two salts.

There have been two X-ray structure studies on selenium dicyanide[83, 84,85,87]. However, both were based on two-dimensional X-ray data and it is not clear how reliable the results are. Hazell[83] reported that selenium dicyanide and sulphur dicyanide were isomorphous and had the space group *Cmca*. However, Emerson[75] and Linke and Lemmer[85,86] showed that $S(CN)_2$ belonged to the space group *Pbca* and Hazell[84] now believes that the space group for both compounds is *Pbca*. Thus his refinement imposed certain inappropriate symmetry constraints and some of the results were chemically unreasonable (e.g., 1·42(15) Å for a C–N bond and 119(6)° for the C—Se—C angle). Linke and Lemmer[85,87] refined the structure of $Se(CN)_2$ in *Pbca* and found it to be isostructural with $S(CN)_2$. While the general features of the structure are probably correct, the fact that only projection data were used makes the details of bond lengths and angles somewhat unreliable. The values given for the two Se–C bonds were 2·01 and 2·08 Å, for the two C–N bonds 1·27 and 1·07 Å, for the two Se—C—N angles 155° and 168° and for the C—Se—C angle 99°.

XI. CRYSTAL STRUCTURE DATA ON METAL COMPLEXES CONTAINING CYANATES, THIOCYANATES AND RELATED LIGANDS

As stated in the introduction, no comprehensive discussion of the geometry of metal complexes containing cyanates, thiocyanates, or selenocyanates will be attempted. Rather we will focus on a few features of the geometry of the ligands themselves and point out the existence of recent review articles on these fairly large areas. Some aspects of the chemistry and bonding properties of the pseudohalide ligands OCN^-, SCN^-, and $SeCN^-$ have been reviewed[102,103]

In general, evidence supports that most organometallic complexes have the isocyanate structure (i.e. coordination through nitrogen) **1b** rather than the cyanate structure (with coordination through oxygen) **1a**. A recent example, studied by Duggan and Hendrickson[104], illustrates that the cyanate ligand can coordinate *both* through nitrogen *and* through oxygen. These authors studied the crystal structure of di-μ-cyanato-bis (2,2′,2″-triaminotriethylamine) dinickel(II) tetraphenylborate (**13**) and



(13)

found a centrosymmetric structure with Ni···O and Ni···N distances of 2·336(5) and 2·108(7) Å. A view of the structure of the cation is shown in Figure 35. The molecular dimensions found in several metal complexes containing the cyanate group are given in Table 17. Two other examples, two forms of a thallium complex, have recently been shown by Britton and coworkers[109] to complex through both N and O. Most of the metal complexes that coordinate only through nitrogen do so in an almost linear fashion. In these determinations, the C–O bond (1·178–1·238 Å) is slightly longer than the N–C bond (1·118–1·146 Å). Comparison with some of the simpler cyanates studied in the gas phase which had M—N—C angles much less than 180° (for example, HNCO[1] and H_3GeNCO[15]), lead Duggan and Hendrickson[104] to propose a correlation between the

TABLE 17. Dimensions in cyanate ligands in metal complexes

Compound	N or O coordination	N—C (Å)	C—O (Å)	N—C—O (deg)	M—N—C (deg)	Reference
$[Ni_2tren_2(OCN)_2](BPh_4)_2$	N and O	1·128(10)	1·220(9)	178·5(9)	155·0(6)[a] (117·1(5))	104
$Cp_2Ti(NCO)_2$[b]	N	1·146(23)	1·210(22)	—[c]	172(3)	105
$Cp_2Zr(NCO)_2$[b]	N	1·131(9)	1·178(9)	—	174·5(5)	105
$Cp\,Cr(NO)_2(NCO)$	N	1·126(5)	1·179(6)	178·6(6)	180·0(4)	106
$Cp\,Mo(CO)(PPh_3)_2NCO$	N	1·118(14)	1·238(16)	179·1(1·2)	178·3(9)	107
$(CH_3)_3SnNCO\cdot(CH_3)_3SnOH$[d]	N	1·07(8)	1·29(10)	162(8)	110(5)[e] 114(5)	108
$(CH_3)_2TlNCO$[f] Orthorhombic	N and O	1·16(10)	1·18(9)	179(10)	129(1)[a] (120(3))	109
Trigonal	N and O	1·23(7)	1·19(7)	180	129(1)[a] (112(2))	109

[a] This angle refers to the nitrogen coordination; the M—O—C angle is in parenthesis.

[b] The values given for this compound are averaged for the two cyanate groups in the molecule; Cp refers to the cyclopentadienyl group.

[c] The values for the N—C—O angles were not given in Reference 105.

[d] The standard deviations in this study were quite high and the lack of agreement with the N-C and C-O bond lengths found the other compounds in this table may arise from the low precision of the analysis.

[e] There are two crystallographically-independent Sn—C—O angles in this structure.

[f] Two crystallographic forms of $(CH_3)_2TlNCO$ were reported in Reference 109; one of them is orthorhombic, the other is trigonal.

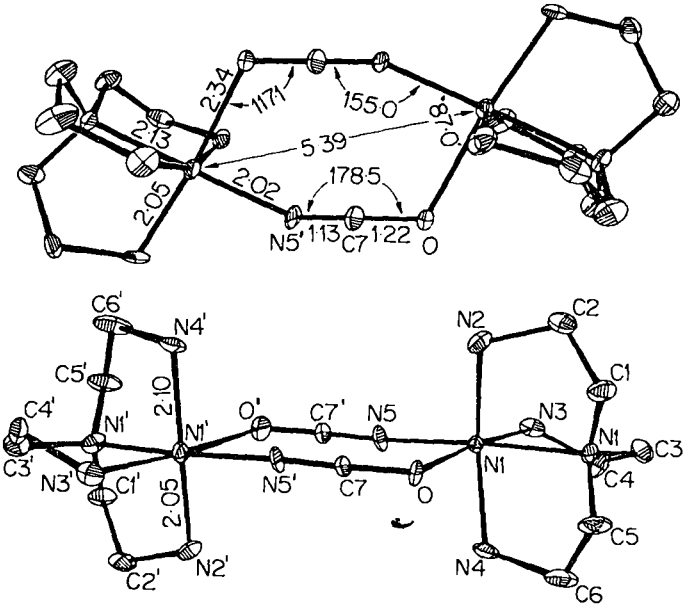


FIGURE 35. ORTEP plotting of $[Ni_2(tren)_2(OCN)_2]^{2+}$ showing some important geometrical parameters characterizing the di-μ-cyanate bridge and the nickel coordination environment. Hydrogen atoms are not shown. [After Duggan and Hendrickson, *Inorg. Chem.*, **13**, 2056 (1974).]

M—N—C angle and the N–C bond length. When the M—N—C angle gets smaller, the N–C length appears to get longer implying double bond rather than triple bond character. It is certainly apparent that the N–C bond lengths in these complexes, which mainly have M—N—C angles close to linearity, are considerably shorter than those in the simpler molecules whose lengths are given in Table 2 and which have M—N—C angles deviating greatly from linearity (Table 4). The values reported by Chow and Britton[109] for the two forms of $(CH_3)_2$-TlNCO would lend some support to the ideas put forward by Duggan and Hendrickson.

The thiocyanate (SCN) and isothiocyanate (NCS) ligands are much more common than the corresponding cyanate ligands and a great many crystal structures containing these ligands have been determined. In a study on isothiocyanatothiocyanato-(1-diphenylphosphino-3-dimethylaminopropane)Pd(II), Clark and Palenik[110] surveyed some molecular dimensions on thiocyanate groups and concluded that while there were some individual anomalies (which may result from errors or artifacts in particular studies), no significant trends in bond lengths in the N—C—S

TABLE 18. Bond distances and angles in thiocyanate groups in metal complexes[a]

	N—C (Å)	C—S (Å)	N—C—S (deg)	M—N—C (deg)	Reference
Thiocyanate anions					
Ammonium silver dithiocyanate[b,c]	1·10(11)	1·71(9)	168(5)		111
Potassium thiocyanate[d]	1·149(14)	1·689(13)	178·3(1·2)		88
4-Phenyl-1,2-dithiolium thiocyanate[d]	1·179(12)	1·598(8)	177·6(0·4)		112
Barium cryptate thiocyanate	1·158(8)	1·646(6)	179·6(4)		113
$Ba(SCN)_2 \cdot C_{20}H_{40}N_2O_7 \cdot 2H_2O$[e]	1·238(15)	1·576(12)	167·2(5)		
Metal isothiocyanates (M—NCS)					
Silver thiocyanate[f]	1·19(7)	1·64(3)	154(3)	163(3)	114
$K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$[g]	1·171	1·634	177·1	168·5	115
Bis(hydrazine)zinc isothiocyanate[h]	1·128(14)	1·655(12)	170·7(1·6)	161·2(9)	116
trans-Dithiocyanatotetrakis-(*N*,*N*'-diethylthiourea)nickel(II)	1·169(16)	1·636(14)	178·8(1·2)	175·0(1·0)	117
Bis-(2-thioimidazolidine)-nickel(II) isothiocyanate[i]	1·16(3)	1·64(2)	178·6(1·2)	162·1(1·7)	118
Bis(thiourea) nickel(II) isothiocyanate[j]	1·169(14)	1·635(13)	178·0(1·0)	162·2(1·0)	119
Trimethyltin isothiocyanate[k]	1·15(7)	1·64(7)	175(6)	173(5)	120
Isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)-Pd(II)[l,m]	1·136(10)	1·611(8)	178·6(7)	177·6(5)	110
Dimethyl diisothiocyanato (terpyridyl) Sn(IV)[n]	1·154(6)	1·608(4)	178·3(4)	177·3(4)	121
	1·151(5)	1·610(4)	176·9(4)	155·1(4)	
Diaquobis-(*N*,*N*-diethylnicotinamide)-diisothiocyanato zinc[o]	1·151(6)	1·623(5)	178·9(4)	164·7(3)	122
Dimethyltin diisothiocyanate[p]	1·15(5)	1·60(4)	179(3)	168(3)	123
Dimer of tetramethyl-1,3-diisothiocyanato-distannoxane[q]	1·17(7)	1·61(6)	177(4)	169(3)	124
	1·10(7)	1·64(5)	180(8)	142(7)	
				132(4)	
Metal thiocyanates (M—SCN)				M—S—C (deg)	
Ammonium silver dithiocyanate[b,r]	1·24(20)	1·60(11)	173(6)	110(2)	111

Silver thiocyanate[f]	1·19(7)	1·64(3)	154(3)	114(1)	114
Bis(ethylenediamine)Cu(II)thiocyanate[s]	1·16(3)	1·62(2)	176·9	79·9	125
Isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)-Pd(II)[t,r]	1·146(11)	1·658(8)	173·0(8)	107·3(3)	110
Thiocyanatopenta-ammine cobalt(III) dichloride	1·14(4)	1·64(3)	175(3)	105(1)	126
Thiocyanatopenta-ammine iridium(III) diperchlorate	1·146(30)	1·604(23)	174(3)	109·0(9)	127

[a] Some of the data in this table were taken from a somewhat similar table presented by Clark and Palenik[110].

[b] In this structure, there are two crystallographically-independent NCS groups, one of these is an anion, the other is coordinated to silver through the sulphur atom.

[c] The one described here is the anion; the NCS angle was calculated by us from coordinates in Reference 111.

[d] In this structure, the thiocyanate anion lies on a crystallographic mirror plane.

[e] There are two crystallographically-independent thiocyanate anions in this structure.

[f] The thiocyanate group in the structure of AgNCS acts as a bidentate ligand (through N and S) to two different Ag atoms. The values for the NCS angle and the M—N—C and M—S—C angles were calculated by us from the coordinates in Reference 114.

[g] In this structure there were four crystallographically independent NCS groups. The values given here are averages of the four independent values. The N-C values range from 1·133(17) to 1·228(29) Å, C-S from 1·571(25) to 1.706(29) Å, N—C—S from 173·5(1·9) to 179·5(1·9), and Mo—N—C from 162·9(1·7) to 176·4(1·3).

[h] In this structure, the two thiocyanate groups are related by C_i crystallographic symmetry.

[i] In this structure the thiocyanate group acts as a bridge between two different Ni(II) species; the details of its bonding through nitrogen are given in this table.

[j] There is one crystallographically unique thiocyanate group in this structure.

[k] In this structure, the thiocyanate group acts as a bidentate ligand (through N and S) between two different Sn atoms. The details of its bonding through nitrogen are given in this table.

[l] There are two independent NCS groups in this structure, one complexes to Pd through nitrogen and one through sulphur.

[m] In this entry, the coordination through nitrogen is described.

[n] In this structure, there are two crystallographically-independent NCS groups, both of which coordinate to Sn through nitrogen; details of both are given in this table.

[o] In this structure the two NCS groups are related by C_i crystallographic symmetry.

[p] There are two isothiocyanate groups related by C_s crystallographic symmetry.

[q] There are two crystallographically distinct NCS groups in this structure. One of these is coordinated to a Sn atom directly, the other acts as a bridge to two Sn atoms, but is coordinated to both through the same Sn atom; in this case there are two distinct M—N—C angles, the latter of which was calculated by us from the coordinates presented in Reference 124.

[r] The NCS group described here is the one coordinated through sulphur. The N—C—S and Ag—S—C angles were calculated by us from the coordinates in Reference 111.

[s] The estimated standard deviations for the angles were not given in Reference 125.

[t] In this entry, coordination through sulphur is described.

group could be discerned. The data included in their survey are given in Table 18 along with a few representative recent data. Apart from the clear difference between the metal (M)—S—C (80–110°) and M—N—C angles (155–178°), there do not appear to be significant differences in dimensions between the case when the NCS group is coordinated through nitrogen and when it is coordinated through sulphur.

XII. CONCLUSIONS

In this chapter we have tried to survey the information available on the structure of cyanates, isocyanates, thiocyanates, and isothiocyanates obtained both in the gas and crystalline phases. While there has been considerable recent interest in gas phase studies on some simple derivatives, there is a dearth of reliable data on organic cyanates and thiocyanates in the crystalline state. It is surprising that with the widespread use of X-ray crystallography that is now taking place, structural data are lacking on such simple organic groups. There is certainly a need for precise studies on this group in the crystal so that the structural results could be compared with those being made by the microwave and electron diffraction methods.

XIII. ACKNOWLEDGMENTS

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22. Some examples of cases where different structures have been obtained in the gas phase and the crystal include:
(a) There are instances where more rotational forms appear in the vapours than in the condensed phases. Thus *anti* and *gauche* conformers of ethane-1,2-dithiol were found in the vapour phase [M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Japan*, **38**, 1734 (1965); I. Hargittai and Gy. Schultz, *J.C.S. Chem. Commun.*, 323 (1972)] and only the *anti* form in the crystal [M. Hayashi *et al.*, *Bull. Chem. Soc. Japan*, **38**, 1734 (1965)].
(b) Biphenyl has been shown to have a planar structure in the crystal [J. Trotter, *Acta Crystallogr.*, **14**, 1135 (1961); A. Hargreaves and S. H. Rizvi, *Acta Crystallogr.*, **15**, 365 (1962); G. B. Robertson, *Nature*, **191**, 593 (1961)], while the two phenyl rings are rotated by about 45° in the vapour [O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949); **4**, 926 (1950); **6**, 205 (1952)].
(c) In the vapour phase bis(cyclopentadienyl)beryllium, $(C_5H_5)_2Be$ (electron diffraction) has two parallel, staggered C_5H_5 rings 3·373 ± 0·010 Å apart, with the Be atom on the common fivefold axis of the two rings. The Be atom may occupy two alternative positions at 1·472 ± 0·006 Å from one ring and 1·903 ± 0·008 Å from the other, [A. Almenningen, O. Bastiansen, and A. Haaland, *J. Chem. Phys.*, **40**, 3434 (1964); A. Haaland, *Acta Chem. Scand.*, **22**, 3030 (1968)]. In the crystal, [C.-H. Wong, T.-Y. Lee, K.-J. Chao, and S. Lee, *Acta Crystallogr.*, **B28**, 1662 (1972)] the distance between the two parallel rings is 3·33 Å. One of the rings, however, is slipped away from the symmetry axis on which the Be atom is located. The distance of the Be atom from one of the rings, under which it lies, is 1·53 ± 0·03 Å and the distance between the Be atom and the plane of the other ring is 1·81 Å.

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 3

Stereochemical and conformational aspects of cyanates and related groups

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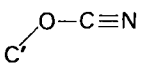
I. INTRODUCTION

Cyanates and related groups are necessarily end groups, attached by a single bond to the rest of the molecule in which they are found. These groups are essentially linear in geometry and when attached to a carbon atom in a molecule, the angle between that atom and the group is between 90° and 180° (**1**–**4**).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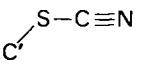
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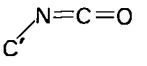
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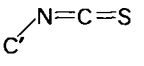
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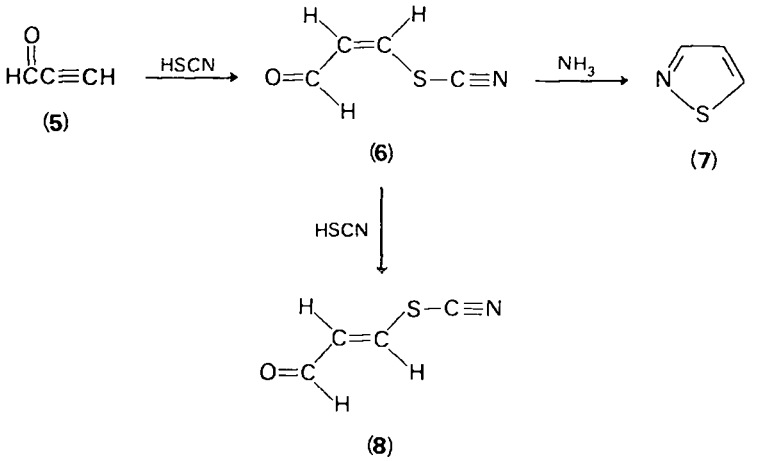
Clearly, these groups do not introduce into molecules the possibility of different stereochemical configurations of a single structure, such as the geometrical isomers found in the alkenes or in the presence of the carbon–nitrogen double bond. However, since rotation about single bonds is, in most instances, not free, certain conformations of these groups with respect to the rest of the molecule will be more stable than others, and hence, different stereoisomers can be recognized, detected even, but not isolated. This chapter will discuss the conformational and configurational analysis

of molecules containing cyanates and related groups and emphasize the relationship between conformational equilibria, configuration and the physical and chemical properties of molecules.

Although different configurations of a single structure do not result from the presence of cyanates and related groups, there are many examples where geometrical or optical isomers have been isolated for molecules containing these groups. In most cases, knowledge of the precise configuration of the molecule was important to an understanding of the chemistry of the functional group. The following examples will illustrate this point.

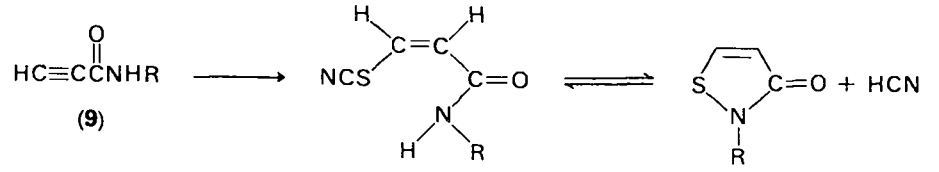
Isothiazole (**7**) can be prepared by the reaction of 3-thiocyanopropenal with liquid ammonia, but success is dependent upon use of the *cis* isomer (**6**)[1–3]. Only a tar results from use of the *trans* isomer (**8**). 3-Thiocyanopropenal is prepared by addition of thiocyanic acid to propynal (**5**). An optimum yield of the *cis* isomer was obtained when an aqueous solution of thiocyanic acid was slowly added to a solution of propynal in acetone at −10 to −15 °C. At higher temperatures the *trans* isomer was favoured. It appears that the addition of thiocyanic acid to propynal occurs in a *trans* manner to yield the *cis* isomer which in the presence of thiocyanic acid isomerizes to the *trans* isomer. The isomers were identified by their nuclear magnetic resonance spectra. The coupling constant for the olefinic protons, $J_{2,3} = 9$ Hz for the *cis* isomer and 15 Hz for the *trans* isomer[4,5].



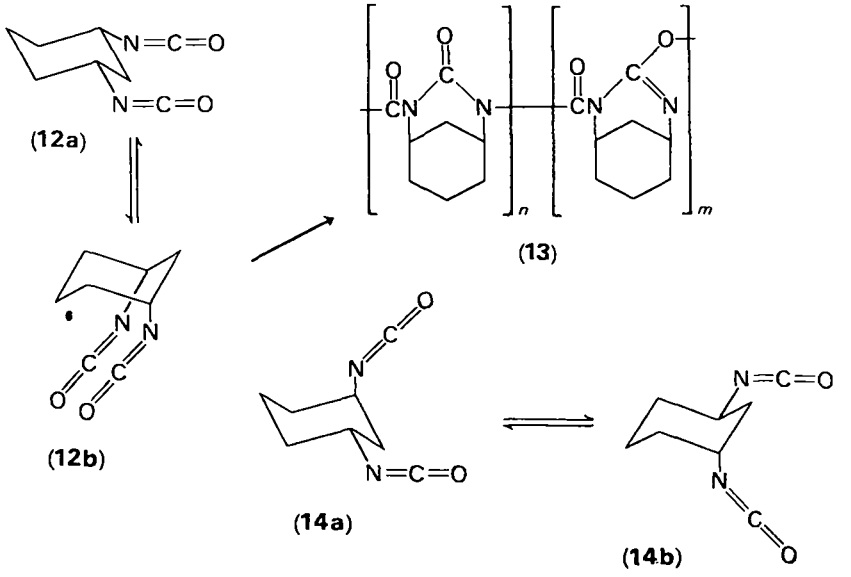
(**5**) (**6**) (**7**) (**8**)

cis-3-Thiocyanoacrylamides (**10**) were obtained, similarly, by the addition of thiocyanic acid to the propiolamides (**9**), and conversion to the corresponding substituted 3-isothiazolones (**11**) was effected readily.

Evidence was provided for equilibria between 3-isothiazolones (+HCN) and *cis*-3-thiocyanoacrylamides[5].

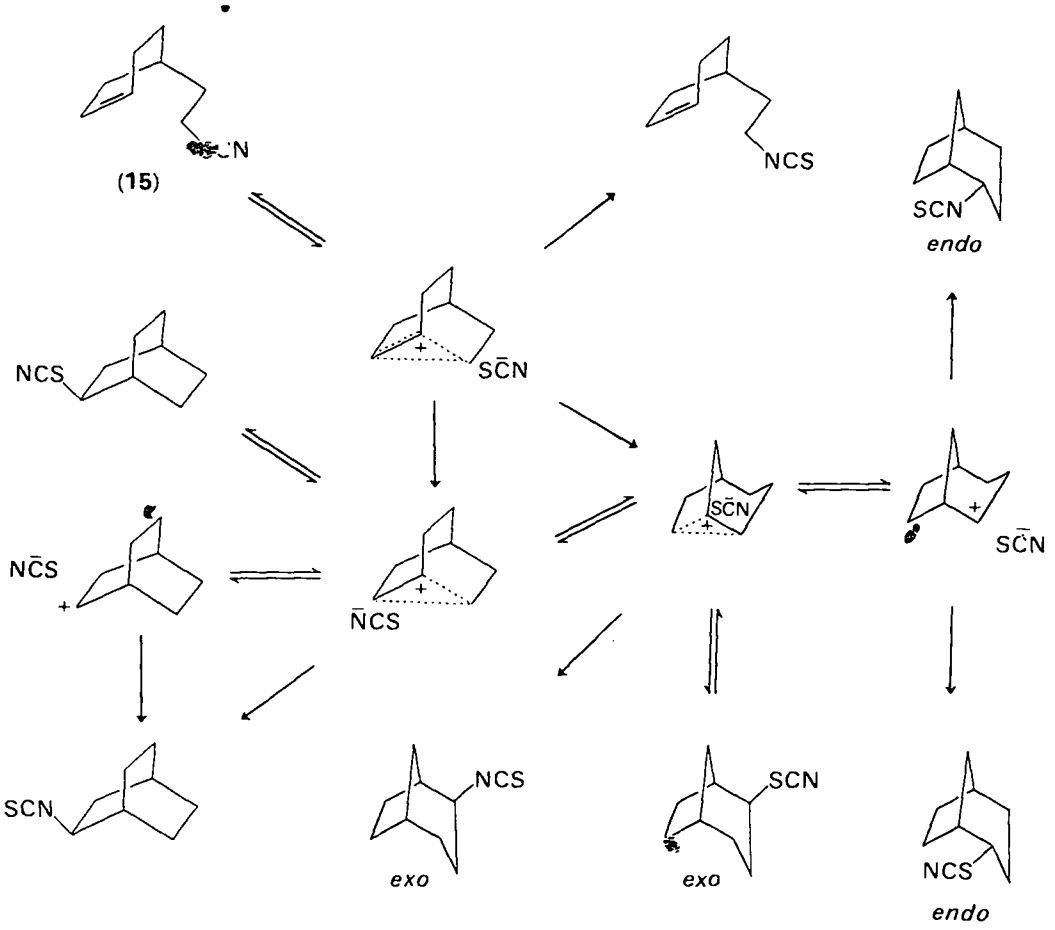


During a study of the mechanism of the cyclopolymerization reaction, *cis*- and *trans*-1,3-diisocyanatocyclohexane were synthesized[6,7]. The polymerization of the *trans* isomer was attempted, using sodium cyanide in DMF as initiator, but no polymerization occurred. Under similar conditions the *cis* isomer produced soluble linear cyclopolymers. *cis*-1,3-Diisocyanatocyclohexane (**12**), because of the diaxial conformation which the molecule can assume (**12b**), is functionally and configurationally capable of polymerizing by the cyclopolymerization mechanism to give linear polymers containing bicyclic units (**13**). The *trans* isomer, if polymerization occurred, might be expected to yield cross-linked polymers eventually because the isocyanato groups would be too far apart, in equatorial and axial positions respectively, for the intramolecular step to occur (**14**). Since it has been found that monoisocyanates in which the



functional group is attached to a secondary carbon atom are not polymerized under these conditions[8–10], and the axial–equatorial arrangement of the isocyanato groups in the *trans* isomer will not allow the formation of a cyclopolymer, there are steric reasons for the inability of this monomer to polymerize.

Considerable effort has been devoted to the elucidation of the mechanisms of thermally induced thiocyanate–isothiocyanate isomerizations[11,12]. Most allylic thiocyanates rearrange via a six-membered cyclic transition state involving little or no charge separation[13,14]. The overall nature of non-allylic isomerizations is of a kinetically preferred thiocyanate having a relatively weak carbon–sulphur bond reacting by bimolecular displacement or unimolecular dissociation–recombination to the thermodynamically preferred isothiocyanate[15,16]. In the study of systems in which



participation by a remote double bond provides a driving force for ionization, most authors use a non-classical intermediate to explain the formation of rearranged products[17]. Thiocyanate isomerizations where ionization occurs involve intimate ion pairs which means that this system provides conditions in which intermediates are captured very rapidly and the nature of the carbonium ions can be investigated[18]. An example is the isomerization of 2-(Δ^3-cyclohexenyl)ethyl thiocyanate (**15**) which has been investigated and a comprehensive interpretation of the results has been proposed involving localized and delocalized ions[19].

(*R*)-2-Butyl thiocyanate ($[\alpha]_D^{25} = -60$) isomerized to racemic 2-butyl isothiocyanate in DMF at 145 °C, indicating a completely non-stereospecific reaction. This, and other results, are explained by involving, again, an ion pair intermediate[20].

However, the emphasis of this chapter will be placed upon the elucidation of the three-dimensional structure of molecules containing cyanates and related groups, and not upon the stereochemistry of the reactions of these groups.

II. CONFORMATIONAL AND CONFIGURATIONAL ANALYSIS

Most of the discussion which follows will be concerned with isocyanates, thiocyanates and isothiocyanates. Because preparative routes to organic cyanates have not been established for too long[21–31] and because alkyl cyanates readily rearrange to isocyanates[26,28,29,31] very little work related to their stereochemistry has been reported.

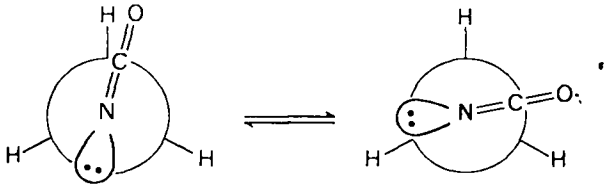
A. Acyclic Molecules

Electron diffraction[32] photographs of gaseous methyl isocyanate have been reported and interpreted[33], with the assumption of a tetrahedral methyl group (C′—H = 1·09 Å), the C′—N bond length as 1·47 Å, and a linear isocyanate group, to give the following structural parameters for the molecule: N—C = 1·19 ± 0·03 Å, C—O = 1·18 ± 0·03 Å, and the angle between the linear isocyanate group and the C′—N bond = 125 ± 5°.

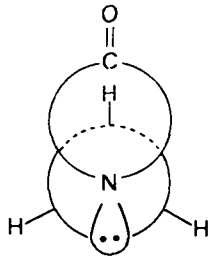
Barriers to internal rotation of methyl groups have been measured in a number of molecules by analysis of characteristic internal rotation splittings found in their microwave spectra[34]. The J0 → 1 and J1 → 2 *a*-type transitions in the microwave spectrum of methyl isocyanate have been studied[35]. A computer program was written to calculate the energy

levels and transition frequencies for any value of the barrier for a molecule containing a methyl group and a plane of symmetry. The model assumed was a rigid methyl group attached to a rigid frame, and the basis chosen was that appropriate for free internal rotation. The spectrum of methyl isocyanate was predicted for a range of values of the barrier from 0 to 1·5 kcal/mol (6·3 kJ mol^{-1}) and for a range of values of the ∠C'NC from 130° to 140°. Apart from the bond angle, the structure assumed for methyl isocyanate was that determined by electron diffraction[33]. Using a bond angle smaller than 130° gave results which were not consistent with the microwave spectrum. In spite of the variation of the spectrum which could be obtained by varying the barrier, the spectrum could not be fit by the model of a rigid methyl group attached to a rigid frame. However, for a barrier less than 0·15 kcal/mol (0·63 kJ mol^{-1}) and a bond angle of 140°, the calculated spectrum is in fair qualitative agreement with the observed spectrum. From the splitting of the J3 → 4, $K = \pm 1$, $m = \pm 3$ transition, the barrier to internal rotation of the methyl group was found to be 0·049 ± 0·003 kcal/mol (0·203 ± 0·13 kJ mol^{-1}). This value is mentioned in a recent review[36] but it is misquoted (as 4·9 ± 3 kcal/mol) and the literature reference is not given.

Two extreme conformations are possible for the methyl isocyanate molecule. The isocyanate group may be staggered or eclipsed with respect to the methyl group (**16a** ⇌ **16b**). In the above work[35], no indication is given of the preferred conformation. In acetaldehyde[37] and propene[38], the preferred conformer is that with the double bond eclipsed with a hydrogen



(16a) **(16b)**



(17)

atom. It is suggested[39] that this is reasonable if the double bond is considered to be of the 'banana-type'. The banana-type double bond would be staggered rather than eclipsed with respect to the carbon–hydrogen bond on the adjacent atom. Since it has been claimed that the volume requirement of a lone pair on a nitrogen atom exceeds that of a covalently bonded hydrogen atom[40], **16a** (**17**) could be more populated than **16b**. The microwave spectrum of methyl thiocyanate has been investigated in the frequency range of 8–34 GHz[41]. The rotational constants determined from the spectrum are A = 15,796·2, B = 4155·4 and C = 3354·2 MHz. With only three rotational constants, it was not possible to make a complete structural determination. However, assuming C′—H = 1·093 Å, ∠HC′H = 109° 28′, C′—S = 1·820 Å and C—N = 1·156 Å, the other two parameters were determined as ∠C′SC = 99° 52′ and S—C = 1·684 Å. Splittings due to internal rotation were observed for rotational transitions in the ground and in the first excited torsional states. Analysis of these splittings gave an internal barrier of 556 cm^{-1}, i.e. 1·59 kcal/mol (6·68 kJ mol^{-1}). Approximate values of 0·28 ± 0·15 kcal/mol[42] (1·18 ± 0·63 kJ mol^{-1}) and 0·91 kcal/mol[43] (3·82 kJ mol^{-1}) have been reported for the rotational barrier about the C—N bond of methyl isothiocyanate.

Later, the microwave spectra of methyl thiocyanate, methyl isocyanate and methyl isothiocyanate were re-examined under high resolution[44]. The barriers to internal rotation of the methyl group were found to be:

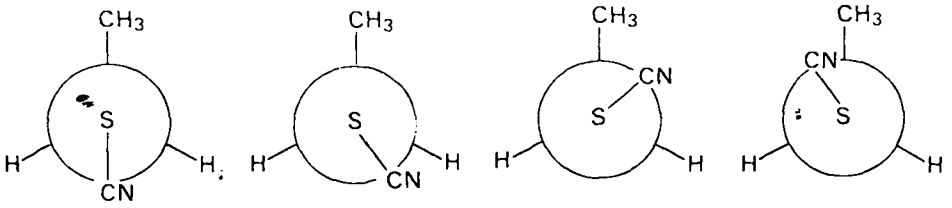
CH_3SCN, 1·60 ± 0·08 kcal/mol (6·72 ± 0·34 kJ mol^{-1}):

CH_3NCO, 0·083 ± 0·015 kcal/mol (0·35 ± 0·06 kJ mol^{-1})

CH_3NCS, 0·304 ± 0·05 kcal/mol (1·28 ± 0·21 kJ mol^{-1}).

The data were consistent with bond angles of 99·6° (∠C′SC), 140° (∠C′NC in CH_3NCO) and 147–148° (∠C′NC in CH_3NCS).

Four conformations of ethyl thiocyanate can be recognized if rotation about the C_α–S bond is considered (**18**–**21**).

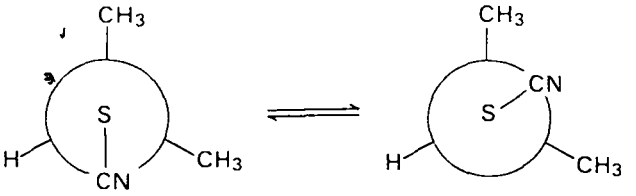


anti-periplanar (**18**) *anti*-clinal (**19**) *syn*-clinal (**20**) *syn*-periplanar (**21**)

From an infrared spectroscopic study of ethyl thiocyanate, the enthalpy difference between the *syn*-clinal (*gauche*) and *anti*-periplanar (*anti*)

conformations was estimated to be 0·49 kcal/mol (2·06 kJ mol^{-1}), with the *anti* being the more stable[45]. However, a microwave investigation[46] showed that the molecule exists mainly in the *gauche* form in the gas phase and that this conformer is at least 0·8 kcal/mol (3·4 kJ mol^{-1}) more stable than the *anti* form. This result was supported by an infrared and Raman reinvestigation in vapour, liquid, amorphous and crystalline states[47]. The spectra revealed only the *gauche* conformation. It is of interest that the *gauche* form (torsion angle = 58°) predominates. Steric interactions, as in the *gauche* form of butane, would suggest the opposite was true. Comparison can be made with derivatives of propane, e.g. 1-cyanopropane[48], where *gauche* forms are also more stable than *anti* forms. It would seem that steric repulsion in ethyl thiocyanate between CH_3 and CN is not severe at all since calculations[46] based upon van der Waals interactions indicate that the *gauche* form is slightly more stable. Calculations involving dipole–dipole interactions also favour the *gauche* form.

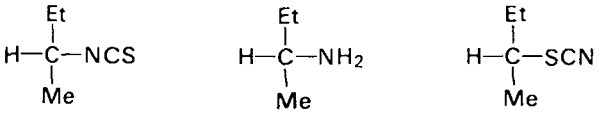
Two staggered conformations are possible for 2-propyl thiocyanate (**22** and **23**). Infrared studies[45,49] are used to suggest that the *gauche–anti* form (**22**) predominates.



(**22**) (**23**)

The enthalpy difference between the two forms is calculated[45] as 1·36 kcal/mol (5·7 kJ mol^{-1}). On the basis of the preceding discussion of ethyl thiocyanate, the *gauche–gauche* conformer (**23**) might have been expected to predominate.

2-Butyl derivatives exist in enantiomeric configurations. The correlation between isothiocyanate and amine is known[50–52] (**24** and **25**). Correlation between thiocyanate (**26**) and amine has been achieved[20] using



(–)-*R* (–)-*R* (–)-*R*

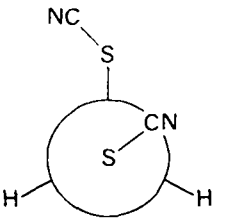
(**24**) (**25**) (**26**)

steps **27–29**. The first step was assumed to occur with net inversion

$$\underset{(27)}{RSCN} \xrightarrow{N_3^-} \underset{(28)}{RN_3} \xrightarrow{LiAlH_4} \underset{(29)}{RNH_2}$$

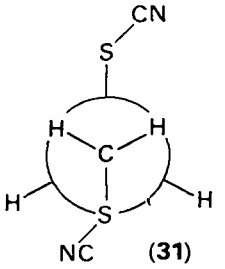
and the second with net retention of configuration. Thus 2-butyl thiocyanate and 2-butyl isothiocyanate of the same configuration have the same sign of rotation. Confirmation of the configurational assignment for (−)-(*R*)-2-butyl thiocyanate was obtained by its conversion to a thiol of opposite configuration to the known (+)-(*S*)-2-butanethiol[53].

The crystal and molecular structure of dithiocyanatomethane, $CH_2(SCN)_2$, has been determined[54]. The molecule in the crystal has symmetry 2. The bond distances are: S—CH_2, 1·808 Å; S—CN, 1·677 Å; C—N, 1·194 Å; and bond angles are: C′—S—C, 98·2°; S—C—N, 176·4°; S—C′—S, 115·0°. An intermolecular distance of 3·17 Å between nitrogen and sulphur atoms on adjacent molecules suggests a weak intermolecular interaction. It is interesting that the molecule adopts a configuration in the crystal in which each thiocyanate group is *syn*-clinal (*gauche*) to the other CH_2—S bond (**30**).

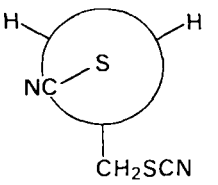


(**30**)

The structure of 1,2-dithiocyanatoethane has also been determined from single-crystal X-ray data[55]. The molecules have a centrosymmetric *trans* form, with the cyanide groups rotated out of the S—C′—C′—S plane. This means that the CH_2–S bonds are *anti*-periplanar (**31**) to each other but that, again, the thiocyanate group is *syn*-clinal (**32**) to the CH_2–CH_2 bond.

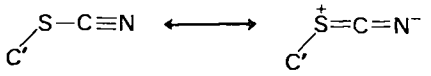


(**31**)



(**32**)

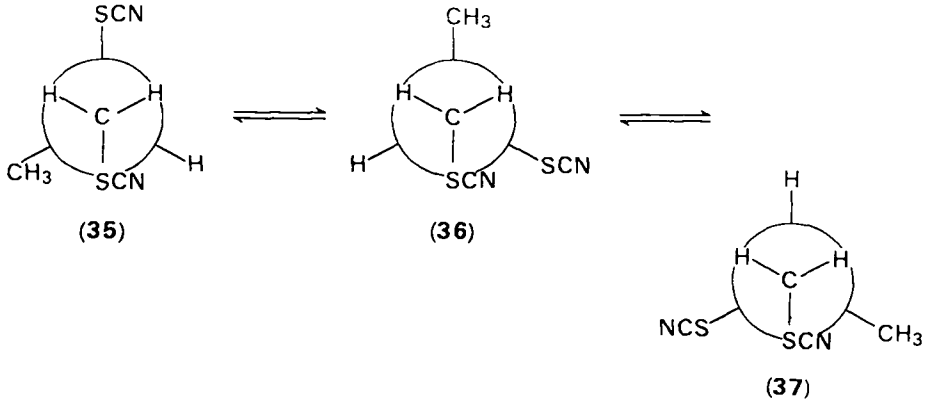
In both $CH_2(SCN)_2$ and $NCSCH_2CH_2SCN$ there is a deviation of the S—C—N angle from linearity. Further, the results found for the S–C and C–N bond lengths can be interpreted in terms of a significant contribution from **34** to the structure of the thiocyanate group.



(33) **(34)**

Infrared and Raman spectral data also suggest the *anti*-periplanar form for 1,2-dithiocyanatoethane in the solid state, but the *syn*-clinal form is observed in chloroform solution[56].

The difference between calculated and experimental dipole moments of a series of aliphatic dithiocyanates suggests the occurrence of a partial hindrance to free rotation at the bonds between the thiocyanate groups and the carbon atoms of the aliphatic chain[57]. Electrostatic interactions and steric effects influence the degree of free rotation. The first effect is evident from the significant increase in the dipole moment on lengthening the aliphatic chain: 1,2-dithiocyanatoethane (3·03 D); 1,3-dithiocyanatopropane (3·90 D); 1,4-dithiocyanatobutane (4·06 D); 1,5-dithiocyanatopentane (4·46 D). The effect of substituting a methyl group for a hydrogen atom in 1,2-dithiocyanatoethane, i.e. to give 1,2-dithiocyanatopropane, is to increase the dipole moment by more than 1 D (to 4·07 D). It is suggested that in benzene solution this molecule exists in conformations **35** and **36** with **36** predominating because of the steric repulsion between the methyl and thiocyanate groups in **35**. There is some evidence to indicate that the steric effect of the methyl group hinders rotation around the neighbouring HC—S bond.

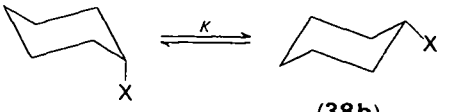


(35) **(36)** **(37)**

B. Cyclohexane Derivatives

1. Monosubstituted cyclohexanes

Monosubstituted cyclohexanes (**38**) can exist in two chair conformations, one with the substituent axial (**38a**), the other with the substituent equatorial (**38b**). The two conformations are readily interconvertible and at room temperature monosubstituted cyclohexanes rapidly pass from one chair form into the other. The equatorial conformation is expected to be the more stable because the non-bonded interactions are larger for an axial substituent than for an equatorial one.



(38a) (38b)

The free energy difference, ΔG_x°, between the two conformations is given by $\Delta G_x^{\circ} = -RT \ln K$.

$-\Delta G_x^{\circ}$ is the 'conformational free energy' of the axial form, i.e. the conformational free energy is the free energy of a conformation above that of the conformation of minimum energy.

The equilibrium constant $K = x/(1 - x)$, where x is the mole fraction of the equatorial conformer in the equilibrium mixture.

In order to calculate K, and hence $-\Delta G_x^{\circ}$, the equation:

$$K = \frac{P - P_a}{P_e - P}$$

has been derived[58] where P_a and P_e are the magnitudes of a property of a molecule with an axial and an equatorial substituent respectively, and P is the measured value of this property in the mixture. This equation was originally used to calculate K from reaction rates but is also used for n.m.r. parameters of isocyanates.

N.m.r. spectroscopy has been established as one of the most accurate and simple methods of determining the free energy difference between the axial and equatorial conformations in cyclohexane derivatives[59,60]. Consider the n.m.r. spectra of 4-*t*-butylcyclohexanes, biased cyclohexane derivatives. When the substituent is an electronegative atom or group the spectrum shows two main regions of absorption; a larger signal at high field and a smaller signal at low field. For example, the spectra of *cis*- and *trans*-4-*t*-butyl-1-isocyanatocyclohexane[61], (a) and (b) respectively in

Figure 1, showed two regions of absorption of relative areas 18:1. The signal at low field is due to the tertiary proton bonded to the same carbon atom as the isocyanate group (α-proton) which has a lower diamagnetic shielding than the other protons. It has been found that axial and equatorial protons generally differ in chemical shift if the chemical environment is otherwise the same[62]. The signal of axial protons usually appears at higher field and is broader than that due to equatorial protons[62–64]. Thus

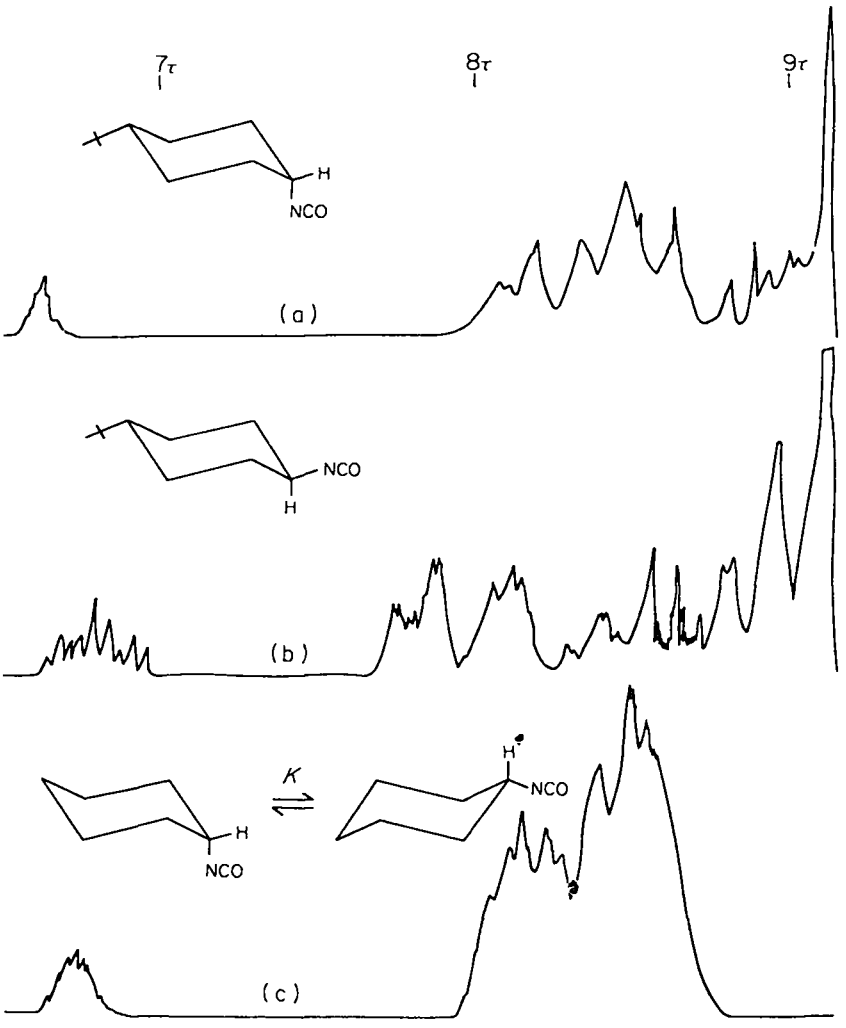


FIGURE 1. N.m.r. spectra recorded at 100 MHz in $CDCl_3$ at 35°C: (a) *cis*-4-*t*-butyl-1-isocyanatocyclohexane; (b) *trans*-4-*t*-butyl-1-isocyanatocyclohexane; (c) isocyanatocyclohexane.

from the relative chemical shifts and band widths of α-protons it is possible to determine the configuration of cyclohexane derivatives.

The spectrum of isocyanatocyclohexane, (c) in Figure 1, might be expected to show two signals for the α-proton; a narrow signal at low field due to the equatorial α-proton and a broader signal at higher field due to the axial α-proton, the ratio of these two signals being a direct measure of the relative abundance of the two conformers in the equilibrium. The spectrum actually obtained, however, shows only one signal for the α-proton. The transition of an excited nuclear spin from the parallel to the anti-parallel state, and back again, by which the n.m.r. signal is produced, is relatively slow compared with the rate of inversion of a cyclohexane ring at room temperature. Thus during one spin transition of the α-proton, the molecule to which it is attached interconverts very often, and the α-proton itself is many times axial and many times equatorial. Thus the magnetic environment of the α-proton during its transition is an average value of the environments of an axial and an equatorial proton and all properties of the measured signal are average values. If the equilibrium constant for isocyanatocyclohexane is to be calculated then the magnitudes of the properties of the individual conformers must be known.

If a mobile system, such as isocyanatocyclohexane, is cooled the rate of interconversion of the conformers is reduced while the transition time of a nuclear spin remains unaltered. On cooling, a distinct broadening of the α-proton signal is observed followed by separation into two bands (Figure 2). This separation is clear evidence that the rate of chair–chair interconversion has been slowed sufficiently at low temperature so that the mean lifetime in any conformation is larger than the transition time of a nuclear spin. The broader peak at low field is assigned to the equatorial proton and the peak at high field to the axial proton. Measurements of the populations of the equatorial and axial α-protons in equilibrium by this method have given $-\Delta G^{\circ}_{NCO}$ as:

0·60 kcal/mol (2·52 kJ mol^{-1}) at −75 °C in $CDCl_3$[61];

0·506 kcal/mol (2·125 kJ mol^{-1}) at −80 °C in CS_2[65];

0·52 kcal/mol (2·18 kJ mol^{-1}) at −70 °C in $CDCl_3$[66];

0·43 kcal/mol (1·81 kJ mol^{-1}) at −60 °C and 0·44 kcal/mol (1·85 kJ mol^{-1}) at −70 °C (solvent not specified)[67].

One of the first methods used to determine the configuration of biased cyclohexane derivatives was measurement of the width of the α-proton signal. The band width is equal to the sum of the coupling constants involved. The signal of the α-proton is the X part of an A_2B_2X system[64] since the axial and equatorial protons adjacent to the α-proton are not identical. Long range coupling can be ignored. The coupling constant

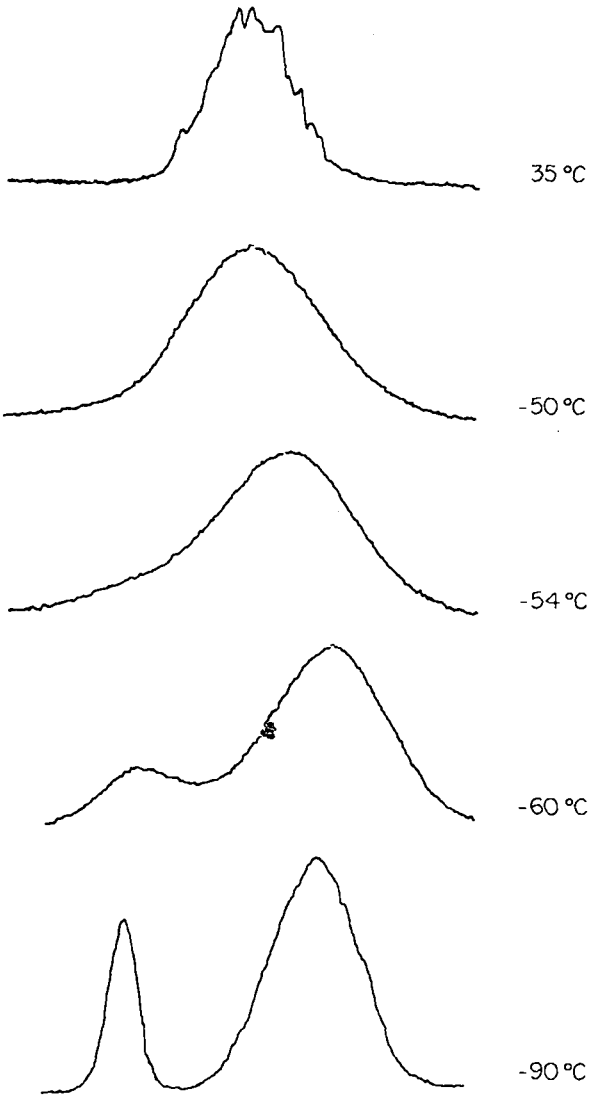


FIGURE 2. α-Proton signal of isocyanatocyclohexane at 60 MHz.

between neighbouring axial protons, J_{aa}, is generally two to three times as large as the coupling constant between an axial and a neighbouring equatorial proton, J_{ae}[62]. The coupling constant between two neighbouring equatorial protons, J_{ee}, is even lower[63]; however, the difference between J_{ae} and J_{ee} is small. The difference in coupling constants results in the signal due to the axial α-proton being broader than that due to the

equatorial α-proton. In mobile cyclohexane systems (**39**) the coupling constants are average values, and hence:

$$\text{band width } H_x \text{ (39)} = 2[x(J_{aa} + J_{ae}) + (1 - x)(J_{ee} + J_{ea})]$$

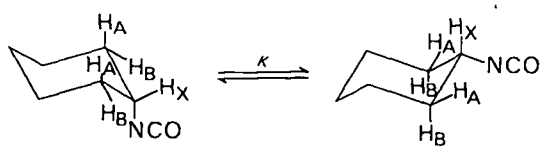
It is assumed that a 4-*t*-butyl substituent has a negligible effect on the coupling constants to the α-proton and therefore that *cis*- and *trans*-4-*t*-butyl-1-isocyanatocyclohexane (**40** and **41**) approximate to the two chair conformations in isocyanatocyclohexane. Thus:

$$\text{band width } H_x \text{ (40)} = 2J_{ea} + 2J_{ee}, \text{ and}$$
$$\text{band width } H_x \text{ (41)} = 2J_{aa} + 2J_{ae}$$

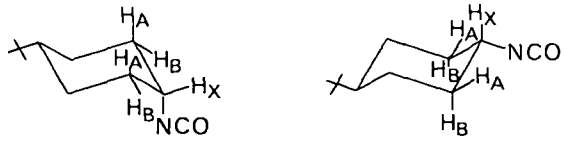
The equilibrium constant may then be expressed as:

$$K = \frac{w - w_{cis}}{w_{trans} - w}$$

where w is the band width of the α-proton signal in isocyanatocyclohexane and w_{cis} and w_{trans} the band widths in the 4-*t*-butyl derivatives.



1 − *x* (**39a**) *x* (**39b**)



(**40**) (**41**)

The signal of the *trans*-isomer shows a fine structure in agreement with expectations[61]. The signal is a triplet, separations J_{aa}, each component itself a triplet, separations J_{ae}. In the *cis* isomer the α-proton signal is largely unresolved and the outermost lines were estimated from inflections in the curve. The outermost peaks in the α-proton signal of isocyanatocyclohexane can be reasonably estimated. The value of $-\Delta G^{\circ}_{NCO}$ obtained is 0·48 kcal/mol (2·02 kJ mol^{-1})[61,67].

Accurate chemical shift measurements were made[61,67] and K determined using:

$$K = \frac{\tau - \tau_{cis}}{\tau_{trans} - \tau}$$

where τ is the chemical shift of the α-proton in isocyanatocyclohexane and τ_{cis} and τ_{trans} the chemical shift in the 4-*t*-butyl derivatives. The results obtained show that the conformer with an equatorial isocyanate group is favoured by 0·39 kcal/mol (1·64 kJ mol^{-1})[61] and 0·37 kcal/mol (1·55 kJ mol^{-1})[67].

From the range of values obtained for $-\Delta G^{\circ}_{NCO}$, there appear to be large uncertainties in the methods. However, $-\Delta G^{\circ}_{NCO}$ values obtained from the chemical shift and band widths of the α-protons in the 4-*t*-butyl substituted systems are in good agreement, considering the assumptions made, with the value obtained by the low-temperature method. Doubts about the validity of the assumptions made when using 4-*t*-butyl derivatives have been expressed on various occasions[68,69]. Thus it would appear that the only theoretically unobjectionable approach is to slow the interconversion of the conformational isomers of the mobile system itself at low temperature and to measure the population of the individual conformers.

The conformational preferences of thiocyanate and isothiocyanate groups in monosubstituted cyclohexanes have been determined by low temperature n.m.r. spectroscopy[65]. Values obtained were $-\Delta G^{\circ}_{SCN}$ = 1·23 kcal/mol (5·17 kJ mol^{-1}) and $-\Delta G^{\circ}_{NCS}$ = 0·284 kcal/mol (1·19 kJ mol^{-1}).

It is apparent that the atom next to the cyclohexane ring determines to a large degree the conformational free energy[65,70]. Thus OH and OMe have similar conformational free energies, as do SH, SMe and SCN with the sulphur containing groups of greater magnitude. Although the conformational preference of the cyanate group has yet to be determined, I would predict a value $-\Delta G^{\circ}_{OCN}$ of 0·5–0·6 kcal/mol (2·10–2·52 kJ mol^{-1}).

The low experimental value for the conformational free energy of the isocyanate group indicates that it is of relatively small steric size with respect to the cyclohexane ring. Although it might be expected, on the basis of van der Waals radii, that isothiocyanate would have a larger conformational free energy, the value is lower. It is suggested[65] that the contribution of **42** to the structure of the isothiocyanate group is more important than that from the analogous form in the isocyanate group. The larger value for $-\Delta G^{\circ}_{SCN}$ is not unexpected when compared with other sulphur containing groups.

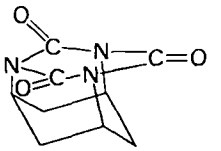
$$-\overset{+}{N}\equiv C-\bar{S}$$

(42)

2. Di- and trisubstituted cyclohexanes

The only studies reported are concerned with isocyanates. During a study of the mechanism of the cyclopolymerization reaction, the conformational equilibria in *cis*- and *trans*-1,3-diisocyanatocyclohexane were determined from n.m.r. studies[71]. As expected, the *trans* isomer exists as equal amounts of equatorial–axial isocyanato and axial–equatorial isocyanato forms in rapid equilibrium. It was shown that the only detectable conformer of the *cis* isomer is that in which the isocyanato groups are in equatorial positions. This was taken as evidence that a ground-state interaction between isocyanato groups in this monomer, which readily cyclopolymerizes, is not a significant factor in the cyclopolymerization mechanism. An interspacial electronic interaction in the ground state of *cis*-1,3-diisocyanatocyclohexane would be expected to decrease the energy of the diaxial conformation of the molecule, thus increasing the proportion of this conformer in the equilibrium mixture.

The *cis*- and *trans*-isomers of 1,3,5-triisocyanatocyclohexane, because of the *cis*-triaxial and *trans*-diaxial–equatorial conformations which can be achieved, also yield linear polymers by the cyclopolymerization mechanism[72]. Attempts to form 1,3,9-triazatetracyclo[4,4,0,$1^{3,9}$,$1^{4,8}$] dodecan-2,10,11-trione (**43**) by intramolecular trimerization of the isocyanato groups of the *cis* isomer were unsuccessful.



(43)

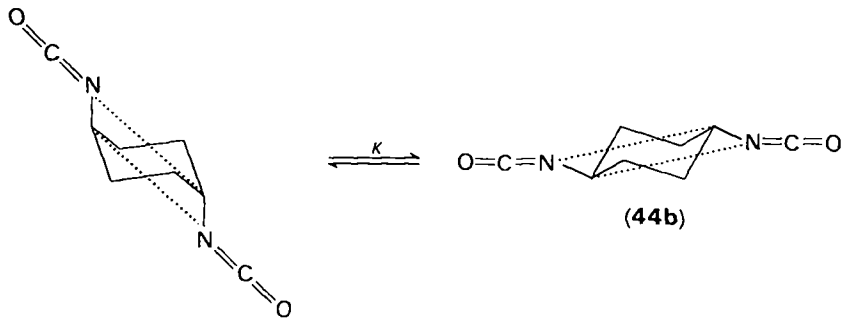
In the course of configurational and conformational investigations on substituted cyclohexanes, 220 MHz n.m.r. spectra of di- and trisubstituted derivatives, having one or two isocyanate groups, were obtained[73]. In many cases detailed assignments of all ring protons were possible.

The conformational free energies of a wide variety of groups on cyclohexane rings are now well known[65,70]. A question which has been considered on numerous occasions concerns the degree to which additivity

of conformational free energies can be assumed such that the conformational equilibrium in cyclohexane derivatives with more than one substituent can be predicted. If two substituents have a 1,1-relationship a quantitative lack of additivity has been observed[74,75]. The steric effect of adjacent groups in 1,2-disubstituted cyclohexanes is sizeable[76]. A 1,3-arrangement of substituents has been found to yield a small but definite lack of additivity[77,78]. In the 1,4 series additivity has generally been assumed and appears to be valid when one or both substituents are alkyl groups[79,66]. For example, *trans*-1-isocyanato-4-methylcyclohexane has been investigated[66]. The signal due to the α-protons was observed as a fairly well defined nonet. On cooling the solution down to −90 °C no measurable effect was observed. Thus, this compound exists exclusively in one conformation (*ee*). Assuming additivity of conformational free energies in this case and using $-\Delta G^{\circ}_{CH_3} = 1{\cdot}7$ kcal/mol (7·10 kJ mol^{-1}), the calculated value, $-\Delta G^{\circ} = 2{\cdot}21$ kcal/mol (9·28 kJ mol^{-1}), predicts 99% diequatorial conformer at −80 °C. A similar result was obtained for *cis*-1-isocyanato-4-methylcyclohexane[66]. The α-proton signal did not change on cooling from room temperature down to −90 °C. Here calculation predicts 96% diequatorial conformer, from $-\Delta G^{\circ} = 1{\cdot}17$ kcal/mol (4·92 kJ mol^{-1}), assuming additivity holds. We would not expect to be able to detect the smaller signal in this case. A comparison of calculated and determined $-\Delta G^{\circ}$ values for 1-isocyanato-4,4-dimethylcyclohexane, where two peaks should be detected at low temperature, would test whether additivity can be assumed in 1,4-derivatives having isocyanate and methyl groups.

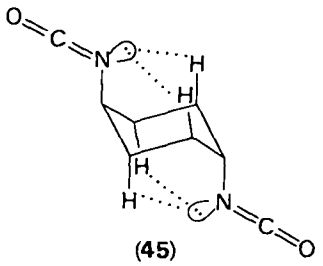
A number of investigations have shown that if two polar groups are *trans* to each other in 1,4-disubstituted cyclohexanes, marked deviations from additivity of conformational free energies are observed[80,81]. The conformational equilibrium in *trans*-1,4-diisocyanatocyclohexane has been studied by low temperature n.m.r. spectroscopy and similar results obtained[66]. The α-proton signal behaved as expected on cooling the solution. A gradual broadening and separation of the signal into two distinct peaks was observed. Peak areas were measured by integration and planimetry, and $-\Delta G^{\circ}$ (−65 °C in $CDCl_3$) was found to be 0·38 kcal/mol (1·58 kJ mol^{-1}). If conformational free energies are additive in this system we would expect $-\Delta G^{\circ} = 1{\cdot}04$ kcal/mol (4·36 kJ mol^{-1}) which is approximately three times the value obtained experimentally. The magnitude of this deviation can be appreciated if it is realized that the predicted value corresponds to a 94:6 ratio of conformers (in favour of diequatorial) whereas the actual ratio *ee*:*aa* = 71:29. This would seem to suggest that with one isocyanato group present in a cyclohexane ring

the conformational preference is decided mainly by the steric size of the group, but with two isocyanato groups *trans*-1,4 to each other steric size is not so important, and for some other reason the conformational equilibrium is disturbed to increase the proportion of the conformer with the two groups axial. To account for this phenomenon an explanation involving electrostatic interactions across the ring has been postulated[80]. In the diisocyanate, electronic attraction between $C_{(1)}$ and 4-NCO and between $C_{(4)}$ and 1-NCO could offset any steric repulsive forces and result in a larger proportion of the diaxial conformer than might otherwise be expected (**44a** ⇌ **44b**). In the diaxial conformer the distance between the centres is shorter than in the diequatorial conformer.



(**44a**) (**44b**)

More recently it has been shown that electrostatic interactions do not explain the observed data and an alternative explanation has been put forward[82]. In the diaxial conformer the axial 2-hydrogen atom, in a planar *trans* arrangement with the axial polar group, becomes more positive than usual. This hydrogen atom is in close proximity to the axial 4-polar group, resulting in an attractive interaction. There are four such interactions in the diaxial conformer. In the diequatorial conformer, although the axial 2-hydrogen atom is also positively charged it is now much further away from the 4-polar group and therefore does not contribute any extra stabilization. The interaction of this hydrogen and the 1-polar group is included in the conformational free energy of the group. The axial isocyanate group would be expected to prefer an orientation such that the plane of the group is perpendicular to the plane of the 3,5-*syn*-axial carbon–hydrogen bonds, with the carbonyl group directed away from this plane. In this conformation, attractive 1,3-interactions between the nitrogen lone pair electrons and the positive hydrogen atoms could be responsible for the extra stability of the 1,4-diaxial conformer (**45**).



(45)

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 4

The optical rotatory dispersion and circular dichroism of the cyanates and related groups

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I. INTRODUCTION

In the last 15 years optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) have found a secure place among the relatively few physical methods which organic and biological chemists employ in the solution of their research problems.

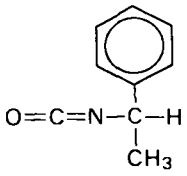
The present review article, which aims to illustrate the chirospectroscopic[1] properties of cyanates, isocyanates, thiocyanates, and isothiocyanates, surveys the literature to May 1976. The related compounds cyanamides and azides are also briefly discussed. Finally, the chirospectroscopic properties of the chromophoric derivatives[2] of amines, alcohols, and thioalcohols (thiols), obtained by reaction with cyanates and related compounds, are also examined. The o.r.d. and c.d. nomenclature is that in common use[3].

II. CHIROSPECTROSCOPIC PROPERTIES OF CYANATES AND ISOCYANATES

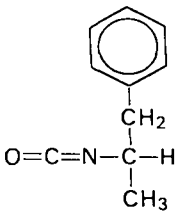
Optically active isocyanates were first prepared in 1904 by Neville and Pickard[4]. In subsequent years such compounds were extensively used for the synthesis of optically active urethanes and ureines, in particular for the resolution of racemic alcohols and amines into their optical antipodes[5].

The chirospectroscopic properties of an optically active isocyanate were first described by Terent'ev and colleagues in 1967[5]. The Russian workers reported the o.r.d. curves in the 600–300 nm region of (−)-α-phenylethyl isocyanate (**1**) without a solvent and at different concentrations in absolute benzene. They were able to show that not only the magnitude of the optical rotation, but the sign of the o.r.d. curves changed with a change in concentration of the benzene solutions of the isocyanate. On the basis of this experiment they could demonstrate that the previous stereochemical designation[6] was incorrect.

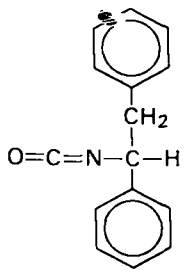
In order to examine the reason for the concentration effect in benzene, the spectropolarimetric behaviour of (−)-α-phenylethyl isocyanate (**1**) was examined in solvents of different polarity and at different temperatures[7,8]. The o.r.d. spectra were obtained in benzene, *o*-xylene, CCl_4, absolute *i*-octane, *i*-octane containing water, and dimethylformamide at 20–50 °C. In the aromatic solvents the sign of the o.r.d. pattern is dependent on concentration and temperature, while this dependence is not observed in other solvents. This inversion of the o.r.d. curve in benzene solutions was explained by assuming the formation of donor–acceptor complexes between the arylalkyl isocyanate and aromatic solvent molecules. Such complex formation changes the composition of the preferred conformers of the isocyanate molecules, involving rotation about the N–C_{sp^3} bond, and consequently it changes the stereochemical environment of the asymmetric carbon atom, which in turn leads to a variation in the course of the o.r.d. curves.



(**1**)



(**2**)



(**3**)

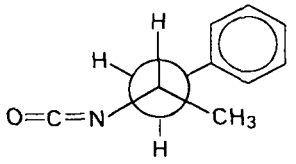
In absolute *i*-octane the o.r.d. curve was reported to 220 nm. It shows a positive Cotton effect near 265 nm, which exhibits fine structure and is associated with the longest-wavelength absorption band (^1L_b) of the monosubstituted benzene chromophore[7,9–13]. This Cotton effect is superimposed on a negative background curve.

The interest in spectropolarimetric analysis of optically active isocyanates was extended to (+)-α-benzylethyl isocyanate (**2**)[7]. In the region down to 270 nm, **2** gives positive rotatory dispersion curves, the pattern of which depends neither on the nature of solvent nor on the temperature. In addition, this arylalkyl isocyanate also exhibits a weak, structured and positive band in the 270–250 nm region. Thus, the aromatic chromophore, either directly bonded to the asymmetric centre, as in **1**, or separated from it by a methylene group as in **2**, determines the course of the o.r.d. curve in the region of the first absorption band.

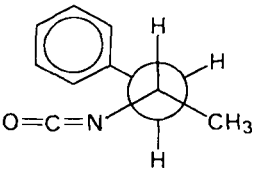
However, an important difference stands out clearly in the chirospectroscopic properties of the two isocyanates **1** and **2**. For (+)-α-benzylethyl isocyanate (**2**) is the 265 nm *positive* Cotton effect superimposed on a *positive* background curve; for (−)-α-phenylethyl isocyanate (**1**) the 265 nm *positive* Cotton effect is superimposed on a *negative* background curve. The sign of the background curve is determined by contributions of short-wavelength bands to rotation. Since it was proposed[9–12] for a number of compounds containing, *inter alia*, a benzene ring, that optical activity below 240 nm is predominantly due to a second absorption band of the aromatic chromophore, Terent'ev and coworkers[7] suggested that the source of the Cotton effect observed for (+)-α-benzylethyl isocyanate (**2**) in the neighbourhood of 210 nm (peak at 219 nm in *i*-octane) is the ^1L_a absorption band of the monoalkylated benzene chromophore at 208 nm. However, the effect of the —NCO group, the second chromophore present in the molecule, on the rotatory dispersion of the two arylalkyl isocyanates was probably not sufficiently considered. Actually in 1965 Turner and Warner reported that ethyl isocyanate has an ultraviolet (u.v.) absorption maximum at 207 nm in an unspecified solvent[14]; more recently it was shown that above 200 nm methyl isocyanate has only a shoulder at 225 nm in cyclohexane[15]. Also, the reason why the 210 nm band, in contrast to the 265 nm band, changes its sign from **1** to **2**, was not discussed by the Russian group. Finally, it should be noted that the sign of rotation of the two isocyanates in the visible (i.e., at 589 nm) is determined by the more intense short-wavelength Cotton effect near 210 nm.

The difference mentioned above in the spectropolarimetric behaviour of isocyanates **1** and **2** in aromatic solvents was tentatively rationalized by Terent'ev and coworkers[7].

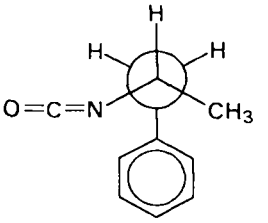
The possible effect of aromatic solvents on the conformational preferences of (−)-α-phenylethyl isocyanate (**1**) was previously discussed. In contrast, three conformations are possible for (+)-α-benzylethyl isocyanate (**2**), namely **2a**, **2b**, and **2c**, of which **2c** is clearly not a favoured conformation owing to the two skew interactions. The stability of conformations **2a** and



(2a)



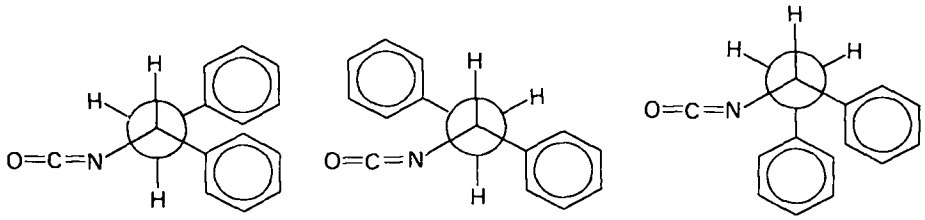
(2b)



(2c)

2b depends on the magnitude of the skew interactions of the benzene ring with the methyl group (in conformer **2a**) or isocyanate group (in conformer **2b**). The two conformers are approximately equal with respect to steric factors. Conformation **2b** could be energetically more favoured because of interactions of the π electrons of the benzene ring and the isocyanate group, i.e. because of formation of an intramolecular donor–acceptor complex. This interaction possibly gives conformation **2b** sufficient stability so that it is not changed by solvent and temperature effects. Such changes cannot be expected for conformation **2a** either. The benzene ring and isocyanate group are removed from each other in this conformation, so that formation of complexes with an aromatic solvent should not change the conformation of the molecule and thereby affect the pattern of the o.r.d. curves. Thus, although it was impossible to arrive at a definite conclusion regarding the preferred conformation of (+)-α-benzylethyl isocyanate (**2**) on the basis of the available experimental data, it is evident that a change in conformation associated with the formation of an intermolecular solvent–solute complex would not be expected.

Finally, Terent'ev and colleagues investigated the o.r.d. properties of (+)-α,β-diphenylethyl isocyanate (**3**)[16]. Both groups, phenyl and benzyl, characteristic of the isocyanates **1** and **2** previously studied, are present in this compound at the asymmetric carbon atom. As in the case of (**1**), in aromatic solvents there is a significant dependence of the o.r.d. patterns of (**3**) on concentration and temperature. In relatively more dilute solutions (< 12%) isocyanate **3** gives negative curves, and with an increase in concentration the o.r.d. curves become positive. Also, an increase in temperature of the dilute solutions leads to a positive shift of the o.r.d. curves. Furthermore, the



(3a) (3b) (3c)

two isocyanates **1** and **3** present analogous chiroptical properties as far as the relative signs of ^1L_b and ^1L_a Cotton effects are concerned. In fact, in both cases the Cotton effect centred near 265 nm has the opposite sign to the 210 nm one.

On the basis of general conformational considerations, Terent'ev and coworkers[16] assumed that **3b** is the more preferred conformer, since in *gauche* conformation **3a**, the two bulky phenyl groups interfere with each other. In order to check this assumption, they calculated the conformational composition by Brewster's method[17]. In *i*-octane 59% of (+)-α,β-diphenylethyl isocyanate is conformer **3b**, 41% conformer **3a** and 0% conformer **3c**.

The formation of a solvent–solute complex in benzene solution was also suggested for isocyanate **3**. An increase in the bulk of the —NCO group due to complex formation could lead to a preference for conformer **3a**, which makes a negative contribution to rotation, and leads consequently to a change in the sign of rotation of **3**, as observed experimentally. An increase in temperature should result in the destruction of such complexes. An increase in the concentration of the isocyanate should lead to a decrease of the complexed isocyanate/free isocyanate ratio. In both cases, rotation should approach that of the isocyanate in the absence of a solvent. Actually, the o.r.d. spectra of (+)-α,β-diphenylethyl isocyanate (**3**) in aromatic solvents undergo a positive shift with an increase in temperature and concentration.

The first c.d. spectrum of an optically active isocyanate[18] is reported in Figure 1. (−)-α-Phenylethyl isocyanate (**1**) in cyclohexane exhibits a structured positive Cotton effect near 260 nm (positive maxima at 267 nm, 261 nm, 255 nm and 249 nm) corresponding essentially to the electric-dipole allowed 0–0 subsystem[12–13]. The progression has 930 cm^{-1} spacing. The intensity of the c.d. band indicates that the aromatic chromophore is directly linked to the asymmetric carbon atom. A stronger negative Cotton effect was also observed at 217 nm. Below 230 nm the u.v. absorption

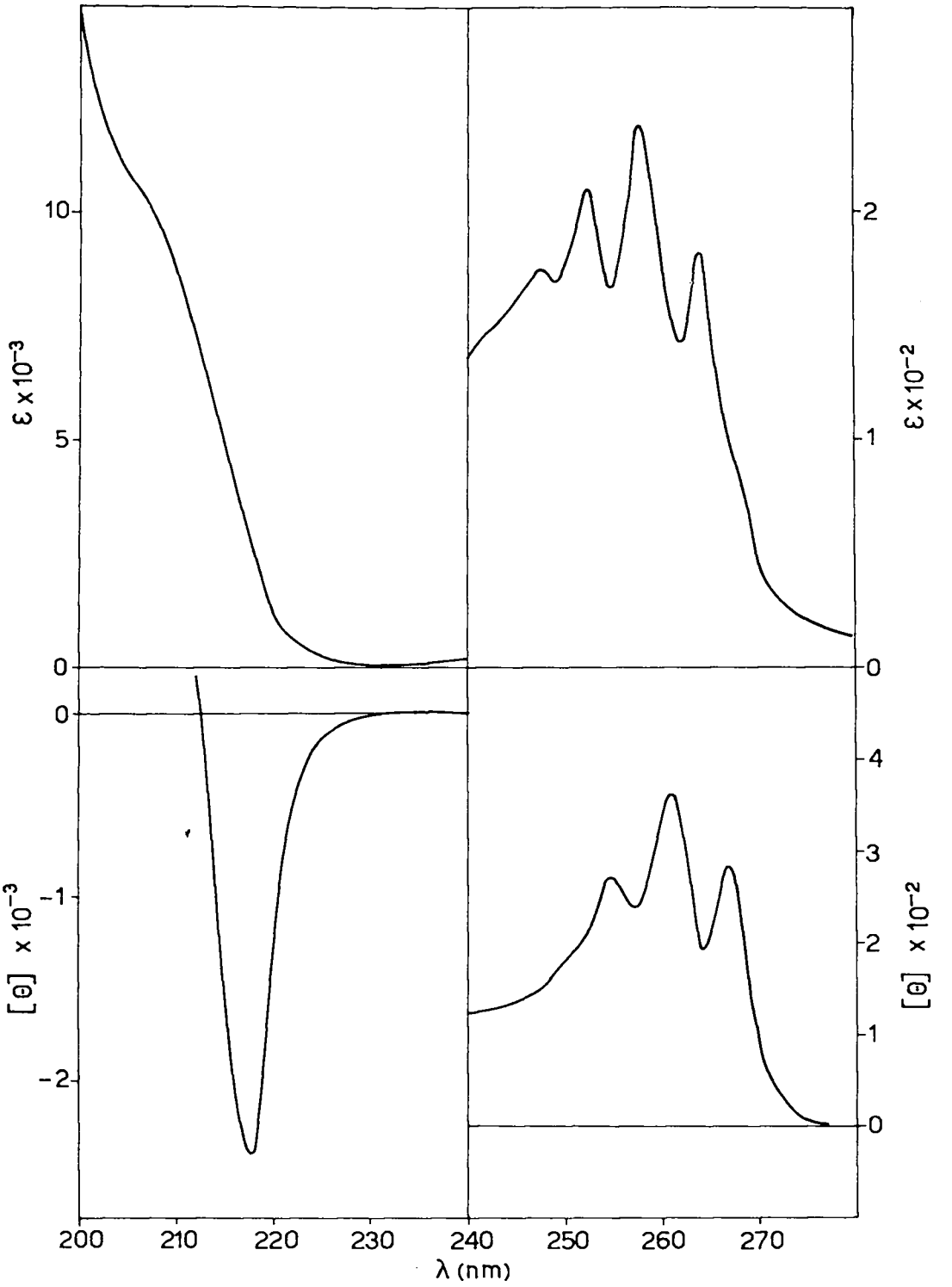
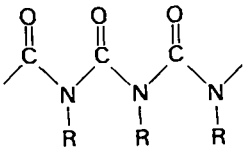


FIGURE 1. Ultraviolet absorption and circular dichroism spectra of (−)-α-phenylethyl isocyanate (**1**) in cyclohexane.

spectrum of **1** shows an inflection at about 210 nm. It should be noted that we purchased the (−)-α-phenylethyl isocyanate from Fluka as (+)-α-phenylethyl isocyanate. Probably the optical rotation at 589 nm of the commercial product was measured under anomalous conditions, i.e. in diluted solutions of an aromatic solvent.

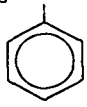
Unfortunately the chirospectroscopic properties of monochromophoric isocyanates are still totally unknown in spite of the fact that a number of optically active alkyl isocyanates was synthesized.

Early in 1959 Shashoua[19] showed that monoisocyanates can be polymerized to linear, high-molecular-weight polymers by an anionic mechanism at low temperatures. Poly-isocyanates (1-nylon polymers) (**4**) are



(**4**)

a: R = $CH_3-\dot{C}H-CH_2-$



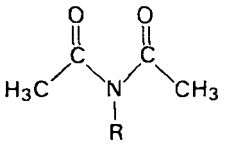
b: R = $CH_3-\dot{C}H-CH_2-$
CH_2-CH_3

interesting molecules in many respects. Not only are they rigid although lacking any notable specific interactions, but also they are polar while being soluble in solvents of low polarity. These unique properties have been responsible for their being subjected to an unprecedented range of different experimental techniques[20].

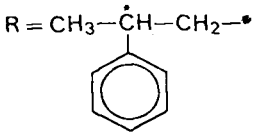
Goodman and Chen synthesized two optically active polyisocyanates, poly-[(+)-β-phenylpropyl isocyanate] (**4a**)[21] and poly-[(+)-β-methylbutyl isocyanate] (**4b**)[22] containing asymmetric carbon atoms in their side-chains. These polymers consist wholly of a ureide-like backbone and, among the common organic solvents, are soluble solely in chloroform.

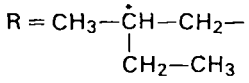
C.d. studies of these polymers were carried out[21–23]. The aromatic polymer (**4a**) in chloroform shows a broad positive dichroism band in the 275–290 nm region. Below 275 nm, it produces a strong negative c.d. with a maximum at 252 nm, probably associated with the $n \rightarrow \pi^*$ transition of the ureide-like chromophore; finally, a region of positive dichroism emerges below 235 nm. In chloroform the dipole–dipole interactions between the polymer and the weakly acidic solvent may be responsible for the solvation of the ureide-like main chain. The c.d. spectrum of the aliphatic polymer (**4b**) in chloroform exhibits a band which is strongly positive and is centred at 253 nm with a cross-over at 235 nm. The beginning of a region of negative

dichroism below 235 nm was also observed. To compare with the chirospectroscopic properties of the polymers in solution, optically active low-molecular-weight model compounds (**5a** and **5b**) were also prepared. The two polymers show substantially enhanced rotatory properties compared with their respective model compounds.



(**5**)





In the aliphatic polymer (**4b**) the main chain has inherently symmetric chromophores which acquire optical activity from dissymmetric perturbations of their environment by the side chain. In the aromatic polymer, in addition to dissymmetric perturbation of inherently symmetric chromophores, the chromophoric effect can also be derived from the interactions between the aromatic side chains. These interactions are probably responsible for the larger magnitudes of the side-chain Cotton effects for the aromatic polymer when compared with the aliphatic polymer.

The comparative study of the two polymers (**4a** and **4b**) and their model compounds (**5a** and **5b**) indicated that dissymmetry in the polymer backbone and the aromatic side chains (obviously, the latter effect is present only in polymer **4a**) contribute to the c.d. spectra of the optically active polymers. The n.m.r. spectra of polymers **4a** and **4b** confirmed that they assume a preferred conformation in chloroform solution[21–23]. In this context it should be noted that recent conformational energy calculations[20] suggest that poly(*n*-alkyl isocyanates) exist as helical structures both in solution and in the solid state, with occasional helix reversals occurring in solution to produce a decrease in the rigidity of the higher-molecular-weight chains. The helix form proposed by Troxell and Scheraga[24] appears to be consistent with most of the experimental data.

The c.d. spectra of polymers **4a** and **4b** in the protonating solvent sulphuric acid were also reported by Goodman and Chen[21–23]. In these experimental conditions the polymers are extended as a polyelectrolyte.

No data concerning chirospectroscopic properties of cyanates are available.

III. CHIROSPECTROSCOPIC PROPERTIES OF THIOCYANATES

As for isocyanates, the optical activity associated with the inherently symmetric thiocyanate chromophore follows as a consequence of its being located in a dissymmetric molecular environment, and the sign and magnitude of the optical activity is determined by the nature and location of the atoms in the extrachromophoric environment. The thiocyanate transition near 245 nm ($\varepsilon \simeq 100$)[25,26] may be attributed to the promotion of an electron from a non-bonding $3p_y$ orbital situated mainly on sulphur to an antibonding π_x^* orbital determined largely by the carbon and nitrogen $2p_x$ atomic orbitals. The schematic representation of the pertinent orbitals is shown in Figure 2.

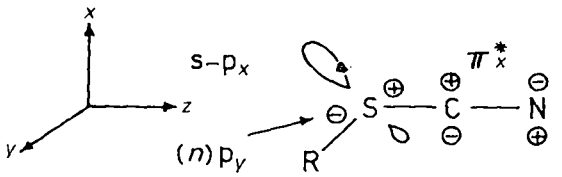


FIGURE 2. Orbitals involved in the 245 nm transition of the thiocyanate chromophore.

The considerations which led to an octant rule for the isoelectronic azide chromophore[27] (see Section V) apply also to thiocyanates insofar as the basic symmetry in the nature of the electronic transitions holds for these two chromophores. It should be noted that, although the chromophores have been called isoelectronic, the sulphur atom contributes bonding and non-bonding electrons from a higher energy level ($n = 3$) in thiocyanates than the corresponding nitrogen atom ($n = 2$) in azides. This distinction may lead to certain quantitative differences; however, it is unlikely to lead to qualitative differences.

On this basis Djerassi and colleagues[26] assumed that thiocyanates should follow the azide octant rule[27]. The thiocyanate octant rule is illustrated in Figure 3. A consideration of the two possible orientations (a and b in Figure 3) gives rise to the same result. Looking along the axis from nitrogen through carbon to sulphur, the symmetry planes are: (1) the xz-plane containing the S, C, and N atoms and the carbon of R attached to sulphur; (2) the yz-plane, orthogonal to the xz-plane, and containing the S, C, and N atoms; and (3) a so-far poorly defined surface approximated by a third plane (xy), orthogonal to the other planes and passing through the carbon atom of the —S—C≡N group.

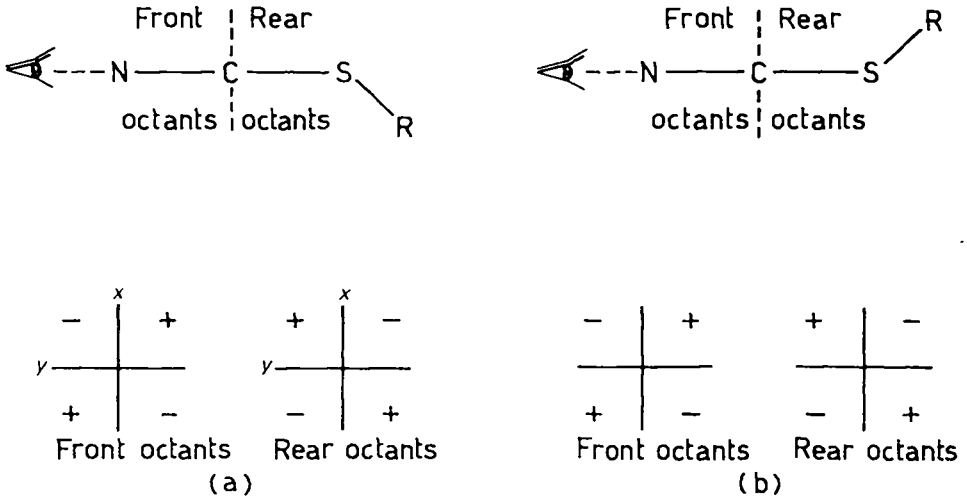
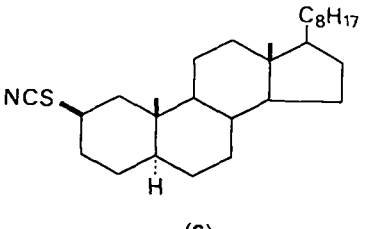


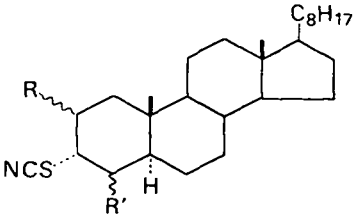
FIGURE 3. The octant rule for the thiocyanate chromophore.

The stereochemical factors which need to be taken into consideration in a thiocyanate octant rule are complicated since the chromophore is subject to rotation about the C_{sp^3}–S bond. Consequently, besides o.r.d., the technique of variable-temperature c.d. was employed to study conformational equilibria, including free rotation of various steroidal thiocyanates.

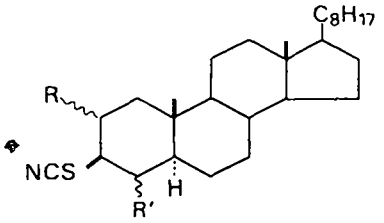
Since, in general, the rotational strength of the —S—C≡N chromophore is rather weak, the Cotton effect in the 250 nm region is discernible only with difficulty by o.r.d. measurements because of the relatively strong background rotation upon which it is superimposed. This represents one of the cases where the superiority of c.d. over o.r.d. is particularly evident. The relevant c.d. data of the monochromophoric steroidal thiocyanates (**6–14**) are summarized in Table 1. The potential utility of the octant rule was tested by analysing the rotameric contributions of the various monochromophoric thiocyanates and those containing additional chromophores, such as the —OH, —$OCOCH_3$ and C=C groups. It was concluded that the interpretations from an octant rule analysis of the c.d. behaviour of thiocyanato steroids are not completely conclusive because of the complications introduced by the very many accessible rotameric conformations and asymmetric solvation effects. But when the chromophore has an obviously preferred orientation, there is generally good coincidence between observed and predicted Cotton-effect signs. Moreover, the thiocyanate group, a long-neglected chromophore, offers a further interesting example of an application of the octant rule to a non-carbonyl-type chromophore.



(6)



(7) R = R' = H
(8) R = β-CH_3—; R' = H
(9) R = α-CH_3; R' = H
(10) R = H; R' = α-CH_3—



(11) R = R' = H
(12) R = β-CH_3—; R' = H
(13) R = α-CH_3—; R' = H
(14) R = H; R' = α-CH_3—

The chirospectroscopic properties of 17-α-thiocyanato-Δ^5-pregnenes containing the dominant 20-carbonyl chromophore (**15**–**16**) were also investigated[28–31]. The c.d. curve of thiocyanohydrin (**15**) and its diacetate (**16**), taken in *n*-hexane, when compared with the c.d. curves of these same compounds in more polar solvents, are characterized by a sharp decrease in the amplitude of the Cotton effect in the region of the $n \rightarrow \pi^*$ transition of the carbonyl chromophore (near 300 nm) for **15**, and a substantially smaller change in amplitude of the c.d. band for diacetate **16**. A change in the intensity of the Cotton effect, observed when the character of the solvent is changed, testifies to the conformational mobility of the 17-acetyl group, which can be due either to the steric or the polar effect of the vicinal groups that are found in the *cis* configuration with respect to it. According to Akhrem and coworkers[28–31] the sharp decrease in the intensity of the c.d. band, clear down to a change in the sign, that is observed for thiocyanohydrin (**15**) when going from polar solvents to *n*-hexane, can be explained only by the formation of an intramolecular hydrogen bond in **15** in the case of solution in *n*-hexane with involvement of the *cis*-arranged acetyl and hydroxy groups, which facilitates a reorientation of the acetyl group to the preferential conformation with the carbonyl group directed towards C_{16}

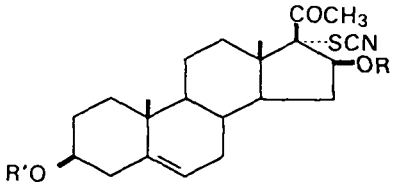
TABLE 1. Circular dichroism data for some monochromophoric steroidal thiocyanates

Compound	Solvent	Temperature (°C)	λ_{max}(nm)	$\Delta\varepsilon_{max}$
(6) 2β-Thiocyanato-5α-cholestane	Decalin	R.T.[a]	272	+0·81
	Decalin	+166	273	+0·32
(7) 3α-Thiocyanato-5α-cholestane	*i*-Octane	R.T.	255	+0·13
	Methanol	R.T.	255	+0·17
	Decalin	R.T.	255	+0·13
	Decalin	+130	255	+0·11
	EPA[b]	R.T.	255	+0·14
	EPA	−192	252	+0·14
(8) 2β-Methyl-3α-thiocyanato-5α-cholestane	Methanol	R.T.	253	+0·42
	i-Octane	R.T.	253	+0·36
	EPA	R.T.	252	+0·33
	EPA	−192	253	+0·34
(9) 2α-Methyl-3α-thiocyanato-5α-cholestane	EPA	R.T.	253	+0·09
	EPA	−192	255	−0·02
(10) 3α-Thiocyanato-4α-methyl-5α-cholestane	EPA	R.T.	278	−0·03
			250	+0·16
	EPA	−192	280	−0·03
			250	+0·53
(11) 3β-Thiocyanato-5α-cholestane	*i*-Octane	R.T.	250	+0·02
	Methanol	R.T.	250	−0·02
	EPA	R.T.	260	+0·01
	EPA	−192	242	−0·13
(12) 2β-Methyl-3β-thiocyanato-5α-cholestane	*i*-Octane	R.T.	248	+0·12
	Methanol	R.T.	248	+0·11
	EPA	R.T.	247	+0·14
	EPA	−192	247	+0·16
(13) 2α-Methyl-3β-thiocyanato-5α-cholestane	*i*-Octane	R.T.	250	−0·36
	Methanol	R.T.	248	−0·43
	EPA	R.T.	249	−0·43
	EPA	−192	245	−0·91
(14) 3β-Thiocyanato-4α-methyl-5α-cholestane	*i*-Octane	R.T.	253	+0·42
	Methanol	R.T.	250	+0·41
	EPA	R.T.	250	+0·41
	EPA	−192	248	+0·59

[a] Room temperature.
[b] EPA: ethyl ether–*i*-pentane–ethanol, 5:5:2 (by volume).

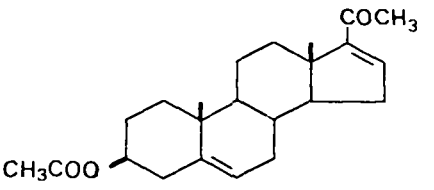
(conformation A of Figure 4). In a polar solvent, due to some failure of intramolecular hydrogen bonding formation, the conformational equilibrium mixture is shifted towards conformations B and C.

The 16 β-acetoxy derivative (**16**) shows an increase in the intensity of the

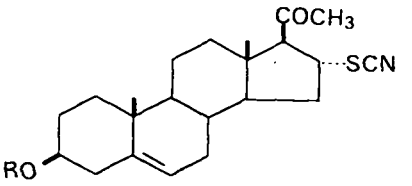


(15) R = R' = H

(16) R = R' = CH_3CO-

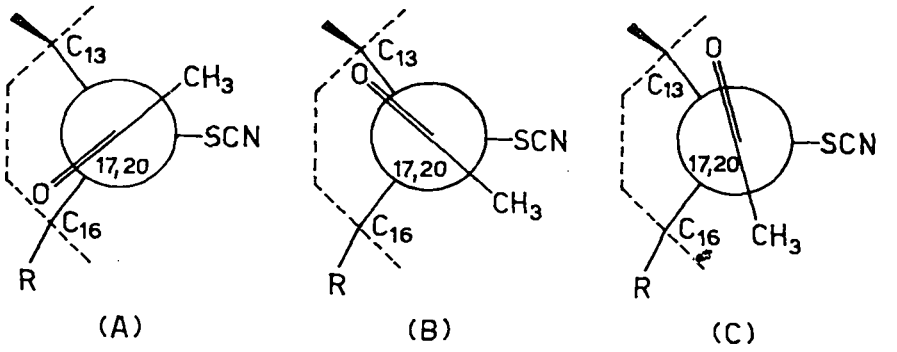


(17)



(18) R = H

(19) R = CH_3CO-



R = -OH (15)

R = $-OCOCH_3$ (16)

FIGURE 4. Possible conformations around the C_{17}–C_{20} bond in 17-α-thiocyanato-Δ^5-pregnenes **15** and **16**.

Cotton effect compared with the corresponding 16β-hydroxy compound (**15**). The introduction of a *cis*-acetoxy function (16β-acetoxy group) into the vicinity of the 17β-acetyl group may be assumed to give rise to strong steric and polar interactions (which are definitely stronger than those in 16β-hydroxy compounds). Therefore, the conformation equilibrium of the

16β-acetoxy pregnene can be expected to shift mainly away from conformation A; in addition, the above explanation is also in accord with the relatively small solvent effect observed in the c.d. spectra of **16**.

In the course of this study Akhrem and coworkers[28–31] were also able to show that:

(a) functional substituents in position 17 with a covalent bond longer than 1·76 Å (the C_{sp^3}–S interatomic distance of thiocyanates is about 1·82 Å) give a negative contribution according to the carbonyl octant rule in the positive Cotton effect of pregnenes in the preferred conformation A;

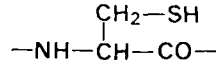
(b) in the conformation B (Figure 4) most of the steroid skeleton lies near to or in one of the planes of the carbonyl group, and therefore has a small effect on the c.d.; the main contribution to the optical rotation is made by the 17α-SCN group, situated close to the plane of the carbonyl group, but in a positive octant, overcoming the negative one experienced by the methyl group in position 18 and the C_{16} methylene (and the substituent at C_{16});

(c) for the 16β acetoxy steroid (**16**), evidently, a partial reorientation of the 17β-acetyl group to the energetically less profitable C conformation (Figure 4) is possible, and the octant diagram shows that the steroid skeleton and the 17α-—S—C≡N group are in a positive octant in this conformation; possibly, the partial contribution of this conformer also explains the rather large amplitudes of the Cotton effect for compound **16**.

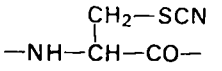
The above discussion pertains to a steroid molecule on the assumption that the D ring is in the half-chair conformation. Since the factors influencing the conformation of the D ring were almost unknown, Akhrem and coworkers[28–31] could not *quantitatively* estimate the influence of the 17α-—S—C≡N substituent.

In an extension of their investigations on the modification of steroids the Russian workers studied the stereochemistry of the addition reaction of HSCN to the 3β-acetate of $\Delta^{5,16}$-dehydropregnen-3β-ol-20-one (**17**)[32]. In particular, the c.d. spectra of the 16-thiocyanato derivatives (**18** and **19**) gave information on their configurations. In both cases a strong positive Cotton effect, associated with the $n \rightarrow \pi^*$ transition of the carbonyl chromophore, was observed near 295 nm. A positive Cotton effect is connected with the 20-carbonyl chromophore of a 17-acetyl side chain in configuration β. The establishment of the α-configuration of the thiocyanato group at C_{16} in the 17β pregnene series also presented no great difficulty. In fact, a significant decrease in the intensity of the c.d. curve is observed in the case of 16β, 17β

substitution, while a 16α substituent shows an influence on the Cotton effect to a significantly lesser extent. This in turn possibly depends on the fact that, as discussed above, 16β, 17β-*cis* substitution induces some reorientation of the acetyl side chain.



(20)



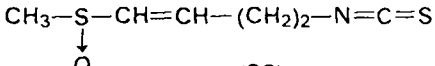
(21)

Cysteine residues (**20**) were modified in peptide and protein chemistry to the derivatives **21**[33]. However, the o.r.d.–c.d. spectra of these optically active thiocyanates are not available.

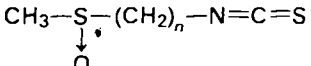
IV. CHIROSPECTROSCOPIC PROPERTIES OF ISOTHIOCYANATES

Only a few examples of the isolation, preparation, characterization and use of optically active isothiocyanates are known, chiefly as a result of needing to obtain physiologically active materials[34]. Interestingly, the optical activity of the naturally occurring isothiocyanates (**22** and **23**) is associated with the presence of an asymmetric sulphur atom in the sulphoxide moiety[35]. The o.r.d. properties of these sulphoxide mustard oils were investigated[36]; however, the discussion was essentially centred on the contribution of the sulphoxide chromophore to the optical rotatory properties. This approach is well justified since in compounds **22** and **23** the isothiocyanato group is separated from the source of the optical activity by three or more carbon atoms and hence it is not expected to contribute significantly to the optical rotation.

The chirospectroscopic properties of (+)-α-phenylethyl isothiocyanate



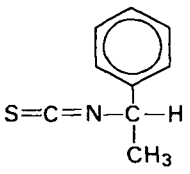
(22)



(23)

$n = 3–5; 8–10$

(**24**) were reported without a solvent and in a number of solvents of different polarity[34]. All o.r.d. curves, taken between 650 nm and 300 nm, were plain and positive. The molar rotation values were greatly dependent on solvent polarity, but this effect was not regular. This very limited chiroptical analysis was not further extended.



(24)

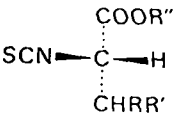
The o.r.d.–c.d. properties of some isothiocyanates derived from amino acids and amino alcohols (**25–34**) were described by Crabbé and colleagues[37]. Table 2 gives the u.v. and c.d. data for isothiocyanates which were derived from the amino groups of some amino alcohol alkyl carbonates.

Above 220 nm only one u.v. transition was detected at 256–259 nm. Corresponding u.v. absorption bands for the isothiocyanates derived from amino acid esters and for alkyl isothiocyanates were found at 240–260 nm[34,38–40]. The delocalized π-system and the role of sulphur d orbitals in the electronic structure of molecules containing the —NCS group have been recently discussed[41].

Three Cotton effects of increasing intensity were detected between 350 nm and 200 nm. From longer wavelengths, a first rather weak Cotton

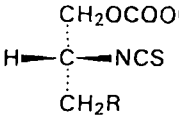
TABLE 2. Ultraviolet absorption and circular dichroism data for isothiocyanates derived from some amino alcohol alkyl carbonates in ethanol

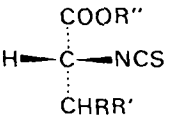
Compound	Ultraviolet		Circular dichroism	
	λ_{max}(nm)	ε_{max}	λ_{max}(nm)	$\Delta\varepsilon_{max}$
D-2-Aminopropanol derivative (**29**)	259	16,940	347	+0·73
			255	−2·60
			200	−9·45
D-2-Aminobutanol derivative (**30**)	259	15,900	338	+0·52
			260	−1·85
			203	−5·55
D-Phenylglycinol derivative (**34**)	259	17,200	341	+0·42
			276	−0·63
D-Phenylalanilol derivative (**31**)	259	16,050	340	+0·71
			260	−4·33
			205	−9·00
D-Serine derivative (**32**)	256	16,280	345	−0·84
			250	−2·27
			214	+5·88
D-Threonine derivative (**33**)	256	22,850	344	−0·43
			248	−1·26
			215	+3·33



(25) R = R′ = H; R″ = CH_3—
(26) R = R′ = CH_3— ; R″ = CH_3CH_2—
(27) R = H; R′ = CH_3—$\underset{\displaystyle CH_3}{CH}$—; R″ = CH_3CH_2—

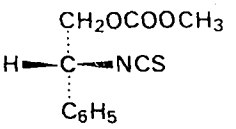
(28) R = H; R′ = $CH_3CH_2OCOCH_2$—; R″ = CH_3CH_2—





(29) R = H
(30) R = CH_3—
(31) R = C_6H_5—

(32) R = H; R′ = CH_3OCOO—; R″ = $CH_3CH_2CH_2$—
(33) R = CH_3—; R′ = CH_3CH_2OCOO—; R″ = CH_3—



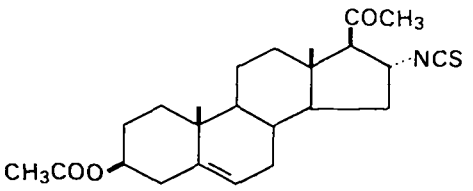
(34)

effect appears around 340 nm. Apparently, this c.d. band does not have any counterpart in the u.v. absorption spectrum. This emphasized that the c.d. technique is a valuable tool in the detection of hidden absorption bands. A second, more-intense, Cotton effect of opposite sign is situated at about 255 nm. The most intense Cotton effect, of the same sign, is observed in the 200–210 nm region, where the —NCS chromophore exhibits a further u.v. absorption band[40].

From this study it was confirmed *inter alia* that the c.d. spectra give a better quantitative evaluation of the Cotton effects exhibited by compounds presenting several optically active transitions. As far as the signs of the c.d. bands are concerned, those of serine (**32**) and threonine (**33**) derivatives at 340 nm and 205 nm are opposite to the ones exhibited by the other amino alcohols listed in Table 2. This was attributed to the second carboxyl group which is present in compound **32** and to a second asymmetric centre which is part of the threonine molecule **33**. Also noteworthy is the enhanced intensity of the 260 nm Cotton effect in the phenylalaninol derivative (**31**).

Besides the 16-thiocyanato derivatives (**18** and **19**) the addition reaction of HSCN to the 3β-acetate of $\Delta^{5,16}$-dehydropregnen-3β-ol-20-one (**17**)

yields the four optically active steroidal isothiocyanates **35–38**[32]. It is worth noting that the addition products which are obtained in high yield, i.e. isothiocyanates (**35**, **37** and **38**), are formed contrary to expectation instead of the addition products of thiocyanic acid. The direct isothiocyanation of steroids under the conditions studied seemed unlikely since such reactions usually require drastic conditions. Nevertheless, the formation of isothiocyanates together with only an insignificant amount of the thiocyanates (**18** and **19**) under relatively mild conditions was strictly proven. Applying the empirical c.d. correlations discussed above for the steroidal thiocyanates[32], Akhrem and coworkers were also able to determine the configurations of the 17-side chain and the —NCS group at C_{16} of the four isothiocyanates (**35–38**). N.m.r. spectra were consistent with the configurations assigned using c.d.



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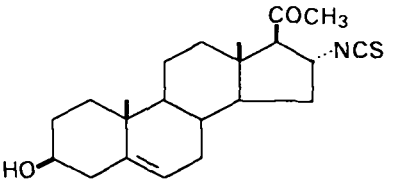

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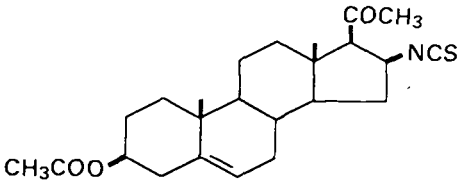

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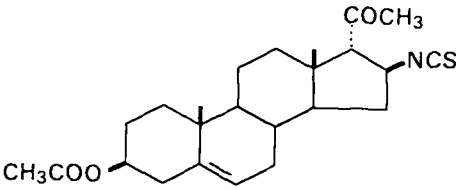


(38)

V. CHIROSPECTROSCOPIC PROPERTIES OF CYANAMIDES AND AZIDES

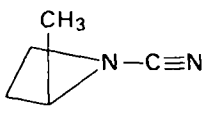
The cyanamide chromophore was investigated using c.d. by Kostyanovsky and coworkers[42]. The c.d. spectra of (+)-1-cyano-2-methylazetidine (**39**) and (−)-1-cyano-2-methylpyrrolidine (**40**) revealed a complex pattern which consists of two superimposed dichroic absorption bands of the same sign near 210–220 nm and below 200 nm, respectively, but in (+)-1-cyano-α-pipecoline (**41**) and (+)-1-cyanocamphidine (**42**) only one c.d. band is observed below 200 nm. The long-wavelength Cotton effect

is related to the u.v. shoulder in the 205 nm region[42], whereas the short-wavelength Cotton effect depends upon an absorption band below 190 nm.

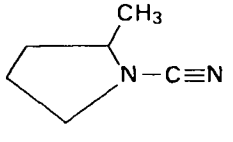
The shift of the u.v. absorption band as a function of the solvent used[42] and extended Hückel-type molecular orbital calculations of dimethylcyanamide (**43**)[43] indicate that the absorption bands can be assigned to transitions of electrons of an amino nitrogen lone pair occupying the three-centre non-bonding orbitals π_z^* to the antibonding π_y^* and π_z^{**} orbitals.

The Cotton effect sign may be unambiguously correlated with the absolute configuration of the asymmetric carbon atom. The quadrant rule[44] must be the common regional rule which is controlled by the symmetry properties of the —NCN chromophore under the assumption of its planarity. From the microwave data it is known that the out of plane angle in dimethylcyanamide (**43**) is near 40°[45]. With such geometry of the chromophore, the equatorial group in **41** is arranged near the nodal surface. Presumably, because of this the long-wavelength Cotton effect is absent in this compound. By analogy with thiocyanate (—NCS) and azide ($—N_3$) chromophores, it is believed that the cyanamide (—NCN) chromophore should also follow the octant rule. The c.d. spectra of **39** and **40** indicate that the —NCN chromophore is governed by the same sign rule as the thiocyanate[26] and azide[27] chromophores. For compound **40**, for example, the projection along the NCN axis and the corresponding quadrant signs are illustrated in Figure 5.

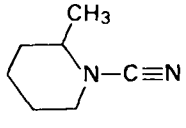
In the u.v. absorption spectra of alkyl azides, two transitions of low intensity are found around 215 nm and 287 nm[46–49] which have been recently assigned to the $s–p_x \rightarrow \pi_y^*$ and $\pi_y \rightarrow \pi_x^*$ transitions, respectively[47]. The non-bonding π_y orbital is mainly localized as the $2p_y$ orbital of N_1; the antibonding π_x^* orbital is associated principally with $2p_x$ atomic orbitals from the remaining two nitrogen atoms (N_2 and N_3) (Figure 6). The 287 nm



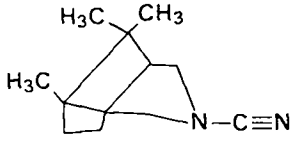
(**39**)



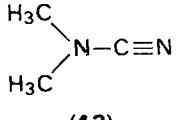
(**40**)



(**41**)



(**42**)



(**43**)

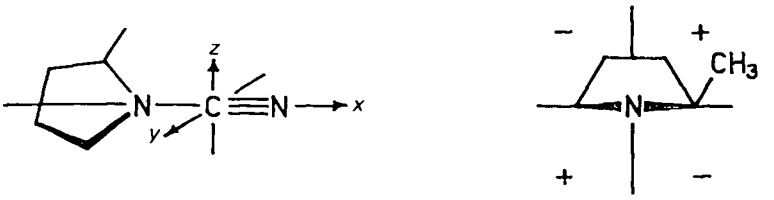
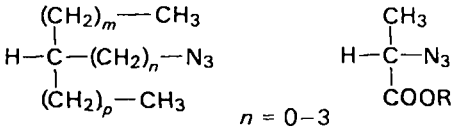


FIGURE 5. Projection along the NCN axis and the corresponding quadrant signs of (−)-1-cyano-2-methyl pyrrolidine (**40**).



(44) **(45)**

band is often considered to be a typical $n \rightarrow \pi^*$ transition, similar to those of carbonyl compounds such as ketones and aldehydes, but this band does not show the characteristic solvent blue-shift of this transition[47]. Also, the 215 nm band seems to be nearly insensitive to solvent polarity[47].

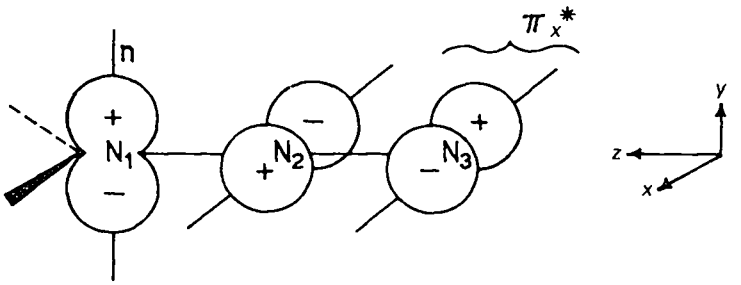
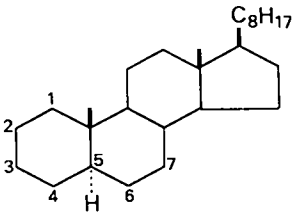


FIGURE 6. Orbitals involved in the 285 nm transition of azides.

The long-wavelength u.v. absorption band of monochromophoric alkyl azides (**44**) was reported to be optically inactive by Levene and Rothen[49]. However, in the case of α-azidopropionic acid and its derivatives (**45**) an anomalous dispersion was observed[49,50].

Cotton effects corresponding to this transition were first investigated in detail by Djerassi and his colleagues[27]. These workers suggested that the sign of the azide Cotton effect should be related to the geometry of the chromophore's environment by an octant rule analogous to that for ketones; in fact, if a compound was viewed along the line of the azide



(46–52)

(46) = 2α, N_3
(47) = 2β, N_3
(48) = 3α, N_3
(49) = 2α, CH_3; 3α, N_3
(50) = 3α, N_3; 4α, CH_3
(51) = 3β, N_3
(52) = 6β, N_3

chromophore, with the lone pair of electrons of N_1 upward and in the vertical plane, then the region around the chromophore could be divided into octants analogous to those for ketones (Figure 7).

The o.r.d. and c.d. properties above 230 nm of a number of steroidal azides were measured and analysis of some of the data in terms of the octant

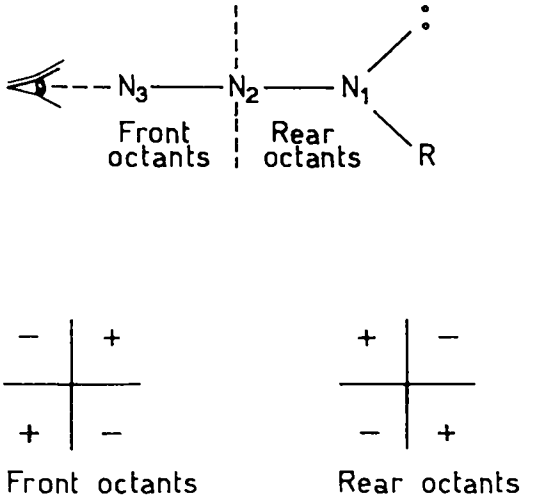
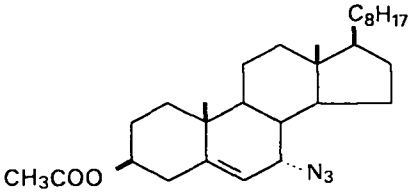


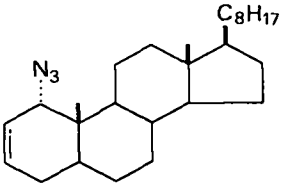
FIGURE 7. The octant rule for the azide chromophore.

rule was attempted[27]. The rotational strength of the azide chromophore is considerably weaker than that of the carbonyl group and, in a number of instances, the Cotton effect in the 280 nm region is discernible only with difficulty by o.r.d. means because of the relatively strong background rotation upon which it is superimposed. The amount of definitive stereochemical information that could be obtained was severely limited because of the very many accessible rotameric conformations. The c.d. data of some monochromophoric azidocholestanes (**46**–**52**) in dioxane solution are reported in Table 3.

Other applications of the octant rule for the azide chromophore in steroids have been reported by Kischa and Zbiral[51] for the allylic azides (**53** and **54**).



(**53**)



(**54**)

TABLE 3. Circular dichroism data for some monochromophoric steroidal azides in dioxane

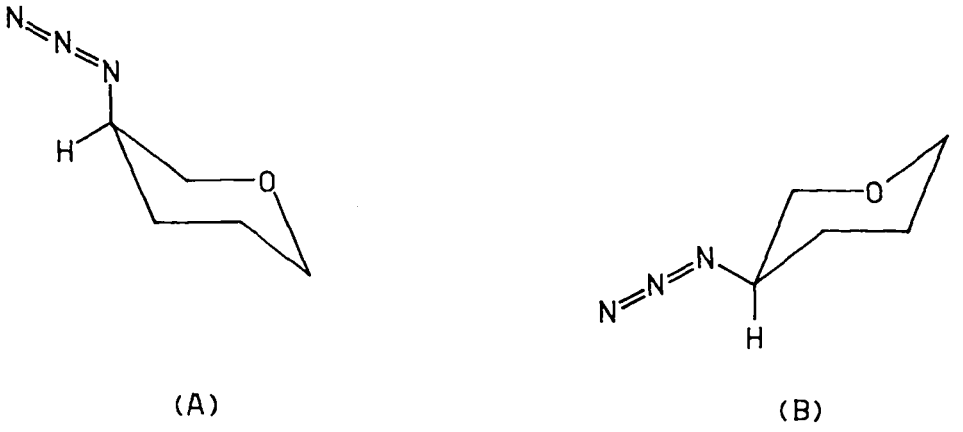
Compound	Position of azide	Other substituents	Temperature (°C)	λ_{max}(nm)	$\Delta\varepsilon_{max}$
(**46**)	2α	—	25	270	−0·07
(**47**)[a]	2β	—	25	284	+0·06
			−192	310	−0·03
			−192	245	+0·04
(**48**)[a]	3α	—	25	290	+0·06
			−192	292	+0·11
(**49**)	3α	2α-Methyl	25	290	−0·16
(**50**)	3α	4α-Methyl	25	284	+0·15
(**51**)	3β	—	25	282	−0·07
(**52**)	6β	—	25	305	−0·03

[a] In EPA solvent mixture.

Subsequently this octant rule was tested for an impressive array of carbohydrate azides by various authors[52–55]. In spite of the large number of possible conformations agreement between the octant rule prediction and the observed sign of the Cotton effect was found in the majority of cases. Paulsen[52] emphasized that for each configuration of the azide group, there are several possible conformations around the C–N_3 bond to be considered. He suggested that the conformation determining the sign of the Cotton effect is that in which the linear azide group is coplanar with the adjacent C–H bond, and pointing away from the pyranose ring [(A) and (B) for axial and equatorial azides, respectively] (Figure 8).

Finally, Akhrem's group discussed the chirospectroscopic properties of the 17α-azido-Δ^5-pregnene-20-ones in terms of the effect of the length of the

C–N_3 bond on the sign of the Cotton effect of the carbonyl chromophore $n \rightarrow \pi^*$ transition[28,30,31].



(A) (B)

FIGURE 8. Application of the azide octant rule to carbohydrate derivatives.

VI. CHIROSPECTROSCOPIC PROPERTIES OF THE REACTION PRODUCTS OF CYANATES AND RELATED GROUPS

Cyanates, thiocyanates, isocyanates and isothiocyanates are capable of reaction with amino, hydroxyl, thiol and other nucleophilic groups. Comparing the reaction rates of cyanates and related groups with compounds containing the above mentioned nucleophiles at pH $\simeq$ 8–9 one obtains the following sequence of nucleophilicity[56–59]:

$$-SH \gg \diagdown N-H > ArOH > -NH_2 \gg ROH$$

Detailed kinetic studies were carried out on the reaction of isothiocyanates with primary amines[34,59–62], phenols[59] and thioalcohols[56,59]. The results obtained demonstrated that the reaction is first order with respect to the —XH component; in addition, the unprotonated form of the amine and the phenolate and thiolate anions are the reactive species. Also, isocyanates are much more reactive than their sulphur analogues.

Over the last 10 years the o.r.d.–c.d. properties of the reaction products of cyanates and related groups with primary and secondary amines, alcohols and thioalcohols (thiols) have been extensively investigated. In this section a

summary of these studies is reported. The main emphasis is placed on those chromophores which have demonstrated their usefulness as chromophoric derivatives[2] of compounds containing $-NH_2$, $>NH$, $-OH$ and $-SH$ functional groups. This is an area where Djerassi's approach[2] has found immediate and widespread acceptance because of the urgent need for new and rapid methods for the determination of absolute configuration and conformational preferences, particularly in the field of natural products. Metal complexes will not be discussed.

A. With Primary and Secondary Amines

The reaction between isothiocyanates and α-NH_2 groups of amino acid residues in a weakly alkaline medium gives N^{α}-alkyl (aryl) thiocarbamoyl derivatives (**55**). Methyl isothiocyanate has to be preferred over aryl isothiocyanates in chiroptical analysis since it has a somewhat higher reactivity towards amino groups, the time required for the reaction to be completed therefore being shortened; it is considerably more soluble in water, which makes it possible to conduct the reaction in aqueous solution without resorting to the addition of organic solvents; and, finally, it does not contain a chromophore which could interfere in the c.d. determinations[63].

The $-NH-C(=S)-NH-$ chromophore was examined in detail by u.v. absorption spectroscopy and was shown to present a low intensity band at 280–290 nm and a much stronger band at 240–250 nm, which are associated to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions within the thiocarbonyl group, respectively[64]. The c.d. data of N^{α}-methylthiocarbamoyl(MTC)-α-amino acids (**55**; R = CH_3) at weakly alkaline pH[63] are reported in Table 4. The results obtained can be summarized as follows:

(a) MTC-amino acids of L-configuration have a positive Cotton effect and, consequently, those of the D-series a negative one: this observation was tested on all the protein amino acids and was demonstrated to hold without exception;

(b) the dichroic bands are centred at 262–263 nm, with the exception of MTC-L-serine which shows a broad band at 265–270 nm;

(c) the reported $A_L - A_R$ values do not have absolute significance, since MTC-amino acids were not isolated but measured directly in the reaction mixtures;

(d) the ε-amino side-chain group of lysine residues reacts with methyl isothiocyanate (as demonstrated with N-α-carbobenzoxy-L-lysine by thin layer chromatography), but the N^{ε}-MTC derivatives do not

complicate the stereochemical correlations, since it does not exhibit a dichroic band in the region of absorption of thioureines, the asymmetric carbon atom being too far removed from the inherently symmetric chromophore;

(e) a second α-carbon atom of opposite configuration is not able to alter the sign of the band;

(f) in the presence of other groups absorbing in this spectral region the Cotton effect associated with the thioureine chromophore can not be assigned unequivocally.

The rates of reaction of methyl isothiocyanate and amino acid residues were also measured and found to be dependent on the degree of substitution of the amino moiety, being rapid for the secondary amino group of proline and considerably slower for the primary amino groups of the various amino acids[63].

The drawback of the superposition of bands related to chromophores absorbing in the 250–300 nm region shown by the MTC derivatives can easily be removed if the reaction mixtures, after about 90 minutes at slightly alkaline pH, are kept at acidic pH for a few hours. The resulting methylthiohydantoins (MTH) (**56**; R = CH_3) show a Cotton effect at 300–315 nm (Table 4) which is positive for the L-series and negative for the D-series[63,65,66]. The location of the dichroic band in correspondence to a low-intensity u.v. band[67] and its red-shift on going from more-polar to less-polar solvents suggests that it is associated with an $n \rightarrow \pi^*$ transition within the chromophore. The position and the dichroic intensities of these Cotton effects are merely indicative, since completion of the reactions and extent of racemization were not assessed. The Cotton effect of MTH above 300 nm does not exhibit inversion of sign on going from aqueous to organic solutions, as has been reported for other —NH—C(=S)—-containing compounds[68]. Hence, the use of the sign of the 305 nm Cotton effect of MTH was proposed as a simple and rapid method for determining the absolute configurations of sequences of α-amino acids in natural occurring peptide compounds[63,65,66].

More recently, the u.v. and c.d. properties of 19 MTH derived from α-amino acids were independently investigated by Suzuki and Tuzimura[69]. The racemization mechanism was also discussed.

A large number of 3-phenyl-2-thiohydantoins (PTH) (**56**; R = C_6H_5), obtained by reacting phenyl isothiocyanate with the α-NH_2 group of α-amino acids, were also examined by c.d.[70–72]. These derivatives suffer the disadvantage of racemizing more easily than MTH. The sign of the 320–330 nm dichroic band of all PTH of the same configuration is the same

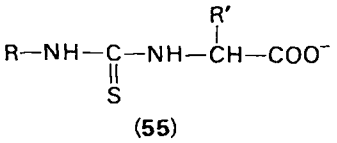
TABLE 4. Circular dichroism of amino acid and peptide derivatives with methyl isothiocyanate

Amino acid/ peptide	Methylthioureine (55)[b] $\Delta A^c \times 10^3$	λ_{max}	Methylthiohydantoin (56)[e] $\Delta A^f \times 10^3$	λ_{max}
L-Alanine	1·1	262	3·85	306
D-Alanine	−1.1	262	−3.85	306
L-Valine	1·0	263	3·9	303
L-Leucine	3·0	262	0.42	308[g]
D-Leucine	−3·0	262	−0·42	308[g]
L-Isoleucine	1·3	262	0·23	308[g]
L-Serine	0·15	265–270[d]	2.25	305[h]
L-Threonine	0·8	263	1·1	305[h]
L-Aspartic acid	1·6	263	2·4	309
L-Asparagine	1·0	263	2·5	304
L-Glutamic acid	1·5	263	2·8	306
L-Glutamine	0·9	263	8·45	302
L-Methionine	3·0	262	3·0	303
L-Lysine	1·6	262	4·45	305
L-Arginine	0·8	262	5·2	307
L-Proline	5·7	262	44·2	308
L-Histidine	—	—	2·05	315
L-Phenylalanine	—	—	0·38	309[g]
L-Tyrosine	—	—	11·0	305[h]
L-Tryptophan	—	—	12·6	302
Z-L-Lysine[a]	—	—	—	—
L-Alanyl-D-Alanine	1·7	267	3·75	303

[a] *N*-α-Carbobenzoxy-L-lysine.
[b] Approximately 90 min at slightly alkaline pH; temperature 23 ± 1 °C; excess of methyl isothiocyanate.
[c] Amino acid or peptide concentrations, 10^{-1} M; 1-mm cell.
[d] Wavelength maximum not clear.
[e] Several hours at acidic pH.
[f] 1-cm cell.
[g] The isolated compound has been measured in methanol solution; Δε values.
[h] Shoulder.

in all solvents tested. As in the case of MTH, positive and negative Cotton effects correspond to L- and D-configurations, respectively. The behaviour of α-methyl-a-amino acids was also investigated, but the authors concluded that the configuration of these compounds is not determinable by the c.d. spectra of their PTH derivatives[72].

Three insulin derivatives containing from one to three groups of the symmetric dye fluorescein isothiocyanate, bound at the amino functions,



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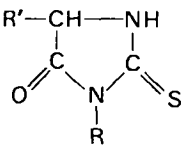

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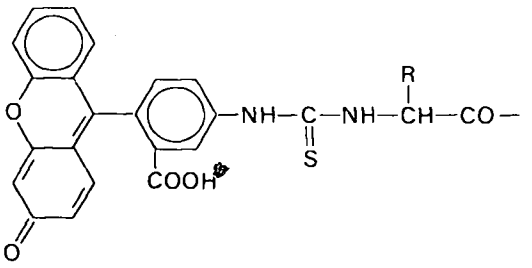


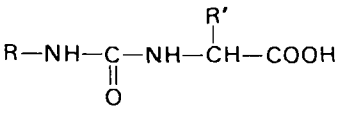
(57)

were examined by absorption and c.d. spectroscopy above 400 nm[73]. The results were interpreted according to Moffitt's exciton theory[74]. This approach was confirmed by the examination of model compounds.

Three samples of fluoresceinthiocarbamoyl-lysozyme were prepared and the average amount of covalently bound dye was 4·2, 2·0 and 1·5 mol/mol of protein, respectively[75]. The c.d. spectra were examined only below 300 nm. No measurable changes occur in the peptide absorption region upon introduction of the dye, whereas in the 250–300 nm region the spectra change considerably with the degree of labelling. It was suggested that at a high degree of labelling there might be some interaction between the fluoresceinthiocarbamoyl group (**57**) and aromatic amino acid residues, probably tryptophyl residues, of the lysozyme molecule.

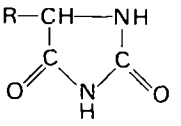
These studies demonstrate that fluorescein isothiocyanate can be considered as a useful chiroptical probe for the investigation of the topography of naturally-occurring peptide molecules. Finally, an o.r.d. study of 16 fluoresceinthiohydantoins from α-amino acids was published by Kawauchi and Tuzimura[76].

In addition to isothiocyanates, KCNO has also been proposed as a suitable reagent for determining $-NH_2$ terminal amino acids[77] and for modifying the ε-NH_2 group of lysine residues in proteins[59] and in peptide hormones[78]. Gravenmade and colleagues reported the c.d. of N^{α}-carbamoyl-α-amino acids (**58a**)[79,80].

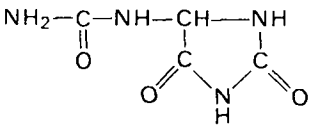


(58)

a: R = H
b: R = CH_3



(59)



(60)

A positive Cotton effect near 230 nm, assigned to the ureido chromophore, is apparent for the D-amino acid derivatives at pH <9. At pH >9 no dichroic bands are evident above 220 nm. Recent results obtained in our laboratory[15] on the chirospectroscopic properties of methyl isocyanate aliphatic amino acid adducts (**58b**) revealed the presence of a Cotton effect in the 220–225 nm region at pH 8·5, which is negative for the L-series (Figure 9). Thus, the location of the dichroic band of the NH—C(=O)—NH— group below 250 nm and its rather low intensity do not seem particularly promising for an extension of this method to proteins. The chiroptical properties of carbamoylpepsinogen[81] and carbamoyl Bence-Jones protein[82] were studied and found to be similar to those of the underivatized proteins.

O.r.d.–c.d. analysis of hydantoins (**59**), obtained by cyclization of the N^{α}-carbamoyl-α-amino acids (**58a**), showed a Cotton effect at 238–245 nm which is negative for L-enantiomers[83]. Hydantoins from aromatic amino acids and proline exhibited different spectra. According to the octant rule the negative Cotton effects were assigned to the C_4 $\diagdown$ $C{=}O$ $\diagup$ chromophore.

In order to assign the absolute configuration of (−)-allantoin (**60**) the c.d. of the hydantoin derived from aspartic acid was examined as a function of pH[79]. A hypsochromic shift was observed on changing the pH from alkaline to acid values.

Attention was paid also to thioureines derived from naturally occurring mustard oils (**61**), the o.r.d. properties of which were examined by Klyne and colleagues[36]. This study substantiated the stereochemical assignments based on the o.r.d. curves of the isothiocyanates.

A number of important studies were published on the chirospectroscopic

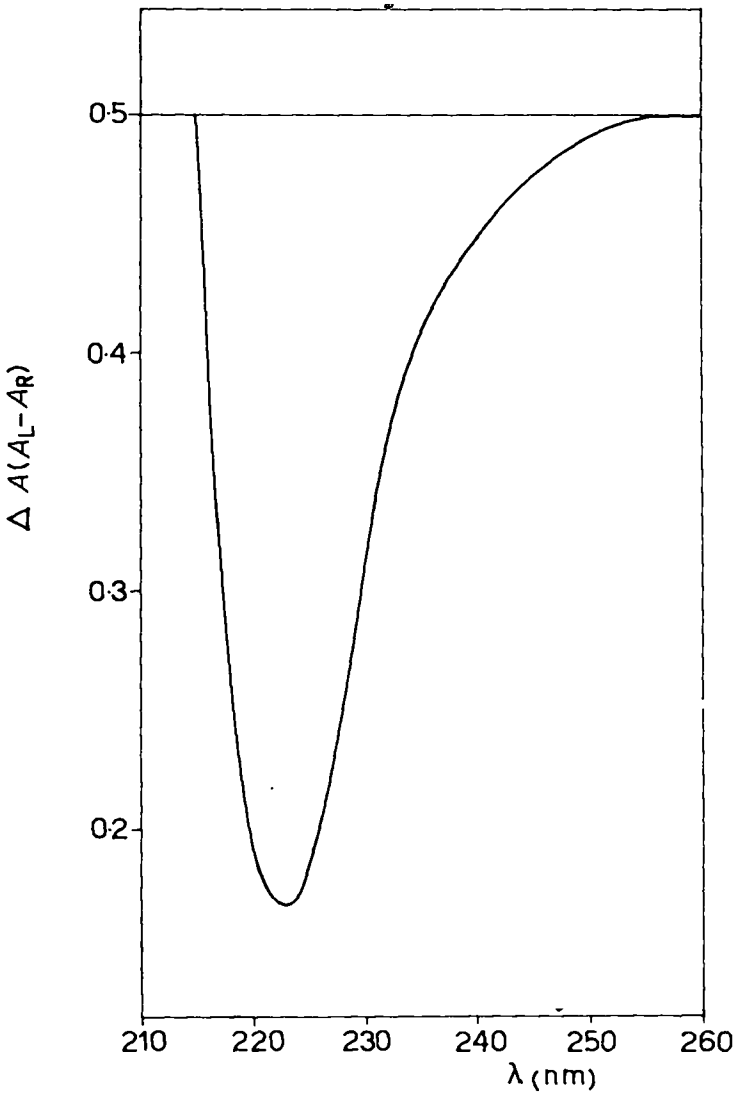
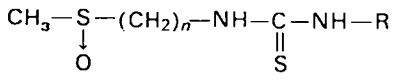
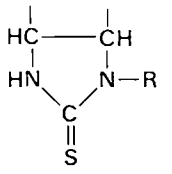


FIGURE 9. C.d. spectra of the reaction product of methyl isocyanate with L-valine at pH 8·5; 1-cm cell; sensitivity 0·2; amino acid concentration 1·16 mg/ml.



(61)



(62)

properties of ureines[5,84,85] and thioureines[86–92] derived from optically active isocyanates and isothiocyanates, respectively. The most interesting conclusion concerns the possibility of determining the composition of mixtures of ethanol with water and methanol[92].

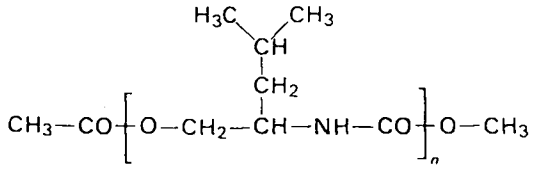
Recently Scott investigated in detail the reaction of 2-amino sugars with isothiocyanates[93]. Among the various products thioureines and imidazolidine-2-thiones (**62**) were identified. Unfortunately, the o.r.d.–c.d. properties of these compounds were not examined.

B. With Alcohols

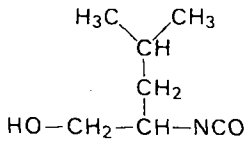
The literature relating to o.r.d.–c.d. studies on molecules obtained by reacting cyanates and related groups with alcohols is disappointingly meagre.

The 1-substituted oligoethyleneurethanes (**63**) from dimer to heptamer were synthesized step-by-step using the optically active α-hydroxymethyl-γ-methylbutyl isocyanate (**64**) as the starting material and their o.r.d. properties investigated in the 300–600 nm region[94,95]. It was found that the o.r.d. patterns are dependent upon the number of repeating units, nature of solvent and temperature. All oligomers showed simple dispersion in solvents such as alcohols, dioxane and chloroform. On the other hand, the hexamer and heptamer showed anomalous dispersion in aromatic solvents such as benzene and toluene, while lower homologues up to the pentamer showed simple dispersion in these solvents. The anomalous dispersions of oligourethanes, which could be destroyed by increasing temperature, were interpreted as a helix formation due to the intramolecular hydrogen bonding, the strength of which is notably weaker compared with that in amide linkages of polypeptides. A detailed c.d. study of these oligourethanes in the region of absorption of the carbamate chromophore (i.e., below 250 nm) would be of particular interest.

Other works worthy of mention in this area are those of Terent'ev[5] and Potapov[96]. The o.r.d. curves were obtained of the optically active urethanes (**65** and **66**) containing aromatic chromophores. (−)-α-Phenylethyl isocyanate (**1**) and (+)-α-benzylethyl isocyanate (**2**) were employed in these

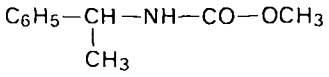


(63) $n = 2–7$

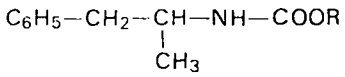


(64)

studies. Above 250 nm a weak and structured Cotton effect was observed for compound **66** associated with the long-wavelength absorption band of the substituted benzene chromophore. The sign of this effect is not dependent on the solvent polarity. Near 210 nm a second Cotton effect was observed which has a positive sign in polar solvents, but a negative sign in *i*-octane, benzene or CCl_4. The conformations of **66** which cause the above o.r.d. changes were discussed.

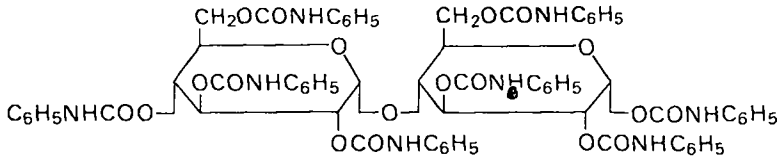


(65)



(66)

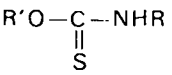
An impressive array of carbamoyl polysaccharides (see for example the maltose derivative **67**) were studied in recent years by o.r.d. and c.d.[97,98]. The reaction of the polysaccharides and the optically inactive phenyl isocyanate was found to be simple and fully substituted products were easily obtained. In addition, in special cases it was possible to substitute selectively the —OH groups. For the β-glycans a small negative c.d. in the region of 238–240 nm was found; in the case of α-glycosides a strong negative c.d. with a maximum at 240–242 nm and a strong positive c.d. with a maximum at 223–225 nm were observed. It was shown[97] that the striking difference of the chirospectroscopic properties between the α- and the β-glycans is not related to the contributions of single independent chromophores influenced by their individual different steric arrangements and their spatial relation to the glycosidic bond. The exciton theory of Moffitt[74], which is suitable for explaining the o.r.d. and c.d. spectra of helical polymers, was applied to carbamoyl α- and β-glycans. This method allowed



(67)

Bittiger and Keilich[97] to propose a structure with helical parts for the α-glycans while a nearly planar arrangement was suggested for the β-glycans.

Some interesting studies in this field, which in our opinion should be carried out in the near future, include the investigation of the chirospectroscopic properties of the reaction products of cyanates and isocyanates with side-chain—OH groups of amino acid residues. In this context it should be mentioned that isocyanates were used to protect the phenolic side chain of tyrosyl residues[99]. Cyanate[59] and isocyanates[100] were also employed to modify the hydroxyl group of the reactive serine residues of various proteases.



(68)

The absence of reports dealing with the o.r.d. and c.d. of thionocarbamates (**68**) obtained by reacting isothiocyanates with alcohols is probably related to the very low rate of this reaction, as mentioned above.

C. With Thioalcohols (Thiols)

The dithiocarbamate (dithiourethane) chromophore present in compounds **69**, which are obtained by reacting the —SH groups of cysteinyl derivatives with isothiocyanates, was investigated by u.v. absorption and c.d. techniques[63,66,101–105]. In water a weak band at about 325 nm is apparent, along with bands of greater complexity near 270 nm and 250 nm[66,101]. When the group is in a dissymmetric environment these transitions have optical activity[63,66,102–105]. Since the long-wavelength absorption, which probably involves promotion of a non-bonding electron of the sulphur atom within the  group to the antibonding orbital π^* exhibits low extinction, being associated with an electrically-forbidden transition, and since it occurs in a spectral range which is transparent in a variety of natural compounds, the c.d. curves of *S*-methylthiocarbamoylcysteinyl derivatives (**69**; R = methyl) were examined in detail only above 300 nm. The sign of the 320 nm band is strictly solvent dependent, as is shown in other thiocarbonyl compounds[68]; therefore it is not automatically transferable from water to organic or aqueous-organic solutions. Since this Cotton effect presents a high dissymmetry factor ($\Delta\varepsilon/\varepsilon$), its sign in

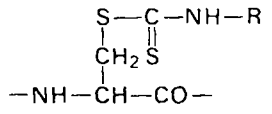
water can be used to determine the optical configuration of the α-carbon atom of cysteine in peptides, being positive for L-cysteinyl derivatives and negative for D-derivatives. In addition, under the experimental conditions employed, no S → N shift of the $S{=}\overset{|}{C}{-}NH{-}CH_3$ group was observed.

Arylalkyl isothiocyanates were also used in these investigations, but no definite advantages over methyl isothiocyanate were observed[105].

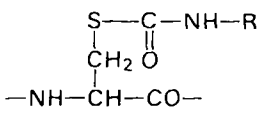
A fascinating aspect of stereospecificity–bioluminescence relationships illustrates the major role of cysteine configuration in the field of natural products[106,107]. In this and similar senses, D-cysteine may be present in other natural compounds and involved in special roles[108–111]. Cysteines have frequently been isolated from various sources, but the reports seldom specify their optical configurations. The above described method can rapidly supply this information. Moreover, the extension of the study of the chirospectroscopic properties of the dithiocarbamate chromophore to the determination of the configuration of optically active mercaptans and —SH acids appears to be particularly attractive[63,112,113].

The analytical application of this method in the quantitative estimation of free thiol groups of cysteine derivatives and in the determination of the number of cysteine units in proteins was also reported[102]. Since the reaction between the —SH group and methyl isothiocyanate at slightly acidic pH, at room temperature and for a few hours is quantitative, stoichiometric and selective, evaluations of the extent of chemical and enantiomeric purities in the synthesis of cysteine-containing peptides by means of the *S*-methylthiocarbamoyl derivative appears to be easily feasible.

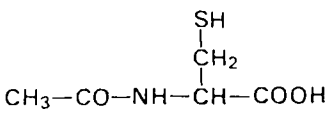
Recently cyanate and alkyl isocyanates have been employed to protect cysteine sulphur in peptide synthesis[114–116] and to react with the free —SH group of cysteine residues of sulphydryl hormones and enzymes[59,117,118]. However, the —S—C(=O)—NH— chromophore (**70**) exhibits the longest wavelength dichroic band at 255–260 nm[102], e.g. in a region of the spectrum where aromatic and disulphide side chains of amino acid residues also show dichroic absorption[11]. On the contrary, the *S*-alkylthiocarbamoyl chromophore (**69**) does not present this drawback. Its stability to acid[67] and the mild conditions for introduction and removal[102] suggest its application as a protective and analytical tool in peptide chemistry. Support for these



(**69**)



(**70**)



(**71**)

conclusions also came from the observation that the concentrations used for the c.d. determinations safely allow one to assume the identity of enantiomeric and optical purities.

The chiroptical properties of the reaction products of the model compound *N*-acetyl-L-cysteine (**71**) with methyl isothiocyanate and methyl isocyanate, respectively, at pH 5 are illustrated in Figure 10.

To our knowledge, the chirospectroscopic properties of the dithiocarbamates (**69**) and thiocarbamates (**70**) obtained by reacting thiols with

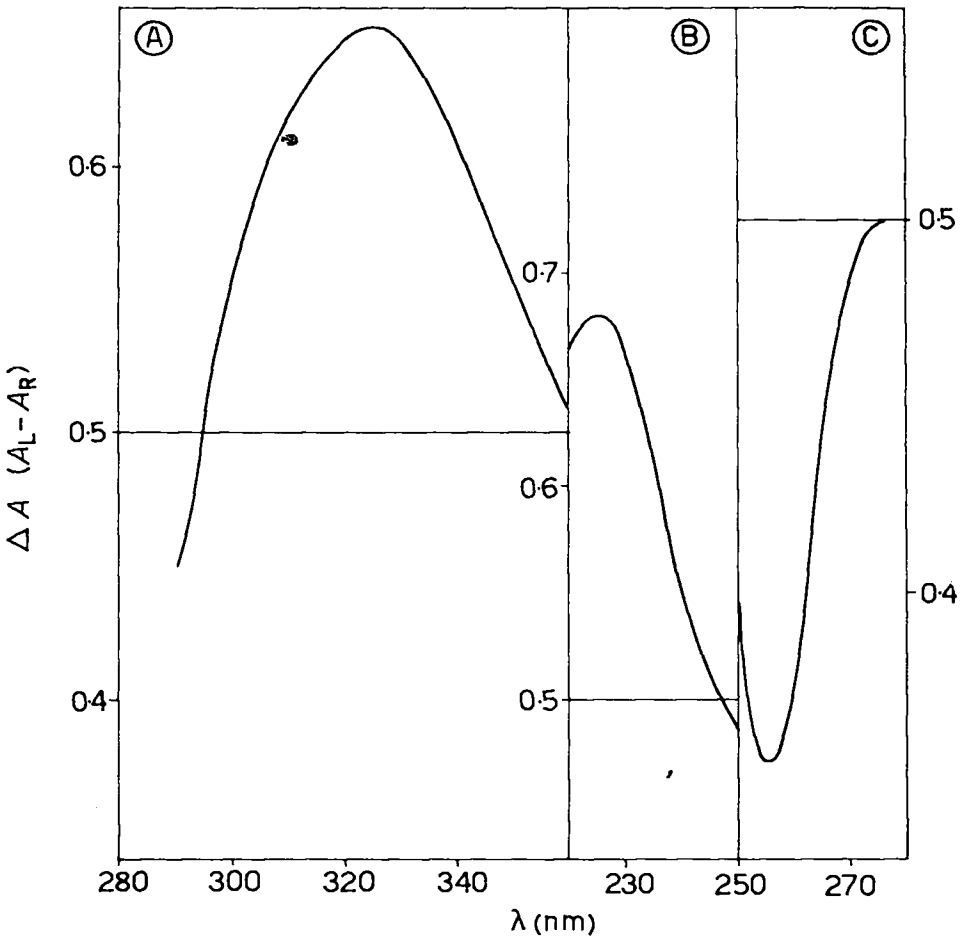


FIGURE 10. C.d. spectra of the reaction products of *N*-acetyl-L-cysteine (**71**) (0·96 mg/ml) with methyl isothiocyanate (A) at pH 5 (1-cm cell; sensitivity 0·02), and with methyl isocyanate (B and C) at pH 5 (B = 0·05-cm cell, sensitivity 0·02; C = 1-cm cell, sensitivity 0·05).

optically active isothiocyanates and isocyanates, respectively, have not yet appeared in the literature.

Note added in proof: Since the completion of this article, three papers discussing the o.r.d.–c.d. properties of steroidal thiocyanates[119], and of carbamoyl derivatives of poly-L-lysine[120] and alkaline peptidase[121] have appeared in the literature.

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 5

Detection and determination of cyanates, isocyanates, isothiocyanates, and thiocyanates

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The four functional groups will be treated separately, but an effort will be made to stress both the similarities and differences in their detection and determination, as well as the methods of their analysis in the presence of each other.

I. CYANATES

A. Introduction and Chemical Methods

The organic cyanates have become available in the last decade[1,2]. Alkyl cyanates are less stable than aryl cyanates and are rapidly isomerized to isocyanates. To date no chemical methods of analysis have been reported for the cyanates. They undergo readily a multitude of reactions, especially nucleophilic additions[1,2] and it seems reasonable to assume that some of these latter reactions may be developed in the future into chemical methods of analysis and characterization. Hence, their reaction with water in alkaline solution[3,4], or with hydrogen sulphide[5,6,7,4], to give high yields of crystalline urethanes or thiourethanes respectively, could be utilized in their characterization. At present, however, spectroscopic methods are the main tools in their analysis.

$$ROC{\equiv}N + H_2O \longrightarrow H_2NCO_2R$$

$$ROC{\equiv}N + H_2S \longrightarrow H_2NCSOR$$

B. Gas Chromatography

Primary alkyl cyanates (alkyl: C_2–C_4) have been separated by gas chromatography from their isomeric isocyanates, using a non-polar Perkin-Elmer 'O-column', operating between 42·5 °C and 80 °C, depending upon the molecular weight of the cyanates[6,8]. The isomeric isocyanates, trimerization products, and other non-volatile products do not appear in these chromatograms. Since isopropyl and *s*-butyl cyanates decompose

on heating, they could not be analysed by gas chromatography[7]. The cyanates show considerably longer retention times than the isomeric isocyanates: at 60 °C on a 2-m 'O-column' and at a flow rate of 120 ml/min the retention time of ethyl isocyanate is 2·8 min and that of ethyl cyanate is 6·8 min[6].

C. Physical Methods

1. Infrared and Raman spectroscopy

Alkyl cyanates[9,10] show a characteristic medium to strong band in the 2280–2240 cm^{-1} region, which is either split into a doublet or is slightly asymmetric in appearance. It has been assigned to the C≡N stretching vibration and the splitting is due to Fermi resonance between the C≡N vibration and the first overtone of the C—O—C asymmetric stretching vibration. This band occurs in the same region as the N=C=O band in isocyanates. Although it is strong, it is much less intense than the corresponding band in isocyanates. The other absorption characteristic of alkyl cyanates[9,10] (and of course missing in isocyanates) occurs in the 1180–1080 cm^{-1} region and has been assigned to the C—O—C asymmetric stretching vibration. This absorption is generally split and very strong. In the far infrared[9] the alkyl cyanates show a band of medium intensity close to 515 cm^{-1}, and another weak band around 600 cm^{-1}.

Aryl cyanates[10] also show the C≡N stretching vibration in the 2280–2240 cm^{-1} region. This strong band is doubly or triply split, but the splitting is not due to Fermi resonance. In the Raman spectrum it occurs at the same frequencies as in the infrared, being likewise doubly or triply split, but of medium intensity. The C—O—C stretching vibration is strong and occurs in the 1235–1160 cm^{-1} region.

The cyanates and isocyanates are most easily distinguished in the infrared by the presence in the former and absence in the latter of the C—O—C vibration in the 1200–1100 cm^{-1} region.

2. Electronic spectroscopy

Only the electronic spectra of aryl cyanates have been reported. Martin[3,1] observed that substituted phenyl cyanates (substituents: *p*-Me, *p*-Cl, *p*-MeO, *o*-MeO, *p*-NO_2, *p*-OCN) exhibited the two typical bands of benzene derivatives: a fine-structured benzenoid band between 256 and 290 nm and an intense K-band around 214–224 nm. For comparison

he presented the absorption curves and tabulated the absorption maxima of phenyl cyanate and isocyanate in cyclohexane (Table 1).

The K-band of the substituted phenyl cyanates is hypsochromically shifted, and is of smaller width at half height, and of lower intensity as

TABLE 1. Ultraviolet absorption maxima of phenyl cyanate and phenyl isocyanate in cyclohexane[3]

Compound	K-Band		Benzenoid band	
	λ (nm)	log ε	λ (nm)	log ε
PhOCN	216	3·21	256, 262, 268	2·58, 2·75, 2·67
PhNCO	227	4·02	264, 271, 278	2·69, 2·75, 2·68

compared with the K-band of substituted phenyl isocyanates. The benzenoid band is also hypsochromically shifted. In the series H < CH_3 < Cl < *o*-MeO < *p*-MeO the vibrational fine structure of the benzenoid band gradually disappears and the band is bathochromically shifted by 27 nm, while that of the K-band is shifted by 10 nm. 4-Biphenylyl cyanate has, in chloroform, a maximum at 251 nm (ε 19,200), while the maximum of the corresponding isocyanate is at 263 nm (ε 22,800)[11,12].

3. Nuclear magnetic resonance spectroscopy

Groving and Holm[9] determined the proton chemical shifts of several alkyl cyanates as pure liquids. Their results can be summarized as follows: α-methylene protons resonate around 4·28–4·54 p.p.m. whereas α-methine protons resonate around 4·67–4·88 p.p.m.; the β-methyl protons of ethyl cyanate have their chemical shift at 1·45 p.p.m., while β-methylene protons of *n*-propyl and *n*-butyl cyanate resonate around 1·80 p.p.m. The chemical shifts of the α-protons of the cyanates were distinctly different from those of the isocyanates, the former resonating 1·17 p.p.m. downfield from the latter. The β-protons of the cyanates similarly resonate 0·25 p.p.m. to lower field from the corresponding isocyanates. Martin[1] tabulated the chemical shifts of the aromatic protons as well as those of the aliphatic protons of the substituents of aryl cyanates. The chemical shifts of the aromatic ring protons appear in the 7·00–7·50 p.p.m. region. In phenyl cyanate the multiplet of the aromatic protons is centred at 7·48 p.p.m., while *p*-phenylene dicyanate has its singlet at 7·31 p.p.m.

In ^{14}N n.m.r. spectroscopy[13,14] ethyl and phenyl cyanate exhibit ^{14}N resonances at 222 p.p.m. and 208 p.p.m. upfield from the nitrate ion, respectively, whereas the corresponding isocyanates resonate at 343 p.p.m. and 330 p.p.m. Consequently ^{14}N n.m.r. spectroscopy allows a distinction to be made between cyanates and isocyanates, and probably also between alkyl and aryl cyanates.

4. Mass spectrometry

Jensen and coworkers[15] examined the mass spectra of alkyl cyanates and isocyanates and recorded their results in tabular form and as plotted spectra. They found that the mass spectra of alkyl cyanates were very similar to those of the isomeric isocyanates, differences occurring mainly in the relative abundance of certain fragments. The alkyl cyanates show a molecular peak which is less abundant than the one in the corresponding isocyanates. In both groups the molecular peak becomes less abundant with rise in molecular weight. As a general rule, fragments containing the functional group (such as M, M-1, M-alkyl) are more abundant in the spectra of alkyl isocyanates, whereas pure hydrocarbon fragments are more abundant in the spectra of cyanates, i.e. the elimination of the functional group occurs to a larger extent in the alkyl cyanates. Alkene eliminations and formation of cyclic structures are dominant features in the mass spectra of alkyl cyanates and isocyanates containing long chains.

In phenyl cyanate[15] the most abundant fragment is $C_6H_5^+$ (*m/e* 77), which is missing in the spectrum of phenyl isocyanate. Both compounds show strong molecular peaks as well as peaks due to the elimination of CO (*m/e* 91).

II. ISOCYANATES

A. Introduction

The organic isocyanates are much more stable than the organic cyanates. Di- and polyisocyanates are important starting monomers in the manufacture of high-performance polymers, such as polyurethanes. It is therefore essential to determine the purity of the commercially available isocyanate monomers and to estimate both the amount of monomer isocyanate still present in the polymers formed, as well as the number of free polymeric NCO groups[16,17].

B. Chemical Methods

1. Introduction

The carbon atom of the isocyanate group is highly electrophilic and readily undergoes a variety of nucleophilic addition reactions. Therefore the two major reactions on which its chemical analysis is based are addition of primary or secondary amines to yield substituted ureas, and in the case of aromatic isocyanates, acid hydrolysis to amines (via the addition of the elements of water) and subsequent analysis of the latter.

$$RN{=}C{=}O + R^1R^2NH \longrightarrow RNHCONR^1R^2$$

$$ArN{=}C{=}O + H_2O \longrightarrow ArNHCO_2H \longrightarrow ArNH_2 + CO_2$$

Addition of alcohols yields urethanes, but as alcohols are less reactive than amines towards the isocyanates, they are also less popular in the quantitative determination of the isocyanates.

$$RN{=}C{=}O + R^1OH \longrightarrow RNHCO_2R^1$$

2. Qualitative analysis

a. *Simple tests.* One qualitative test is based on treatment of an acetic acid solution of the isocyanate with a drop of 20% sulphuric acid and observation of the escaping carbon dioxide[18]. In a second test, a urethane is prepared by dissolving the sample in excess methanol, whereby the urethane usually crystallizes after a short time[18].

b. *Hydroxamic acid test.* This test is based on the following reactions:

$$RN{=}C{=}O + NH_2OH \longrightarrow RNHCONHOH$$

$$3\,RNHCONHOH + FeCl_3 \longrightarrow (RNHCONHO)_3Fe + 3\,HCl$$

The sample is treated with hydroxylamine hydrochloride in 95% ethanol, heating to boiling, and after cooling it is acidified with M hydrochloric acid. Addition of a 10% ferric chloride solution yields a deep magenta colour. The test is positive for aryl isocyanates but negative for aryl isothiocyanates. Carboxylic acids, acid chlorides and acid anhydrides may also give positive tests[19].

c. *Malachite green–n-butylamine reagent.* This colourless reagent,

obtained from malachite green and *n*-butylamine, reacts within 20–30 sec with the isocyanate group to develop a green colour. It has been used in the detection of unreacted monomer isocyanates in urethane-based polymers and it is claimed to detect less than 0·005 mmol isocyanate per g of sample[20].

d. *Reaction with peroxy compounds.* When aryl mono- and diisocyanates and isothiocyanates are treated in dimethylformamide with hydroperoxides, such as cumene or *t*-butyl hydroperoxide, or with peracetic acid, they develop characteristic colours. On making the solution basic with tetrabutylammonium hydroxide, more intense but distinct characteristic colours are obtained, which are specific for each isocyanate. The qualitative method therefore provides a tool for the identification of specific aromatic isocyanates. The method is also applicable quantitatively as discussed in Section II.B.5[21].

3. Determination by amine addition to isocyanate

This is the most widely used method of determination and it is based on the addition of amine to the isocyanate group to give a substituted urea (Section II.B.1). Aliphatic primary and secondary amines add readily and quantitatively to the isocyanate to give a urea which is soluble in the reaction solvent. Excess of a standard amine solution is added to a weighed amount of isocyanate. The reaction is exothermic and complete within a few minutes or up to 1 h. The solution can be titrated with an aqueous acid if methanol is added. The excess amine is then back-titrated with standard acid, using an indicator.

A variety of amines, solvents, reaction conditions, and modes of determination of excess amine have been used. The most popular amines are *n*-butylamine and dimethylamine. Most frequently used solvents include dioxane and chlorobenzene. It should also be pointed out that this method is equally applicable to isothiocyanates. Several representative procedures are summarized in the following.

The method of Siggia and Hanna[22] requires the addition of 20 ml of a 12·5% solution of *n*-butylamine in dioxane to 2 mequiv of isocyanate (or isothiocyanate). In the case of alkyl isocyanates and isothiocyanates the mixture is allowed to stand for 45 min at room temperature for complete reaction. With aromatic isocyanates reaction is complete almost at once and back-titration can be carried out as soon as the amine is added. After addition of water the solution is back-titrated with 0·1 N-sulphuric

acid, using methyl red as an indicator. Siefken[23] determined a large number of aliphatic and aromatic isocyanates in similar fashion using di-*n*-butylamine in chlorobenzene, then adding methanol and back-titrating with hydrochloric acid, with bromophenol blue as indicator. The method of Siefken was adapted by Roth[24] to the micro-scale, using 5–10 mg samples when reaction time was reduced to 5 min. The precision of the method is ±0·5%.

Karten and Ma[25] modified the method of Siggia and Hanna to the semimicro (1 mequiv) and micro scale (0·1 mequiv). They used *n*-butylamine in dioxane as reagent. Reaction time was 15 min for aromatic isocyanates and 45 min for aliphatic isocyanates. The mixture was back-titrated with hydrochloric acid to the methyl red end-point.

Other amines used include piperidine[26,27], aniline[26], diisobutylamine[28,29,30], diethylamine[31,32], and dicyclohexylamine[33]. Other solvents used include tetrahydrofuran[20,34] and dimethylformamide[33,35,36,37]. In two cases the back-titration was done *potentiometrically*[28,31].

Down to *c.* 1 μmol residual isocyanate group per g sample of soluble polyurethanes could be detected *radiochemically*. After dissolution of the sample in dimethylformamide in the presence of a solution of [1-^{14}C]-butylamine in chlorobenzene, the labelled urea was precipitated by adding water, filtered off, washed and dried and dissolved in a suitable solvent for scintillation counting[34].

In one case the isocyanate was determined *gravimetrically*. Aniline was added to the isocyanate and after heating 30 min on a water bath, the excess aniline was steam-distilled and the urea residue dried and weighed[26].

Kubitz[20] determined traces of isocyanate groups in urethane-based polymers by treating the polymer with excess *n*-butylamine in tetrahydrofuran solution, and then determined the excess amine by adding to it a malachite green solution and measuring by absorption spectroscopy the decrease in absorbance of the latter (Section II.B.2.c).

The above variations of the method were applied not only to alkyl and aryl isocyanates (and isothiocyanates) as such, but as already indicated in several instances above, also to the determination of isocyanate groups in rubber bonding agents[28], to unreacted NCO groups in polyurethane resins and coatings[31], and to polymeric isocyanate in the presence of reactive halides[33].

Alkyl and aryl isocyanates were also determined by using excess benzhydrazide (instead of an amine):

$$RN{=}C{=}O + PhCONHNH_2 \longrightarrow RNHCONHNHCOPh$$

The excess unreacted benzhydrazide was back-titrated with a sodium nitrate solution[38].

4. Determination via the derived amine

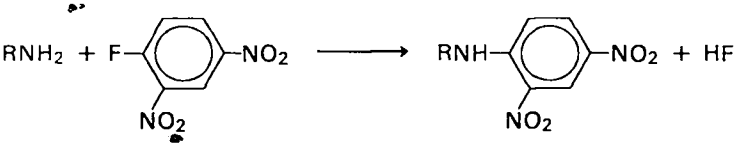
In this method the isocyanate is first hydrolysed in acid solution to the amine and the latter is then determined. Two methods have been used in this determination.

a. *Diazotization and coupling.* The amine is diazotized and then coupled with aromatic amines or with phenols to yield azo dyes. The dyes are determined either colorimetrically or photometrically.

Marcali[39] modified this principle to the micro-determination of toluene diisocyanates in the air. Air was drawn at a specific rate through a bubbler containing acid. The generated amine was then diazotized and coupled with *N*-1-naphthylethylenediamine to give a reddish-blue colour which was measured at 550 nm. As little as 0·01 p.p.m. of toluene-2,4-diisocyanate can be detected by this method in air samples.

The above principle with minor modifications was used in the determination of aromatic diisocyanates in the atmosphere after application of paints containing them[40]. It was applied in similar fashion in the determination of aromatic isocyanates in the air in the absence[41] and in the presence[42] of primary aromatic amines. A chronological list of additional determinations by the same method is given in Reference 43.

b. *Reaction with 2,4-dinitrofluorobenzene.* Amines react with 2,4-dinitrofluorobenzene to yield *N*-alkylamino-2,4-dinitrobenzenes, the absorbance of which is measured.



The method has been applied to the determination of isocyanates in the air. Thus, air containing hexamethylene diisocyanate is passed through a known quantity of concentrated hydrochloric acid–dimethyl sulphoxide (1:9), water is then added, followed by addition of a known quantity of 1-fluoro-2,4-dinitrobenzene and a molar $NaHCO_3$ solution. The solution is heated, sodium hydroxide is added and the mixture is heated again, cooled and extracted with chloroform. The amine is determined by measuring the extinction of the filtered extract at 350 nm. The method is applicable to 1–1000 μg of the above diisocyanate[44]. The method has

been modified in order to be able to determine air samples containing 10^{-2} p.p.m. or less hexamethylene diisocyanate[45]. It has also been used in the determination of methyl isocyanate[46].

5. Determination by reaction with peroxy compounds

This method has already been described in Section II.B.2.d as a tool in the qualitative analysis of aromatic isocyanates and isothiocyanates. In the quantitative determination, a molar excess of peroxy compound is added to a dioxane solution of a weighed sample of isocyanate. Tetrabutylammonium hydroxide is added dropwise until no further colour change occurs. The absorbance of the solution is measured either in the visible region, or with an additional 100-fold dilution at λ_{max} in the ultraviolet region, and compared with the known molar absorptivities of the compounds in question[21].

6. Derivatives

As indicated, isocyanates react with amines to give *N*,*N*′-disubstituted ureas as crystalline derivatives which may be utilized in the characterization of both isocyanates and amines. The isocyanate and the amine are heated in 95% ethanol and the product is generally recrystallized from the same solvent.

The reaction between an isocyanate and an alcohol or phenol yields urethanes as crystalline derivatives, which may also be utilized in the characterization of both isocyanates and alcohols and phenols. The mixture of isocyanate and alcohol or phenol is heated on a water bath at 60–70 °C for 10–15 min. The crude urethane solidifies and is extracted with petroleum ether from which it is also recrystallized.

Siefken[23] lists the melting points of a very large number of substituted ureas (mainly phenylureas) and urethanes (mainly methyl carbamates). Additional urethane derivatives of 1- and 2-naphthol and several *N*-alkyl-*N*′-phenylureas and *N*-aryl-*N*′-phenylureas are also listed in the literature[47].

C. Polarography

The polarographic reduction of phenyl isocyanate[48], α,ω-diisocyanates[49], and aromatic diisocyanates[50] has been reported, but only in one publication has its analytical application been described.

Polarographic reduction was applied to the determination of phenyl

isocyanate, tolylene diisocyanate, and hexamethylene diisocyanate. The polarographic waves were recorded in 0·2 M-tetrabutylammonium iodide and 0·1 M-tetraethylammonium iodide in dioxane–dimethylformamide (3:1), in dimethylformamide, or in acetone, from −1·0 V to −2·2 V. The isocyanates were determined from standard curves with an error of less than 1–2%[51].

D. Gas Chromatography

Ruth[52] has separated aliphatic and aromatic isocyanates and diisocyanates in the presence of reactive organic halides on a column of 10% polyphenyl ether on 40–60 mesh Chromosorb-T at 200°C, using thermal conductivity detection. Methyl isocyanate and carbon tetrachloride were determined on a stainless steel column packed with 15% polyoxy ethylene glycol 4000 on INZ-600 diatomite at 50°C and detected by thermal conductivity. For mixtures containing ≃25% of methyl isocyanate, the absolute error was ≃1% for each component[53]. Traces of 2,4-diisocyanatotoluene in polluted air were determined on a column of 15% Apiezon L and 1% Epikote, using electron capture detection[54]. Optimum conditions have been established for the determination of mixtures of 2,4- and 2,6-diisocyanatotoluenes on a column of dinonyl phthalate on Celite 545 at 110°C. Equations are also given for determining the area ratio of two component peaks when the peaks overlap and the detector response is non-rectilinear[55]. Mono- and polychlorophenyl isocyanates were also separated by gas chromatography[56].

E. Physical Methods

1. Infrared and Raman spectroscopy

The isocyanate group is characterized in the infrared by a very strong asymmetric stretching vibration in the 2290–2240 cm^{-1} region ($\varepsilon \sim 1300$–2000)[57], which can easily be differentiated from that of the N=C=S, SC≡N, N=N=N, and N=C=N groups[58]. Bellamy has tabulated this band for numerous alkyl and aryl isocyanates, as well as the corresponding band in the other aforementioned groups[58]. The band is usually a singlet but occasionally shows signs of broadening, apparently as a result of a Fermi resonance effect[59].

The above band occurs very closely to the nitrile stretching vibration, but its intensity is about a hundred times greater. The band is insensitive

to the nature of the substituent it carries since both alkyl and aryl isocyanates display the band in the same region[58]. In the Raman spectrum the band is relatively weak[60,61].

The symmetric stretching vibration occurs in the 1450–1420 cm^{-1} region, being very weak in the infrared and strong in the Raman spectrum[60,61,62,63].

Perfluoroalkyl isocyanates show the asymmetric stretching frequency around 2295 cm^{-1} and the symmetric frequency around 1465 cm^{-1} [64]. The infrared and Raman spectra of *trans*-vinylene diisocyanate have also been discussed[61]. The characteristic band near 2250 cm^{-1} has been used by several workers in the quantitative determination of NCO groups in polyurethanes[65]. For the determination of the isomeric ratio in a mixture of 2,4- and 2,6-diisocyanatotoluenes the bands at 12·35 μm and 12·8 μm have been used[66]. Grasselli's atlas[67] lists with references, major infrared bands for ten alkyl and aryl isocyanates. Yukawa[68] lists the asymmetric stretching vibration of 32 isocyanates.

The near-infrared spectra of 33 aliphatic and aromatic isocyanates have been recorded[69]. The NCO group has the characteristic first overtone of its stretching vibration near 2·64 μm (molar absorptivity ~1–2). The band sometimes occurs as a doublet. In addition, the aromatic isocyanates show a characteristic band in the 1·65–1·68 μm region (first overtone of aromatic methine), and another one, mostly as a doublet, near 2·14 μm (aromatic combination band). The NCO band at 2·64 μm can be used to obtain quantitative data from mixtures containing isocyanates.

In the far infrared and in the Raman spectrum the isocyanates have two medium-to-weak bands near 595 cm^{-1} and 615 cm^{-1} (out-of-plane skeletal bending vibrations)[61,62].

2. Electronic spectroscopy and fluorescence

The absorption spectrum of ethyl isocyanate in the gaseous state has been recorded: it possesses a broad transition at ~210 nm ($\varepsilon \sim 60$) and end absorption: no fine structure is exhibited by this band. Methyl isocyanate has a more or less similar spectrum[70]. It has also been reported that the NCO group does not absorb in the ultraviolet even if attached to a vinyl group[71]. However, the ultraviolet spectrum of *trans*-vinylene diisocyanate in isooctane solution shows a maximum at 225 nm (ε 19,770)[61].

A detailed comparison between the electronic spectra of aromatic isocyanates and cyanates has already been made in Section I.C.2. The ultraviolet spectra of several aryl isocyanates are collected in Table 2[67]. All these compounds show an intense K-band around 230 nm (ε 10,000–

TABLE 2. Ultraviolet spectra of aryl isocyanates, ArNCO[67]

Ar	Solvent	λ_{max} (nm)	ε
Ph	Hexane	226, 263, 277	10,965, 457, 468,
2-ClC_6H_4	Methanol	235, 268, 276, 284	12,200, 672, 715, 554
3-ClC_6H_4	Methanol	238, 278, 286	16,200, 1060, 846
4-ClC_6H_4	Hexane	235, 273, 287	16,596, 661, 437
2-$NO_2C_6H_4$	Hexane	222, 259, 316	16,982, 4366, 2291
3-$NO_2C_6H_4$	Hexane	222, 253, 300, 335	23,442, 6918, 479, 166
4-$NO_2C_6H_4$	Hexane	215, 276, 324	10,233, 13,804, 550
2-MeC_6H_4	Hexane	228, 273, 280	10,233, 631, 562
3-MeC_6H_4	Hexane	229, 273, 281	9550, 550, 490
4-MeC_6H_4	Hexane	230, 274, 283	13,183, 776, 759
1-Naphthyl	Cyclohexane	318, 290, 226	

20,000), and a fine-structured benzenoid band with two or three peaks in the 270–300 nm region (ε 500–1000). The ultraviolet band of *p*-chlorophenyl isocyanate at λ_{max} 234 nm (ε 16,300) has been utilized in the determination of the disappearance of the compound during its reaction with methanol in *n*-heptane[72].

The emission spectrum of ethyl isocyanate, which is due to NCO free radicals has been recorded[73].

3. Nuclear magnetic resonance spectroscopy

It has been indicated in Section I.C.3 that α- and β-protons of alkyl isocyanates resonate 1·17 p.p.m. and 0·25 p.p.m., respectively, upfield from the corresponding protons in alkyl cyanates. This places the chemical shifts of α-methylene protons of alkyl isocyanates around 3·2 p.p.m., and those of α-methine protons around 3·6 p.p.m.; the β-methyl protons and the β-methylene protons will then resonate around 1·20 p.p.m. and 1·55 p.p.m., respectively[9].

The α-protons in cyclohexyl isocyanate and in *cis*- and *trans*-(4-*t*-butyl)cyclohexyl isocyanates resonate around 3·4 p.p.m.[74]. In a series of α-alkoxyethyl isocyanates the α-methine and β-methyl protons have been found to resonate in the 4·6–5·0 p.p.m. region and 1·2–1·45 p.p.m. region, respectively[75]. The methyl proton resonance in a series of α,α-dimethylbenzyl isocyanates occurs in the 1·5–1·7 p.p.m. region[76]. Grasselli's atlas[67] records the proton chemical shifts of several aryl isocyanates. Hence, phenyl isocyanate has its proton chemical shift centred at 7·1 p.p.m.

The c.m.r. chemical shifts (in $CDCl_3$) of the NCO group occur in methyl,

ethyl, and cyclohexyl isocyanates at 121·4, 122·5, and 123·6 p.p.m. downfield from tetramethylsilane, respectively, whilst that of phenyl isocyanate appears at 125·2 p.p.m.[77]. The c.m.r. chemical shift of NCO in trichloroacetyl isocyanate occurs at 130·2 p.p.m.[78]. The proton noise-decoupled c.m.r. spectrum of phenyl isocyanate has been recorded (see however Reference 77)[79]. The chemical shift of the methyl carbon in methyl isocyanate resonates 99·2 p.p.m. upfield from benzene (as neat liquid)[80].

The ^{14}N chemical shifts of methyl, ethyl, *n*-propyl, and phenyl isocyanates (as neat liquids) occur at 361, 343, 346, and 330 p.p.m. upfield from the nitrate ion[13,14]. The ^{14}N chemical shifts of several trialkylsilyl and trialkylgermyl isocyanates have also been tabulated[13]. It has already been indicated in Section I.C.3 that this method can distinguish between isocyanates and cyanates.

4. Mass spectrometry

In Section I.C.4 a detailed comparison between the mass spectra of alkyl and aryl cyanates and isocyanates has been made, and many features of the mass spectral behaviour of the latter are described there. In addition[81], it has been shown that in the mass spectra of *n*-alkyl isocyanates the intensity of the molecular ion attains a minimum when the alkyl chain-length is most favourable for the formation of the rearrangement ion $C_5H_9NO^+$. Another important ion in these spectra is CH_2NCO^+. Finally, it can be said that the mass spectra of straight-chain isocyanates and cyanates become more and more alike with increasing chain-length.

In aryl isocyanates the M, M-28, and M-55 peaks are strong. Other strong peaks in these mass spectra depend more on the structures of individual compounds[15,81]. The most abundant peaks of 2-chlorophenyl isocyanate are at *m/e* 155 (relative intensity 33), 153 (100), 125 (41), 90 (34), 63 (35), 62 (19), 38 (19), 37 (20)[67].

III. ISOTHIOCYANATES

A. Introduction

Isothiocyanates occur in higher plants in free form or as thioglycosides from which they are set free by enzymic hydrolysis or by chemical conversion[82]. The low-boiling isothiocyanates are isolated by steam-distillation as essential oils. They are also referred to as mustard oils, since many occur in mustard plants. Allyl isothiocyanate is the principal constituent (*c.* 94 %) of the volatile oil obtained from black mustard seeds.

The mustard oils are widely used in flavouring of all kinds of food products and as active ingredients in mustard plasters and other medicinal preparations. Therefore their identification and determination in combined form and as free esters in plant seeds and in the above-mentioned products is indispensable.

B. Chemical Methods

1. Introduction

Although the isothiocyanates are, in general, considerably less reactive than the corresponding isocyanates, with whom they are isoelectronic, their methods of analysis are, in the main, also based on nucleophilic addition reactions. In the case of the isothiocyanates, however, ammonia addition plays a more prominent role than amine addition. Addition of ammonia yields a monosubstituted thiourea. Fission of the isothiocyanate group is also used as an analytical tool but to a lesser extent.

$$RN{=}C{=}S + NH_3 \longrightarrow RNHCSNH_2$$

The literature abounds with references on the analysis of isothiocyanates. The majority of these discusses the detection and determination of isothiocyanates in plant seeds and in mustard oils extracted from them, and most of them deal with allyl isothiocyanate.

2. Qualitative analysis

The isothiocyanates or mustard oils can be detected by colour reactions and identified in the form of their derivatives.

a. *Reaction with sodium azide.* On adding dimethylformamide to a mixture of an isothiocyanate and sodium azide, an instantaneous evolution of nitrogen takes place and the solution turns blue or green. Thiocyanates and isocyanates give negative tests[83].

b. *Reaction with zinc acetate.* This is a very sensitive test which can detect 0·1 to 0·5 mg mustard oil. A mixture of less than 1 mg sample, 4 ml 0·033 M-secondary sodium phosphate, and 0·4 ml saturated zinc acetate solution is heated in a sealed tube on a water bath for 1 h. After cooling, 2 ml of a solution of 6·5 mg *N.N*-dimethyl-*p*-phenylenediamine sulphate in 100 ml 4 N-sulphuric acid is added, followed by 0·4 ml of a 10% solution of ferric ammonium sulphate in N-sulphuric acid: the mixture turns blue[84].

c. *Reaction with peroxy compounds.* This test, which has been described in Section II.B.2.d is also applicable to isothiocyanates.

d. *Test for isothiocyanates and thiocyanates in presence of each other.* This test is common to both aliphatic and aromatic isothiocyanates and thiocyanates and is based on the following reactions:

$$RNCS + 3\,KOH \longrightarrow RNH_2 + KSH + K_2CO_3$$

$$2\,RSCN + 2\,KOH \longrightarrow KOCN + KCN + H_2O + RSSR$$

A mixture of the sample and M-potassium hydroxide in 80% ethanol is heated and then centrifuged. To the lower ethanolic layer a sodium hydroxide solution of picric acid is added. A blood-red colour which becomes deep yellow or orange on heating indicates the presence of a primary amine which originates from an isothiocyanate. If a deep red colour is observed only after heating, this indicates the presence of hydrocyanic acid which originates from a thiocyanate. If both esters are present in the sample, a blood-red colour is obtained at once, and it becomes darker on heating. If no colour is produced, the sample does not contain any isothiocyanates or thiocyanates[85].

e. *Test for allyl isothiocyanate.* An ethanolic solution of the sample is treated with phloroglucinol and concentrated hydrochloric acid: a pale red coloration is obtained which intensifies on heating[86].

f. *Spot test for phenyl isothiocyanate.* To detect less than 50 μg phenyl isothiocyanate the sample is heated with a 2% lead nitrate solution and concentrated aqueous ammonia on a water bath for 1 to 3 min: black lead sulphide is formed. To detect less than 0·5 μg of the above compound, it is heated with a sodium hydroxide solution in glycerol at 180 °C, and its vapour is exposed to a filter paper impregnated with a 2% aqueous solution of sodium 1,2-naphthoquinone-4-sulphonate: a red-violet colour is produced in 1 to 2 min[87].

g. *Reaction with ammonia.* Reaction of an isothiocyanate with strong aqueous ammonia in ethanol yields crystalline thioureas which can be purified and then identified by melting point. Allylthiourea from allyl isothiocyanate gives rhombic prisms, melting point 74 °C. The thioureas obtained can also be separated and identified by paper chromatography[88].

3. Determination by ammonia addition to isothiocyanate

Addition of alcoholic ammonium hydroxide to isothiocyanates to yield monosubstituted ureas is a reaction which goes to completion.

For this reason, and since thioureas have served most effectively in the purification and identification of mustard oils, the determination of isothiocyanates via their thiourea derivatives has practical advantages. The thioureas formed in solution can be analysed by numerous methods as described below. Because of the very large number of references in the literature, only a minor but representative fraction of the references can be cited here.

Conversion to the thiourea occurs generally by heating the mustard oil in ethanolic or aqueous ammonia for several minutes or by letting the mixture stand at room temperature for *c.* 24 h.

a. *Spectrophotometric determination.* Thioureas absorb in the 230–260 nm region of the ultraviolet. In this method of determination thioglucosides in plant seeds are enzymically hydrolysed and the generated mustard oils are extracted with an organic solvent. They are converted by aqueous or ethanolic ammonia to thioureas, which are dissolved in organic solvents and determined spectrophotometrically[89].

b. *Reaction with silver ions.* This popular method of determination is based on the reaction of thioureas with silver ions to precipitate silver sulphide:

$$RNHCSNH_2 + 2\,AgNO_3 + 2\,NH_3 \longrightarrow RNHCN + Ag_2S + 2\,NH_4NO_3$$

Determination is accomplished either gravimetrically, by weighing the filtered and dried silver sulphide, or argentimetrically, i.e. by adding a known excess of a silver nitrate solution, filtering off the precipitated silver sulphide, and back-titrating the excess silver ions in the filtrate with thiocyanate ions, using ferric ions as indicator (Volhard method). In the majority of cases reported in the literature the volumetric method has been the method of choice.

Fürst and Poethke[90] determined allyl isothiocyanate by heating a mixture of 5 ml of a 2% solution of the isothiocyanate, 5 ml 25% aqueous ammonia, and 5 ml ethanol for 10 min, then more strongly for another 10 min. Ten millilitres of a 10% ammonium nitrate solution was added, the mixture was cooled, and 50 ml of a 0·1 N-silver nitrate solution were added and the mixture was diluted to 100 ml with water, and filtered. To a 50 ml aliquot of the filtrate 10 ml 25% nitric acid were added, and the mixture was titrated with 0·1 M-ammonium thiocyanate, using ferric ammonium sulphate as indicator. To determine the allyl isothiocyanate in mustard seed, a 5-g sample of seeds was macerated with 100 ml water for 2 h, 50 ml ethanol was added, the mixture was distilled, and 50 ml of

distillate was collected. The distillate was heated with 10 ml 25% aqueous ammonia, 10 ml 10% ammonium nitrate solution and 20 ml 0·1 N-silver nitrate solution were added, and the determination was completed as described above.

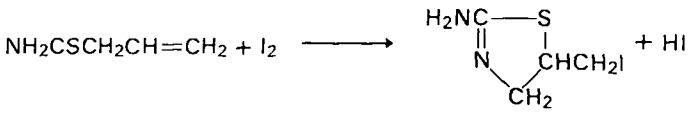
Fürst[91] has improved the above method by applying electroanalytical detection. He used it to determine allyl isothiocyanate in mustard seed, and in this case it was not necessary to isolate the isothiocyanate by distillation. The isothiocyanate was converted to allylthiourea in the usual manner, and 2 to 10 mg quantities of the latter were determined by titration in aqueous ammonia–ammonium nitrate buffer solution with 0·01 N-silver nitrate with amperometric detection of the end-point, using a dropping-mercury electrode at −0·6 V versus the NCE.

Additional examples are listed in Reference 92.

c. *Oxidation.* Various oxidizing agents were used in this method. Böhme[93] oxidized the thiourea with hydrogen peroxide and excess standard alkali, and after 2 h at room temperature added excess hydrochloric acid and back-titrated with potassium hydroxide to methyl orange. The method is based on the following reaction:

$$RNHCSNH_2 + 2\,HO^- + 4\,H_2O_2 \longrightarrow RNHCONH_2 + 5\,H_2O + SO_4^{2-}$$

Oxidation of allylthiourea (from allyl isothiocyanate) by iodine and back-titration with thiosulphate ions is the standard method used by the Swiss[94] and German[95] pharmacopoeia. The method is apparently based on the following reaction[96]:



Fürst[91] determined 0·2 to 2 mg quantities of allylthiourea (from allyl isothiocyanate) polarographically by anodic oxidation, measuring at −0·38 V versus the NCE in 0·1 N-sodium hydroxide.

d. *Reaction with o-hydroxymercuribenzoic acid.* Recently Wronski[97] determined thioureas originating from isothiocyanates which contain labile sulphur, by heating them with excess of alkaline *o*-hydroxymercuribenzoic acid. Excess reagent was removed by adding a dithiofluorescein solution in excess, and determining the excess of the latter spectrophotometrically at 578 nm. The absolute relative error and the limit of determination are ≃0·0015 and ≃0·002 microequivalents of sulphur, respectively.

e. *The iodine–azide reaction.* Exceedingly small quantities of sulphur compounds induce this reaction:

$$I_2 + 2\,N_3^- \longrightarrow 2\,I^- + 3\,N_2$$

The reaction is faster with thioureas than with isothiocyanates. Kurzawa and Krzymien[98] obtained best results by adding 10 ml of 0·02 M-iodine to a solution containing 2 to 30 μg of thiourea and sufficient sodium azide to give a concentration of 2% in the final solution, which was adjusted to pH 6 with 0·1 M-hydrochloric acid. After 30 sec the unconsumed iodine was titrated with 0·02 N-sodium arsenite. Under the above conditions the induction coefficient, i.e. mole ratio of consumed iodine to thiourea, was ≃ 80, and from this value the amount of thiourea could be determined. The method was utilized in the determination of isothiocyanates (via their thiourea derivatives) in plant seeds[99]. It was also adapted to the microdetermination of 3-butenyl isothiocyanate in rape seed[100], by its conversion with methylamine to *N*-methyl-*N'*-(3-butenyl)thiourea, which is fourteen-times more effective than the isothiocyanate, as the inducer of the iodine–azide reaction. The concentration range for the determination in the last example was 0·2 to 1·0 μg of isothiocyanate per ml of test solution, and the error was less than ±5%.

4. Determination by amine addition to isothiocyanate

This method which is based on the addition of excess primary or secondary amine to an isothiocyanate to yield a di- or trisubstituted thiourea and back-titration of excess added amine, proceeds in the same manner as with isocyanates. It has been described in detail in Section II.B.3. Thus, Siggia and Hanna[22] used *n*-butylamine in dioxane in the determination of methyl and ethyl isothiocyanates, and back-titrated the excess amine with aqueous sulphuric acid, using methyl red as indicator. Roth[24] used di-*n*-butylamine in chlorobenzene and back-titrated with hydrochloric acid, using bromophenol blue as indicator. Karten and Ma[25] applied the method on a micro and semimicro scale, using *n*-butylamine, and letting the reaction proceed for 15 min in the case of aromatic isothiocyanates and 45 min in the case of aliphatic isothiocyanates. Venkataraghavan and Rao[27] used piperidine in dioxane. Vinson[36] used *n*-butylamine in dimethylformamide in the determination of aromatic and aliphatic isothiocyanates.

Wronski[101] described procedures for the determination isothiocyanates under special circumstances. In one of these procedures 0·05–0·5 mmol of

a sample is dissolved in 10 ml ethanol, 1 ml 40% dimethylamine is added, and in the case of aromatic and allyl isothiocyanates, the mixture is allowed to stand 1 min, whereas in the case of aliphatic isothiocyanates, it is heated on a steam bath for 1 min. The mixture is cooled and 20 ml ethanol, 2 ml 60% perchloric acid and 0·5 ml of a saturated solution of *p*-dimethylaminobenzylidenerhodanine solution in 95% ethanol are added. The mixture is then titrated with 0·05 N-*o*-hydroxymercuribenzoate until the colour changes from yellow to red. This procedure can also be used to determine aromatic isothiocyanates in the presence of thiocyanates.

In the case of a mixture of aliphatic and aromatic isothiocyanates, the sum of both isothiocyanates is determined according to the above procedure. A second sample is then dissolved in 10 ml ethanol, 1 ml dimethylamine is added, and the mixture is heated for 1 min on a steam bath. After cooling, 20 ml ethanol and 5 ml M-NaOH are added and the solution is titrated with 0·05 N-*o*-hydroxymercuribenzoate, using dithiofluorescein as indicator, until the blue colour disappears: this yields the content of aromatic isothiocyanates.

5. Determination by release of thiocyanate ion

This method is based on the release of thiocyanate ion by alkali. *p*-Hydroxybenzyl isothiocyanate, obtained by enzymic hydrolysis of thioglucosides of plant seeds, is treated with M-sodium hydroxide. Trichloroacetic acid is added to the solution of the released thiocyanate ions and the precipitate formed is filtered. Ferric nitrate is added to the filtrate and the red colour which develops is estimated spectrophotometrically versus a control at 460 nm[102].

6. Derivatives

The principal method of characterization of isothiocyanates consists in their conversion to substituted thioureas by reaction with ammonia or amines. The isothiocyanate and the amine are mixed in ethanol and the mixture is refluxed. The derivative usually separates as an oil which solidifies when carefully rubbed. It is dried rapidly between filter papers and extracted with a minimum volume of petroleum ether. It is generally recrystallized from ethanol–ether. Melting points of derivatives with aniline and benzylamine have been recorded[103a]. The thioureas can also be identified by paper chromatography[88].

Another method of derivatizing isothiocyanates is the reaction with phenylhydrazine or *p*-carboxyphenylhydrazine to yield substituted arylthiosemicarbazides[103b]:

$$RN{=}C{=}S + ArNHNH_2 \longrightarrow RNHCSNHNHAr$$

C. Electroanalytical Methods

Tur'yan[104] devised an electroanalytical method for the determination of organic compounds. The method is based on the reduction of the molecule at a mercury cathode, with a simultaneous setting free of iodine on a platinum anode, and the volumetric determination of the iodine by thiosulphate titration at the end of the electrolysis, the end-point being indicated by the fall in current. The method is applicable when the cathode reaction takes place with 100% yield. Among compounds investigated was 2,4-dinitroisothiocyanatobenzene.

Bipotentiometric titration was successfully applied to the oxidation of various non-aromatic sulphur compounds, including isothiocyanates. In this method various types of compound can be identified because different compounds give different types of titration curves. The oxidants used were lead(IV) acetate and cobalt(III) acetate, and the potential was measured against the volume of oxidant solution added. The method was not applicable to non-aromatic thiocyanates[105].

The polarographic reduction of isothiocyanates was investigated by several workers, and in a few cases the results seem suitable for use in the quantitative determination. The polarographic reduction of phenyl isothiocyanate at a dropping mercury cathode was investigated[106]. Half-wave potentials of the polarographic reduction of 45 aromatic isothiocyanates were reported and were found to be little dependent on the structures of the substituents on the aromatic ring, but the wave heights were proportional to the concentrations in the range between $6{\cdot}6 \times 10^{-5}$ and $4{\cdot}10 \times 10^{-5}$ M. and in the range of pH 2·2–8·1[107]. In the case of 1- and 2-naphthyl isothiocyanates, well-developed polarographic waves were observed which were suitable for analytical purposes[108]. *p*-Substituted isothiocyanates were determined by polarographic reduction, using suitable supporting electrolytes and solvents[109]. The half-wave potentials of the polarographic reduction of eighteen *m*-substituted phenyl isothiocyanates were measured[110].

D. Separation Methods

1. Isolation

Isothiocyanates or mustard oils are natural products which occur in plant seeds in the free form or as thioglucosides. Generally the isothiocyanates are set free by enzymic hydrolysis and steam-distilled. If they are

labile or non-volatile they are isolated by extraction with organic solvents. For direct identification they may be directly converted with ammonia into thiourea derivatives which can be purified by recrystallization and chromatographic separation[111,82].

2. Distillation, distribution, and crystallization

The mustard oils isolated from plant material are mixtures containing isothiocyanates. Several methods are available for their separation into individual constituents. Mustard oils were separated by fractional distillation[112], partition chromatography between partially miscible solvents[113], as well as by distribution, followed by column chromatography on alumina[114].

The mustard oil hydrolysate can also be directly converted on reaction with ammonia to thioureas which can be separated and purified either by fractional crystallization[115], or by distribution between partially miscible solvents[116].

3. Gas chromatography

Gas chromatography has been applied very extensively in the analysis of isothiocyanates, therefore only a few examples from the literature can be cited here.

A very detailed investigation of the gas-chromatographic behaviour of 32 saturated and unsaturated, branched and unbranched aliphatic isothiocyanates, aromatic isothiocyanates, ω-methylthio-substituted compounds of the type $MeS(CH_2)_nNCS$, and isothiocyanates containing ester or sulphone groupings, has been conducted, using various stationary phases. The results were presented mainly as retention time–reciprocal temperature diagrams. They indicate that gas chromatography is an efficient method for the separation and identification of isothiocyanates[117]. Several authors have analysed, by gas chromatography, the isothiocyanate constituents of mustard oils[118,119,120].

Recently, 20 alkyl and aryl isothiocyanates and 17 3-substituted rhodamines obtained from them were investigated gas-chromatographically, on a column packed with Diatoport (80–100 mesh) and coated with 10% silicon gum UCW 98. It was found that the retention times of the 3-substituted rhodamines were higher than those of the corresponding precursor isothiocyanates, and that therefore not only mixtures of isothiocyanates could easily be separated from each other, but that the

corresponding compounds of the two groups could be separated from each other as well[121].

Straight-line relationships between $\log R_t$ and the number of carbon atoms were obtained by gas–liquid chromatography of 20 synthetic isothiocyanates on 10% SE-30 and 2·5% DEGS columns, thus affording a method for identification[122].

4. Paper chromatography

Direct analysis of allyl and aryl isothiocyanates was done on Whatman paper No. 4 with 2% acetic acid in carbon tetrachloride as mobile phase, and 30% acetic acid as stationary phase. Detection was accomplished with 0·5% silver nitrate–ammonia (1:1)[114]. Similarly, aryl isothiocyanates in the presence of their methyl thiocarbonates were chromatographed on paper impregnated with dimethylformamide–methanol (1:3), nonane being used as mobile phase, and detection was accomplished with an iodine–sodium azide reagent[123].

Isothiocyanates were also chromatographed as thiourea derivatives. Kjaer and Rubinstein[88] described a successful separation on Whatman paper No. 1 using chloroform saturated with water as the mobile phase, and detection either by the Groth reagent (sodium nitroprusside treated with hydroxylamine hydrochloride and sodium carbonate, then with bromine), or by an iodine–azide–starch reagent. Instead of applying the thioureas to the paper, they can be prepared directly on the paper by applying the isothiocyanates to the paper, and exposing the paper to gaseous ammonia. Thus allyl and aryl isothiocyanates were converted on Whatman paper No. 1 in the presence of ammonia to the thioureas. The paper was then treated with bismuth nitrate to give yellow complexes which were separated by developing with water saturated with butanol or with 40% aqueous ethanol[124].

Instead of thioureas, thiosemicarbazides (from isothiocyanates and 2,4-dinitrophenylhydrazine) were also analysed by paper chromatography, using ethanol–pyridine–water (40:5:55) as the mobile phase[125].

5. Thin-layer chromatography

Alkyl and aryl isothiocyanates in mustard oils were satisfactorily separated as thiourea derivatives on activated silica gel with ethyl acetate–chloroform–water (3:3:4), and detected by spraying with 1% potassium ferricyanide solution–5% ferric chloride solution (1:1)[126].

Several compounds based on *N*,*N*-dimethylaniline and substituted in

the 4-position with a phenylazo moiety and containing an isothiocyanate group were separated on silica gel by development with hexane–benzene (1:1)[127].

E. Physical Methods

1. Infrared and Raman spectroscopy

Bellamy[128] has tabulated the N=C=S asymmetric stretching mode of various alkyl and aryl isothiocyanates. In alkyl isothiocyanates[129] this broad and intense absorption occurs in the region of 2140–2080 cm^{-1}. The absorption of the aryl isothiocyanates[129] is also broad but it is more intense and occurs between 2100 and 2040 cm^{-1}. It has been shown that alkyl and aryl isothiocyanates and thiocyanates can be distinguished by their characteristic vibration frequencies between 2105–2060 cm^{-1} and around 2140 cm^{-1}, respectively; in the latter this band is sharp and of medium intensity, whereas in the former it is broad and strong[130]. In addition, this band in isothiocyanates is sensitive to solvents, whereas the corresponding one in thiocyanates is not; hence an additional means of differentiation between the two groups is available[129].

When the infrared spectra of alkyl and aryl isothiocyanates are recorded at the higher resolving power of a lithium fluoride prism (instead of using a sodium chloride prism) it is found that the above band actually consists of a moderately intense band at 2221–2170 cm^{-1} (30–40% absorption), accompanied by a group of two to three strong bands at 2150–2050 cm^{-1} (50–80% absorption), as well as a very weak band in the 2000 cm^{-1} region (20–40% absorption)[131]. The position and intensity of these bands depend on the polarity of the solvents employed.

Alkyl isothiocyanates exhibit a second, very strong, characteristic band at 1348–1318 cm^{-1} which has been tentatively assigned to the bending vibration of the CH atoms of the $-CH_2N=C=S$ or $\diagdown\!\!\diagup CHN=C=S$ groupings. It is evidently missing in the spectra of methyl, *t*-butyl, phenyl, and α-naphthyl isothiocyanates[131].

Ham and Willis[132] have summarized their extensive investigation[59] of the infrared and Raman spectra of isothiocyanates as follows: (i) aliphatic and aromatic isothiocyanates have a broad and strong infrared band around 2100 cm^{-1} with an integrated intensity of about 15×10^4 l/mol cm and half-width of about 100 cm^{-1}, and a moderately strong and broad Raman band which is split into a doublet; (ii) the symmetric stretching

vibration of aliphatic isothiocyanates is strong in both the Raman and infrared spectra and occurs around 1090 cm^{-1}; (iii) aromatic isothiocyanates have a very strong Raman band, and a very weak infrared band around 1250 cm^{-1}, and another band, strong in the infrared and moderately weak in the Raman spectrum around 930 cm^{-1}.

The far infrared spectra of 22 saturated aliphatic isothiocyanates have been recorded[133a]. Eighteen of these compounds exhibit characteristic frequencies at 641–599 cm^{-1} (medium–strong), 562–510 cm^{-1} (strong), and 470–439 cm^{-1} (strong)[133b]. Modes of vibration have been tentatively assigned to these absorptions[133c]. Far infrared and Raman spectra of several isothiocyanates have also been recorded by other authors[59].

The band around 2100 cm^{-1} has been used in the determination of methyl isothiocyanate occurring as a degradation product in soil. Methyl isothiocyanate was estimated by comparison with the infrared band of standard samples[134].

Grasselli's atlas[135] lists the major infrared bands of eight isothiocyanates and the references whence they have been obtained. Yukawa[68] lists the asymmetric stretching frequencies of 13 isothiocyanates and their references.

2. Electronic spectroscopy and fluorescence

Alkyl isothiocyanates invariably display a maximum of moderate intensity ($\varepsilon \sim 10^3$) in the 244–248 nm region, as is evidenced by the tabulated spectra of 21 alkyl and aralkyl isothiocyanates[131]. Thus ethyl isothiocyanate has its maximum in dioxane at 245 nm ($\log \varepsilon$ 2·86) and allyl isothiocyanate at 246 nm ($\log \varepsilon$ 2·94).

Aryl isothiocyanates exhibit more complex spectra, with strong absorption bands in the 270–350 nm region ($\log \varepsilon \sim 4$). These bands often display fine structure. The spectra of 45 aryl isothiocyanates have been tabulated, and the absorption curves of some of them have been presented[136]. Also the spectra of a series of 4-substituted derivatives of 4′-isothiocyanatoazobenzenes have been tabulated[137].

The ultraviolet spectra of several alkyl and aryl isothiocyanates are collected in Table 3[135].

The emission spectrum of methyl isothiocyanate, which is due to NCS free radicals, has been recorded[73].

3. Nuclear magnetic resonance spectroscopy

Mathias[138] has reported on the p.m.r. chemical shifts of the α-protons of alkyl isothiocyanates in carbon tetrachloride as follows (in p.p.m.):

Me 3·37 $MeCH_2$ 3·64 Me_2CH 3·95

The chemical shifts of the α-protons of allylic isothiocyanates occur at a somewhat lower field (in p.p.m.):

$MeCH{=}CHCH_2$ 4·04 $CH_2{=}CHCH_2$ 4·18 $CH_2{=}CHCMeH$ 4·35

The same author found that a distinction can easily be made between isothiocyanates and thiocyanates since the latter resonate more than 0·5 p.p.m. to higher field.

TABLE 3. Ultraviolet spectra of isothiocyanates, RNCS[135]

R	Solvent	λ_{max} (nm)	ε
Et	Methanol	244	
n-Bu	Cyclohexane	248, 270	1738, 126
Cyclohexyl	Cyclohexane	249, 275	1202, 45
MeCO	Ethanol	333	54
$PhCH_2$	Ethanol	248	1318
Ph	Cyclohexane	268, 279	
4-ClC_6H_4	Cyclohexane	228, 276, 288, 304	30,199, 15,136, 14,791, 1778

The p.m.r. chemical shift of the methyl group in ethyl isothiocyanate appears at 1·40 p.p.m.[139]; that of the phenyl in phenyl isothiocyanate at 7·2 p.p.m.[135]. The chemical shifts and coupling constants of several aliphatic isothiocyanates and sulphur-containing isothiocyanates have been tabulated[140].

The c.m.r. chemical shift of the NCS group in isothiocyanates occurs at about 10 p.p.m. downfield from the corresponding one in isocyanates (p.p.m. downfield from tetramethylsilane)[77,80]:

Me 128·6 Et 130·7 Cyclohexyl 132·3 Ph 135·7

It appears however, about 20 p.p.m. upfield from the corresponding chemical shift in thiocyanates[141].

The ^{14}N resonances of the NCS group in isothiocyanates occur at the following chemical shifts, upfield from the nitrate ion (in p.p.m.):

H 265[142]. Me 291[143], 285[142] Et 273[143], 271[144]. Ph 265[142]

Therefore the isothiocyanates can be easily distinguished from the cyanates

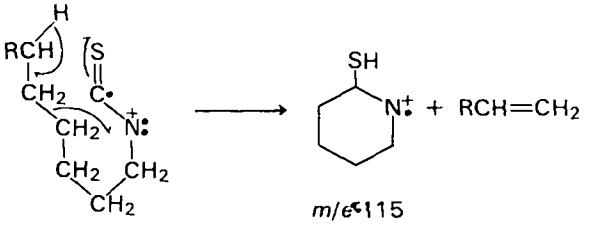
(EtOCN 222 p.p.m.)[13,14], isocyanates (MeNCO 363 p.p.m.)[143], and thiocyanates (EtSCN 103 p.p.m.)[143]. The ^{14}N chemical shifts of silyl and germyl isothiocyanates and their trialkyl and triphenyl derivatives are also 260 to 280 p.p.m. upfield from the nitrate ion[142].

The ^{15}N chemical shift of methyl isothiocyanate occurs 93 p.p.m. downfield from ammonia[145]. In this compound the coupling constant $J_{^{15}N-^{13}Me}$ was found to be 13·4 Hz[146].

4. Mass spectrometry

The existence of the 4·2% ^{34}S isotope may assist in the recognition of sulphur-containing ions.

Kjaer and coworkers[147] have examined 40 diversely-substituted isothiocyanates. They found that the molecular ion of straight-chain alkyl isothiocyanates is of appreciable intensity up to *n*-pentyl isothiocyanate, and then it becomes quite weak. The molecular peak is also intense in the lower branched and unsaturated alkyl isothiocyanates. All the straight-chain alkyl isothiocyanates exhibit an important peak at *m/e* 72, corresponding to the CH_2NCS^+ ion, which is due to α-cleavage. Lower alkyl isothiocyanates exhibit an *m/e* 59 ion ($NCSH^+$), while higher ones, containing at least five carbon atoms in a contiguous chain, show one peak at M-33 (loss of SH), and another one at *m/e* 115, which is due to ring-closure:



Branching in the α- or β-positions in the alkyl portion of isothiocyanates still leads to the fragmentation pattern described above. In the mass spectra of unsaturated isothiocyanates allylic fission dominates. Where the allylic bond is α to the nitrogen atom, the most abundant ion will be the allyl ion; but when the allylic bond is β to the nitrogen atom, as in 3-butenyl isothiocyanate, the predominant ionized fragment is $CH_2{=}\overset{+}{N}CS$ at *m/e* 72. The above results have been reviewed[148].

The mass spectra of several alkyl isothiocyanates and thiocyanates were compared[15]. The differences between them are discussed in Section IV.E.4.

Aryl and benzyl isothiocyanates exhibit a molecular peak. Phenyl isothiocyanate also loses the NCS group to give the Ph^+ (*m/e* 77) ion, which eliminates acetylene to give another ion, *m/e* 51. Benzyl isothiocyanate also expels the NCS group to yield the tropylium ion (*m/e* 91)[147,148].

The eight most abundant peaks and relative intensities of several isothiocyanates are collected in Table 4[135].

TABLE 4. The most abundant ions and relative intensities in the mass spectra of isothiocyanates, RNCS[135]

R									
Me	*m/e*	73	72	70	45	44	32	28	15
	Rel. int.	100	49	9	26	15	11	8	14
Et	*m/e*	87	72	60	59	29	28	27	26
	Rel. int.	100	33	14	74	38	16	48	12
n-Pr	*m/e*	101	72	45	43	42	41	39	27
	Rel. int.	100	51	11	56	24	46	14	34
n-Bu	*m/e*	115	72	57	56	41	39	29	27
	Rel. int.	91	57	50	32	100	30	99	67
dl-*s*-Bu	*m/e*	115	86	57	56	41	29	28	27
	Rel. int.	0	54	51	49	100	82	74	54
d-*s*-Bu	*m/e*	115	86	57	56	41	29	28	27
	Rel. int.	0	54	51	49	100	82	74	54
l-*s*-Bu	*m/e*	115	86	57	56	41	29	28	27
	Rel. int.	0	54	51	49	100	82	74	54
Ph	*m/e*	136	135	77	67·5	51	50	39	38
	Rel. int.	9	100	76	9	34	16	8	6
4-ClC_6H_4	*m/e*	171	169	134	108	82	69	63	39
	Rel. int.	37	100	13	26	14	33	16	11

5. Cotton effects

The n–π^* transition of optically active amino acids appears at very short wavelengths in the ultraviolet, and therefore it is sometimes advantageous to obtain optical rotatory dispersion and circular dichroism data by means of a chromophoric derivative.

The isothiocyanato derivatives of amino acids, $RCH(NCS)CO_2R^1$, and

those of amino alcohol carbonate esters, $RCH(NCS)CH_2OCO_2R^1$, have their maxima in the ultraviolet around 250 nm ($\varepsilon \sim 700$–2000), and 260 nm ($\varepsilon \sim 15{,}000$–22,000), respectively[149]. Both types of derivative show multiple Cotton effects. The latter derivatives, in particular, exhibit three Cotton effects of different intensity around 340, 260, and 205 nm, which can be used in stereochemical assignments. Thus, the 2-isothiocyanato derivative of D-2-aminobutanol methyl carbonate (λ_{max} 259 nm, ε 15,900) exhibits the following circular dichroism data: $[\theta]_{338} + 1700$; $[\theta]_{260} - 6100$; $[\theta]_{203} + 18{,}320$. Optical rotatory dispersion and circular dichroism data and curves of several of these derivatives are also given[149].

IV. THIOCYANATES

A. Introduction

Thiocyanates are isomers of the isothiocyanates and are isoelectronic with the cyanates. They are, however, more stable than the latter. On heating alkyl and allyl thiocyanates they isomerize to isothiocyanates. Several organic thiocyanates have been used as insecticides and fungicides, whereas others serve as solvents and stabilizers, and in these fields their detection and determination is of significance. On the whole, however, their use has not been widespread[150].

B. Chemical Methods

1. Introduction

In contrast to the chemical analysis of isocyanates and isothiocyanates, which to a large extent is based on nucleophilic addition reactions, that of thiocyanates is predominantly based on fission reactions. The thiocyanates are first converted by chemical methods of reduction, oxidation, or cleavage to anionic species such as cyanide, thiocyanate, mercaptide or sulphide, which are subsequently detected and determined. Many of the analytical methods used in the detection and determination of all kinds of sulphur-containing compounds, are also applicable to thiocyanates, but are not specific to them. Only representative and more recent references will be cited.

2. Qualitative analysis

Brückner and coworkers[151] tested several methods of identification on 22 organic thiocyanates. In one method they reduced the thiocyanate

with sodium amalgam in refluxing ethanol to cyanide ions. These were detected by adding a picric acid–sodium carbonate solution and subsequent boiling to yield a red to red-brown colour. Reduction on boiling with an aqueous solution of sodium sulphite also gave cyanide ions which were detected by adding ferric chloride to give a blue colour. The cyanide ions can also be detected by the benzidine–cupric acetate reaction. In another qualitative test the authors converted the organic thiocyanate to thiocyanate anions by reaction with sodium sulphide and detection with ferric chloride, which gives a red colour. Two other methods which are less sensitive have been used by these authors and are based on the oxidation of the thiocyanate to the mercaptide. In these two methods the thiocyanate is treated either with lead tartrate or with sodium plumbite to give lead mercaptide which separates as a yellow precipitate. One of the methods described above, which was based on the reduction of the thiocyanate with sodium sulphite to the cyanide, and detection of the latter by addition of ferric chloride to give Prussian blue, was modified to the spot-test scale[152].

Organic thiocyanates and disulphides were also detected by reduction with zinc powder and hydrochloric acid to the corresponding thiols. The thiols were then treated with pyridine, sodium nitroprusside, and zinc chloride to give a pink colour, which could be detected at a sample concentration of 10 to 25 μg in 2 ml[153].

A qualitative test for the detection of thiocyanates and isothiocyanates in the presence of each other has been described in Section III.B.2.d[85].

3. Quantitative analysis

a. *Reduction with Raney nickel.* This method is applicable to many sulphur-containing compounds, including thiocyanates. It is based on the desulphurization of the sulphur-containing compound with Raney nickel and the determination of the evolved hydrogen sulphide with *o*-hydroxymercuribenzoic acid. A sample of 3–15 mg is heated with Raney nickel in water or ethanol and the evolved gases are absorbed in a 0·25 M-sodium hydroxide solution. The sodium sulphide formed is then titrated with *o*-hydroxymercuribenzoic acid, using dithiofluorescein as indicator. The method was tested on *p*-thiocyanatoaniline and *p*-thiocyanatodimethylaniline[154].

b. *Cleavage with sodium plumbite solution.* This method which has already been mentioned in Section IV.B.2 is based on the following reaction:

$$2\,RSCN + Na_2Pb(OH)_4 \longrightarrow (RS)_2Pb + 2\,NaOCN + 2\,H_2O$$

The analysis is carried out by treating an alcoholic solution of the sample with an excess of a standard sodium plumbite solution. The precipitated lead mercaptide is filtered off and the excess lead in the filtrate is precipitated as sulphate, which is collected, redissolved in ammonium acetate and the lead titrated with a standard ammonium molybdate solution, using tannin as indicator. The method has a precision of $\pm 0{\cdot}5\%$. It is also applicable to other sulphur-containing compounds, such as thioureas, thiocarbonates, thiols, and disulphides[155].

c. *Cleavage with ammoniacal silver nitrate solution.* Cleavage of thiocyanates with an ammoniacal silver nitrate solution also leads to mercaptide ions. In one example, benzyl thiocyanate was determined by adding a standard silver nitrate solution to an ammoniacal solution of the sample. The precipitated silver mercaptide was filtered off and the excess of silver ions in the filtrate was determined argentimetrically by the Volhard method. The method is applicable also to other sulphur-containing compounds[156]. 2,4-Dinitrophenyl thiocyanate in a fungicide was similarly treated with ammoniacal silver nitrate solution but in this case the precipitated silver mercaptide was determined gravimetrically[157].

d. *Cleavage with sodium hydroxide in aqueous ethanol.* This method has been described in Section III.B.2.d as a qualitative test for the detection of thiocyanates and isothiocyanates in the presence of each other. In its quantitative version it has been applied to the determination of aliphatic and aromatic thiocyanates. As shown in Section III.B.2.d, hydrolysis with alkali in aqueous solution yields among other products cyanide ions. Hydrolysis is effected by treatment with sodium hydroxide in alcohol–water at about 40 °C. The cyanide in the hydrolysed solution is then determined by the picric acid reaction using a Duboscq colorimeter[85]. It has been suggested that more accurate results could be obtained by using a photoelectric colorimeter or spectrophotometer[158]. The method yields results that are accurate and precise to about $\pm 1\%$ relative, when applied to insecticide preparations containing small amounts (0·1–0·3%) of alkyl or aralkyl thiocyanates.

Wronski[101] has described methods for the determination of thiocyanates which are also based on cleavage with alkali in aqueous ethanol. In his methods, however, hydrolysis yields thiols by the following reaction:

$$RSCN + 2\,OH^- \longrightarrow RS^- + CNO^- + H_2O$$

In the case of easily hydrolysable thiocyanates, the formed thiols are titrated directly with an alkaline solution of *o*-hydroxymercuribenzoate,

using dithiofluorescein as indicator. Thiocyanates which are more resistant to decomposition are determined by heating with excess *o*-hydroxymercuribenzoate in alkaline solution, adding a known excess amount of cysteine, and back-titrating the latter with *o*-hydroxymercuribenzoate as above. The same author has described in his paper also the determination of thiocyanates in the presence of aliphatic isothiocyanates, and the determination of thiocyanates and aromatic isothiocyanates in the presence of each other.

e. *Cleavage with sodium ethoxide.* This method is also based on the basic hydrolysis of thiocyanates to cyanides (Section III.B.2.d). It was applied in the microdetermination of 1-butoxy-2-(2-thiocyanatoethoxy)-ethane (Lethane 384) in milk and animal tissue. Samples are extracted with hexane and then treated with sodium ethoxide in dimethylformamide. Aqueous sodium hydroxide is added and the aqueous layer acidified and the liberated hydrocyanic acid absorbed in a sodium hydroxide solution. Addition of bromine yields cyanogen bromide, which after removal of excess bromine with sodium arsenite, is treated with a pyridine–benzidine reagent, the extinction read at 352 nm and compared with a calibration curve[159].

f. *Cleavage with sulphide ions.* This cleavage which yields thiocyanate ions is based on the following reaction:

$$2\,RSCN + Na_2S \longrightarrow R_2S + 2\,NaSCN$$

Panchenkov and Smirnov[160] were the first to utilize this principle. They determined the liberated thiocyanate ions by adding a known excess of silver nitrate and filtering off the silver thiocyanate. The excess silver ions were determined by the Volhard method.

The principle was adapted to the micro- and macroscale analysis. In the macroscale method 100 to 200 mg samples are heated with sodium polysulphide to liberate the thiocyanate ions, which are determined by titration with a 0·1 N-silver nitrate solution, and ferric ions as indicator. On the microscale 10 to 60 μg samples are heated with sodium polysulphide and the liberated thiocyanate ions are treated with bromine in a potassium bromide solution to convert them to thiocyanogen bromide. The latter reacts with a benzidine–pyridine reagent to form a polymethine dye. The extinction of the dye is measured at 520 nm and compared with a calibration curve[161].

The same principle has also been used to estimate benzyl thiocyanate

in plant seeds. The liberated thiocyanate ions were determined colorimetrically from the colour conferred by ferric ions[162].

4. Derivatives

Thio acids, such as thioacetic acid or thiobenzoic acid add quite readily to thiocyanates, in organic solvents, without a catalyst, to give crystalline *N*-acyldithiocarbamates:

$$RSC{\equiv}N + R^1COSH \longrightarrow RSCSNHCOR^1$$

This reaction is useful for distinguishing thiocyanates from isothiocyanates, which under the same conditions yield *N*-acylamines and carbon disulphide[163].

C. Polarography

The polarographic reduction of aromatic thiocyanates was investigated by several authors but was not specifically utilized in analytical determinations.

The half-wave potentials of *p*-thiocyanatoaniline and *p*-thiocyanato-*N*,*N*-dimethylaniline at a dropping mercury electrode were shown to be independent of pH, but dependent upon solvent and concentration. The reduction involves the following reaction[164]:

$$ArSCN + 2e^- + 2H_2O \longrightarrow ArSH + HCN + 2OH^-$$

In *o*-, *m*-, and *p*-nitrophenyl thiocyanates the SCN group is reduced in the region -1 to -2 V versus SCE, and the reduction potential is apparently unaffected by the presence of the nitro substituent[165]. In the case of the three isomeric thiocyanatoacetophenones, it has been observed that in the *ortho* compound the SCN group is not reduced, in the *meta* compound it is very slightly reduced, but in the *para* compound it is readily reduced. By contrast, the CO group is reduced in all three isomers, showing two reduction waves[166].

The half-wave potentials observed on polarographic reduction of the three isomeric dithiocyanobenzenes, the three isomeric thiocyanatoacetophenones, and of 3,4- and 2,5-dithiocyanatoacetophenones were reported. It was found that the half-wave potentials of the SCN group

were independent of pH, whereas those of the carbonyl group were dependent on it[167]. Similar pH dependence was observed with isomeric aminothiocyanatoacetophenones[168].

D. Separation Methods

1. Gas chromatography

Methyl thiocyanate and methyl isothiocyanate were separated on a Perkin–Elmer K-column at 132 °C, the isothiocyanate being eluted first after 2 min, and the thiocyanate after 3 min[169].

Benzyl cyanide, benzyl isothiocyanate, and benzyl thiocyanate, extracted from plant seeds, were separated on a stainless steel column (1·8 m, 1·8 mm) of 8% butanediol succinate polyester on silanized chromosorb W (mesh 80–100) at 190 °C. The cyanide was eluted first, the isothiocyanate second, and the thiocyanate last. For quantitative determination anethole was added as an internal standard. The relative sensitivity in the quantitative determination was also investigated. Elution temperatures of the three corresponding allyl compounds are also given[170].

2. Paper chromatography

Of the numerous articles reporting the paper-chromatographic separation of thiocyanates, only a few are cited here. Thiocyanato fatty acids[171] (occasionally from thiocyanogen addition to unsaturated acids[172]) were analysed on paper impregnated with undecane, developed with undecane–acetic acid[171], or with various concentrations of aqueous acetic acid[172], and detected by exposure to ammonia vapour and spraying with ferric ions[171], or by conversion to cupric salts and spraying with potassium ferrocyanide[172].

The paper-chromatographic separation and R_f values of several aromatic thiocyanates were reported[173]. Paper impregnated with 50% methanolic dimethylformamide was used, the chromatograms were developed with xylene or cyclohexane–benzene (3:1), and detected with a mercuric acetate–fluorescein reagent, or with a sodium sulphide–ferric chloride reagent[173]. The R_f values of a very large series of phenols, phenol ethers, and phenol ketones, and their corresponding thiocyanato derivatives were measured on paper impregnated with 25% methanolic dimethylformamide, and developed with different solvent mixtures. Various spray reagents were used for detection[174].

E. Physical Methods

1. Infrared and Raman spectroscopy

Bellamy[128] has tabulated the asymmetric stretching vibration of aliphatic and aromatic thiocyanates. In alkyl thiocyanates[130] this vibration occurs in the 2160–2130 cm^{-1} region, whereas in aryl thiocyanates[129] it appears around 2170 cm^{-1}. This band is sharp and of medium intensity. It can be differentiated from the corresponding band in isothiocyanates by the characteristics described in detail in Section III.E.1. In addition, a band occurring in the region of 722–683 cm^{-1} has been assigned to a C–S vibration of thiocyanates[130].

The vibrational frequencies of methyl thiocyanate in the infrared[59] and in the Raman spectrum[59,175] have been recorded, as well as those of ethyl, *n*-propyl, isopropyl, *n*-butyl, and *s*-butyl thiocyanates[176]. The infrared and Raman spectra of methyl thiocyanate and methyl-d_3-thiocyanate have also been compared[177].

The far infrared spectra[178a] of 16 alkyl thiocyanates have been discussed, assigned[178a,b] and recorded[178c]. The primary thiocyanates exhibit three characteristic peaks at 405–403 cm^{-1} (strong), 649–641 cm^{-1} (weak–medium), and 621–617 cm^{-1} (medium–strong). The secondary thiocyanates show characteristic bands at 658–657 cm^{-1} (weak), 641–633 cm^{-1} (weak), 609–602 cm^{-1} (strong), 578–575 cm^{-1} (medium), and 405–403 cm^{-1} (strong).

Grasselli's atlas[179] lists the major bands of seven thiocyanates and the references from where they have been obtained. Yukawa[180] lists the asymmetric vibration of nine thiocyanates and their references.

2. Electronic spectroscopy and fluorescence

The spectra of ethyl and butyl thiocyanates have been recorded. They absorb around 250 nm ($\log \varepsilon \sim 1{\cdot}6$–$1{\cdot}7$) and show hypsochromic shifts in polar solvents. They absorb at essentially the same wavelength as alkyl isothiocyanates, but the intensity of their absorption is much lower than that of the isothiocyanates[181]. It has been reported that *n*-butyl thiocyanate has its maximum at 244 nm in cyclohexane[179].

Ultraviolet spectra of a series of aryl thiocyanates have been measured[182], and some data are given in Table 5[179].

The emission spectrum of methyl thiocyanate which is due to NCS free radicals, has been recorded[73].

TABLE 5. Ultraviolet spectra of thiocyanates, ArSCN[179]

Ar	Solvent	λ_{max} (nm)	ε
Ph	Cyclohexane	226, 270	9333, 1349
4-$NH_2C_6H_4$	Ethanol	262, 280	15,849, 5623
4-ClC_6H_4	Ethanol	238	12,303
1-Naphthyl	Ethanol	225, 280, 287, 315	56,234, 6761, 8511, 955
$PhCH_2$	Methanol	253, 259	

3. Nuclear magnetic resonance spectroscopy

The proton chemical shifts of some alkyl thiocyanates are given in Table 6[138,179]. As indicated in Section III.E.3, the α-protons of alkyl thiocyanates resonate about 0·5–0·7 p.p.m. upfield from those in the corresponding isothiocyanates. The chemical shifts and coupling constants of thiocyanates containing the following groups have been tabulated[183]: Me, Et, 5-(2-methylthio-2-methoxycarbonyl)ethyl, 1-methyl-2-(methylthio)ethyl, 1,1-dimethyl-2-(methylthio)ethyl, 2-methyl-2-(methylthio)propyl, 2-thienyl, and 3-thienyl.

The c.m.r. chemical shifts of the SCN group in alkyl thiocyanates have been recorded for those with the following alkyl groups (in p.p.m. downfield from tetramethylsilane)[141]:

Me 113·5 Et 112·1 Bu 112·1

TABLE 6. P.m.r. chemical shifts of alkyl thiocyanates. RSCN[138,179], measured in carbon tetrachloride, except where indicated otherwise

R	δ (p.p.m.)	
	α-Protons	Other protons
Me	2·61	
Et	2·98	Me 1·5 ($CDCl_3$)
i-Pr	3·48	
n-Bu	3·01	β and γ CH_2 1·2–2·1 Me 1·0
$MeCH{=}CHCH_2$	3·55	
$PhCH_2$	4·2	Ph 7·4 ($CDCl_3$)

As has been indicated in Section III.E.3, these chemical shifts are about 20 p.p.m. upfield from those in the corresponding isothiocyanates.

The proton noise-decoupled c.m.r. spectrum of ethyl thiocyanate has been recorded (in p.p.m. downfield from tetramethylsilane)[184]:

Me 15·4 CH_2 28·6 SCN 111·9

In this decoupled spectrum the Me and CH_2 singlets have enhanced intensity, as compared with the SCN singlet, because of a nuclear Overhauser effect.

The ^{14}N chemical shift of ethyl thiocyanate occurs 103 p.p.m. upfield from the nitrate ion[143,144]. Therefore, as indicated in Section III.E.3, ^{14}N n.m.r. can serve to distinguish thiocyanates from isothiocyanates, as well as from cyanates and isocyanates.

4. Mass spectrometry

Alkyl thiocyanates and isothiocyanates[15] display similar differences in their mass spectra to those found for alkyl cyanates and isocyanates. These differences, however, are much more pronounced in the sulphur-containing compounds. Alkyl fragments, formed by α-cleavage predominate in the spectra of the lower straight-chain thiocyanates. Thus ethyl, *n*-propyl, and *n*-butyl thiocyanates exhibit peaks of high relative intensity due to Et^+, *n*-Pr^+, and *n*-Bu^+ ions. *n*-Propyl and *n*-butyl thiocyanates show also a peak at *m/e* 41 which may be due to the allyl ion. On the other hand, NCS-containing fragments, especially CH_2NCS^+ (*m/e* 72) predominate in the alkyl isothiocyanates and are practically absent in the spectra of alkyl thiocyanates. $HSCN^+$ and $HNCS^+$ (*m/e* 59) occur approximately to the same extent in alkyl thiocyanates and isothiocyanates. *n*-Butyl and *n*-hexyl thiocyanates show peaks of low intensity due to the elimination of HCN. As indicated in Section III.E.4, apart from ring-closure reactions and the occurrence of the ion CH_2NCS^+ (*m/e* 72) in greater abundance in the spectra of isothiocyanates, the spectra of straight-chain thiocyanates and isothiocyanates become more and more alike with increasing chain-length, as was the case for cyanates and isocyanates. Finally it should be pointed out that while the molecular ions are the base peaks in the lower isothiocyanates, the most abundant peaks in the lower thiocyanates are the propyl and allyl ions. Table 7 shows the eight most abundant peaks of several lower straight-chain thiocyanates[179].

The molecular ions are the base peaks of phenyl and 3-indolyl thiocyanates. The phenyl thiocyanate also displays strong peaks originating

from elimination of CN, HCN, CS, and SCN, while the indolyl thiocyanate shows peaks originating from the elimination of CN and S[185].

TABLE 7. The most abundant ions and relative intensities in the mass spectra of alkyl thiocyanates, RSCN[179]

R = Me		R = Et		R = n-Pr	
m/e	Rel. int.	*m/e*	Rel. int.	*m/e*	Rel. int
73	6	87	59	101	55
72	100	58	10	45	11
71	67	57	31	43	100
46	20	45	8	42	14
45	45	32	8	41	82
44	63	29	100	39	22
31	19	28	30	28	11
15	53	27	48	27	56

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 6

Thermochemistry of cyanates, isocyanates, and their thio derivatives

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We must strive for the best solution possible not the best possible solution—*Anon.*

I. INTRODUCTION

This chapter is concerned with the thermochemistry of the cyanates, isocyanates, thiocyanates, and isothiocyanates. A search of literature has revealed very little in the way of experimental data, so the emphasis will be on estimation. The literature searched included *Chemical Abstracts*, IUPAC's *Bulletin of Thermochemistry and Thermodynamics*, and the two classic monographs[1,2], Stull, Westrum, and Sinke's *The Chemical Thermodynamics of Organic Compounds*, and Cox and Pilcher's *Thermochemistry of Organic and Organometallic Compounds*.

The methods of estimation will be based on additivity techniques developed by Benson and his coworkers[3–5]. It would not be appropriate to give a detailed discussion of additivity principles here because they have been adequately covered previously, in earlier volumes in this series[6,7]. Nor would it be appropriate in a review article of this size to estimate the thermodynamic properties of all possible compounds of interest. The H-, methyl-, ethyl-, vinyl-, phenyl-, derivatives of the cyanates, isocyanates, thiocyanates, and isothiocyanates have been discussed in the hope that they will form a basis for further work. A few other compounds have been included.

The thermodynamic properties of interest here are the heat of formation, the entropy, and the heat capacity. The ideal gas state was chosen because more numbers are available than for the liquid or solid state, and equilibrium constants in the gas and condensed phases are often very similar. All of the values discussed here will be for a temperature of 298·15 K (25 °C). For the sake of brevity, the terms molar, gas, and 298·15 K will be omitted from the thermochemical symbols. Otherwise, the nomenclature will be that recommended by IUPAC[8a,8b]. For example, the symbol for the heat of formation of methyl isocyanate in the ideal gas state at 298·15 K is denoted here by $\Delta_f H^0$ (CH_3NCO). The unit of energy recommended by IUPAC is the joule, so all heats of formation will be in units of kJ/mol, followed by a value in the previously accepted unit, kcal/mol. The conversion factor is cal = 4·18 J. The symbol for the standard molar entropy is S^0 (chemical compound) and that for the standard molar heat capacity is c_p^0 (chemical compound). The units for all entropies and heat capacities will be J/(mol K). As with the heats of formation, the value of

the entropy and heat capacity in the previously accepted unit cal/(mol K) will also be given.

Most of the measurements reported in this review are good to ±10 kJ/mol, 2 kcal/mol for the heat of formation and ±5 J/(mol K), 1 cal/(mol K) for the entropy and heat capacity. Most of the estimates are good to ±20 kJ/mol, 5 kcal/mol for the heat of formation and ±10 J/(mol K), 2 cal/(mol K) for the entropy and heat capacity.

II. CYANATES

A. Hydrogen Cyanate or Cyanic Acid

No experiments have been reported on the thermochemical properties of hydrogen cyanate, but several methods of estimation are available. The estimated results are summarized in Table 1.

If it is assumed that the difference in the properties of the O–C bond in hydrogen cyanate and cyanogen chloride is the same as the difference in the properties of the O–C bond in acetic acid and acetyl chloride, equation (1)

$$HO(CN) - Cl(CN) = HO(COCH_3) - Cl(COCH_3) \quad (1)$$

then the thermochemical properties of hydrogen cyanate can be estimated from equation (2) and the known[1] thermochemical properties of cyanogen chloride, acetic acid, and acetyl chloride

$$HO(CN) = Cl(CN) + HO(COCH_3) - Cl(COCH_3) \quad (2)$$

Another way to estimate the entropy and heat capacity of hydrogen cyanate is to assume that there is no entropy or heat capacity change between hydrogen cyanate HOCN and hydrogen isocyanate HNCO, for which the thermochemical properties are known[9]. This is a reasonable assumption for entropies and heat capacities, to which a major contribution is from the mass of the molecule. This is the basis for atom additivity[3], (see later). However, it is a poor assumption for heats of formation, because they depend so much on the bonding between N, C, and O atoms. The bonding is very different in HOCN and HNCO.

As mentioned above, entropies and heat capacities can be estimated to within about 15 J/(mol K), 4 cal/(mol K) using atom additivity[3]. The atomic contributions[3] are as follows in units of J/(mol K) [cal/(mol K)]. For C_p^0: H 3·55 (0·85), C 15·68 (3·75), N 14·21 (3·40), and O 14·21 (3·40); for S^0: H 87·78 (21·0), C (ligancy 2) 22·15 (5·3), N (ligancy 1) 95·72 (22·9), and O (ligancy 2) 36·78 (8·8). The heat capacity and entropy of HOCN are

TABLE 1. Estimation of the standard molar heat of formation, entropy, and heat capacity of hydrogen cyanate or cyanic acid (HOCN) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^\circ$		S°		c_p°		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
−58·5	−14·0	222·8	53·3	43·5	10·4	HO(CN) − Cl(CN) = HO($COCH_3$) − Cl($COCH_3$)
		237·8	56·9	45·1	10·8	By analogy with HNCO
		240·8	57·6	47·6	11·4	Atom additivity
		252·5[a]	60·4[a]	52·2	12·5	By analogy with CH_3CN
−58·5	−14·0	230·3	55·1	44·3	10·6	Recommended value

[a] R ln 3 has been added to correct for symmetry.

obtained by adding the values for the four atoms, and the results are in Table 1.

A quick and simple estimate of entropy and heat capacity to within about 20 J/(mol K), 5 cal/(mol K) can be made by comparing molecules that have approximately the same shape and mass. In the case of HOCN, a molecule that has approximately the same shape and mass is CH_3CN. The values from the literature[1] for CH_3CN are in Table 1. The methyl group in CH_3CN has a symmetry of 3. So, the 'intrinsic' entropy of CH_3CN is obtained by adding the symmetry correction of $R \ln 3$ to the entropy of CH_3CN.

Of the four methods for estimating the entropy and heat capacity of hydrogen cyanate, the cyanogen chloride/acetic acid/acetyl chloride method and the analogy with hydrogen isocyanate method are probably the best. Therefore, the recommended value in Table 1 is the average of these two methods. The other methods are included for completeness.

B. Methyl Cyanate

No experiments have been reported on the thermochemical properties of methyl cyanate, but several methods of estimation are available. The estimated results are summarized in Table 2.

The first two methods are related. In the one, the difference between methyl cyanate and cyanic acid is taken to be the same as the difference between methyl acetate and acetic acid, equation (3)

$$CH_3(OCN) - H(OCN) = CH_3(OCOCH_3) - H(OCOCH_3) \quad (3)$$

In the other, the difference between methyl cyanate and cyanic acid is taken to be the same as the difference between methyl formate and formic acid, equation (4)

$$CH_3(OCN) - H(OCN) = CH_3(OCOH) - H(OCOH) \quad (4)$$

Returning to the first method, from equation (3)

$$CH_3(OCN) = H(OCN) + CH_3(OCOCH_3) - H(OCOCH_3) \quad (5)$$

Unfortunately, Stull, Westrum, and Sinke[1] do not list the thermochemical properties of methyl acetate. However, methyl acetate and acetic acid can be broken down into groups, equations (6) and (7)

$$CH_3(OCOCH_3) = [C-H_3,O] + [O-C,CO] + [CO-C,O] + [C-CO,H_3] \quad (6)$$

$$H(OCOCH_3) = [O-CO,H] + [CO-C,O] + [C-CO,H_3] \quad (7)$$

TABLE 2. Estimation of the standard molar heat of formation, entropy, and heat capacity of methyl cyanate (CH_3OCN) and ethyl cyanate (CH_3CH_2OCN) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
Methyl cyanate						
−38·0	−9·1	290·1	69·4	70·2	16·8	$CH_3(OCN) - H(OCN) = CH_3(OCOCH_3) - H(OCOCH_3)$
−29·7	−7·1	275·5	65·9	64·8	15·5	$CH_3(OCN) - H(OCN) = CH_3(OCOH) - H(OCOH)$
		272·5	65·2	70·6	16·9	Atom additivity
		295·5	68·5	73·2	17·5	By analogy with CH_3CH_2CN
−33·9	−8·1	283·0	67·7	67·7	16·2	Recommended value
Ethyl cyanate						
−69·4	−16·6	326·1	78·0	88·6	21·2	

Substituting equations (6) and (7) in equation (5), we obtain equation (8)

$$CH_3(OCN) = H(OCN) + [C—H_3,O] + [O—C,CO] - [O—CO,H] \quad (8)$$

Values for the heat of formation[10] and entropy[4] of these groups are available, and for the heat capacity of all the groups except the [O—C, CO] group. However, a value of 15·9 J/(mol K), and 3·8 cal/(mol K) for the [O—C, CO] group is obtained from the listed[1] heat capacity of ethyl acetate and the other known[4] groups for ethyl acetate. Substitution of the group values and the values for cyanic acid from Table 1 into equation (8) gives the thermochemical properties of methyl cyanate in Table 2.

Returning to the second method, from equation (4),

$$CH_3(OCN) = H(OCN) + CH_3(OCOH) - H(OCOH) \quad (9)$$

Values for the thermochemical properties of cyanic acid, were taken from Table 1 and for methyl formate and formic acid from Stull, Westrum, and Sinke[1]. The results are in Table 2.

The entropy and heat capacity of methyl cyanate can be estimated by atom additivity[3]. The atomic contributions[3] used for cyanic acid were also used for methyl cyanate with the additional atomic contribution of −136·3 J/(mol K), −32·6 cal/(mol K) for carbon (ligancy 4) for the entropy. The results are in Table 2.

Finally, the entropy and heat capacity of methyl cyanate may be estimated from those for propionitrile, which has a similar mass and shape. A symmetry correction of $R \ln 3$ is added to the entropy of propionitrile, to give its 'intrinsic' entropy. The results are in Table 2.

The first two methods of estimating the thermochemical properties of methyl cyanate are probably significantly more accurate than the last two methods. The recommended values in Table 2 are, therefore, the average of the first two methods. The last two methods are given for comparison.

C. Ethyl Cyanate

No measured thermochemical properties of ethyl cyanate have been reported. However, the heat of formation, entropy, and heat capacity can be easily and accurately estimated from those for methyl cyanate, with the addition of the group values for [C—C, O, H_2], which takes care of the extra methylene group. The group values are[4] for heat of formation −35·5 kJ/mol, −8·5 kcal/mol, for entropy 43·1 J/(mol K), 10·3 cal/(mol K), and for heat capacity 20·9 J/(mol K), 5·0 cal/(mol K). The thermochemical properties of ethyl cyanate are summarized in Table 2.

D. Vinyl Cyanate

No experiments have been reported on the thermochemical properties of vinyl cyanate, and there are few methods of estimation. The heat of formation, entropy, and heat capacity of vinyl cyanate can be estimated by assuming that the difference between vinyl cyanate and cyanic acid is the same as the difference between vinyl acetate and acetic acid, equations (10) and (11).

$$CH_2CH(OCN) - H(OCN) = CH_2CH(OCOCH_3) - H(OCOCH_3) \quad (10)$$

then

$$CH_2CH(OCN) = H(OCN) + CH_2CH(OCOCH_3) - H(OCOCH_3) \quad (11)$$

Unfortunately, Stull, Westrum, and Sinke[1] do not list the thermochemical properties of vinyl acetate. However, vinyl acetate and acetic acid can be broken down into groups, equations (12) and (13)

$$CH_2CH(OCOCH_3) = [C_d - H_2] + [C_d - H,O] + [O - C_d, CO] + [CO - C,O] + [C - CO,H_3] \quad (12)$$

where C_d is a vinyl carbon atom and

$$H(OCOCH_3) = [O - CO,H] + [CO - C,O] + [C - CO,H_3] \quad (13)$$

Substituting equations (12) and (13) in equation (11), we obtain equation (14)

$$CH_2CH(OCN) = H(OCN) + [C_d - H_2] + [C_d - H,O] + [O - C_d,CO] - [O - CO,H] \quad (14)$$

For the heat of formation, all the values for the right hand side of equation (14) are available[4,10]. However, for the entropy, there are no values in the literature for the groups $[C_d - H, O]$ and $[O - C_d, CO]$. A value of 33·4 J/(mol K), 8·0 cal/(mol K) has been determined for the $[C_d - H, O]$ group, using a previous assumption that the $[C_d - H, O]$ group can be assigned to the equivalent to a $[C_d - H, C]$ group. In order to obtain values for the entropy and heat capacity of the $[O - C_d, CO]$ group, it is necessary to estimate the entropy and heat capacity of vinyl acetate. If it is assumed that the difference between vinyl acetate and ethyl acetate is the same as the difference between acrylic and propionic acid, equation (15)

$$CH_2CH(OCOCH_3) - CH_3CH_2(OCOCH_3) = CH_2CH(COOH) - CH_3CH_2(COOH) \quad (15)$$

From equation (15), it follows that

$$CH_2CH(OCOCH_3) = CH_3CH_2(OCOCH_3) + CH_2CH(COOH) - CH_3CH_2(COOH) \quad (16)$$

Equation (16) and values from Stull, Westrum, and Sinke[1] for ethyl acetate and acrylic acid, and the values calculated from group additivity[4,10] for propionic acid were used to estimate the entropy of vinyl acetate to be 354·9 J/(mol K) 84·9 cal/(mol K), and the heat capacity of vinyl acetate was estimated to be 99·1 J/(mol K), 23·7 cal/(mol K). From these values for vinyl acetate, the intrinsic entropy of the [O—C_d, CO] group was found to be 26·3 J/(mol K), 6·3 cal/(mol K) and the heat capacity of the [O—C_d, CO] group was found to be 9·2 J/(mol K), 2·2 cal/(mol K).

Substitution of group values into equation (14) then gave the thermochemical properties of vinyl cyanate that are recommended in Table 3. Values estimated by atom additivity are included for comparison.

E. Phenyl Cyanate

No experiments have been reported on the thermochemical properties of phenyl cyanate. The heat of formation, entropy, and heat capacity of phenyl cyanate can be estimated by assuming that the difference between phenyl cyanate and cyanic acid is the same as the difference between phenyl acetate and acetic acid, equation (17)

$$Ph(OCN) - H(OCN) = Ph(OCOCH_3) - H(OCOCH_3) \quad (17)$$

Then

$$Ph(OCN) = H(OCN) + Ph(OCOCH_3) - H(OCOCH_3) \quad (18)$$

Unfortunately, Stull, Westrum, and Sinke[1] do not list the thermochemical properties of phenyl acetate. However, the thermochemical properties of phenyl acetate can be estimated by assuming that the difference between phenyl acetate and ethyl acetate is the same as the difference between benzoic acid and propionic acid, equation (19).

$$Ph(OCOCH_3) - CH_3CH_2(OCOCH_3) = Ph(COOH) - CH_3CH_2(COOH) \quad (19)$$

From equation (19), it follows that

$$Ph(OCOCH_3) = CH_3CH_2(OCOCH_3) + Ph(COOH) - CH_3CH_2(COOH) \quad (20)$$

By using equation (19) and values from Stull, Westrum, and Sinke[1] for ethyl acetate, benzoic acid, and the values calculated from group additivity[4,19], for propionic acid, the heat of formation of phenyl benzoate was found to be −277·6 kJ/mol, −66·4 kcal/mol, the entropy of phenyl benzoate was found to be 408·8 J/(mol K), 97·8 cal/(mol K), and the heat capacity of phenyl benzoate was found to be 124·6 J/(mol K), 29·8 cal/(mol K).

TABLE 3. Estimation of the standard molar heat of formation, entropy, and heat capacity of vinyl cyanate (CH_2CHOCN) and phenyl cyanate (PhOCN) in the ideal gas state at 298·15 K (25° C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
Vinyl cyanate						
57·7	13·8	295·5	70·7	75·7	18·1	$CH_2CH(OCN) - H(OCN) = CH_2CH(OCOCH_3) - H(OCOCH_3)$
		305·1	73·0	86·1	20·6	Atom additivity
57·7	13·8	295·5	70·7	75·7	18·1	Recommended value
Phenyl cyanate						
98·2	23·5	357·0	85·4	102·4	24·5	$Ph(OCN) - H(OCN) = Ph(OCOCH_3) - H(OCOCH_3)$

Substituting these values for the thermochemical properties of phenyl benzoate into equation (18) together with Stull, Westrum, and Sinke's[1] values for acetic acid, and the values for cyanic acid estimated in this work, the heat of formation of phenyl cyanate was found to be 98·2 kJ/mol, 23·5 kcal/mol, the entropy of phenyl benzoate was found to be 357 J/(mol K), 85·4 cal/(mol K), and the heat capacity of phenyl benzoate was found to be 102·4 J/(mol K), 24·5 cal/(mol K). The results are summarized in Table 3.

III. ISOCYANATES

A. Hydrogen Isocyanate or Isocyanic Acid

JANAF[9] reports experimentally obtained values for the heat of formation of hydrogen isocyanate. The results by several different methods are in good agreement, and the value JANAF has adopted is in Table 4. JANAF also reports statistical mechanical calculations of the entropy and heat capacity that are in Table 4. Values for the entropy and heat capacity of hydrogen isocyanate can be obtained by atom additivity. The results are necessarily identical to those obtained earlier (see Table 1) for hydrogen cyanate. The results of the atom additivity estimates are included in Table 4 for completeness.

B. Methyl Isocyanate

Stull, Westrum, and Sinke[1] list a value of −89·9 kJ/mol, −21·5 kcal/mol for the heat of formation of liquid methyl isocyanate. What is needed is the heat of vaporization at 298·15 K (25 °C) of methyl isocyanate, to convert the heat of formation in the liquid phase to that in the gas phase.

One method of estimating the heat of vaporization is to assume that the heat of vaporization of methyl isocyanate is the same as the heat of vaporization of methyl isocyanide[1] (32·6 kJ/mol, 7·8 kcal/mol).

Another method of estimating the heat of vaporization of methyl isocyanate is based[4] on its boiling point of 332·6 K (59·6 °C). The method is empirical, but sufficiently accurate for the present purposes. The equation is

$$\Delta H_{vap}/(\text{kJ mol}) = [S_T/(\text{J/mol K})][1{\cdot}76 \times 10^{-3} \times (t_B/^{\circ}\text{C}) + 0{\cdot}253] \quad (21)$$

where ΔH_{vap} is the heat of vaporization

S_T is Trouton's constant taken to be 92 J/(mol K), 22 cal/(mol K)

t_B is the boiling point in °C.

TABLE 4. Estimation of the standard molar heat of formation, entropy, and heat capacity of hydrogen isocyanate or isocyanic acid (HNCO) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
−100·7	−24·3	237·8	56·9	45·1	10·8	Measured[9]
		242·4	58·0	47·6	11·4	Atom additivity
−100·7	−24·3	237·8	56·9	45·1	10·8	Recommended value

In the case of methyl isocyanate, the heat of vaporization from equation (21) is 32·9 kJ/mol, 7·9 kcal/mol in excellent agreement with the previous estimate. Taking an average value of 32·8 kJ/mol, 7·8 kcal/mol gives a value of −57·1 kJ/mol, −13·7 kcal/mol for the heat of formation of methyl isocyanate in the ideal gas state at 298·15 K (25 °C).

Methyl isocyanate is therefore 23·2 kJ/mol, 5·6 kcal/mol more stable than methyl cyanate (Table 2), and hydrogen isocyanate is 42·2 kJ/mol, 10·3 kcal/mol more stable than hydrogen cyanate. These heats of isomerization are significantly greater than in the hydrocarbon analogues[1]. For example, 1,2-butadiene is only 2·9 kJ/mol, 0·7 kcal/mol more stable than ethyl acetylene, and allene is 6·7 kJ/mol, 1·6 kcal/mol less stable than methyl acetylene.

No values of the entropy or heat capacity of methyl isocyanate have been reported. Perhaps the best method of estimation is to assume that the entropy and heat capacity of methyl isocyanate are the same as those for methyl cyanate (see Table 1). An alternative method is to use atom additivity to estimate the difference between hydrogen isocyanate and methyl isocyanate. From the atomic contributions[3] listed earlier for carbon and hydrogen atoms, the CH_2 increment is 39·3 J(mol K), 9·4 cal/(mol K) for entropy and 22·8 J/(mol K), 5·4 cal/(mol K) for heat capacity. The use of the values for hydrogen isocyanate in Table 4 with the foregoing CH_2 increment gives 277·1 J/(mol K), 66·3 cal/(mol K) for the entropy and 67·7 J/(mol K), 16·2 cal/(mol K) for the heat capacity.

The thermochemical properties of methyl isocyanate are summarized in Table 5.

C. Ethyl Isocyanate

Stull, Westrum, and Sinke[1] list a value of −117·9 kJ/mol, −28·2 kcal/mol for the heat of formation of ethyl isocyanate in the liquid state. The boiling point[11] of ethyl isocyanate is 333·2 K (60 °C), so from equation (21) the heat of vaporization is 32·9 kJ/mol, 7·9 kcal/mol. The heat of formation of ethyl isocyanate in the ideal gas state at 298·15 K (25 °C) is therefore −85·0 kJ/mol, −20·3 kcal/mol.

No experimental values have been reported for the entropy and heat capacity of ethyl isocyanate. Perhaps the simplest way to estimate the entropy and heat capacity of ethyl isocyanate is to add a CH_2 increment based on atom additivity to methyl isocyanate. The results are in Table 6.

TABLE 5. Estimation of the standard molar heat of formation, entropy, and heat capacity of methyl isocyanate (CH_3NCO) in the ideal gas state at 298·15 K (25° C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
−57·1	−13·7					$\Delta_f H$ (liquid)[1] + estimated ΔH_{vap}
		283·0	67·7	67·7	16·2	By analogy with methyl cyanate
		272·5	64·8	70·6	16·9	Atom additivity
		277·1	66·3	67·7	16·2	Hydrogen isocyanate + CH_2 atomic increment[3]
−57·1	−13·7	283·0	67·7	67·7	16·2	Recommended value

TABLE 6. Estimation of the standard molar heat of formation, entropy, and heat capacity of ethyl isocyanate (CH_3CH_2NCO) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
−85·0	−20·3					$\Delta_f H$(liquid)[1] + estimated ΔH_{vap}
		322·3	77·1	90·5	21·6	Methyl isocyanate + CH_2 atomic increment[3]
−85·0	−20·3	322·3	77·1	90·5	21·6	Recommended value

D. Vinyl Isocyanate

No experiments have been reported on the thermochemical properties of vinyl isocyanate. The thermochemical properties of vinyl isocyanate may be estimated from those of vinyl cyanate by assuming that the difference between vinyl isocyanate and vinyl cyanate is the same as the difference between methyl cyanate and methyl isocyanate, equations (22) and (23)

$$CH_2CH(NCO) - CH_2CH(OCN) = CH_3(NCO) - CH_3(OCN) \quad (22)$$

therefore,

$$CH_2CH(NCO) = CH_2CH(OCN) + CH_3(NCO) - CH_3(OCN) \quad (23)$$

As discussed earlier, methyl isocyanate is 23·2 kJ/mol, 5·6 kcal/mol more stable than methyl cyanate. From the heat of formation of vinyl cyanate in Table 3, the heat of formation of vinyl isocyanate is 80·9 kJ/mol, 19·4 kcal/mol.

Because the entropy and heat capacity of methyl isocyanate were assumed to be equal to those of methyl cyanate, it follows from equations (22) and (23) that the entropy and heat capacity of vinyl isocyanate are assumed to be equal to those of vinyl cyanate.

The thermochemical properties of vinyl isocyanate are in Table 7.

E. Phenyl Isocyanate

No experiments have been reported on the thermochemical properties of phenyl isocyanate. The thermochemical properties of phenyl isocyanate have been estimated in the same way as was done above for vinyl isocyanate, namely from equations (24) and (25).

$$Ph(NCO) - Ph(OCN) = CH_3(NCO) - CH_3(OCN) \quad (24)$$

therefore,

$$Ph(NCO) = Ph(OCN) + CH_3(NCO) - CH_3(OCN) \quad (25)$$

The results are in Table

IV. THIOCYANATES

Barroeta[12] has recently reviewed the thermodynamics of organic thiocyanates. Much of the work discussed here will be based on this review. The standard state of sulphur has been taken as the solid.

TABLE 7. Estimation of the standard molar heat of formation, entropy, and heat capacity of vinyl isocyanate [$CH_2CH(NCO)$] and phenyl isocyanate [Ph(NCO)] in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
Vinyl isocyanate						
81·1	19·4	295·5	70·7	75·7	18·1	$CH_2CH(NCO) - CH_2CH(OCN) = CH_3(NCO) - CH_3(NCO)$
Phenyl isocyanate						
121·6	29·1	357·0	85·4	101·4	24·5	$Ph(NCO) - Ph(OCN) = CH_3(NCO) - CH_3(OCN)$

A. Hydrogen Thiocyanate or Thiocyanic Acid

No experimental results have been reported for the thermochemical properties of thiocyanic acid. If it is assumed that the difference in the thermochemical properties of thiocyanic acid and isothiocyanic acid is the same as the difference in the thermochemical properties of cyanic and isocyanic acids, equation (26)

$$H(SCN) - H(NCS) = H(OCN) - H(NCO) \tag{26}$$

then the thermochemical properties of thiocyanic acid can be estimated from the known thermochemical properties of isothiocyanic acid (Table 12), cyanic acid (Table 1), isocyanic acid (Table 4) and equation (27)

$$H(SCN) = H(NCS) + H(OCN) - H(NCO) \tag{27}$$

The results are in Table 8.

Values for the entropy and heat capacity of thiocyanic acid estimated by group additivity[3] are included in Table 8 for completeness.

B. Methyl Thiocyanate

Measured values have been reported[12–16] for the thermochemical properties of methyl thiocyanate. The measured values are in Table 9 along with estimates based on atom additivity and (hydrogen thiocyanate + CH_2 increment) for the entropy and heat capacity. The method of estimating is that used earlier for methyl isocyanate.

C. Ethyl Thiocyanate

The heat of formation of liquid ethyl thiocyanate has been measured[12,13] to be 71·1 kJ/mol, 17·0 kcal/mol. Using an estimated heat of vaporization of 32·6 kJ/mol, 7·8 kcal/mol, Barroeta[12] has recommended 107·8 kJ/mol, 25·8 kcal/mol for the heat of formation of ethyl thiocyanate in the ideal gas state. This value is in excellent agreement with 109·5 kJ/mol, 26·2 kcal/mol calculated from the heat of formation of methyl thiocyanate (Table 9) plus the value[4] for the [C—C, H_2, S] group, which allows for the additional methylene group.

No experimental values have been reported for the entropy or heat capacity of ethyl thiocyanate, but they can be estimated easily from the values for methyl thiocyanate (Table 9) and for the [C—C, H_2, S] group[4]. The results are in Table 10, along with estimates based on atom additivity.

TABLE 8. Estimation of the standard molar heat of formation, entropy, and heat capacity of hydrogen thiocyanate or thiocyanic acid (HSCN) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
175·1	41·9	240·4	57·5	45·6	10·9	H(SCN) − H(NCS) = H(OCN) − H(NCO)
		259·2	62·0	53·1	12·7	Atom additivity
175·1	41·9	240·4	57·5	45·6	10·9	Recommended value

TABLE 9. Estimation of the standard molar heat of formation, entropy, and heat capacity of methyl thiocyanate (CH_3SCN) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
133·3	31·9					Measured[13–15] and reviewed[12]
		299·3	71·6	72·7	17·4	Measured[6] and reviewed[12]
		289·3	69·2	76·1	18·2	Atom additivity
		279·6	66·9	68·1	16·3	Hydrogen thiocyanate + CH_2 atomic increment[3]
133·3	31·9	299·3	71·6	72·7	17·4	Recommended value

The thermochemical properties of ethyl thiocyanate are summarized in Table 10.

D. Vinyl Thiocyanate

There are no measured values for the thermochemical properties of vinyl thiocyanate. Perhaps the most accurate way to estimate the thermochemical properties of vinyl thiocyanate is to assume that the difference between vinyl thiocyanate and vinyl cyanate is the same as the difference between methyl thiocyanate and methyl cyanate, equation (27)

$$CH_2CH(SCN) - CH_2CH(OCN) = CH_3(SCN) - CH_3(OCN) \quad (27)$$

therefore,

$$CH_2CH(SCN) = CH_2CH(OCN) + CH_3(SCN) - CH_3(OCN) \quad (28)$$

The thermochemical properties of vinyl cyanate (Table 3), methyl isocyanate (Table 5), and methyl cyanate (Table 2) and equation (28) were used to calculate the heat of formation, entropy, and heat capacity of vinyl thiocyanate in Table 11. Estimates of the entropy and heat capacity of vinyl thiocyanate were also made using atom additivity and are included in Table 11.

E. Phenyl Thiocyanate

There are no measured values for the thermochemical properties of phenyl thiocyanate. The estimated values in Table 11 were obtained by assuming that the difference between phenyl thiocyanate and phenyl cyanate is the same as the difference between methyl thiocyanate and methyl cyanate, equation (29)

$$Ph(SCN) - Ph(OCN) = CH_3(SCN) - CH_3(OCN) \quad (29)$$

therefore

$$Ph(SCN) = Ph(OCN) + CH_3(SCN) - CH_3(OCN) \quad (30)$$

The thermochemical properties of phenyl isocyanate were calculated from equation (30) and the known thermochemical properties of phenyl cyanate (Table 3), methyl isocyanate (Table 5), and methyl cyanate (Table 2).

TABLE 10. Estimation of the standard molar heat of formation, entropy, and heat capacity of ethyl thiocyanate (CH_3CH_2SCN) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		C_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
107·8	25·8					Measured[13] and reviewed[12]
		328·6	78·6	98·7	23·6	Atom additivity
		338·6	81·0	95·3	22·8	Methyl thiocyanate + CH_2 atomic increment[3]
109·5	26·2	340·7	81·5	95·3	22·8	Methyl thiocyanate + [C—C, H_2, S] group increment[4]
107·8	25·8	340·7	81·5	95·3	22·8	Recommended value

TABLE 11. Estimation of the standard molar heat of formation, entropy, and heat capacity of vinyl thiocyanate (CH_2CHSCN) and phenyl thiocyanate (PhSCN) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
Vinyl thiocyanate						
224·9	53·8	311·8	74·6	80·7	19·3	$CH_2CH(SCN) - CH_2CH(OCN) = CH_3(SCN) - CH_3(OCN)$
		321·9	77·0	91·5	21·9	Atom additivity
224·9	53·8	311·8	74·6	80·7	19·3	Recommended value
Phenyl thiocyanate						
265·4	63·5	373·3	89·3	107·4	25·7	$Ph(SCN) - Ph(OCN) = CH_3(SCN) - CH_3(OCN)$

V. ISOTHIOCYANATES

A. Hydrogen Isothiocyanate or Isothiocyanic Acid

The thermochemical properties of hydrogen isothiocyanate or isothiocyanic acid have been measured[17-19] and reviewed[1,12]. They are reproduced in Table 12 with estimates of the entropy and heat capacity of hydrogen isothiocyanate, using atom additivity.

B. Methyl Isothiocyanate

Barroeta[12] has reviewed the experimental measurements on the heat of formation[20-23] and the statistical mechanical calculations of the entropy and heat capacity[24,25] of methyl isothiocyanate. The results are in Table 13 with two estimates of the entropy and heat capacity based on atom additivity.

C. Ethyl Isothiocyanate

The heat of formation of ethyl isothiocyanate was measured by Berthelot[12,26] in 1901. Berthelot's heat of combustion of methyl isocyanate[12,26] differed by 42·6 kJ/mol, 10·2 kcal/mol from Sunner's more recent measurement[20], using the rotating bomb calorimeter. Although the absolute value of Berthelot's heat of formation of ethyl isothiocyanate may therefore also be in error by about 40 kJ/mol, 10 kcal/mol, the relative values may be much closer. Thus, Berthelot[12,26] found that methyl isothiocyanate was 28·8 kJ/mol, 6·9 kcal/mol more stable than methyl thiocyanate, whereas the more recent work (Tables 9 and 13) shows that methyl isocyanate is 20·1 kJ/mol, 4·8 kcal/mol more stable than methyl thiocyanate. Specifically, Berthelot[12,26] found that ethyl isothiocyanate was 38·5 kJ/mol, 9·2 kcal/mol more stable than ethyl thiocyanate. With the value for ethyl thiocyanate (Table 10) of 107·8 kJ/mol, 25·8 kcal/mol, the heat of formation of ethyl isothiocyanate is then 69·3 kJ/mol, 16·6 kcal/mol.

Another method of calculating the thermochemical properties of ethyl isothiocyanate is to assume that the difference between ethyl isothiocyanate and ethyl thiocyanate is the same as the difference between methyl isothiocyanate and methyl thiocyanate, equation (31)

$$CH_3CH_2(NCS) - CH_3CH_2(SCN) = CH_3(NCS) - CH_3(SCN) \qquad (31)$$

Therefore,

$$CH_3CH_2(NCS) = CH_3CH_2(SCN) + CH_3(NCS) - CH_3(SCN) \qquad (32)$$

TABLE 12. Estimation of the standard molar heat of formation, entropy, and heat capacity of hydrogen isothiocyanate or isothiocyanic acid (HNCS) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^\theta$		S^θ		c_p^θ		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
127·5	30·5	247·9	59·3	46·4	11·1	Measured[17,18] and reviewed[1]
132·1	31·6					Measured[17–19] and reviewed[12]
		247·0	59·1	53·1	12·7	Atom additivity
132·1	31·6	247·9	59·3	46·4	11·1	Recommended value

TABLE 13. Estimation of the standard molar heat of formation, entropy, and heat capacity of methyl isothiocyanate (CH_3NCS) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
114·6	27·42					Measured[20-23] and reviewed[12]
133·3	27·10					
		289·7	69·3	65·2	15·6	Measured[24,25] and reviewed[12]
		289·3	69·2	76·1	18·2	Atom additivity
		287·2	68·7	69·0	16·5	Hydrogen isocyanate + CH_2 atomic increment[3]
113·3	27·10	289·7	69·3	65·2	15·6	Recommended value

The thermochemical properties of ethyl isothiocyanate calculated from equation (32), and from the thermochemical properties of ethyl thiocyanate (Table 10), methyl isothiocyanate (Table 13), and methyl thiocyanate (Table 9) are summarized in Table 14.

D. Vinyl Isothiocyanate

No experiments have been reported on the thermochemical properties of vinyl thiocyanate. An estimate of the thermochemical properties of vinyl thiocyanate has been made, assuming that the difference between vinyl isothiocyanate and vinyl thiocyanate is the same as the difference between methyl isothiocyanate and methyl thiocyanate, equation (33)

$$CH_2CH(NCS) - CH_2CH(SCN) = CH_3(NCS) - CH_3(SCN) \quad (33)$$

Therefore,

$$CH_2CH(NCS) = CH_2CH(SCN) + CH_3(NCS) - CH_3(SCN) \quad (34)$$

The thermochemical properties of vinyl isothiocyanate calculated from equation (34) and from the thermochemical properties of vinyl thiocyanate (Table 11), methyl isothiocyanate (Table 13), and methyl thiocyanate (Table 9) are summarized in Table 15.

E. Phenyl Isothiocyanate

Bertholet has measured the heat of combustion of phenyl isothiocyanate[1,12,26]. Stull, Westrum, and Sinke[1] have listed the heat of formation of liquid phenyl isothiocyanate to be 214·4 kJ/mol, 51·3 kcal/mol. The boiling point[11] is 494 K, 221 °C. From equation (21), ΔH_{vap} = 59·9 kJ/mol, 14·1 kcal/mol. The heat of formation of phenyl isothiocyanate in the ideal gas state is then 273·4 kJ/mol, 65·4 kcal/mol.

The thermochemical properties of phenyl isothiocyanate can also be estimated by assuming that the difference between phenyl isothiocyanate and phenyl thiocyanate is the same as the difference between methyl isothiocyanate and methyl thiocyanate equations (35) and (36)

$$Ph(NCS) - Ph(SCN) = CH_3(NCS) - CH_3(SCN) \quad (35)$$

Therefore,

$$Ph(NCS) = Ph(SCN) + CH_3(NCS - CH_3(SCN) \quad (36)$$

The thermochemical properties of phenyl isothiocyanate calculated from equation (36) and from the thermochemical properties of phenyl

TABLE 14. Estimation of the standard molar heat of formation, entropy, and heat capacity of ethyl isothiocyanate (CH_3CH_2NCS) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
69·3	16·6					Bertholet's[12,26] measurement of $CH_3CH_2(NCS) - CH_3CH_2(SCN)$ and recent value for $CH_3CH_2(SCN)$ (Table 10)
87·8	21·0	331·1	79·2	87·8	21·0	$CH_3CH_2(NCS) - CH_3CH_2(SCN) = CH_3(NCS) - CH_3(SCN)$
		329·0	78·7	88·0	21·0	Methyl isothiocyanate + CH_2 atomic increment[3]
78·6	18·8	331·1	79·2	87·8	21·0	Recommended value

TABLE 15. Estimation of the standard molar heat of formation, entropy and heat capacity of vinyl isothiocyanate (CH_2CHNCS) and phenyl isothiocyanate (PhNCS) in the ideal gas state at 298·15 K (25 °C)

$\Delta_f H^0$		S^0		c_p^0		
kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
Vinyl isothiocyanate						
204·9	49·0	302·2	72·3	73·2	17·5	$CH_2CH(NCS) - CH_2CH(SCN) = CH_3(NCS) - CH_3(SCN)$ and recommended value
Phenyl isothiocyanate						
273·4	65·4					$\Delta_f H$ (liquid)[1,12,26] + estimated ΔH_{vap}
245·4	58·7	363·7	87·0	99·9	23·9	$Ph(NCS) - Ph(SCN) = CH_3(NCS) - CH_3(SCN)$
259·4	62·1	363·7	87·0	99·9	23·9	Recommended value

TABLE 16. Measured and estimated standard molar heats of formation, entropies, and heat capacities of hydrogen-, methyl-, ethyl-, vinyl- and phenyl- cyanates, isocyanates, thiocyanates, and isothiocyanates in the ideal gas state at 298·15 K (25° C)

Compound	$\Delta_f H^0$		S^0		c_p^0		Table
	kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	
Cyanates							
Hydrogen (cyanic acid)	−58·5	−14·0	230·3	55·1	44·3	10·6	1
Methyl	−33·9	−8·1	283·0	67·7	67·7	16·2	2
Ethyl	−69·4	16·6	326·1	78·0	88·6	21·2	2
Vinyl	57·7	13·8	295·5	70·7	75·7	18·1	3
Phenyl	98·2	23·5	357·0	85·4	102·4	24·5	3
Isocyanates							
Hydrogen (isocyanic acid)	−100·7	−24·4	237·8	56·9	45·1	10·8	4
Methyl	−57·1	−13·7	283·0	67·7	67·7	16·2	5
Ethyl	−85·0	−20·3	322·3	77·1	90·5	21·6	6
Vinyl	80·9	19·4	295·5	70·7	75·7	18·1	7
Phenyl	121·6	29·1	357·0	85·4	102·4	24·5	7

Thiocyanates							
Hydrogen (thiocyanic acid)	175·1	41·9	240·4	57·5	45·6	10·9	8
Methyl	133·3	31·9	299·3	71·6	72·7	17·4	9
Ethyl	107·8	25·8	340·7	81·5	95·3	22·8	10
Vinyl	224·9	53·8	311·8	74·6	80·7	19·3	11
Phenyl	265·4	63·5	373·3	89·3	107·4	25·7	11
Isothiocyanates							
Hydrogen (isothiocyanic acid)	132·1	31·6	247·9	59·3	46·4	11·1	12
Methyl	113·3	27·1	289·7	69·3	65·2	15·6	13
Ethyl	78·6	18·8	331·1	79·2	87·8	21·0	14
Vinyl	204·9	99·0	302·2	72·3	73·2	17·5	15
Phenyl	259·4	62·1	363·7	87·0	99·9	23·9	15

thiocyanate (Table 11), methyl isothiocyanate (Table 13), and methyl thiocyanate (Table 9) are summarized in Table 15.

VI. SUMMARY OF THERMOCHEMICAL PROPERTIES OF CYANATES, ISOCYANATES, AND THEIR THIO DERIVATIVES

For convenience, the measured and estimated heats of formation, entropies, and heat capacities discussed in the previous sections have been collected in Table 16.

VII. GROUP VALUES FOR ESTIMATING THE THERMOCHEMICAL PROPERTIES OF CYANATES, ISOCYANATES, AND THEIR THIO DERIVATIVES BY GROUP ADDITIVITY

The principles and use of group additivity have been described in considerable detail elsewhere[3-7,10]. A simple example will be given here. Suppose it is necessary to calculate the heat of formation of *n*-propyl cyanate. *n*-Propyl cyanate is made up of the following groups:

$$CH_3CH_2CH_2OCN = [C—C,H_3] + [C—C_2,H_2] + [C—C,H_2,O] + [O—C,CN] \quad (37)$$

The values for the [C—C, H_3], [C—C_2, H_2], and [C—C, H_2, O] groups are already available[4,10], so it is necessary to obtain a value for the [O—C, CN] group. This group occurs in methyl cyanate:

$$CH_3OCN = [C—H_3,O] + [O—C,CN] \quad (38)$$

The heats of formation of CH_3OCN (Table 16) and the [C—H_3, O] group[10] are known, so the value of the [O—C, CN] group is found from equation (39)

$$[O—C,CN] = CH_3OCN - [C—CH_3,O] \quad (39)$$

to be 8·36 kJ/mol, 2 kcal/mol. Substitution of this group value and the other known group values in equation (37) gives the heat of formation of *n*-propyl cyanate to be −88·6 kJ/mol, −21·2 kcal/mol.

Values of the thermochemical properties of the [O—C, CN] groups were calculated from methyl cyanate and other groups as indicated in Table 17.

TABLE 17. Group values for estimating the thermochemical properties of cyanates, isocyanates, thiocyanates, and isothiocyanates in the ideal gas state at 298·15 K (25 °C)

Group	Source molecule	$\Delta_f H^\theta$		S^θ		c_p^θ	
		kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)
O—C, CN	CH_3OCN	8·4	2·0	165·1	39·5	41·8	10·0
O—C_d, CN	CH_2CHOCN	31·4	7·5	180·2	43·1	54·3	13·0
O—C_B, CN	PhOCN	29·3	7·0	122·1	29·2	34·7	8·3
C—C, H_2, NCO	CH_3CH_2NCO	−42·6	−10·2	204·4	48·9	64·4	15·4
C_d—H, NCO	CH_2CHNCO	7·9	1·9	180·2	43·1	54·8	13·1
C_B—NCO	PhNCO	5·8	1·4	122·0	29·2	34·7	8·3
S—C, CN	CH_3SCN	175·6	42·0	182·2	43·4	46·8	11·2
S—C_d, CN	CH_2CHSCN	198·6	47·5	196·5	47·0	59·4	14·2
S—C_B, CN	PhSCN	196·5	47·0	138·4	33·1	39·7	9·5
C—C, H_2, NCS	CH_3CH_2NCS	120·8	28·9	213·2	51·0	61·9	14·8
C_d—H, NCS	CH_2CHNCS	178·5	42·7	186·8	44·7	51·8	12·4
C_B—NCS	PhNCS	190·6	45·6	122·9	29·4	32·2	7·7

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CHAPTER 7

Mass spectra of cyanates, isocyanates, and related compounds

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I. GENERAL COMMENTS

This chapter discusses the mass spectra of cyanates, isocyanates, thiocyanates, isothiocyanates, selenocyanates and isoselenocyanates. The systematic investigations of the mass spectra of these six classes of compound were carried out by four different groups of chemists in the period from 1963 to 1975 as can be seen from Table 1.

TABLE 1. Main investigations on the mass spectra of cyanates, isocyanates and related compounds

Group	Investigators	Year	Reference
—N=C=S	Kjær, Djerassi *et al.*	1963	1
—N=C=S	Kjær, Djerassi *et al.*	1965	2
—O—C≡N —N=C=O —S—C≡N —N=C=S	Jensen *et al.*	1966	3
—N=C=O	Ruth and Philippe	1966	4
—Se—C≡N	Agenäs *et al.*	1968	5, 6
—S—C≡N	Agenäs	1969	7
—Se—C≡N	Agenäs	1969	8, 9
—Se—C≡N —N=C=Se	Jensen *et al.*	1975	10

The results of the earlier investigations[1–4] are reported in most textbooks on mass spectrometry, one of which presents a detailed discussion of the mass spectra of isocyanates and isothiocyanates[11].

The aim of this review is partly to describe the electron impact induced decompositions of the six types of compound, and partly to compare the mass spectral behaviour of the six different functional groups. The latter purpose has determined the way in which the mass spectra are presented in the figures.

Use of the term *α-cleavage* is in this review restricted to *α-fissions* with charge retention on the functional group containing fragment. Thus, the process:

$$R{-}CH_2{-}N{=}C{=}O]^{+\bullet} \longrightarrow R^{\bullet} + CH_2{=}\overset{+}{N}{=}C{=}O$$

is according to this definition an *α-cleavage*, whereas the complementary *α-fission*:

$$R{-}CH_2{-}N{=}C{=}O]^{+\bullet} \longrightarrow R^{+} + {}^{\bullet}CH_2{-}N{=}C{=}O$$

is not.

Finally, it should be noted that the mass spectra of the selenium compounds are reduced corresponding to a 100% content of the ^{80}Se isotope. This makes the mass spectra more clear and facilitates the comparisons with the spectra of the oxo- and thio-analogues.

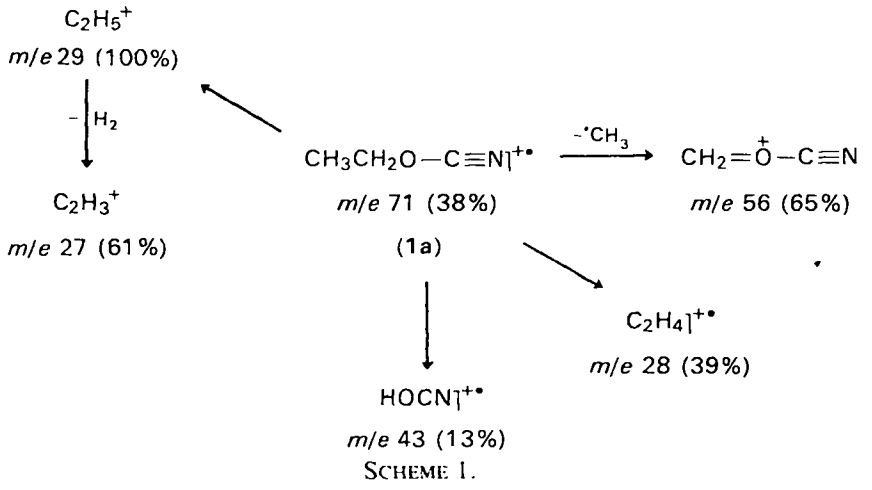
II. CYANATES

A. Alkyl Cyanates[3]

The facile isomerization of alkyl cyanates to isocyanates requires the utmost care when recording the mass spectrum of an alkyl cyanate. If the mass spectrum obtained differs from that of the corresponding isocyanate, significant isomerization during the introduction of the sample can be excluded. But if the two mass spectra are almost identical, the possibility of isomerization has to be taken into consideration. The two extremes are shown in Figures 1 and 2. The mass spectra (Figure 1) of ethyl cyanate (**1a**) and ethyl isocyanate (**1b**) display well-defined differences, whereas the mass spectra (Figure 2) of hexyl cyanate (**2a**) and hexyl isocyanate (**2b**) are hardly discernible.

The mass spectra of 10 alkyl cyanates and those of the corresponding 10 alkyl isocyanates have been examined by Jensen and coworkers[3]. From the reported spectra it can be seen that it is not possible to distinguish between butyl, pentyl, hexyl and heptyl cyanates and isocyanates by mass spectrometry. The mass spectra of ethyl, propyl, isopropyl, *s*-butyl, isobutyl and neopentyl cyanates and isocyanates are sufficiently different for a distinction between the two classes of compound by mass spectrometry to be possible. Finally, since the alkyl cyanates investigated (with the exception of hexyl and heptyl cyanates) can be purified by gas chromatography without isomerization[3], the combined g.l.c.–m.s. analysis is probably the best method for detection and identification of the lower alkyl cyanates.

The mass spectrum (Figure 1) of ethyl cyanate (**1a**) displays peaks corresponding to the fragmentation scheme:



SCHEME 1.

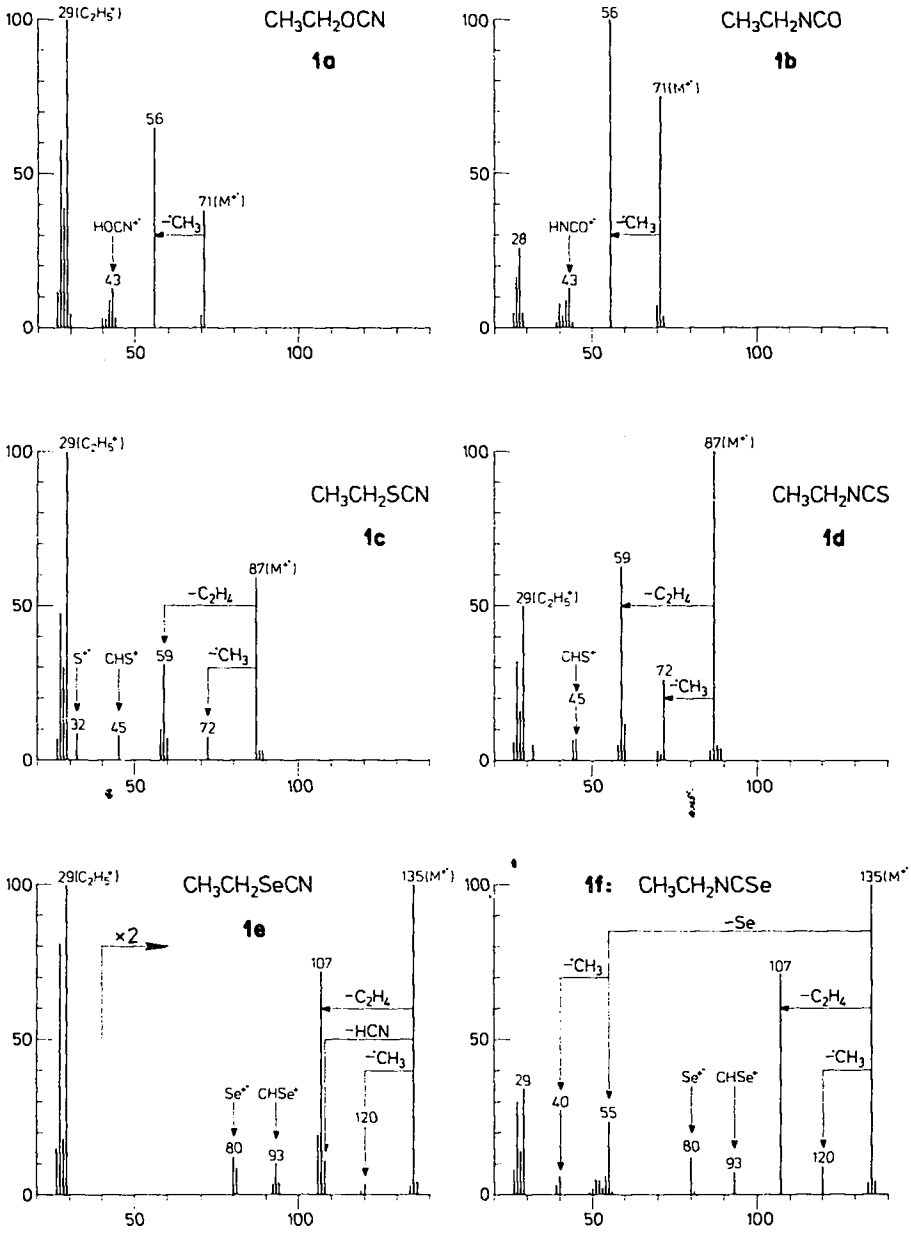


FIGURE 1. Mass spectra of alkyl cyanates and isocyanates.

Propyl cyanate behaves similarly but the spectrum displays in addition peaks corresponding to the decomposition of the propyl cation. α-Branched alkyl cyanates (isopropyl and *s*-butyl cyanate) display highly abundant α-cleavage ions ($CH_3CH{=}\overset{+}{O}{-}C{\equiv}N$, *m/e* 70), whereas β-branching (isobutyl and neopentyl cyanates) apparently impedes the α-cleavage (cf. Section III.A).

The striking resemblance between the mass spectra (Figure 2) of hexyl cyanate (**2a**) and hexyl isocyanate (**2b**) can be due either to an isomerization of hexyl cyanate to hexyl isocyanate or to a fragmentation triggered entirely by the alkyl groups and not by the functional group. The latter possibility is supported by the fact that about 85% of the total ion current is in both cases due to ions containing only hydrogen and carbon atoms. However, the remaining 15% of the total ion current is in both cases mainly due to two types of ions, M − C_2H_4 (*m/e* 99, *c.* 10% $\sum_{25}$) and the α-cleavage products (*m/e* 56, *c.* 4% $\sum_{25}$). This similarity in the abundance of the functional group containing ions indicates that hexyl cyanate isomerizes to hexyl isocyanate. Comparison with the mass spectra (Figure 2) of hexyl thiocyanate (**2c**) and of hexyl isothiocyanate (**2d**) leads to the same conclusion. No appreciable isomerization of **2c** to **2d** takes place, since the mass spectra of **2c** and **2d** are very different. Further, whereas **2d** forms abundant ions corresponding to M − C_2H_4 (*m/e* 115, 13·8% $\sum_{25}$) and to the α-cleavage product (*m/e* 72, 5·8% $\sum_{25}$), **2c** does not.

It would appear reasonable to conclude from this evidence that hexyl cyanate isomerizes to hexyl isocyanate in the inlet system, were it not for the fact that the thermal stabilities of the alkyl cyanates increase with the chain length. That is to say, since the rather unstable ethyl cyanate can be introduced into the mass spectrometer without isomerization, the more stable hexyl cyanate should not isomerize either under the same conditions.

It seems at the present stage that we cannot give a satisfactory explanation of the observation that the mass spectra of the higher alkyl cyanates and isocyanates are practically identical.

B. Phenyl Cyanate[3]

The mass spectrum (Figure 3) of phenyl cyanate (**3a**) is rather simple. The base peak (*m/e* 77) is due to the phenyl cation formed by expulsion of a OCN radical from the molecular ion. The *m/e* 77 peak is as usual accompanied by an intense peak at *m/e* 51 ($C_4H_3^+$). In competition with the loss of ·OCN the molecular ion eliminates carbon monoxide leading to an ion of mass 91. This cation radical undergoes further degradation

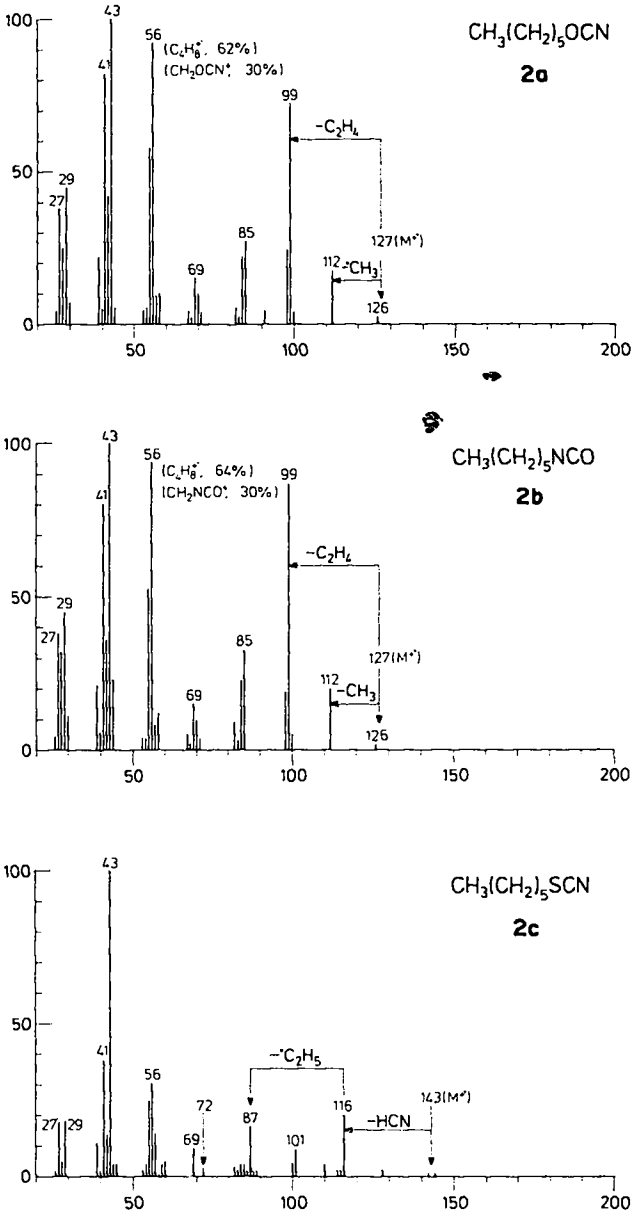


FIGURE 2. Mass spectra of alkyl cyanates and isocyanates.

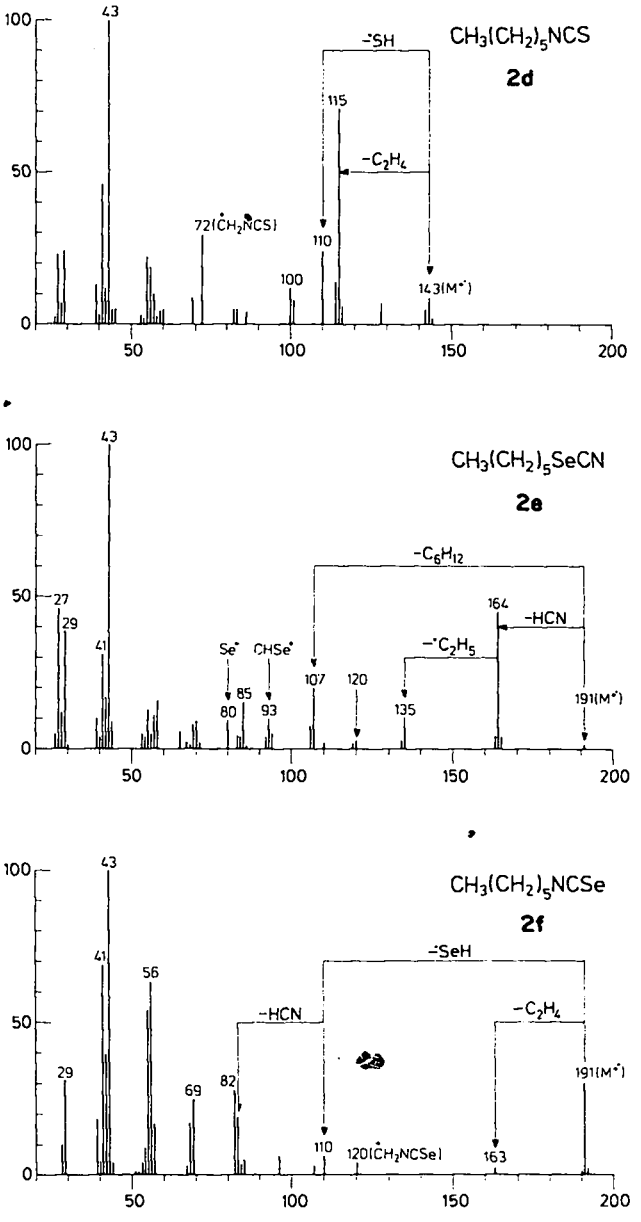


FIGURE 2 (*continued*).

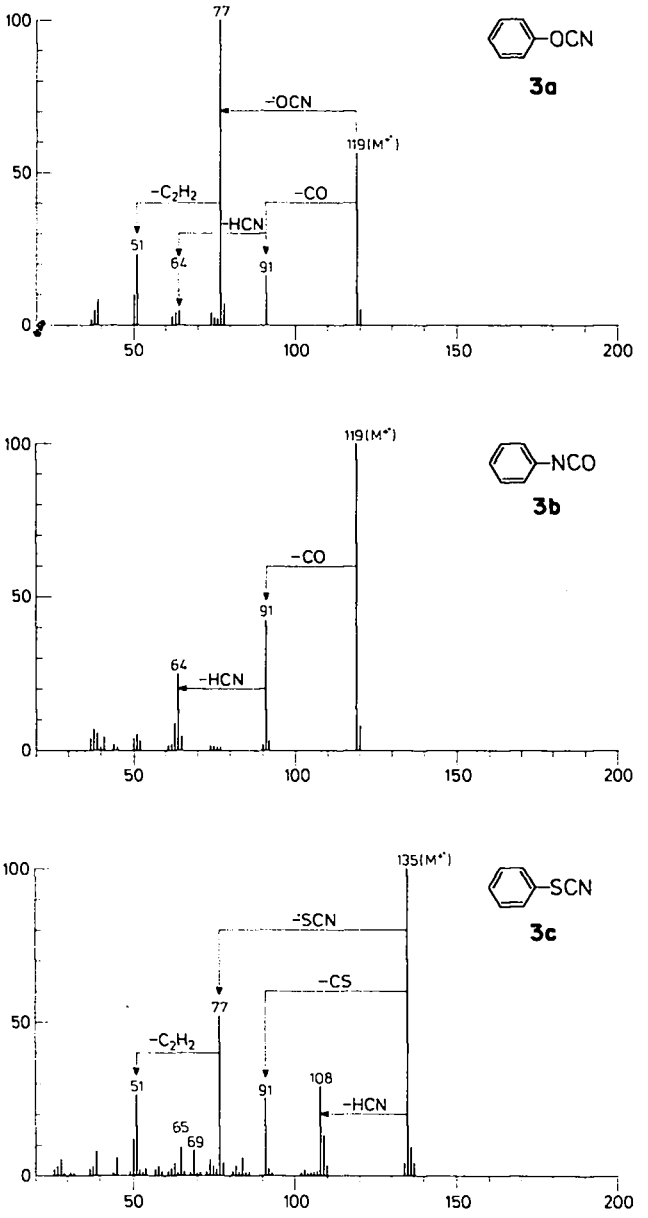


FIGURE 3. Mass spectra of phenyl cyanates and isocyanates.

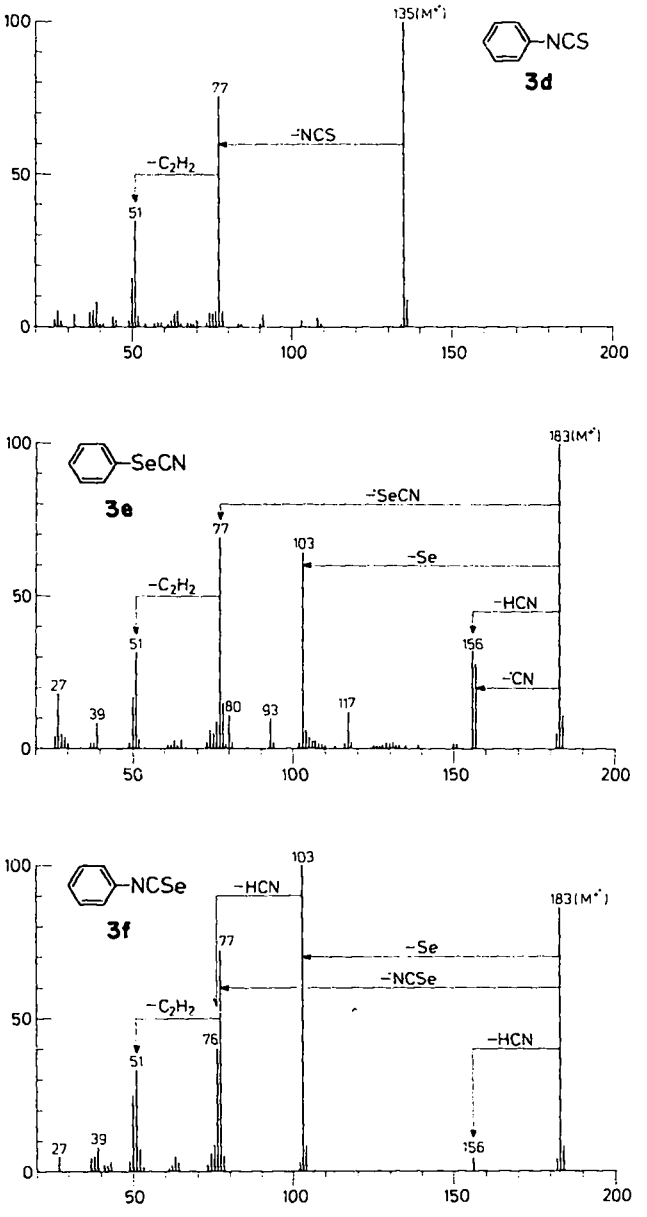


FIGURE 3 (*continued*).

by loss of HCN. This two step process ($M^{+\cdot} \rightarrow 91^{+\cdot} \rightarrow 64^{+\cdot}$)—being of minor importance in the case of **3a**—constitutes the main decomposition path of phenyl isocyanate (**3b**). The initial loss of CO from **3a** requires a skeletal rearrangement of the molecular ion.

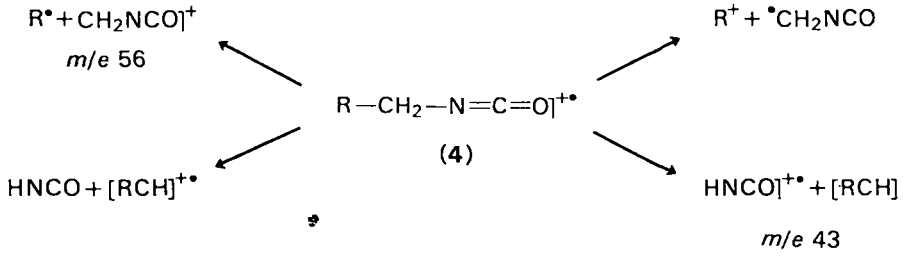
III. ISOCYANATES

The mass spectra of various alkyl and aryl isocyanates have been recorded on a conventional mass spectrometer[3] (Atlas CH4) and on a time-of-flight instrument[4] (Bendix Model 14-101). The spectra obtained on the two instruments are in fair agreement, showing the same decomposition pattern of the isocyanates, even though the relative peak intensities vary. Generally, in the time-of-flight mass spectra of the isocyanates the lighter ions are more abundant, in contrast to what is normally observed[1,2].

The mass spectra given in Figures 1–3 were recorded on conventional instruments.

A. Alkyl Isocyanates[3,4]

The electron impact induced decompositions of the lower alkyl isocyanates are shown in Scheme 2.



SCHEME 2.

Rupture of the $R-CH_2$ bond in **4** with charge retention on CH_2NCO (α-cleavage) is the most important process for $R = CH_3$ and C_2H_5, whereas the complementary reaction—formation of R^+ and $^{\cdot}CH_2NCO$—is the more important for $R = n\text{-}C_3H_7$ and $i\text{-}C_3H_7$, as seen from Table 2.

According to Stevenson's rule[14,15] the positive charge will remain on the fragment of lower ionization potential. From the data reported in Table 2 the IP of $^{\cdot}CH_2NCO$ can be estimated to be in the range of 8·1 to 8·4 eV. This is supported by the low voltage mass spectra of butyl iso-

cyanate which show that the $[CH_2NCO^+]/[C_3H_7^+]$ ratio decreases from 0·23 at 20 eV to 0·03 at 10 eV (unpublished results from the authors' laboratory).

TABLE 2. Competitive formation of CH_2NCO^+ and R^+ from $R{-}CH_2{-}N{=}C{=}O$

R	$[CH_2NCO^+]^a$	$[R^+]^a$	$IP(R^\cdot)^b$
CH_3	36·7	—	9·8 eV
C_2H_5	32·2	10·0	8·4 eV
n-C_3H_7	6·7	16·2	8·1 eV
i-C_3H_7	5·9	33·7	7·5 eV

[a] % $\sum_{25}$ (Reference 3)
[b] Ionization potentials of the alkyl radicals [13]

The remaining two decomposition modes of the lower alkyl isocyanates are also complementary. Cleavage of the bond between the alkyl and the functional group with concomitant transfer of a hydrogen atom leads to HNCO and a C_nH_{2n} molecule, either of which may retain the charge. The IP of HNCO is unknown, but it is probably high. (The IP of HNCS has been determined[16] to be 10·6 eV). The abundance of the HNCO and C_nH_{2n} ions from various alkyl isocyanates are listed in Table 3 together with the IP of the alkenes which may be formed. The 'Stevenson's rule correlation' is less unambiguous than in the case of the α-fission. This can be due to the mechanism of the process. If the C_nH_{2n} fragments are not alkenes the basis of the comparison between abundance and ionization potential disappears.

TABLE 3. Competitive formation of $HNCO^{+\cdot}$ and $C_nH_{2n}^{+\cdot}$ from $C_nH_{2n+1}{-}N{=}C{=}O$

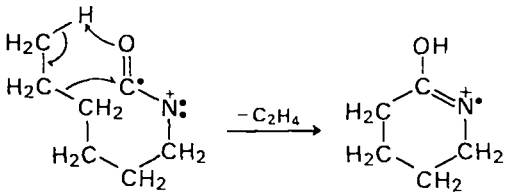
Alkyl	$[HNCO^{+\cdot}]^a$	$[C_nH_{2n}^{+\cdot}]^a$	Alkene	IP (Alkene)[b]
C_2H_5	4·7	9·4	$CH_2{=}CH_2$	10·5 eV
n-C_3H_7	0·1	8·1	$CH_2{=}CHCH_3$	9·7 eV
i-C_3H_7	5·8	14·3	$CH_2{=}CHCH_3$	9·7 eV
n-C_4H_9	1·1	8·4	$CH_2{=}CHCH_2CH_3$	9·6 eV
i-C_4H_9	—	3·8	$CH_2{=}C(CH_3)_2$	9·2 eV
s-C_4H_9	—	6·1	$CH_3CH{=}CHCH_3$	9·1 eV

[a] % $\sum_{25}$ (Reference 3)
[b] Ionization potentials from Reference 13.

α-Branching in the alkyl group favours α-cleavage. Thus 46·1% of the total ion current from isopropyl isocyanate is due to the M − CH_3 ions (*m/e* 70, CH_3CHNCO^+). *s*-Butyl isocyanate can undergo α-cleavage by loss of $^{\bullet}CH_3$ (*m/e* 84, $CH_3CH_2CHNCO^+$, 3·9% $\sum_{25}$) as well as by loss of $^{\bullet}CH_2CH_3$ (*m/e* 70, 40·7% $\sum_{25}$).

β-Branching in the alkyl group impedes the α-cleavage. In the case of isobutyl isocyanate this is due to the competition from the isopropyl cation formation as stressed above. Not surprisingly neopentyl isocyanate displays only a small α-cleavage peak (1·3% $\sum_{25}$), but the peak corresponding to the *t*-butyl ion formed in competition with the α-cleavage is also small (*m/e* 57, 4·6% $\sum_{25}$). The mass spectrum of neopentyl isocyanate displays more peculiarities. About 15% of the total ion current is due to M − C_2H_5. This process necessitates a skeletal rearrangement.

The mass spectrum (Figure 2) of hexyl isocyanate (**2b**) displays an intense peak at *m/e* 99 (10·7% $\sum_{25}$) corresponding to M = 28. The mass spectrum of heptyl isocyanate displays a peak at *m/e* 99 of similar intensity; also the time-of-flight mass spectra[4] of octyl isocyanate and octadecyl isocyanate display intense *m/e* 99 peaks. The elemental composition of the *m/e* 99 ion formed from octyl isocyanate has been found to be C_5H_9NO by high resolution mass measurements[4]. Assuming the elimination of ethene from hexyl isocyanate, the formation of the C_5H_9NO ions can be formulated as the rearrangement:



(**2b**) (**5**) *m/e* 99

B. Phenyl Isocyanate[3,4]

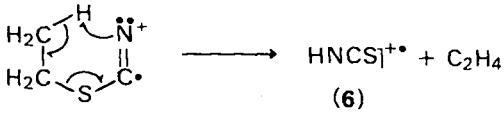
The mass spectrum (Figure 3) of phenyl isocyanate (**3b**) is dominated by three peaks: *m/e* 119 (M, 40·1% $\sum_{25}$), 91 (M—CO, 16·9% $\sum_{25}$) and 64 (M—CO—HCN, 10·1% $\sum_{25}$). The time-of-flight mass spectra of *o*-, *m*-, and *p*-tolyl isocyanate display peaks corresponding to M, M—H, M—CO, M—H—CO, M—CO—HCN and M—H—CO—HCN[4]. The M—H ions are probably isocyanatotropylium ions[11].

IV. THIOCYANATES

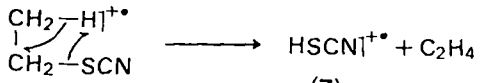
A. Alkyl Thiocyanates[3]

The mass spectra of the lower straight-chain alkyl thiocyanates (ethyl, propyl, and butyl) are dominated by peaks corresponding to the alkyl cations and their daughter ions. The molecular ion peaks are of decreasing intensity, being totally absent in the case of hexyl thiocyanate (**2c**).

The mass spectrum (Figure 1) of ethyl thiocyanate (**1c**) displays a minor peak at *m/e* 72 (CH_2SCN^+) and a larger at *m/e* 59 ($M-C_2H_4$). The former corresponds to the product of the α-cleavage. Two mechanisms (Scheme 3) can be proposed for the ethene elimination from **1c**, involving hydrogen rearrangement to nitrogen and sulphur, respectively.



(**6**)



(**7**)

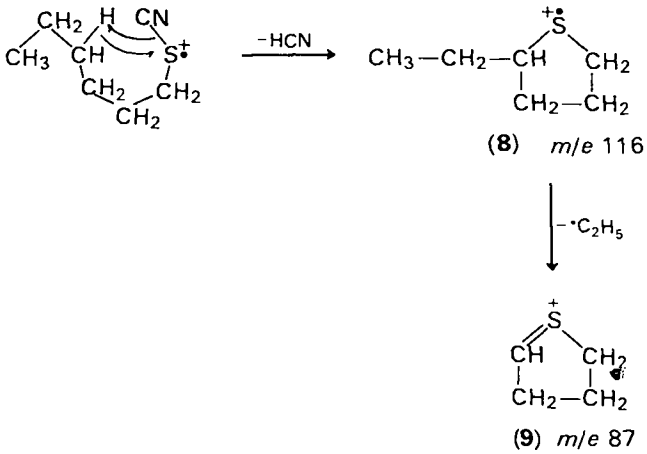
SCHEME 3.

It is often possible to determine the structure of ions formed by fragmentations and rearrangements by comparing the ΔH_f for a given ion with the appearance potential. But, since the ions **6** and **7** have the same heat of formation, it is not possible from the appearance potential alone to determine which process is the most likely. The same ambiguity makes it impossible to decide from this evidence whether $HNCS^{+\cdot}$ or $HSCN^{+\cdot}$ is formed by the ethene elimination from ethyl isothiocyanate (Figure 1, **1d**)[17].

α-Cleavage and $HSCN^{+\cdot}$ formation are unimportant for the higher alkyl thiocyanates. The mass spectrum (Figure 2) of hexyl thiocyanate (**2c**) displays peaks at *m/e* 116 (M—HCN) and at *m/e* 87. A 'metastable peak' indicates the transition $116^+ \rightarrow 87^+$. Since the elimination of HCN from the molecular ion is of no importance in the fragmentation of the lower homologues, the mechanism illustrated on the next page (Scheme 4) appears likely.

B. Phenyl Thiocyanate[7]

The mass spectrum (Figure 3) of phenyl thiocyanate (**3c**) resembles that of phenyl cyanate (**3a**). Both compounds eliminate the functional group



SCHEME 4.

followed by loss of C_2H_2. The elimination of CS from **3c** corresponds to the loss of CO from **3a**. Additionally, phenyl thiocyanate undergoes loss of ·CN and elimination of HCN to produce the ions of mass 109 and 108.

V. ISOTHIOCYANATES

A. *Alkyl Isothiocyanates*[1-3]

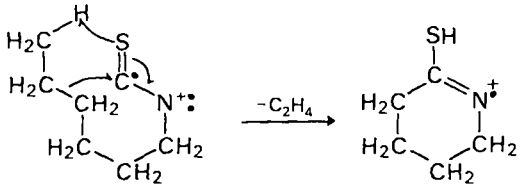
The mass spectra of alkyl isothiocyanates display intense molecular ion peaks for the lower homologues (CH_3NCS to $C_5H_{11}NCS$) and even hexadecyl isothiocyanate gives rise to a 1% molecular ion peak[1]. Hydrocarbon fragments are responsible for peaks between *m/e* 27 and 43 in most spectra, the intensities of which increase when the temperature of the inlet system is raised[3].

The mass spectrum (Figure 1) of ethyl isothiocyanate (**1d**) displays intense peaks at *m/e* 87 (M, 29·0% $\sum_{25}$), 72 (CH_2NCS^+, 7·5% $\sum_{25}$), 59 ($HNCS^{+\cdot}$ or $HSCN^{+\cdot}$, 18·3% $\sum_{25}$), 29 ($C_2H_5^+$) and 27 ($C_2H_3^+$).

The formation of CH_2NCS^+ (α-cleavage) is an important process for all straight chain alkyl isothiocyanates, whereas alkene elimination (to give *m/e* 59) is only important in the case of **1d**.

The mass spectrum (Figure 2) of hexyl isothiocyanate (**2d**) contains two peaks (*m/e* 115, M, $-C_2H_4$, 13·8% $\sum_{25}$, and *m/e* 110, M − SH, 4·6% $\sum_{25}$) which are characteristic for the higher straight chain alkyl isothiocyanates. Loss of ·SH from the molecular ion requires that the alkyl chain is to be at least five carbon atoms long, whereas the formation of 115^+ requires a six-carbon chain and first takes place with hexyl iso-

thiocyanate. Deuterium-labelling experiments[2] indicate that the 115^+ ion contains the NCS group, the four next methylene groups and a hydrogen atom from the sixth methylene group. In accordance with this, the following mechanism appears likely:



(2b) (10) *m/e* 115

B. Aromatic Isothiocyanates[1]

Phenyl isothiocyanate (**3d**) undergoes a simple electron impact induced decomposition, the major peaks (Figure 3) corresponding to M, M—NCS and M—NCS—C_2H_2 ions. Benzyl isothiocyanate fragments in a similar way, forming a very abundant $C_7H_7^+$ ion (*m/e* 91).

VI. SELENOCYANATES

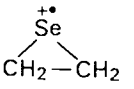
The mass spectra of aromatic and heteroaromatic selenocyanates have been subject to detailed investigations by Agenäs[5,6,8,9], but no description of the mass spectrometry of alkyl selenocyanates has previously been published.

Selenium has six stable natural isotopes: ^{74}Se (0·87%), ^{76}Se (9·02%), ^{77}Se (7·58%), ^{78}Se (23·52%), ^{80}Se (49·82%) and ^{82}Se (9·19%)[18]. The natural abundance of the ^{74}Se isotope is so low that it is unimportant for the appearance of the mass spectrum. The presence of five relatively abundant selenium isotopes makes it easy to recognize a selenium containing ion and to determine the number of selenium atoms incorporated. Knowing that a given ion contains a selenium atom the information contained in the isotope cluster is no longer necessary, and we have therefore reduced the mass spectra of the selenocyanates and isoselenocyanates corresponding to a 100% content of the ^{80}Se isotope. As selenium contains no isotopes of mass 79 and 81 this reduction can be made simply by increasing the intensity of the ^{80}Se peaks by a factor of 2, and removing the peaks corresponding to ions with other Se isotopes.

A. Alkyl Selenocyanates[10]

The mass spectrum (Figure 1) of ethyl selenocyanate (**1e**) is typical for the lower alkyl selenocyanates. Due to the high mass number of selenium these spectra are divided into two parts, the light-ion half displaying peaks corresponding to the very abundant hydrocarbon ions, and the heavy-ion half due to less abundant selenium containing ions.

The abundances of the molecular ions of the lower alkyl selenocyanates are high, whereas the α-cleavage ions (*m/e* 120 from **1e**) are unimportant. Loss of HCN from the molecular ion was observed in the mass spectrum of **2c**, but not in the spectra of the lower thiocyanates. All alkyl selenocyanates undergo this reaction, but probably following different mechanisms. Thus, hexyl selenocyanate (**2e**) consecutively eliminates HCN and $^{\cdot}C_2H_5$ as does the thiocyanate (**2c**). These processes may be interpreted by a mechanism similar to that suggested for the sulphur compounds (Scheme 4). The loss of HCN from ethyl selenocyanate (**1e**) must, however, take place by a different mechanism. The M — HCN ion from **1e** may be assigned the structure **11**.



(11)

All alkyl selenocyanates form fairly abundant ions of mass 107 and 106 corresponding to $HSeCN^{+\cdot}$ (or $HNCSe^{+\cdot}$) and $SeCN^{+}$, respectively; in addition $CHSe^{+}$ and $Se^{+\cdot}$ ions are usually formed in moderate abundance.

B Aromatic Selenocyanates[5,6,8–10]

Phenyl selenocyanate (**3e**) fragments primarily by successive losses of $SeCN^{\cdot}$ and C_2H_2 in analogy to the decompositions of **3a**, **3c** and **3d**. M — $^{\cdot}$CN and M — HCN peaks are observed in the mass spectra of phenyl selenocyanate and of phenyl thiocyanate. Compounds **3a** and **3b** eliminate CO and **3c** eliminates CS to give $C_6H_5N^{+\cdot}$ (*m/e* 91), whereas phenyl selenocyanate forms $C_7H_5N^{+\cdot}$ (*m/e* 103) by loss of Se. The *m/e* 103 peak in the mass spectrum of **3e** has been assigned the structure of ionized benzonitrile[5]. If this is correct, $C_6H_5CN^{+\cdot}$ is formed with a minimum of excess energy, since the elimination of HCN from $103^{+\cdot}$ (leading to $76^{+\cdot}$) which is characteristic for the decomposition of benzonitrile[19] (and of phenyl isocyanide[20,21]) is not observed. Introduction of a methyl group

in the *p*-position[5] does not lead to drastic changes of the decomposition pattern.

4-Aminophenyl selenocyanate splits off HSe$^{\bullet}$ upon electron impact, whereas 2- and 3-methyl-4-aminophenyl selenocyanate have M – Se as the base peak[8]. This is in striking contrast to what could have been expected. A strong M – HSe$^{\bullet}$ peak in the mass spectra of 2- and 3-methyl-4-aminophenyl selenocyanate could be explained as tropylium ion formation.

N,N-Dialkyl-4-aminophenyl selenocyanates fragment to a large extent by reactions involving the dialkylamino group[8].

VII. ISOSELENOCYANATES

A. Alkyl Isoselenocyanates[10]

The mass spectra (Figure 1) of ethyl selenocyanate (**1e**) and ethyl isoselenocyanate (**1f**) are qualitatively similar, but the differences are characteristic of the mass spectra of alkyl selenocyanates and isoselenocyanates. One significant difference is that the alkyl selenocyanates display M—HCN peaks in their mass spectra (*m/e* 108 from **1e**), whereas the corresponding isoselenocyanates display M—Se peaks (*m/e* 55 from **1f**). The mass spectrum (Figure 2) of hexyl isoselenocyanate (**2f**) resembles the mass spectra of the corresponding isocyanate (**2b**) and isothiocyanate (**2d**) more than that of hexyl selenocyanate (**2e**). Compound **2f** eliminates C_2H_4 as do **2b** and **2d**, forming an ion which can be assigned a structure similar to **5** and **10**. In analogy to the loss of $^{\bullet}$SH from **2d**, hexyl isoselenocyanate undergoes loss of $^{\bullet}$SeH. Assuming that two hydrogens are transferred during the reaction leading to the M – $^{\bullet}$SH ion from **2d**, this ion has been assigned the structure **12**[1]. Loss of HCN from **12** then explains the intense peak at *m/e* 83 in the mass spectrum of **2f**. Loss of $^{\bullet}$H from **13** is supported by a 'metastable peak'.

$$\underset{\textbf{(12)}\ m/e\ 110}{CH_3CH{=}CHCH_2CH_2CH_2{-}\overset{+}{N}{\equiv}CH} \longrightarrow \underset{\textbf{(13)}}{C_6H_{11}^{+}} \longrightarrow \underset{m/e\ 82}{C_6H_{10}^{+\bullet}}$$

B. Phenyl Isoselenocyanate[10]

The differences in the mass spectra (Figure 3) of phenyl selenocyanate (**3e**) and of phenyl isoselenocyanate (**3f**) reflect the differences in the structures of the two functional groups. **3f** undergoes loss of Se followed by elimination of HCN. The latter process was not observed from **3e**.

M — HCN is only of minor importance in the case of **3f** and M − CN is not observed.

VIII. COMPARISONS

It is a well established practice within organic mass spectrometry to make comparisons. The mass spectra of homologues are recorded and compared, and from the similarities (and differences) conclusions are made concerning the mass spectral behaviour of the said class of compound. Much of the argumentation in the preceding paragraphs is actually based upon comparisons. However, when making comparisons it is important to know what is being compared.

TABLE 4. Selected peaks from the mass spectra of butyl isocyanate recorded on various instruments[a]

m/e	Atlas	CH4[b]	Bendix 14–101[c]	AEI MS902[d]	Finnigan 1015[d]
99 (M^+)	3	(3)	5	6	1
98	20	(18)	10	27	5
71	9	(9)	8	8	11
70	17	(17)	8	16	21
56	87	(85)	63	97	100
43	100	(94)	82	100	73
41	100	(100)	82	88	78
30	27	(25)	25	31	21
29	19	(24)	28	15	21
28	34	(34)	70	32	45
27	49	(46)	100	45	65

[a]Intensity relative to that of the base peak.
[b]Figures given in parenthesis are the intensities of the corresponding peaks in the mass spectrum of butyl cyanate. Data from Reference 3.
[c]Reference 4.
[d]Unpublished spectra from the authors' laboratory.

As mentioned previously and as can be seen from Table 4, the mass spectra of the six classes of compound under discussion are very dependent on the instrument. The four mass spectra of butyl isocyanate differ more than the two Atlas CH4 spectra of butyl cyanate and isocyanate. The differences between the four isocyanate spectra are entirely due to differences in instrumentation and in the conditions of recording. If the mass spectra of two isomers recorded on different instruments or under different conditions are different, it is difficult to ascertain which deviations

are due to structure and which to instrumentation. If the mass spectra are very similar, it becomes impossible to distinguish between structural and instrumental effects.

In addition to the comparisons between the mass spectra of the six classes of compound made above, the following can be said.

The ethyl derivatives display prominent alkyl peaks (*m/e* 29) in the mass spectra (Figure 1) of **1a**, **1c** and **1e**, increasing in the order —OCN, —SCN, —SeCN. α-Cleavage decreases in importance, whereas C_2H_4 elimination increases in the same order.

The mass spectra of **1b**, **1d** and **1f** display minor alkyl peaks, increasing in importance in the order —NCO, —NCS, —NCSe. The α-cleavage becomes less important in the same order, whereas loss of ethene is most prominent from the isoselenocyanate.

In general the iso-compounds (**1b**, **1d** and **1f**) display the highest M, M − CH_3 (α-cleavage) and M − C_2H_4 peaks, and the smallest alkyl ion peaks. The mass spectra of the six hexyl derivatives display abundant hydrocarbon ion peaks, *m/e* 43 ($C_3H_7^+$) being the base peak in all spectra. The molecular ion peak is absent in the spectra of **2a**, **2b** and **2c**, small in the spectra of **2d** and **2e**, and abundant only in the case of **2f**.

The elimination of C_2H_4 from $C_6H_{11}NCX$ is most important for X = O, whereas the consecutive losses of HCN and $^{\cdot}C_2H_5$ from $C_6H_{11}XCN$ (X = S and Se) are most important for X = Se.

The fragmentation sequence: $C_6H_5Y^{+\cdot} \rightarrow C_6H_5^+ \rightarrow C_4H_3^+$ is important for all six phenyl analogues with the exception of **3b** (Y = —NCO), which instead undergoes the decomposition: $C_6H_5NCX^{+\cdot} \rightarrow C_6H_5N^{+\cdot} \rightarrow C_5H_4^{+\cdot}$. Loss of CX is also observed from **3a** and **3c**, requiring in both cases a skeletal rearrangement. It is quite unexpected that C_6H_5SCN eliminates CS whereas C_6H_5NCS does not. Loss of CSe has not been observed from **3e** or **3f**.

Whereas the mass spectra of the alkyl compounds (**1a–f** and **2a–f**) revealed various general trends (e.g., α-cleavage is more important for the lower alkyl compounds, gains importance when going from R—XCN to R—NCX, and decreases in the order: X = O, S, Se), the aromatic compounds (**3a–f**) as a group behave less systematically upon electron impact, although each single spectrum is quite simple.

IX. CONCLUSIONS

The mass spectra of cyanates, isocyanates and related compounds can be of interest as a means of identifying these six classes, but they can also be studied in order to interpret the very processes taking place in the ion

source of the mass spectrometer when these types of compound are introduced.

With regard to the first purpose it can be stated that the mass spectra of alkyl thiocyanates, isothiocyanates, selenocyanates and isoselenocyanates can be used as quite dependable fingerprints for the purpose of identification. The mass spectra of the higher alkyl cyanates and isocyanates are too similar to allow a distinction between the two groups, whereas inference about the structure of the alkyl can be made.

The mass spectra of the aromatic compounds are useful for the purpose of identification. The molecular ion peak is important in all spectra.

Regarding the second purpose, our present knowledge of the ion chemistry involved is rather limited. Important information can be obtained in future studies involving high-resolution mass measurements, isotopic labelling, metastable defocusing and low voltage mass spectrometry. Thus we can only encourage reinvestigations in this field of organic mass spectrometry.

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CHAPTER 8

Hydrogen bonding and complex formation

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I. INTRODUCTION

The availability of data on any kind of complexes of organic cyanates and related compounds strongly contrasts the amount of data on the chemical behaviour of these compounds. Also, the literature on metallic coordination compounds of the cyanate and, particularly, thiocyanate ions is incomparably richer than on their organic counterparts. Moreover, the available data were published in widely scattered sources and truly physical facts leading to unequivocal interpretation of the structure of complexes are very scant. For example, we could not find any reference to the structure, established by diffraction methods, of a complex with any organic cyanate or related group as ligand. Hence the writing of any sort of review of complexes of organic cyanates and related compounds is unrewarding and it is not surprising that no such review seems to have been written up to now. The reason for this is probably not the lack of any connection between the complex formation and the chemical reactions of cyanate and related groups. For example, the formation of urethanes from

isocyanates and hydroxylic compounds has great significance for the production of polyurethanes, but nevertheless only very few hard facts were published about the intermediate complexing with the catalyst and only one datum is available about the hydrogen bonding between an isocyanate and a hydroxylic component. Besides the reaction, mechanistic interest in complexes of cyanate and related groups, these complexes offer a number of problems of bonding which originate in the electronic structure of these groups. The atoms in the —N—C—X and —X—C—N (X = O,S,Se) groups are bonded by what may be approximately described as a system of cumulated π orbitals in two orthogonal planes with the σ orbitals in the intersection of the two π planes. In addition, the lone pairs on the nitrogen and the X atoms may interact with π orbitals of appropriate symmetry. The excess electronic charge on the N and X atoms and, in particular, the electrons in lone-pair orbitals with rather low ionization potentials confer on these groups electron donating properties. Since in all of them there are two negatively charged, lone-pair-bearing atoms the problem arises which of them will enter complex bonding. Some results of MO calculations[1-4] are available in the literature and they may serve as an orientation as to which atom may be expected to enter the complex bonding. Reliable, *ab initio* calculations on the HNCO molecule show[1,2] that in HNCO the negatively charged nitrogen atom has a larger gross population than oxygen, carbon being positively charged. The nitrogen lone-pair orbital is also the highest one so that this is likely to be the best site both for electrostatic and charge-transfer donation. The corresponding calculation[4] on HNCS shows again the largest negative charge to be on nitrogen but the highest energy comes with the sulphur n_y lone pair. It is rather unlikely that substitution of alkyl or aryl radicals for hydrogen would reverse the charge distribution although HMO calculations[5] show a larger electronic charge on sulphur in aromatic isothiocyanates. For cyanates only HMO calculations are available[6] which show a larger negative π-electron charge on the oxygen. This atom is very likely also to have the largest overall negative charge, but the difference between N and O may not be large. Thus the prediction of the bonding site from calculated charges is rather uncertain and it would be quite interesting to have experimental evidence as to which atom in cyanate and related groups is actually undergoing complex bonding.

In this chapter we are treating the cyanates along with other related groups mainly because in this way it is possible to compare better their complexing properties. The present division of the subject matter has been adopted mainly for practical reasons, the scarcity of data preventing a more rigorous subdivision.

II. HYDROGEN BONDING

Unlike the cyanides[7] the organic cyanates and related compounds have no major significance as solvents, hence the study of their behaviour as proton acceptors in hydrogen bonding is motivated mainly by the problem of their electronic structure and reactivity. This also includes the question of which atom is actually involved in the hydrogen bond.

Quantities which are most often used to express the hydrogen bonding propensity of a proton acceptor are the difference, $\Delta\nu$, between the stretching frequency, ν_{X-H}, of a proton-donating compound in the gas phase or in an inert solvent and its frequency with the acceptor added, the equilibrium constant of the hydrogen bond formation, K_{ass}, and the enthalpy of formation, ΔH^0. The latter quantities may be determined by various methods[8]. The most commonly used method is infrared spectroscopy and the most often used reference donors are methanol and phenol. By far the easiest obtainable characteristic of hydrogen bonding is the frequency shift, $\Delta\nu_{OH}$, and this has been also mostly used to characterize the hydrogen bonding propensity of the cyanate and related groups.

Thermodynamic quantities of hydrogen bonding have also been determined from infrared data. The most extensive collection of data is given by Martin and coworkers[9]. They have studied the hydrogen bonding of a large number of cyanates of the type ArXCN and RXCN (X = N,O,S,Se) with methanol, phenol, and *p*-chlorophenol in CCl_4 and have included for comparison also the data on the corresponding cyanides and some alkyl thiocyanates obtained by Igarashi and coworkers[10]. Kovač and coworkers have investigated[11] the bonding of some alkyl isothiocyanates with phenol in CCl_4. Apart from this only a few scattered references to cyanates and thiocyanates are found in the literature[12-14]. In general, there is quite good agreement between the data given by various authors. The $\Delta\nu_{OH}$ values for phenol depend in the series RXCN both on R and X. Perhaps the best way of comparing the difference impaired by the atom X are the relative proton accepting propensities (RAP) as defined by Martin and coworkers[9] for R = phenyl.

$$\mathrm{RAP} = \frac{\Delta\nu_{OH}(\mathrm{PhXCN}\ldots\mathrm{HOPh})}{\Delta\nu_{OH}(\mathrm{PhCN}\ldots\mathrm{HOPh})}$$

When this is extended to the RNCX compounds (Table 1) the resulting RAP values show that the cyanate, thiocyanate and isothiocyanate groups are weaker bases than the nitrile, but that isocyanate is the strongest proton accepting group.

TABLE 1. Relative proton accepting propensities (RAP) of phenyl pseudohalides and the phenol OH stretching frequency shifts

Proton acceptor	RAP	$\Delta\nu_{Pho-H}$ (cm^{-1})
PhCN	1	153[a]
PhOCN	0·928	143[a]
PhSCN	0·902	138[a]
PhSeCN	0·941	145[a]
PhNCO	1·18	180[b]
PhNCS	0·56	85[b]

[a] Data from Reference 9.
[b] Data from Reference 13.

The order of propensities as shown by the frequency shifts is also reflected in the thermodynamic quantities. The data for the thermodynamic quantities are not available for the whole series of PhXCN and PhNCX compounds and hence Table 2 contains only two benzene derivatives and two methyl derivatives compared to the cyanides. Combining these data with the fact that there exists an at least roughly linear relationship between the frequency shifts, the association constant K_{ass}, and also the ΔH^0 values the following sequence of decreasing propensity for hydrogen bonding is obtained: —NCO > —CN > —SeCN > —OCN > —SCN > —NCS. In connection with an extended investigation of the infrared

TABLE 2. Frequency shifts and thermodynamic quantities of association between phenol and some organic pseudohalides

Proton acceptor	$\Delta\nu_{OH}$ (cm^{-1})	k_{ass} (l/mol)	G^0 (kcal/mol)	H^0 (kcal/mol)	S^0 (cal/mol deg)
C_6H_5CN[a]	153	4·70	−0·92	−4·62	−12·4
C_6H_5OCN[a]	143	4·57	−0·90	−4·1	−10·7
C_6H_5SCN[a]	138	3·87	−0·79	−3·59	−9·4
MeCN[b]	159	—	—	−4·70	—
MeSCN[c]	146	3·11	—	−3·79	−10·50
MeSCN[d]	168	—	—	−3·3	—
MeNCS[c]	107	0·723	—	1·70	6·35
MeNCS[d]	117	—	—	−2·5	—

[a] Data from Reference 9.
[b] Data from Reference 17.
[c] Data from Reference 12.
[d] Data from Reference 22.

spectra and hydrogen bonding characteristics of isothiocyanic acid, which itself is a rather weak proton acceptor, but a strong donor. Pullin and coworkers[15] have also determined the ν_{NH} shifts of this acid when bonded to ethyl thio and isothiocyanate, and the corresponding thermodynamic quantities. The values obtained show again that the thiocyanate is a stronger proton acceptor than is isothiocyanate. Given the sequence of the hydrogen bond accepting propensities of the groups, the question of which atom is actually the proton accepting one follows immediately. The only direct answer would be given by a molecular structure determination of crystalline adducts. Since this has not been done, only circumstantial evidence can be used. Thus Martin and Brause[16] offer an acceptable argument in favour of the terminal nitrogen atom in cyanates being the proton acceptor. The argument is based on the fact that 2,6-di-*t*-butylphenyl cyanate produces a larger shift of the phenol ν_{OH} band ($\Delta\nu = 157\,cm^{-1}$) than the unsubstituted phenyl cyanate. If oxygen were the acceptor the bulky *ortho*-substituents would prevent the approach of the acid. This conclusion apparently contradicts that which might have been made by considering the π electron charges as obtained from simple HMO calculations[6] which indicate more charge on oxygen. However, only good all-electron calculations of the energy differences between free molecules and variously-bonded complexes would have some predictive value.

A different approach to the question of which is the acceptor atom in alkyl isothiocyanates is followed by Kovač and coworkers[11]. These authors believe that the nitrogen atom is the actual acceptor because sulphur would produce larger phenol frequency shifts and also the enthalpies of association would be larger. The argument is based upon a comparison with data on shifts and enthalpies of hydrogen bonding with acceptor groups having definite accepting sites which were collected by Wayland and Drago[17]. In particular, thioanisole was used for comparison. Apart from the fact that sulphur is not equally bonded in both cases, the reasoning is dubious, for if sulphur in the —NCS group had the same hydrogen bonding propensity as in, say, dimethylthioacetamide[17], there is no reason why the weaker hydrogen bond would be formed with nitrogen as acceptor if the stronger acceptor atom sulphur was available. However, the weakness of the argument does not mean that the conclusion is incorrect. In fact, the results of the *ab initio* calculations on isothiocyanic acid mentioned in Section I show the nitrogen atom to be more negatively charged and its lone-pair orbital to be high in energy. The corresponding differences between nitrogen and oxygen atoms in isocyanates are smaller and, lacking any experimental evidence, the problem

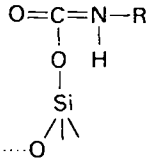
of the accepting site in this group remains unsolved. No attempt seems to have been made to use the heavy-atom vibrational shifts as indicators of the site of bonding.

The influence of the radicals on the hydrogen bonding propensity has been studied in the cyanate series by Igarashi and coworkers[10] and by Martin and coworkers[9]. The first group of authors have determined the frequency shifts and the equilibrium constants in the range 20–50 °C for the bonding of phenol in CCl_4 to methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *s*-butyl thiocyanates. The $\Delta\nu_{OH}$ increases from 146 cm^{-1} to 158 cm^{-1} linearly with the inductive effect of the alkyl radicals as reflected by Taft's σ constants thus showing the inductive effect of the substituents on hydrogen bonding. These authors also obtained a linear relationship between $\log k_{ass}$ and $\Delta\nu_{OH}$ and noted an almost constant value of the $\Delta S^0/\Delta H^0$ ratio. This has been found also by Joesten and Drago[18] for a number of N-containing bases and is considered to be evidence for the RSCN...OH bonding. The ΔH^0 values vary between −2·85 and −4·14 kcal/mol.

Martin and coworkers have collected the $\Delta\nu_{OH}$ values for several proton donors bonded to 85 nitriles, cyanamides, cyanates, thiocyanates, selenocyanates and halogen cyanides as well as some thermodynamic quantities for substituted phenyl cyanates and phenyl thiocyanates. The $\Delta\nu_{OH}$, ΔH^0 and ΔS^0 values for phenol bonding are linearly related to Jaffe's σ^0 constants. The data allowed a quantitative estimate of a relative transmission factor for substituent effects of the atom X in the RXCN systems. The transmission factor becomes smaller with increasing size of the atom X. From the known pK_a values of selected proton donors covering a range of 9 pK_a units, and their ν_{OH} shifts on association with phenyl cyanate, phenyl thiocyanate, and phenyl selenocyanate combined with the linear relationship between the $\Delta\nu_{OH}$ and the substituent constants σ^0 the pK_a values for the whole series of substituted analogues were derived. Since these pK_a values are based on the proton-accepting propensity in hydrogen bonding, their reliability is limited by the well-known general problem of the connection between the basicity in hydrogen bonding and in full protonation, respectively. There are, however, no independently determined protonation constants available for organic cyanates and related compounds.

The interaction of isocyanates with hydroxyl groups on a silica surface has attracted some attention because of their eventual reaction with polyurethanes. The latter are in use as coatings for solid siliceous surfaces. Kulik and coworkers[19] have investigated the infrared spectra of the system aerosil–adsorbed butyl isocyanate and have concluded from the partial

reversibility of the disappearance of part of the free OH groups, that in the first stage the isocyanate is adsorbed on the silica by hydrogen bond formation of the type



However, Rochester and coworkers[20] have shown that the reversible reduction of the OH absorption is in fact due to the formation of a surface urethane which is stable to evacuation at 373 K but is desorbed at 453 K.

III. CHARGE-TRANSFER COMPLEXES

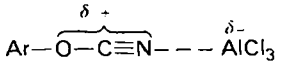
Although the broad notion of charge-transfer (CT) complexes includes also the complexes treated in the previous, as well as in some of the following, paragraphs we shall treat here only the CT complexes in the more restricted sense[21], i.e. in which the (iso)thiocyanate acts as a mixed n and $b\pi_a$ donor to the $x\sigma$ acceptor and the charge-transfer band is observed.

Quantitative data exist[22–24] only for complexes between iodine and MeSCN, MeNCS, EtNCS and allyl isothiocyanate. Although charge-transfer bands of considerable strength were observed in the ultraviolet with the last two they were not suitable for the determination of equilibrium constants. However, this was possible from the blue-shifted internal iodine band. In heptane solution the absorption curves passed through an isosbestic point by varying the thiocyanate concentration. Thus formation constants of 1·00 mol^{-1} for EtNCS and 0·94 mol^{-1} for allyl isothiocyanate were obtained[24] at 20 °C. From the temperature dependence of the formation constants ΔH^0 of 3·9 ± 0·8 and 3·6 ± 0·8 kcal/mol, respectively, resulted. For MeSCN the data were unreliable[24] because the formation constant was too low. However, Wayland and Gold[22] give for this complex $K = 0{\cdot}17 \pm 0{\cdot}02$ mol^{-1} (25 °C, CCl_4) and $\Delta H^0 = 2{\cdot}2$ kcal/mol. Their values for MeNCS even in a different solvent, are in good agreement with those of the former authors. Thus, it is clear that the isothiocyanates are better donors towards iodine than the thiocyanates but weaker than the sulphides[25]. Wayland and Gold[22] have also observed the phenolic OH shift on bonding to MeSCN and MeNCS and the latter turned out to be smaller. This result is used in connection with the theories of 'soft' and 'hard' acids and bases as evidence for the site of bonding: the 'hard' acid

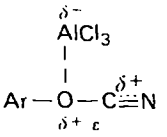
phenol bonds to the 'hard base' nitrogen, whereas the 'soft acid' iodine bonds preferentially to the 'soft base' sulphur.

IV. COMPLEXES WITH LEWIS ACIDS

The catalytic role of metal salts with Lewis acid character ($CdCl_2$, $ZnCl_2$) has long been known to exist in the isomerization of alkyl thiocyanates to isothiocyanates, alkyl cyanates to isocyanates, and in the trimerization of aryl isocyanates to cyanuric acid esters. The formation of complexes appeared likely from the solubility of such salts in the cyanates and thiocyanates and was confirmed by i.r. spectroscopic data. Thus Martin and Weise[26] observed the formation of oily adducts of phenyl, substituted phenyl, and alkyl cyanates with $AlCl_3$ and $SnCl_4$. The antisymmetric stretching was shifted by 70–80 cm^{-1} to higher frequencies in the $AlCl_3$ complexes whereas the shift with $SnCl_4$ was only 18 cm^{-1}. The shifts are similar in magnitude to those obtained with the corresponding cyanides. Because of the appearance of several new bands in the lower frequency regions of the infrared spectra these authors suggest that besides the possible O-, N- and aryl-coordinated 1:1 Lewis acid complexes (**1a–c**) 1:2 complexes and dimers of the structure **2** and **3** are also formed:



(1a)



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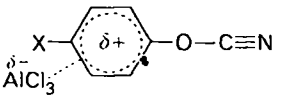

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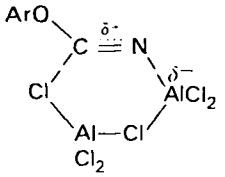
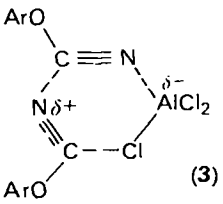
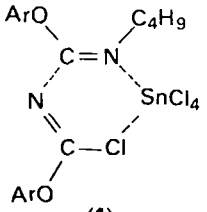


(2)



(3)

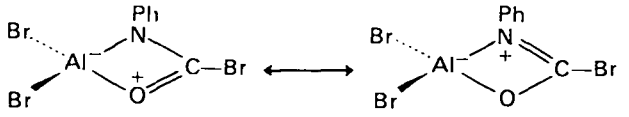
This would explain also the aromatic proton–n.m.r. shifts. The dimer type of structure would be even more pronounced in the $SnCl_4$ complexes which actually have the ArOCN · $\frac{1}{2}$ $SnCl_4$ stoichiometry (**4**).



(4)

Formation of a $CH_3SCN \cdot AlCl_3$ complex occurs[26a] when the gaseous thiocyanate is adsorbed on solid $AlCl_3$. The complex is characterized by a high frequency shift of the CN stretching band from 2168 cm^{-1} to 2214 cm^{-1} and the displacements as well as intensity changes of the CS bands near 700 cm^{-1}. The electron donation is attributed to the nitrogen atom.

Phenyl isocyanate and methyl isocyanate also form oily complexes with $AlBr_3$ as indicated by the high frequency shifts of the antisymmetric NCO stretching for about 155 cm^{-1}. These complexes are obtained by the addition of PhNCO and MeNCO, respectively, to a hexane solution of Al_2Br_6, but the complex $PhNCO \cdot AlBr_3$ reacts within 3 hours at 20 °C to yield a solid compound for which the structure **5** has been suggested[27].



(5)

This is based on the fact that the strong 2400 cm^{-1} band is replaced by C=O and C=N bands near 1640 and 1570 cm^{-1}, respectively. $MeNCO \cdot AlBr_3$ remains liquid and the infrared spectrum indicates the presence of both the coordination complex and the insertion compound. Phenyl isothiocyanate first yields also an oily product with Al_2Br_6, but this turns almost instantly to a solid which is likely to be the sulphur analogue of the above mentioned insertion compound[27]. In view of these results the earlier interpretation of Pestemer and Laurer[28] of the infrared spectra of adducts of phenyl isocyanate and of alkyl and phenyl isothiocyanates with $Al(OC_2H_5)_3$ in terms of coordination compounds have to be revised. The spectra do not show the typical bands near 2200 cm^{-1} of the –NCX groups but only bands that indicate double-bonded nitrogen and oxygen, similarly as in the previous case. Thus obviously the reaction leading to insertion compounds took place.

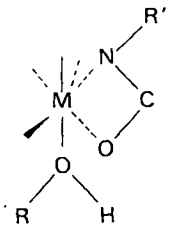
Quite stable complexes are formed[29] between thiocyanates (methyl, chloromethyl, isopropyl, phenyl) and trichloroborane. They are solids with melting points around 100 °C. Their infrared bands between 2230 and 2250 cm^{-1} are indicative of the persistence of the (essentially) R—S—C≡N bonding and the high frequency shift relative to the free molecules of the order of 150 cm^{-1} is quite comparable with shifts observed in the isocyanate–aluminium bromide complexes. The $H_3CSCN \cdot BCl_3$ complex can be recrystallized from CCl_4 whereas the others rearrange to bis(amino)borane derivatives or tris(isothiocyanate) borane[29].

A weak complex of phenyl isocyanate with BF_3 is mentioned by Lappert and Prokai[30]. Such complexes are believed to be the first step in the diamidoborane formation from aryl isocyanates and boranes, possibly also in the analogous reaction of isothiocyanates to dithioamidoboranes. At any rate the isocyanate–borane complexes appear to be much less stable than those of thiocyanates and no characteristics could be obtained. The reaction of phenyl isothiocyanate with diborane in inert solvents yields[31] a solid product in which $PhNCS \cdot BH_3$ has been identified by mass spectrometry as one component, but no details of the structure were obtained with other methods.

V. COMPLEXES OF ISOCYANATES WITH CATALYSTS

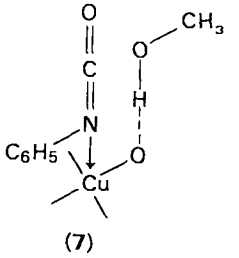
The reaction of hydroxyl compounds with isocyanates leading to urethanes is catalysed by organometallic compounds as well as by metal carboxylates and amines. It has been suggested[32,33] that this catalysis involves ternary complexes. Frisch and coworkers[34] have endeavoured to detect complex formation in mixtures of phenyl isocyanate and the catalysts stannous octoate and lead naphthenate using nuclear magnetic resonance, infrared and ultraviolet spectroscopy. However, they observed no significant shifts although such shifts appeared with the catalyst dissolved in methoxypropanol which was used as the hydroxylic component in the reaction leading to urethane. Later on, Reegen and Frisch[35] used the cryoscopic method with benzene to show the complex formation between dibutyltin dilaurate and triethylamine, respectively, and phenyl isocyanate. They found a rather high degree of association, i.e. of the order of 50% complexed catalyst. It is surprising that this did not show up in the spectra even if considering the fact that the catalyst ratio was lower in the previous experiments. Abbate and Ulrich[36] have concluded from kinetic measurements using organometallic derivatives of lead, tin and mercury in the reaction of *n*-butyl alcohol that the ternary complex is unfavourable

and that it appears only in low concentration. They postulated the following structure (**6**):



(**6**)

Lipatova and Nizel'ski[37–40] considered in a series of papers the possible complex formation between isocyanates and β-diketone chelates of transition metals, particularly copper acetylacetonate, ethyl acetoacetate and 3-ethyl acetylacetonate. Both the binary complexes of the metal chelates with isocyanates and with alcohols, respectively, and ternary complexes of those three components were investigated by means of electronic spectra and, in the last[39] paper, also by electron paramagnetic resonance spectra. Blue shifts and intensity changes of the *d–d* transitions of copper in presence of isocyanate were observed and opposite shifts for the π–π^* transitions of the ligand caused by, for example, methanol. Phenyl isocyanate caused distinct changes in the g factors and constants of the hyperfine structure of the copper quartet, chelated by 3-ethylacetylacetonate with further changes occurring on addition of methanol. Corresponding changes occurred also with phenyl isothiocyanate. The authors interpreted these results in terms of binding of the isocyanate and isothiocyanate as fifth ligand to copper and of the alcohol to the oxygen of the acetylacetonate as in the following scheme (**7**):



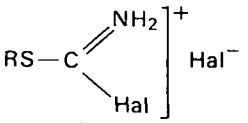
(**7**)

The kinetic analysis[40] of the urethane formation confirmed the role of the ternary complex.

VI. SALTS AND ADDITION COMPOUNDS

There is actually no satisfactory delimitation between salts, adducts, addition compounds and reaction intermediates for organic cyanates and related groups. Neither does the existing structural basis warrant systemization and therefore we have to content ourselves with a rough grouping of the compounds described in the literature.

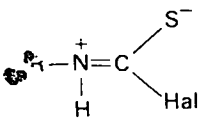
By analogy with the addition compounds of nitriles with two molecules of hydrogen halides, isocyanates, thiocyanates, and isothiocyanates also yield addition compounds in either 1:2 or 1:1 ratios with HCl and HBr. They were prepared by Allenstein and Quis[41] and the structures proposed on the basis of characteristic infrared bands similarly to the nitrilium salts studied previously by the same authors. Solid methyl thiocyanate adducts with two molecules of either HCl or HBr are obtained by saturating the ether solution of the thiocyanate with hydrohalide gas whereas phenyl thiocyanate yields under these conditions an adduct with HBr only. The spectra show a strong and broad band centred near 2740 cm^{-1} and another strong, complex one with the main peak near 1580 cm^{-1}. These bands are attributed to the stretching and bending modes of the hydrogen bonded NH_2 group, the latter being coupled with the C=N stretching. Hence the structure **9**



(9)

appears the most likely one.

Methyl isothiocyanate forms 1:1 adducts with HCl and HBr. The latter adduct appears in two isomeric forms, depending on the conditions of preparation which differ in some details of the infrared spectra[41]. Characteristic are the strong bands near 2800 and 1640 cm^{-1} which are assigned to the NH and C=N stretchings. Structure **10**



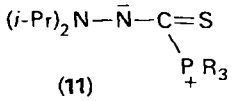
(10)

is therefore acceptable. Phenyl isothiocyanate yields at low temperature an adduct with HBr but this is very unstable.

Methyl and phenyl isocyanate yield with HCl and HBr in CH_2Cl_2 crystalline adducts in 1 : 1 ratio which have been known[42] to exist for a long time, but their structure has been elucidated by i.r. spectroscopy only[41].

Several alkyl and aryl diisocyanate–HCl adducts were prepared by Roginskaya and coworkers[43] and their i.r. spectra recorded. For example hexamethylene diisocyanate forms with HCl one product which is soluble in the diisocyanate and one which is an insoluble solid. A complete separation of both was not possible. However, in the former product the dominant infrared feature is a strong band near 1757 cm^{-1} indicating the bis-carbaminoyl chloride structure whereas in the latter a weak band near 2060 cm^{-1} persists besides a strong and broad band near 3000 cm^{-1}. The authors interpret this in terms of the structure of the solid such as $[R-NH=C=O]^+Cl^-$. It is rather surprising that the band near 2060 cm^{-1} in this and in the spectrum of the analogous *m*-phenylene diisocyanate is so weak.

Finally, some addition products of isothiocyanates with tertiary phosphines should be mentioned because they are formulated as inner salts. Thus *N*-isothiocyanato diisopropylamine treated with trimethyl and triethyl phosphine in dry ether yield rather stable adducts of structure **11**.

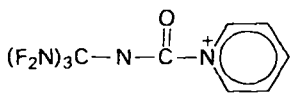


(11)

The structure is deduced from infrared and nuclear magnetic resonance data[44].

The corresponding formulation for isothiocyanate–trialkyl phosphine adducts has been proposed earlier[45]. These adducts appear in the form of yellow solids, but no proofs of the structure were given.

The electrophilic character of the carbon atom in cyanates and, particularly, in tris(difluoramino)methyl isocyanate is manifested in the adduct[46] formation of this isocyanate with pyridine (**12**):



(12)

In contrast with aliphatic nitriles, aliphatic thiocyanates are not reduced in the Stephen reaction. Instead, white crystalline molecular complexes

of butyl and amyl thiocyanates were obtained[47] ($SnCl_2(BuSCN)_2 \cdot 5HCl$ and $SnCl_2$ $(AmSCN)_2 \cdot 5HCl$). The compounds are unstable in air at room temperature and on treatment with ice-water the initial reactants are obtained. The analogous compound with propyl thiocyanate was so unstable that the composition could not be determined. The formation of an adduct with dimethyl sulphoxide has been postulated[48] on the basis of the specific solvent effect of dimethyl sulphoxide in the tritylation of aryl isocyanates. Similarly, the activating role of triethylamine in the addition of alcohols to cyanates is explained by the formation of a cyanate–amine complex by Martin[48] and analogously isocyanate–amine complexes has been advanced by Pestemer and Laurer[28]. Adduct formation in this sense has also been postulated by Mukaiyama and coworkers[49] between phenyl isocyanate and phenyl isothiocyanate, respectively, and tetramethylsulphurane diamide. The evidence is based on the disappearance of the characteristic isocyanate band when the components are mixed in a non-polar solvent. Several more addition compounds have been proposed to appear in the course of various reactions[50] but since no evidence of their structure is given we shall not treat them here.

VII. TRANSITION METAL COMPLEXES

Although the investigations of metal complexes of cyanates and related groups seem to have been conducted for specialized reasons, such as trying to get some insight into the bonding of coordinated pseudohalide ions or searching for optical isomerism of bidentate thiocyanato ligands, rather than in order to acquire data systematically, the examples described in the literature cover roughly all classes of transition metals. However, the structures of these complexes are deduced only from spectroscopic data. Although not as reliable as X-ray structure determinations, they give at least some indication as to which is the actual coordination site amongst the potential n and π donors in cyanate and related groups. More subtle problems such as the influence of the difference between the energies of the n_x and n_y lone pair orbitals of sulphur on the geometry of the complexes remain, of course, to be answered in the future. There is little possibility of comparing the (iso)cyanate and (iso)thiocyanate groups between them because nearly all of the examples of metal complexes are from the thio groups. From the few data on (iso)cyanates it appears that they are rather difficult to prepare, hence these groups may be considered as less stable than the (iso)thiocyanates. In the following we shall try to treat first general relations and this will be followed by an account of the existing evidence.

TABLE 3. Spectroscopic parameters of nitrogen coordinated species in carbon tetrachloride solutions[51]

	$10\,Dq^a$	β^b
$[Cr(AllylNCS)_6]Cl_3$	18·18 kK	0·5
$[Cr(NCS)_6]^{3-}$	17·80 kK	0·6
$[Co(AllylNCS)_4]Cl_2$	5·1 kK	0·65–0·67
$[Co(NCS)_4]^{2-}$	4·55 kK	0·69

[a] Crystal field splitting.
[b] Ratio of Racah's B values for the complexed and free ion (nephelauxetic ratio).

One of the interesting questions from the point of view of coordination chemistry is how the change from the free ions to the organic derivatives influences the ligand properties. Lacking directly determined thermodynamic quantities, the spectrochemical and nephelauxetic parameters should be the most relevant to this question. Only data on Cr^{3+} and Co^{2+} complexes obtained by Ahmed[51] are available and they are reproduced in Table 3. From infrared data and, in fact, in agreement with the nitrogen position in both series N-coordination is present in all these complexes. The difference between the ionic and covalently bonded isothiocyanate is surprisingly small. The $10\,Dq$ and β values place both somewhere near the middle of the nephelauxetic and spectrochemical series and may be taken as indicative of significant π propensity.

TABLE 4. Shifts in uranyl asymmetric stretching vibration in the spectra of complexes $R_4N[UO_2Cl_3L]$ ($\nu_3 = 943\ cm^{-1}$) and $R_4N[UO_2Br_3L]$ ($\nu_3 = 944\ cm^{-1}$) (R_4N^+ = tetradecylammonium ion)[52] in benzene solvent

Ligand L.	$[UO_2Cl_3L]^-$ $\Delta\nu_3$	$[UO_2Br_3L]^-$ $\Delta\nu_3$
MeCN	−12	−10
MeSCN	−13	−10
$(C_4H_9)_2O$	−14	−10
MeNCS	−15	—
$(C_4H_9O)_3PO$	−16	−14
ClO_4^-	−17	−15
$(C_4H_9)_3PO$	−21	−18
NO_3^-	−25	−23
I^-	−26	−24
SCN^-	−26	−25
Br^-	−29	−26
Cl^-	−31	−26

The effect of the ligands on the asymmetric stretching vibration ν_3 of the uranyl group in equatorially bonded complexes as observed by Vdovenko and coworkers[52] can be interpreted according to Dyatkina and Mikhaylov[53], and to McGlynn and Smith[54], in terms of stronger donating ability of the SNC^- ion, but the perturbation of the U–O bonds might be also connected with the overall charge as obvious from the data in Table 4. The higher formation enthalpy of the thiocyanate ion in charge transfer complexes with iodine (Table 5) may reasonably be attributed to the lower ionization potential of π electrons in the ion. The difference in this sense appears at least in the MO calculation[4] on the $HNCO–NCO^-$ pair and may be expected also for the corresponding sulphur pair.

TABLE 5. Formation enthalpies of charge transfer complexes with iodine

	ΔH (kcal/mol)
$SCN^- + I_2$[a]	−8·1
MeSCN + I_2[b]	−2·2
MeNCS + I_2[b]	−3·3
EtNCS + I_2[c]	−3·9
AllylNCS[c]	−3·6

[a] From Reference 55.
[b] From Reference 22.
[c] From Reference 24.

In the above mentioned investigation and also in connection with the charge-transfer complexes studied by Wayland and Gold[22] the concept of 'hard' and 'soft' bases is involved which brings us to the problem of the site of complexing. In the charge-transfer complexes with iodine, sulphur as the 'soft' base was supposed to be the donor atom towards iodine[22]. Again, MeNCS turns out to yield a larger enthalpy of interaction with the softer palladium whereas the harder base MeSCN has a higher enthalpy on interacting with the harder nickel[56] (Table 6).

TABLE 6. Estimated enthalpies, in kcal/mol, of interactions in methyl isothiocyanate and methyl thiocyanate with bis(methyl-*n*-octyl glyoxime)metal(II)[56]

	Ni(II)	Pd(II)
MeNCS	0	1·03 ± 0·36
MeSCN	0·79 ± 0·21	0·71 ± 0·35

The gas-chromatographic technique was used in the determinations of enthalpies with metal glyoximates as stationary phase. However, absolute enthalpy values of the axial coordination were not determined because of the lack of data on the strength of the metal–metal bonds (of the order of 1 kcal/mol) which are replaced by the ligand bonds. Unfortunately, the known enthalpy (2·2 kcal/mol) of formation of the corresponding monothiocyanate nickel(II) complex in solution[57] cannot be used for comparison because it includes the solvation effects.

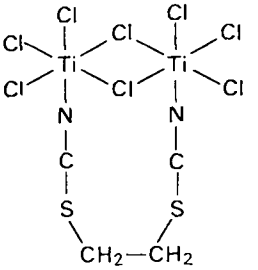
Coordination through sulphur of EtNCS to the aluminium ion was assumed by Haraguchi and Fujiwara[58]. These authors have measured the chemical shifts and line width in the magnetic resonance of the ^{27}Al nucleus of aluminium halides in a series of organic solvents. In particular, the existence of the complex of $[Al(EtNCS)]^{3+}$ was noted in the solution of AlI_3 in EtNCS. From these results a sequence of the strength of interaction could be established as follows: $H_2O > C_2H_5OH$, $C_3H_7OH \gg Cl^-, Br^-, I^- \gtrsim C_2H_5NCS > C_6H_5CN > CH_2{=}CHCN >$ MeCN. This sequence corresponds to the UO_2 stretching shifts as shown in Table 4.

Most of the evidence for the structure of complexes of the organic (iso)thiocyanates and hence of the site of bonding originates from infrared spectroscopy. This is most often used in connection with synthetic work. The high frequency shift of the 2100 cm^{-1} band is usually taken as a criterion for N-coordination in thiocyanate. The S-coordination leaves this band with little change. In the isothiocyanates, the S-coordination is assumed to cause a high frequency shift whereas N-coordination causes a low frequency shift because of a reduced N–C and C–S vibrational interaction. π coordination to the C–S bond seems to reduce the former antisymmetric frequency to as little as 1600 cm^{-1}. However, the implications of the actually observed frequencies regarding the electronic changes on complexing and hence to the site of coordination should be taken with some caution in view of the mass and steric effects which are very lucidly exposed by Bellamy[59]. Some of the conclusions based on infrared frequencies are fortunately also corroborated by steric considerations. For instance, in the case of chelating dithiocyanates, sulphur coordination[60] is only possible on steric grounds. The frequency of the CN band is in agreement with this.

From the existing data it may be concluded that the soft, 'b class' transition elements prefer bonding to sulphur, selenium, or the π-electron system whereas elements of the border region prefer bonding to nitrogen. However, no conclusion about the steric influence of the position of the ligating atom in organic cyanates and thiocyanates can be drawn.

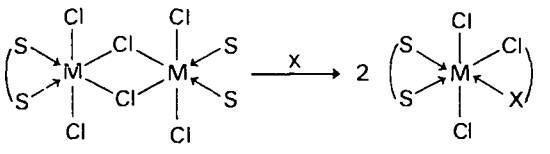
1,2-Dithiocyanatoethane and 1,2-diselenocyanatoethane form the most

numerous group of complexes with a surprising versatility of bonding modes. Bridging structures with ligating nitrogen atoms were proposed for a yellow, moisture sensitive complex with the 'class a' metal titanium(IV) $(TiCl_4)_2 \cdot NCSCH_2CH_2SCN$)[61] and for a temperature unstable complex of the 'class b' metal silver(I)[62]. White crystals of $AgClO_4 \cdot NCSCH_2CH_2SCN$ detonate on heating to 165 °C. The crystal is presumably made up of polymeric $Ag \cdot NCSCH_2CH_2SCN-$ units held together by perchlorate ions (**13**). Attempts to prepare complexes with methyl, allyl or cinnamyl thiocyanates were unsuccessful[62].



(13)

Comparing 1,2-dithiocyanatoethane with 1,2-diselenocyanatoethane as ligands, Goodall emphasized the similarity of behaviour towards cobalt(II), rhodium(III) and iridium(III)[63,64]. Cobalt(II) halides form complexes of the type $[CoX_2 \cdot L]_n$ (with L = $NCSCH_2CH_2SCN$, X is Cl, Br, I and with L = $NCSeCH_2CH_2SeCN$, X is Cl) which are stable in dry air. Solid reflectance spectroscopy in the visible, infrared spectroscopy and magnetic measurements suggest octahedrally coordinated high-spin polymeric complexes with a non-chelating ligand in the *trans* form bonded through nitrogen and sulphur (selenium) and with each pseudohalide group acting as a bridge between two cobalt atoms. Rhodium(III) and iridium(III) form stable dimeric diamagnetic complexes $MX_3 \cdot L$ (M = Rh, Ir; with L = $NCSCH_2CH_2SCN$, X is Cl, Br, I and with L = $NCSeCH_2CH_2SeCN$, X is Cl). The chelating ligand should be in the *gauche* form, coordinated

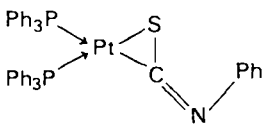


(14)

through sulphur or selenium, respectively. By splitting the chlorine bridges in **14** through unidentate ligands, monomeric complexes result ($MCl_3 \cdot L \cdot X$, M = Rh, Ir; with L = $NCSCH_2CH_2SCN$, X is *p*-toluidine or pyridine and with L = $NCSeCH_2CH_2SeCN$, X is *p*-toluidine).

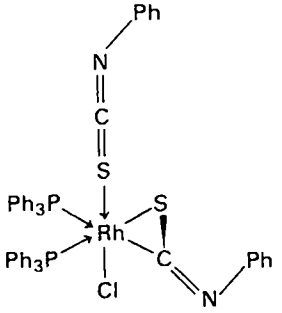
1,2-Dithiocyanatoethane shows no tendency to form complexes with nickel(II), but with palladium(II) products of indefinite composition were obtained[63]. However, a complex with platinum(II) chloride($PtCl_2 \cdot L$) has been described[60,65]. A special type of optical isomerism in complex compounds is produced by the chelating ligand in the *gauche* form, coordinated through sulphur atoms. While the possible configurations were thoroughly discussed using infrared spectra, no experimental information on the complex proper was presented. On the other hand, 1,2-diselenocyanatoethane yields complexes with both palladium(II) and platinum(II) ($MCl_2 \cdot L$)[66]. The complexes are insoluble in all common solvents and thus the molecular weight was not determined. These complexes are diamagnetic. On the basis of infrared spectra they were formulated as monomeric and square planar. The ligand is coordinated through selenium atoms in the *gauche* configuration which is necessary for chelation. However, the appearance of a broad band at about 2200 cm^{-1} suggests that some bonding may be taking place through the nitrogen atom also[64,66]. Obviously, more work is needed in order completely to elucidate the structure of these complexes.

Methyl and phenyl isothiocyanate yield crystalline air stable complexes with platinum(II)[67] ($Pt \cdot L \cdot (Ph_3P)_2$; L = MeNCS, PhNCS). Infrared evidence supports the assumption that the ligands are coordinated through the C–S bond (structure **15**) by analogy with the structure of the planar CS_2 complex[68]. No evidence was found for the existence of the possible *cis–trans* isomerism about the C=N bond. No equivalent products with phenyl isocyanate were isolated. This was directly attributed to the low affinity of the metal for oxygen. But, very interesting complexes of $PtO_2(Ph_3P)_2 \cdot 2PhNCO$ and $PtO_2(Ph_3P_2) \cdot PhNCS$ were obtained as intermediate products in the synthesis of nitrene complexes[69]. Infrared spectra suggest cyclic structures with the participation of the peroxo group similar to the structures of adducts of $PtO_2(Ph_3P)_2$ with aldehydes and ketones[70]. Crystal structure determinations are mentioned as being



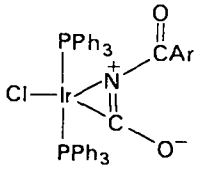
(15)

in progress. There are both π bonded and σ bonded ligands in the proposed structure (**16**) of the stable complexes of $RhCl(L)_2(PPh_3)_2$ (L = PhNCS[67], PhNCO[69]).



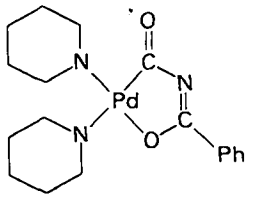
(16)

A series of iridium(I) complexes and a rhodium(I) complex with acyl isocyanates was obtained in the course of investigating complexes which fix molecular nitrogen. π bonding of the isocyanate group to the central metal atom (**17**) was proposed[71,72].



(17)

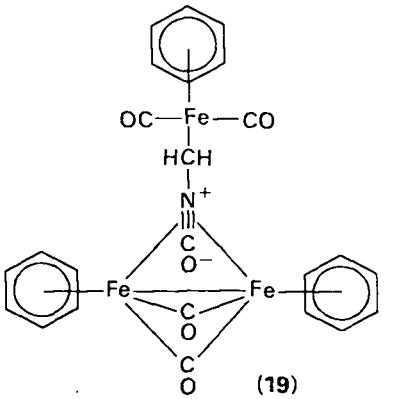
On the other hand, metallocyclic structures composed of M—O—C—N—C or M—S—C—N—C skeletons (**18**) were suggested for a number of related complexes of benzoyl and thiobenzoyl isocyanates and some organometallic compounds of rhodium(I) and palladium(0)[73]



(18)

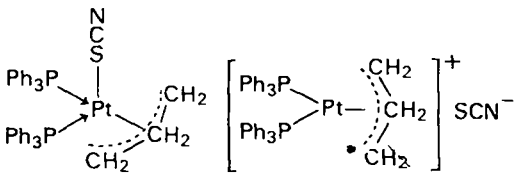
An unusual structure (i.r. and n.m.r. evidence) with bridging isocyanate was assumed for the complex (**19**) of $(C_5H_5)_3Fe_3(CO)_4CH_2NCO$[74]. The

structure was supported by the analogy with the carbon–carbon triple bond in acetylenes acting as a similar bridging group in $(RC{\equiv}CR)Co_2(CO)_6$[75] and in $(RC{\equiv}CR)(NiC_5H_5)_2$[76].



(19)

Both platinum and palladium form stable complexes with allyl isothiocyanate ($Pt(C_3H_5NCS)(PPh_3)_2$[67] and $Pd(C_3H_5NCS)_2Cl$[51]). A critical discussion of the platinum complex (**20**) indicates a π-bonded allyl group and a sulphur-bonded thiocyanate ion, dissociating in polar solvents (**21**). It is implied that similar bonding conditions are possible in the palladium complex also. Further study is promised in this paper[51].



(20) (21)

Three iron complexes of butyl and phenyl isocyanates were claimed[77]. The crystal structure determination of one of them, $[Fe(CO)_3 \cdot PhNCO]_2$, revealed that it is actually an adduct of diphenylurea[78], and one may conclude, by analogy, that the other two cognate complexes are likewise urea adducts. The only reported stable phenyl isocyanate adduct of the border region transition elements seems to be the complex of $Ni(PhNCO)_2(PPh_3)_2$[79]. It was isolated as an intermediate in nickel-catalysed trimerization reaction of phenyl isocyanate. The structure determination is in progress. Nitrogen bonding was postulated, as a result of the thermal

decomposition studies, in the unstable hygroscopic adduct of $VOCl_3 \cdot 2PhNCO$[80,81]. Some unstable phenyl isocyanate and isothiocyanate complexes were proved to exist in solutions. Indications for nitrogen coordination were found in chromium(III) and cobalt(II) complexes with phenyl isothiocyanate, studied by spectroscopy in the visible region. Cr/PhNCS and Co/PhNCS ratios were determined to be 1/6 and 1/4 respectively[51]. A 3:1 complex of phenyl isocyanate with cobalt(II) naphthenate and a 2:1 complex with manganese(II) naphthenate were postulated from electron spectra[82]. $TaCl_5 \cdot PhNCS$ is stable under an inert atmosphere in hexane or heptane solutions under mild conditions[83].

The complexes with alkyl esters are more stable. Thus the isomerization equilibria of the crystalline niobium(V) and tantalum(V) complexes in melt were studied[84]:

$$TaCl_5 \cdot MeNCS \underset{}{\overset{175\,^{\circ}C}{\rightleftharpoons}} TaCl_5 \cdot MeSCN$$

$$NbCl_5 \cdot MeNCS \underset{}{\overset{165\,^{\circ}C}{\rightleftharpoons}} NbCl_5 \cdot MeSCN$$

These are the only reported isomerization equilibria between the sulphur and nitrogen coordinated species that we are aware of. There are well-defined 1:1 solid complexes of methyl thiocyanate with $MeMCl_4$ and Me_2MCl_3 (M = Nb, Ta)[85]. Indications for a mixture of sulphur and nitrogen bonded isomers were presented. The complexes, with the exception of $Me_2NbCl_3 \cdot MeSCN$, slowly disproportionate in organic solvents. In contrast, methyl isothiocyanate yields a series of insertion reaction products. The complexes of ethyl thiocyanate with titanium(IV) and tin(IV) halides are remarkably stable[86]. It is possible to purify them by sublimation. Coordination through sulphur is suggested. A great difference in colour, melting point and infrared spectra between $TiCl_4 \cdot EtSCN$ and $TiCl_4 \cdot EtNCS$ is stressed. The second one has a spectrum very different from that of the pure ligand. It was concluded that this indicates a great change in the electron distribution of the ligand in the complex. The same is true of the $TiCl_4 \cdot 2EtNCO$[86]. However, this complex exhibits, in CH_2Cl_2 solutions, both the original peaks and the new peaks indicating considerable dissociation. This was taken as evidence that the molecular changes occurring in the ligand on bonding are reversible if the ligand is liberated. An oily, unstable product of the composition of $TiCl_4 \cdot 2AllylSCN$ was isolated[61]. A very unstable, air-sensitive *t*-butyl

isocyanate complex with nickel of the formula Ni(*t*-BuNCO)(*t*-BuNC)$_2$ was isolated at low temperature (−40 °C) from a reaction mixture involving Ni(*t*-BuNC)$_2$ and *t*-BuNCO[87]. Its instability prevented characterization. Coordination was proved by the shifted infrared bands due to the isocyanate group and by the reaction of the complex with excess *t*-BuNC in toluene at room temperature, giving Ni(*t*-BuNC)$_4$ and 98% of coordinated *t*-BuNCO. Last to be mentioned are actually the first reported—in 1934 and 1939—complexes with these ligands. These are Co(SCN)$_2$(MeSCN)$_2$[88] and Co(SCN)$_2$(EtSCN)$_2$[89] which were obtained during solubility studies of metal salts in MeSCN and EtSCN. The complexes lose coordinated esters when exposed to air.

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 9

The electrochemistry of cyanates and related compounds

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I. INTRODUCTION

In spite of the importance of cyanates and their thio derivatives in organic chemistry, electrochemical studies dealing with these compounds are very limited in number. For example, only one paper, which appeared in 1912, was found on the electrochemical oxidation of these compounds. The bulk of the work reported has involved polarographic studies and only a few have been supported by preparative work. Obviously, this is a neglected area which could conceivably produce interesting and worthwhile chemistry.

Since practically all the work in this area has involved polarographic studies, half-wave potentials for the different classes of compounds are tabulated in Tables I, II, and III.

TABLE 1. Half-wave potentials of isocyanates

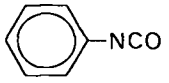
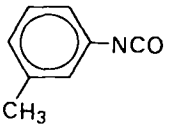
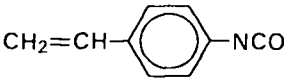
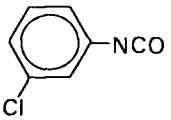
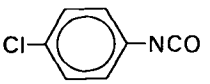
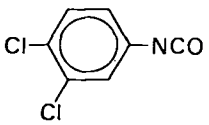
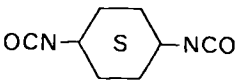
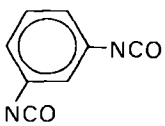
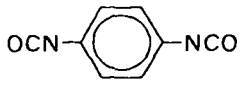
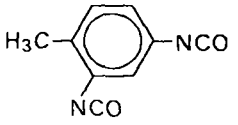
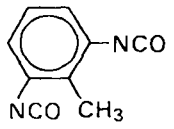
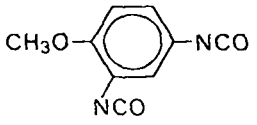
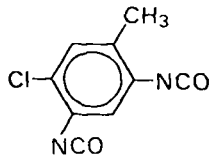
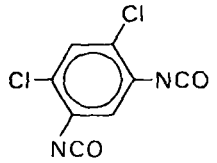
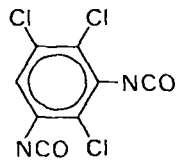
Substrate	$-E^a_{1/2}$	Solvents etc.	Reference
OCN—$(CH_2)_n$—NCO			
$n = 4$	1·93	0·2 M-Bu_4NI in DMF	13
$n = 5$	2·12	0·2 M-Bu_4NI in DMF	13
$n = 6$	2·18	0·2 M-Bu_4NI in DMF	13
$n = 7$	2·23	0·2 M-Bu_4NI in DMF	13
$n = 8$	2·235	0·2 M-Bu_4NI in DMF	13
$n = 9$	2·24	0·2 M-Bu_4NI in DMF	13
$n = 10$	2·25	0·2 M-Bu_4NI in DMF	13
	1·55	0·2 M-Bu_4NI + 0·02 M-Et_4NI in dioxane/DMF = 3/1	11
	2·06	0·05 M-Bu_4NI in DMF	15 28
	2·08	0·05 M-Bu_4NI in DMF	15
	1·93	0·05 M-Bu_4NI in DMF	15
	1·62	0·05 M-Bu_4NI in DMF	15 28
	1·74	0·05 M-Bu_4NI in DMF	15 28
	2·00	0·05 M-Bu_4NI in DMF	28
	2·25	Bu_4NI in DMF	14
	2·10	Bu_4NI in DMF	14
	1·83	0·05 M-Bu_4NI in DMF	15 28

TABLE 1. (*continued*)

Substrate	$-E^a_{1/2}$	Solvents etc.	Reference
	1·98	0·05 M-Bu_4NI in DMF	15 28
	2·15	Bu_4NI in DMF	14
	2·13	0·08 M-Et_4NI in dioxane/DMF = 3/1	29
	2·15	0·05 M-Bu_4NI in DMF	15
	2·22	0·05 M-Bu_4NI in DMF	15
	2·22	Bu_4NI in DMF	14
	2·17	Bu_4NI in DMF	14
	1·87	0·05 M-Bu_4NI in DMF	15
	2·05	0·05 M-Bu_4NI in DMF	15
	2·09	Bu_4NI in DMF	14
	2·07	Bu_4NI in DMF	14
	2·07	0·05 M-Bu_4NI in DMF	28
	1·97	0·05 M-Bu_4NI in DMF	28
	1·99	Bu_4NI in DMF	14

[a] All potentials are in V vs Hg-pool.

TABLE 2. Half-wave potentials of thiocyanates

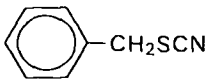
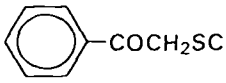
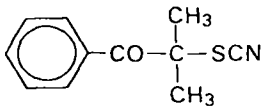
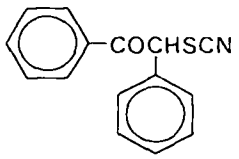
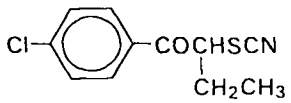
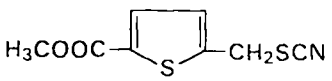
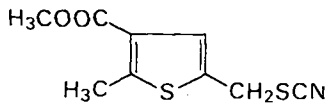
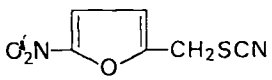
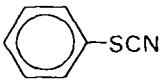
Substrate	$-E_{1/2}$	Solvents etc.	Reference
	1·52	40% EtOH, LiCl	30
	0·66 1·22	pH = 3·5	7
	0·67 1·59	pH = 9·7	7
	0·38	pH = 3·5	7
	0·20	pH = 3·5	7
	0·44	pH = 3·5	7
	0·44 1·59	pH = 9·7	7
	0·75	pH = 2·4	6
	0·75	pH = 8·9	6
	1·6	pH = 2·4	6
	1·18	pH = 8·9	6
	0·18 0·35 0·59 0·88 1·35	pH = 2·9	6
	0·22 0·64 1·17 1·69	pH = 8·9	6
	1·51	40% EtOH, LiCl	30

TABLE 2. (*continued*)

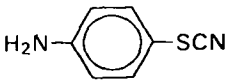
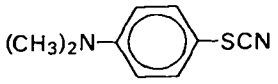
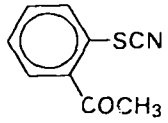
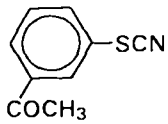
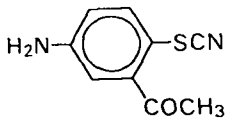
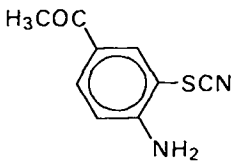
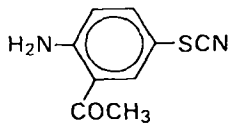
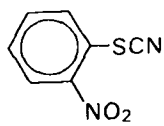
Substrate	$-E_{1/2}$	Solvents etc.	Reference
	1·83[a]	80% EtOH	1
	1·89[a]	80% EtOH	1
	1·17 1·42	pH = 5	5
	0·95 1·29 1·53	pH = 5	5
	1·10 1·22	pH = 5	5
	0·86 1·26	pH = 5	5
	1·04 1·15	pH = 5	5
	0·19 1·07	pH = 3·10	3
	0·57 0·89 1·26	pH = 8·70	3

TABLE 2. (*continued*)

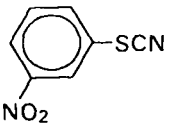
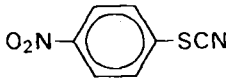
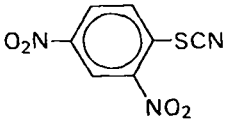
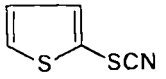
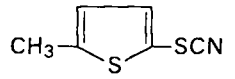
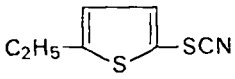
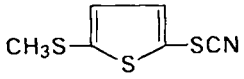
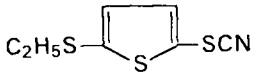
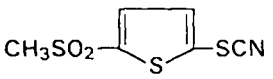
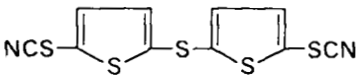
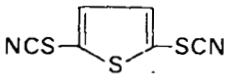
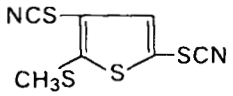
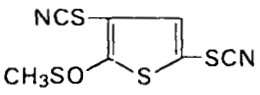
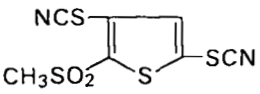
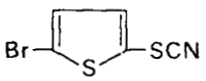
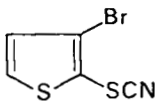
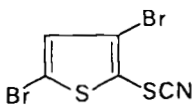
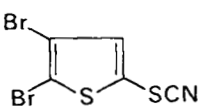
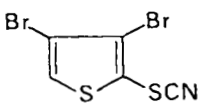
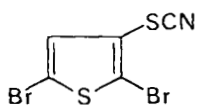
Substrate	$-E_{1/2}$	Solvents etc.	Reference
	0·24 0·83 1·19	pH = 3·10	3
	0·62 0·80 1·39	pH = 8·70	3
	0·17 0·79 1·29	pH = 3·10	3
	0·60 0·82 1·39	pH = 8·70	3
	0·26[b] 0·67[b]	0·1 N-HOAc/NaOAc in 50% acetone	31
	0·43[b] 0·83[b]	0·1 N-AmCl/AmOH in 50% acetone	31
	1·26[c]	60% EtOH, 0·05 N-Et_4NI	32
	1·20[c]	60% EtOH, 0·05 N-Et_4NI	32
	1·17[c]	60% EtOH, 0·05 N-Et_4NI	32
	1·02[c]	60% EtOH, 0·05 N-Et_4NI	32
	1·02[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·83[c] 2·24[c]	60% EtOH, 0·05 N-Et_4NI	32

TABLE 2. (*continued*)

Substrate	$-E_{1/2}$	Solvents etc.	Reference
	0·71[c] 0·95[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·75[c] 1·31[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·74[c] 1·56[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·70[c] 1·24[c] 2·19[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·69[c] 1·38[c] 2·35[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·98[c] 1·79[c]	60% EtOH, 0·05 N-Et_4NI	32
	1·00[c] 2·21[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·73[c] 1·52[c] 2·12[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·86[c] 1·57[c] 2·11[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·95[c] 2·15[c]	60% EtOH, 0·05 N-Et_4NI	32
	0·77[c] 1·57[c] 2·17[c]	60% EtOH, 0·05 N-Et_4NI	32

Potentials are in V vs. SCE except [a] V vs. 0·1 N-calomel.
[b] V vs. Ag/AgCl/sat. KCl, and [c] V vs. Hg-pool. When pH values are given, water was the solvent.

TABLE 3. Half-wave potentials of isothiocyanates

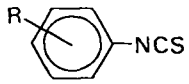
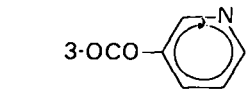
Substrate	$-E_{1/2}$	Solvents etc.	Reference
			
R = H	1·18	pH = 9·1	19
3-CH_3	1·12	pH = 9·1	21
3-Cl	1·03	pH = 9·1	21
4-Cl	1·09	pH = 9·1	19
	1·06	$MeOH/H_2O$	20
3-Br	1·07	pH = 9·1	19
4-Br	1·11	pH = 9·1	19
	1·06	$MeOH/H_20$	20
3-I [4]	1·00	pH = 9·1	21
	1·05	pH = 9·1	19
	1·02	$MeOH/H_2O$	20
2-Cl, 4-Cl	1·09	pH = 9·1	19
3-CN	0·99	pH = 9·1	21
3-NCS	0·93	pH = 9·1	21
3-OH	1·12	pH = 9·1	21
3-OCH_3	1·06	pH = 9·1	21
3-$N(CH_3)_2$	1.13	pH = 9·1	19
4-$N(CH_3)_2$	1·15	pH = 9·1	19
	1·15	$MeOH/H_2O$	20
3-COOH	1·22	pH = 9·1	19
4-COOH	1·22	pH = 9·1	19
3-$COOCH_3$	0·99	pH = 9·1	21
3-$COOC_2H_5$	1·02	pH = 9·1	21
4-$COOC_2H_5$	1·06	pH = 9·1	19
	1·04	$MeOH/H_2O$	20
3-$COOC_5H_{11}$	1·01	pH = 9·1	21
3-$COOC_6H_{13}$	0·98	pH = 9·1	21
3-$COOC_8H_{17}$	1·00	pH = 9·1	21
3-$OCOC_6H_5$	1·01	pH = 9·1	21
	1·00	pH = 9·1	21
3-$COCH_3$	1·02	pH = 9·1	21
3-COC_6H_5	1·00	pH = 9·1	21
3-$NHCOCH_3$	1·05	pH = 9·1	21
3-C_6H_5	1·04	pH = 9·1	21
4-C_6H_5	1·11	pH = 9·1	19
2-CH=CH-C_6H_5	1·10	pH = 9·1	19
3-CH=CH-C_6H_5	1·09	pH = 9·1	19

TABLE 3. (*continued*)

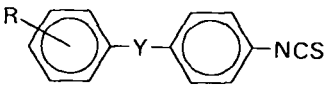
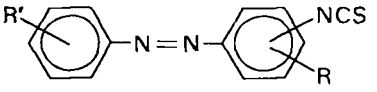
Substrate			$-E_{1/2}$	Solvents etc.	Reference
1-Naphthyl isothiocyanate			1·12	pH = 9·1	19
2-Naphthyl isothiocyanate			1·07	pH = 9·1	19
4-Bromo-1-naphthyl isothiocyanate			1·05	pH = 9·1	19
1-Bromo-2-naphthyl isothiocyanate			1·04	pH = 9·1	19
2-Acridinyl isothiocyanate			1·14	pH = 9·1	19
3-Acridinyl isothiocyanate			1·15	pH = 9·1	19
4-Acridinyl isothiocyanate			1·15	pH = 9·1	19
5-Acridinyl isothiocyanate			1·07	pH = 9·1	19
					
Y = O	R = H		1·13	pH = 9·1	19
			1·18	pH = 9·15	24
		4-NHOH	1·19	pH = 9·15	24
		4-CH_3	1·20	pH = 9·15	24
		4-Cl	1·17	pH = 9·15	24
		4-Br	1·18	pH = 9·15	24
		4-NCS	1·17	pH = 9·15	24
Y = S	R = H		1·00	pH = 9·15	24
		4-$N(CH_3)_2$	1·03	pH = 9·15	24
		4-CH_3	1·01	pH = 9·15	24
		4-Cl	0·00	pH = 9·15	24
		4-Br	0·98	pH = 9·15	24
		4-NCS	0·98	pH = 9·15	24
Y = CH_2	R = H		1·02	pH = 9·15	24
		4-$N(CH_3)_2$	1·03	pH = 9·15	24
		4-NHOH	1·02	pH = 9·15	24
		4-CH_3	1·03	pH = 9·15	24
		4-$NHCOCH_3$	1·01	pH = 9·15	24
		4-NCS	0·99	pH = 9·15	24
Y = SO_2	R = H		0·95	pH = 9·15	24
		4-$N(CH_3)_2$	0·95	pH = 9·15	24
		4-NHOH	0·94	pH = 9·15	24
		4-CH_3	0·95	pH = 9·15	24
		4-Cl	0·94	pH = 9·15	24
		4-Br	0·94	pH = 9·15	24
		4-NCS	0·94	pH = 9·15	24
Y = CH=CH	R = H		1·12	pH = 9·15	24
			1·07	pH = 9·1	19
		4-$N(CH_3)_2$	1·16	pH = 9·15	24
		4-NHOH	1·14	pH = 9·15	24
		4-OCH_3	1·14	pH = 9·15	24
		4-CH_3	1·13	pH = 9·15	24

TABLE 3. (*continued*)

Substrate		$-E_{1/2}$	Solvents etc.	Reference
	4-Cl	1·11	pH = 9·15	24
	4-Br	1·11	pH = 9·15	24
	4-NCS	1·09	pH = 9·15	24
Y = CO	R = 4-OCH_3	1·01	pH = 9·2	25
	4-CH_3	1·00	pH = 9·2	25
	H	0·99	pH = 9·2	25
	4-Br	0·98	pH = 9·2	25
	4-NCS	0·97	pH = 9·2	25
	4-NHOH	1·01	pH = 9·2	25
Y = COO	R = 4-OCH_3	1·02	pH = 9·2	25
	4-CH_3	1·01	pH = 9·2	25
	4-$CH(CH_3)_2$	1·01	pH = 9·2	25
	3-CH_3	1·01	pH = 9·2	25
	H	1·01	pH = 9·2	25
	4-Cl	1·00	pH = 9·2	25
	4-Br	1·00	pH = 9·2	25
	4-I	0·99	pH = 9·2	25
	4-NCS	1·04	pH = 9·2	25
Y = OCO	R = 4-OCH_3	1·08	pH = 9·2	25
	4-$C(CH_3)_3$	1·08	pH = 9·2	25
	4-CH_3	1·08	pH = 9·2	25
	3-CH_3	1·08	pH = 9·2	25
	H	1·07	pH = 9·2	25
	4-Cl	1·07	pH = 9·2	25
	4-Br	1·07	pH = 9·2	25
	3-Cl	1·07	pH = 9·2	25
	4-$COCH_3$	1·06	pH = 9·2	25



NCS = 4	R' = H	R = H	1·12	pH = 9·1	19
			1·15	pH = 9·2	25
4	4'-OCH_3	H	1·16	pH = 9·2	25
4	4'-CH_3	H	1·16	pH = 9·2	25
4	3'-CH_3	H	1·16	pH = 9·2	25
4	4'-Cl	H	1·15	pH = 9·2	25
4	4'-Br	H	1·15	pH = 9·2	25
4	3'-Cl	H	1·15	pH = 9·2	25
4	4'-NCS	H	1·14	pH = 9·2	25
4	3'-Br	H	1·14	pH = 9·2	25
4	4'-$N(CH_3)_2$	H	1·17	pH = 9·2	25
			1·16	pH = 9·1	19
3	4'-$N(CH_3)_2$	H	1·15	pH = 9·1	19

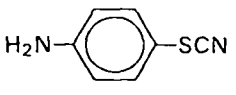
TABLE 3. (*continued*)

Substrate			$-E_{1/2}$	Solvents etc.	Reference
2	4′-$N(CH_3)_2$	3-CH_3	1·16	pH = 9·1	19
3	4′-$N(CH_3)_2$	4-CH_3	1·13	pH = 9·1	19
4	4′-$N(CH_3)_2$	2-CH_3	1·13	pH = 9·1	19
4	4′-$N(CH_3)_2$	3-CH_3	1·14	pH = 9·1	19
5	4′-$N(CH_3)_2$	2-CH_3	1·15	pH = 9·1	19
4	2′-CH_3	3-CH_3	1·15	pH = 9·1	19

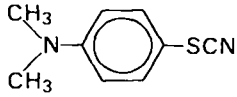
Potentials are in V vs SCE. When pH values are given, water was the solvent.

II. THIOCYANATES

A polarographic study of the reduction of **1** and **2** at the DME in aqueous solution led to the proposal that the reaction involves the uptake of 6 e



(1)



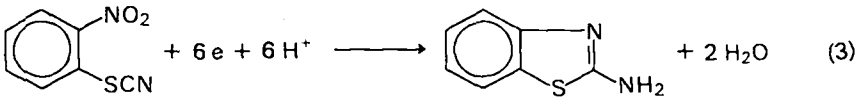
(2)

$$RSCN + 6e + 6H_2O \longrightarrow RSH + CH_3NH_2 + 6OH^- \quad (1)$$

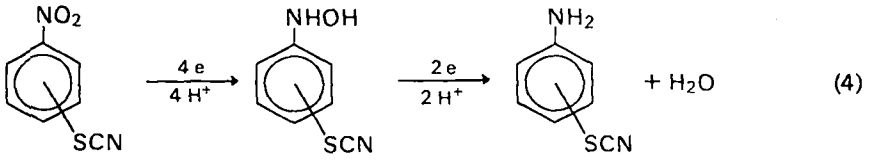
generating the corresponding thiophenol and methyl amine[1] according to equation (1). The polarographic reduction potential was found to be pH independent but dependent upon substrate concentration. The reaction was later reinvestigated using preparative electrolysis with product identification[2]. Both the thiophenol and cyanide ion were established as the products and coulometry showed that a 2 e reduction had occurred according to (2).

$$RSCN + 2e + H_2O \longrightarrow RSH + CN^- + OH^- \quad (2)$$

The reduction of the three isomers of nitrophenyl thiocyanate revealed that the nitro group could selectively be reduced in the presence of thiocyanate groups[3]. In acidic solution the *ortho* substituted compound, 3, gave a single 6 e wave while the *meta* and *para* substituted compounds were reduced in two steps involving four and two electrons, respectively. The reactions were rationalized according to equations (3) and (4). At higher pH (8·7) an additional 2 e wave was observed which was attributed



(3) (4) (3)

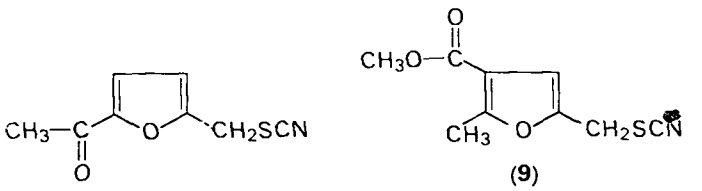


(5) (6) (7) (4)

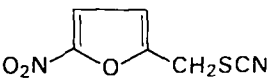
to reductive cleavage of the thiocyanato group of the *ortho* and *para* isomers.

Similar results were reported for the reduction of thiocyanato substituted acetophenones[4,5] where the reduction of –SCN to –SH and $\diagdown\!\!\diagup C{=}O$ to $\diagdown\!\!\diagup CHOH$ was postulated.

While all of the aromatic thiocyanates studied were found to undergo reductive cleavage of the cyanide ion, cleavage of both cyanide and thiocyanate ions have been observed in aliphatic systems. It was found that the 5-substituted furfuryl thiocyanates, **8** and **9**, gave reversible 2 e

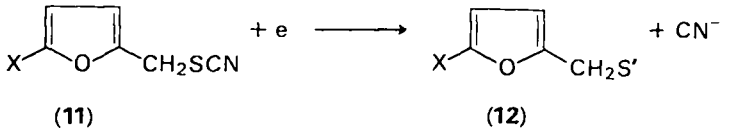


(8) (9)

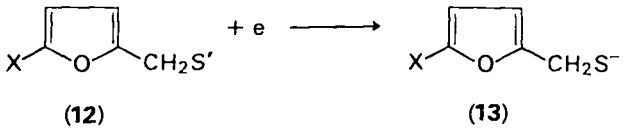


(10)

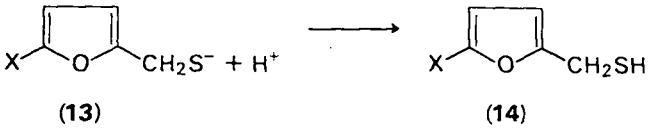
polarographic waves which were nearly independent of both pH and concentration[6]. Microcoulometry also indicated that the reductions involve the transfer of 2 e. The pH independence of $E_{1/2}$ was taken as evidence that the primary step does not involve protons and the mechanism in equations (5)–(7) was suggested.



(11) (12) (5)



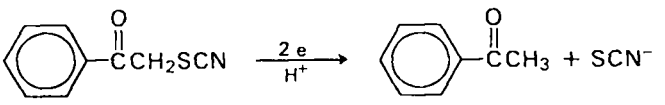
(12) (13) (6)



(13) (14) (7)

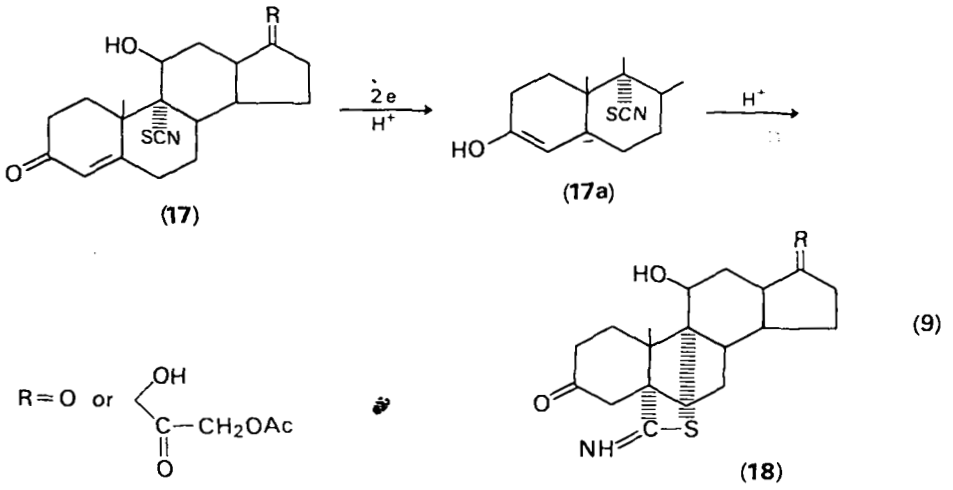
Very complicated results were obtained for the polarographic reduction of **10**. Five reduction waves were observed, some of which must involve reduction of the nitro group.

Both polarography and controlled potential electrolysis were used to establish the reduction pathway of phenacyl thiocyanates[7]. The reaction was found to involve the uptake of two electrons accompanied by the cleavage of the thiocyanato group according to equation (8). The same overall reaction was observed for several substituted phenacyl thiocyanates.



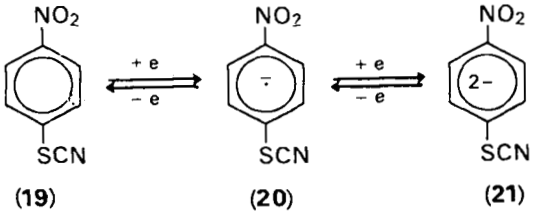
(15) (16) (8)

A reaction which indirectly involves the thiocyanate group was observed when two thiocyanato substituted steroids were reduced electrochemically[8]. The reactions apparently involve reduction of the α,β-unsaturated keto group to an enolate anion which attacks the thiocyanate group (9).

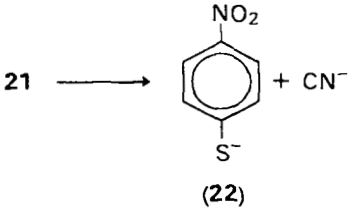


(9)

A recent electroanalytical study of the decomposition pathways of electrolytically generated anion radicals of both aromatic and benzyl thiocyanates further illustrates the different reaction pathways[9]. Cyclic voltammetry and chronoamperometry were used to show that *p*-nitrophenyl thiocyanate is reduced in two successive, one-electron steps (−1·02 and −1·12 V vs. SCE) to an unstable dianion (equation 10). The dianion was found to decompose rapidly generating thiophenolate and cyanide ions (equation 11).

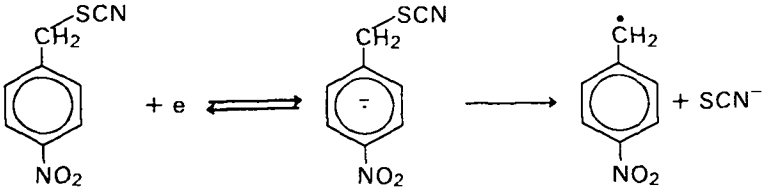


(10)

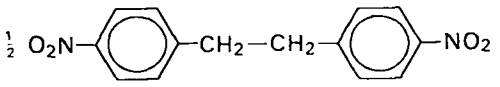


(11)

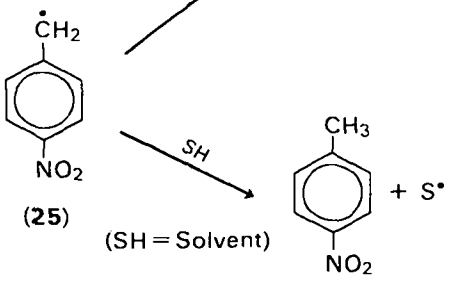
The intermediate anion radical (**20**) was found to decompose as well in a first order reaction with a rate constant of 0·23 sec^{-1} in acetonitrile at 22·5 °C. Two reduction peaks were observed during cyclic voltammetric experiments on *p*-nitrobenzyl thiocyanate in acetonitrile. The first process involves the reduction of the substrate to the corresponding anion radical. The anion radical was found to decompose rapidly giving rise to an electroactive species which was reduced at the second reduction peak. Exhaustive electrolysis of *p*-nitrobenzyl thiocyanate in acetonitrile resulted in the formation of both 4,4′-dinitrobibenzyl and *p*-nitrotoluene. Coulometric *n* values were found to be independent of the presence of added proton donors which was taken as evidence that the formation of *p*-nitrotoluene occurs by a hydrogen atom abstraction reaction rather than by further reduction of the intermediate *p*-nitrobenzyl radical. Hence, the results could be explained by the following equations. The rate constant for decomposition of **24** was estimated from cyclic voltammetry to be equal to about 2×10^4 sec^{-1}.



(23) (24) (25) (12)



(26) (13)

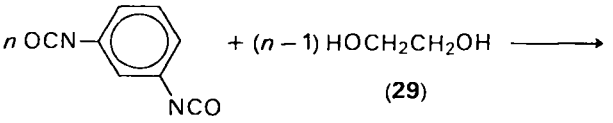


(25) (SH = Solvent) (27)

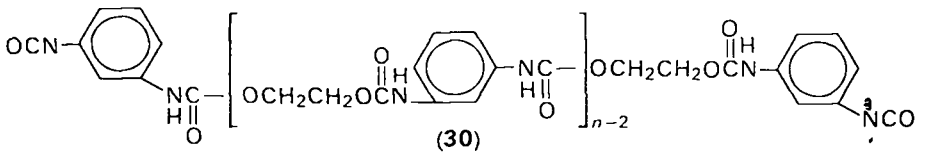
III. ISOCYANATES

The widespread use of aliphatic and aromatic isocyanates and diisocyanates for the preparation of plastic foams (i.e. polyurethane foam) has effectively stimulated research on the physical and chemical properties of these compounds. Despite this electrochemical studies are scarce.

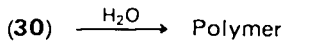
Polyurethane formation involves the reaction with a divalent alcohol, e.g., ethylene glycol, producing a linear polymer, which can be further polymerized by addition of water.



(28) (29)



(30) (14)



(15)

However, isocyanates are also capable of undergoing polymerization by themselves under formation of 'polyisocyanates'. This type of reaction is initiated by anionic catalysts[10], but Shapoval and coworkers[11] have shown that a good yield of a crystalline stereoregular polyphenylisocyanate could be obtained by cathodic reduction of phenylisocyanate in dimethylformamide. The reaction was conducted in a divided cell† at nickel grid electrodes at controlled current (0·01 mA/cm^2) and tetrabutylammonium iodide as supporting electrolyte. The isolated yield was up to 75%. Similar results were obtained with diisocyanatotoluene (a mixture of 65% of the 2,4 isomer and 35% of the 2,6 isomer) and 1,6-diisocyanatohexane. The stereoregularity of the polymer formed was explained by an effect similar to that of an ordinary stereospecific catalyst.

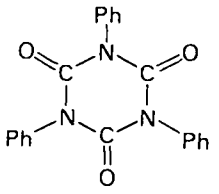
The possibility of initiating polymerization electrochemically has

†In absence of a diaphragm no polymer was formed indicating that the reaction in fact is electrochemical generation of an anionic polymerization catalyst. When an undivided cell is used, the catalyst is trapped by protons generated at the anode.

demonstrated the need for knowledge of the electrochemical (polarographic) behaviour of the isocyanates. Unfortunately no detailed product study has been reported, although a number of interesting proposals have been mentioned in another paper by the Russian workers[12]. It seems likely, however, that under protic conditions an isocyanate, **31**, is reduced in a two-electron process to the corresponding *N*-formyl amine, **32**, analogous to the reduction of isothiocyanates [see next section] (equation 16).

$$\underset{\textbf{(31)}}{RNCO} + 2e + H_2O \longrightarrow \underset{\textbf{(32)}}{RNHCHO} + 2OH^- \qquad (16)$$

In aprotic solvents the reaction appears to be somewhat more complicated, both the limiting current and the polarographic α-value being dependent on the substrate concentration. In addition to the polymerization reaction already mentioned also the formation of dimers and trimers of the type **33** has been discussed[12].



(33)

The assumption that the polarographic half-wave potential could serve as a parameter reflecting the reactivity of an aliphatic diisocyanate towards the formation of polyurethanes was the basis for the study of a series of compounds with the general formula $OCN-(CH_2)_n-NCO$[13]. A key step in urethane formation is the nucleophilic attack on the isocyanate group by a hydroxyl group, a process which was compared to the nucleophilic combination of an isocyanate with an electron. The half-wave potential was demonstrated to be strongly dependent on the number of methylene groups, n, inserted between the two isocyanate groups as illustrated in Figure 1.

An attenuation factor of the value 0·4 could be obtained from a plot of $\log E_{1/2}(n+1)$ versus $\log E_{1/2}(n)$. This is a rather high value demonstrating a strong effect of n on $E_{1/2}$ for small n values and a mild effect for high

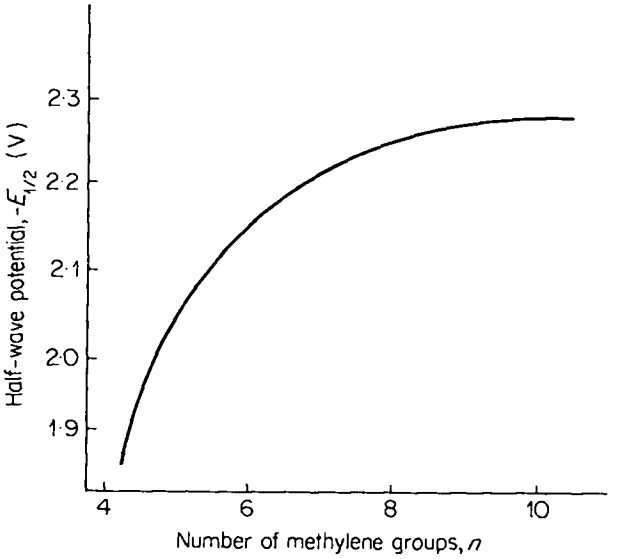


FIGURE 1.

n values, which is also supported by the Figure. The polarographic α-value was for all the compounds under investigation found to be close to 0·07 indicating a highly irreversible electrochemical reduction.

Also the aromatic isocyanates and diisocyanates are irreversibly reduced at the dropping mercury electrode[14,15], but the reported α-values are higher. A typical found value is 0·12[15].

It is of interest to note that, similar to the aliphatic diisocyanates, aromatic compounds substituted by two isocyanate groups give rise to only a single polarographic wave. The observed limiting currents are twice those of the corresponding monosubstituted compounds indicating simultaneous reduction of the two isocyanate groups by a four-electron process[14,15]. Electron-donating substituents, methyl and methoxy, were found to shift the $E_{1/2}$ values toward more negative values, while the electron-withdrawing chlorine had the opposite effect. An analogous effect was observed on the rate of formation of polyurethanes. Electron-donating substituents lower the rate of polyurethane formation, while electron-withdrawing substituents increase the rate when introduced into a diisocyanate molecule.

Further elaboration on this subject showed that a linear relationship exists between the half-wave potentials of isocyanates and the value of the substitution constant, σ[15]. Such relationships have been reported in

numerous cases[16], and it was possible to obtain values of the substituent constants for $-NCO$[15]. The slopes, ρ, were identical for a series of mono- and diisocyanates, and it was concluded that the susceptibility to the influence of substituents for the two groups of compounds is the same. Furthermore the positive sign of the slope (the value is not given) indicates the electrochemical step in the reduction process to be rate determining.

IV. ISOTHIOCYANATES

The isothiocyanates have been by far the most extensively studied class of compounds in this context.

Zahradnik[17] appears to have reported the first polarographic study of an isothiocyanate. Phenyl isothiocyanate was found to be reducible at the dropping mercury electrode in alkaline aqueous solution at $-1{\cdot}04$ V vs NCE independent of pH. Lund reported a combined polarographic and preparative study of the same compound[18]. In acidic solutions, two two-electron waves were observed, while in alkaline solution only one two-electron wave was observed. A preparative experiment under alkaline conditions resulted in the isolation of thioformanilide (**35**) according to the reaction scheme in equation (17).

$$\underset{\textbf{(34)}}{C_6H_5{-}N{=}C{=}S} + 2e + 2H_2O \longrightarrow \underset{\textbf{(35)}}{C_6H_5{-}NH{-}CHS} + 2OH^- \qquad (17)$$

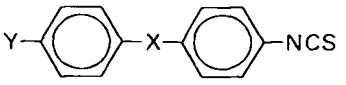
Thioformanilide was also suggested to be the product under acidic conditions, but the rapid hydrolysis of thioformanilide under these circumstances precluded a verification. Lund explained the appearance of a second polarographic wave in acidic solution by the further reduction of thioformanilide to *N*-mercaptomethylaniline, **36**, the fate of which was not reported.

$$\underset{\textbf{(35)}}{C_6H_5NHCHS} + 2e + 2H_2O \longrightarrow \underset{\textbf{(36)}}{C_6H_5NHCH_2SH} + 2OH^- \qquad (18)$$

However, in another preparative study by Zahradnik and coworkers[19] exhaustive electrolysis led to aniline, formaldehyde and hydrogen sulphide supporting the reaction scheme suggested by Lund. In the same paper[19] half-wave potentials for not less than 38 isothiocyanates were given.

Several polarographic studies have been reported where $E_{1/2}$ is correlated with the Hammett substituent constant[19–25]. Linear plots were

generally obtained and have been discussed in terms of electron-withdrawing and -donating effects of the various substituents. Extensive measurements were made on compounds of the general structure **37**[24–25].



(37)

X = CH=CH, S, O, CO, CH_2, COO, NH—NH, OCO, SO_2
Y = non-electroactive substituent

From the effect of Y on the half-wave potential for reduction of the NCS group, the ability of X to transfer electron-withdrawing or -donating effects could be studied. The results were in agreement with those obtained from i.r.-spectroscopic measurements and the coefficient of the electron transfer effects, π',[26] was calculated. The hindering effect was found to increase in the order given below compound **37**.

In all product studies reported, the products identified were always the corresponding thioformamides. An ECE mechanism (*e*lectron transfer followed by a *c*hemical step and further *e*lectron transfer) has been proposed for the electrochemical reduction of isothiocyanates in general[27] (equations 19–22).

$$\underset{\textbf{(38)}}{Ar{-}N{=}C{=}S} + e \xrightarrow{E} \underset{\textbf{(39)}}{Ar{-}\bar{N}{-}\dot{C}{=}S} \qquad (19)$$

$$\underset{\textbf{(39)}}{Ar{-}\bar{N}{-}\dot{C}{=}S} + H^{+} \xrightarrow{C} \underset{\textbf{(40)}}{Ar{-}\overset{H}{N}{-}\dot{C}{=}S} \qquad (20)$$

$$\underset{\textbf{(40)}}{Ar{-}\overset{H}{N}{-}\dot{C}{=}S} + e \xrightarrow{E} \underset{\textbf{(41)}}{Ar{-}\overset{H}{N}{-}\bar{C}{=}S} \qquad (21)$$

$$\underset{\textbf{(41)}}{Ar{-}\overset{H}{N}{-}\bar{C}{=}S} + H^{+} \xrightarrow{C} \underset{\textbf{(42)}}{Ar{-}\overset{H}{N}{-}CHS} \qquad (22)$$

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CHAPTER 10

Photochemistry of cyanates and related groups

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I. INTRODUCTION

Compared with thermal reactions of cyanates and related groups the photochemical reactions applied to this field of chemistry have been greatly neglected. This treatise deals with scientific findings of interest to the organic chemist, and with some physicochemical aspects which result from the irradiation of isocyanic acid vapour, methyl thiocyanate and methyl isothiocyanate. The photochemistry of SCN^- in aqueous solution has been omitted.

Photochemical conversions of the considered class of compounds can be reduced essentially to three mechanisms, all of which consist primarily of a homolytic scission of the molecule:

(a) The whole functional group dissociates as a radical from the fragment R:

$$\begin{aligned} RXCY + h\nu &\longrightarrow R^{\bullet} + {}^{\bullet}XCY \\ {}^{\bullet}XCY &\longleftrightarrow XCY^{\bullet} \\ XCY^{\bullet} + {}^{\bullet}R &\longrightarrow RYCX \end{aligned} \qquad (1)$$

On recombination often the more stable isomers are produced (e.g., isocyanates from cyanates, isothiocyanates from thiocyanates).

(b) In the case of cyanates, isocyanates and thiocyanates additional formation of a diatomic molecule occurs:

$$\begin{aligned} ROCN + h\nu &\longrightarrow RO^{\bullet} + {}^{\bullet}CN \\ RSCN + h\nu &\longrightarrow RS^{\bullet} + {}^{\bullet}CN \\ RNCO + h\nu &\longrightarrow RN + CO \end{aligned} \qquad (2)$$

The production of reactive alkoxy radicals, thiyl radicals and nitrenes leads to complex reaction mixtures.

(c) Finally it was found that on irradiation isothiocyanates have a tendency to form atomic sulphur and isonitriles:

$$RNCS + h\nu \longrightarrow RNC + S \qquad (3)$$

Aside from these major fragmentations a large number of side reactions, depending on temperature, concentration and nature of solvent, occur; these are discussed in the respective chapters. Moreover, as is characteristic for photochemical reactions, they are accompanied by the formation of polymers.

II. SPECTRA

In accordance with the little work that has been done on cyanates and related compounds only a small number of u.v. absorption spectra are available.

Alkyl cyanates show an absorption maximum at 260 nm ($\varepsilon = 13$), the exact position being solvent dependent; moreover, strong absorption occurs under 220 nm[1]. However, the cyanates were far less investigated than the isocyanates. Isocyanic acid vapour, photolysed at 200 mm pressure in order to suppress polymerization, absorbs continuously under 224 nm and shows diffuse bands between 257 and 225 nm[2]. The long-wave limit of the absorption continuum for alkyl isocyanates occurs at approximately 230 nm. Acetyl isocyanate shows an additional band

with a minor extinction at 248 nm, which may be ascribed to the acetyl carbonyl chromophore[3].

More u.v. spectra are available for isothiocyanates[4–6]. Independent of the structure, absorption is observed at 244–249 nm (see Table 1).

TABLE 1. Position and intensity of u.v. absorption maxima of alkyl isothiocyanates[6]

Alkyl group	Wave length (nm)	Extinction (log ε)
Methyl	244	2·8
Ethyl	245	2·9
Isopropyl	246	2·90
t-Butyl	248	3·05
Isobutyl	245	2·86
n-Butyl	245	2·85
n-Amyl	245	2·83
n-Hexyl	245	2·78
n-Octyl	245	2·94
Cyclohexyl	246·5	2·94
Allyl	246	2·94
DL-α-Methallyl	248	2·98
β-Methallyl	247	2·97
trans-Crotyl	246·5	3·04
3-Butenyl	246	2·94
4-Pentenyl	245	2·85
Benzyl	248	3·08
DL-α-Phenetyl	247·5	3·19
3-Methylthiopropyl	245·5	3·01
4-Methylthiobutyl	245	2·98
5-Methylthiopentyl	245	2·97
Phenyl	270	3·98

The order of magnitude of the molar extinction amounts to 10^3, and the absorption is assigned to an allowed $\pi \rightarrow \pi^*$ transition. This should lead from the dipolar structure of the isothiocyanate, which can be attributed from i.r. and Raman spectra analysis, to the cumulated arrangement of the double bonds[6].

$$R-\overset{+}{N}\equiv C-\overline{S} + h\nu \longrightarrow R-N=C=S \qquad (4)$$

On the other hand the isomeric alkyl thiocyanates absorb much less ($\varepsilon = 30$) in the 240 nm region[5] and the maximum apparently results from a forbidden transition. In fact, in the case of thiocyanates the $\pi \rightarrow \pi^*$ transition is accompanied by a charge distribution and leads to a dipolar structure containing trivalent sulphur[6].

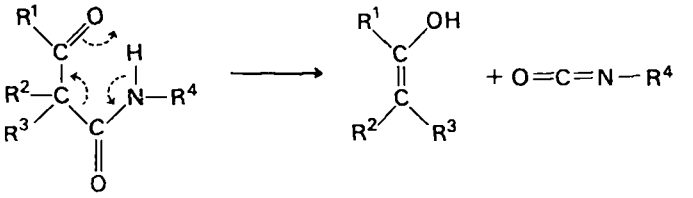
$$R{-}S{-}C{\equiv}N + h\nu \longrightarrow R{-}\overset{+}{S}{=}C{=}\bar{N} \qquad (5)$$

Methyl thiocyanate as well as methyl isothiocyanate absorb continuously in the vacuum u.v., where the isothiocyanate shows an extensive maximum from 165 to 185 nm[7].

III. ISOCYANATES

A. Photochemical Synthesis of Isocyanates

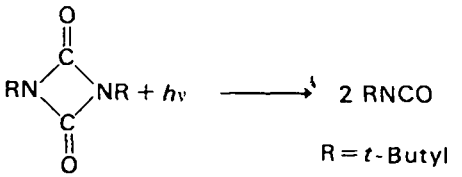
An intramolecular hydrogen transfer caused by a CO group (as observed with numerous photochemical reactions) leads on irradiation of *N*-substituted β-oxo-amides to the scission of the molecule. The isocyanate and the enol form of the ketone are produced by way of a six-membered cyclic transition state whose conformation is facilitated by hydrogen bonding[8].



(6)

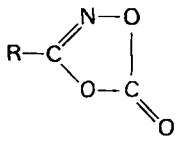
The yields achieved correspond approximately to normal preparative methods, if R^4 = phenyl, *p*-tolyl, benzyl, α-naphthyl or cyclohexyl. Pyridine-2-isocyanate has been prepared for the first time according to this reaction and was isolated as α-pyridyl urea due to the presence of NH_3 during irradiation.

Furthermore, isocyanates appear as the products of the light-induced decomposition of acyl azides[9], 1,3-di-*t*-butyl-1,3-diazetidinedione (**1**) (equation 7)[10] and of the five-membered heterocycles **2** and **3** (equations 8 and 9)[11].



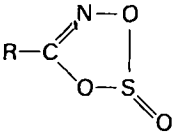
(7)

(**1**)



$$+ h\nu \xrightarrow[-CO_2]{} 2\ \text{RNCO} \qquad \text{R = Aryl} \tag{8}$$

(2)



$$+ h\nu \xrightarrow[-SO_2]{} 2\ \text{RNCO} \qquad \text{R = Aryl} \tag{9}$$

(3)

A complete agreement could not be achieved on the question of whether the formation of the isocyanate from the dioxazolone **2** and from the dioxathiazole **3** proceeds over a discrete acyl nitrene intermediate, or whether—as was proved in the case of the photolysis of pivaloyl azide[12]—a photo-Curtius rearrangement takes place[13].

B. Nitrenes from Isocyanates

Like organic azides, isocyanates on irradiation represent a potential source of nitrenes. However, not only the desired dissociation of the RN–CO bond occurs, but also the scission of the R–NCO bond, contrary to azides which dissociate much more cleanly at the RN–NN bond. The photochemical synthesis of nitrenes from isocyanates proceeds in a far less specific manner than their preparation from azides and has therefore found no interest in laboratory praxis.

1. Photolysis of isocyanic acid vapour

From the possible isomers with the formula CHNO only isocyanic acid, H—N=C=O, is stable in the vapour phase. The vapour of isocyanic acid absorbs continuously at wave lengths below 224 nm (see Section II) so that in irradiation experiments mainly unfiltered medium-pressure mercury lamps were used.

Because of the structural similarity with ketene, isocyanic acid shows similar photolytic behaviour and produces primarily the NH radical[14,15] and carbon monoxide. Besides the N–C bond also the H–N bond is split producing the NCO radical[16,17].

$$HNCO + h\nu \longrightarrow \begin{cases} NH + CO \\ H^{\bullet} + {}^{\bullet}NCO \end{cases} \longrightarrow N_2 + CO + H_2 \qquad (10)$$

Both primary processes proceed with a quantum yield higher than 0·5; as end-products N_2, H_2 and CO can be identified[18]. The production of H_2 does not occur when the irradiation of isocyanic acid takes place in the presence of ethylene, O_2 or NO[19]. Although the formation of the simplest nitrene, NH, according to this photolysis has no preparative significance, the strong emission bands from NCO and NH allow the determination of bond energies and heat of formation of the isocyanic acid[20].

If the photolysis of HNCO is not carried out in the gas phase but in a matrix (Ar, Ne, N_2 or CO) at a few degrees Kelvin, then isomerization to cyanic acid (equation 11 and 12) accompanies the formation of NCO (equation 13 and 14)[21].

$$HNCO + h\nu \longrightarrow NH + CO \qquad (11)$$

$$NH + CO \longrightarrow HOCN \qquad (12)$$

$$HOCN + h\nu \longrightarrow NCO^{\bullet} + {}^{\bullet}H \qquad (13)$$

$$HNCO + h\nu \longrightarrow NCO^{\bullet} + {}^{\bullet}H \qquad (14)$$

2. Alkyl and acyl isocyanates

Analogous to isocyanic acid, two reaction mechanisms operate when methyl isocyanate is irradiated in the vapour phase between 240 and 210 nm[22].

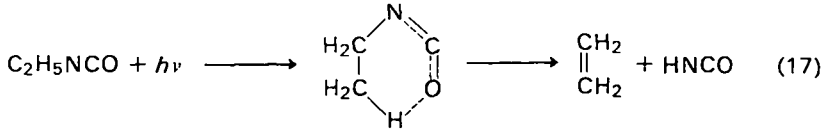
$$CH_3NCO + h\nu \longrightarrow \begin{cases} CH_3^{\bullet} + {}^{\bullet}NCO \\ CH_3N + CO \end{cases} \qquad (15)$$

If the decomposition is Hg-sensibilized, reaction of two NCO radicals yields N_2 and CO. In direct photolysis, on the other hand, the NCO radical seems to abstract hydrogen and isocyanic acid is formed. In both cases the methyl nitrene polymerizes due to its reaction with CH_3NCO or further nitrene molecules.

With the next higher homologue, ethyl isocyanate, an additional third primary process can be observed[3].

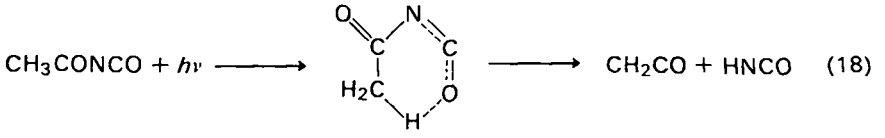
$$C_2H_5NCO + h\nu \longrightarrow C_2H_4 + HNCO \quad (16)$$

Ethylene is formed besides C_2H_5N and the NCO radical—probably as the product of a Norrish Type II process, which proceeds over a six-membered cyclic transition state (equation 17).



(17)

The photolysis of acetyl isocyanate, CH_3CONCO, seems to occur through a similar cyclic transition state which yields ketene as the main product[3].

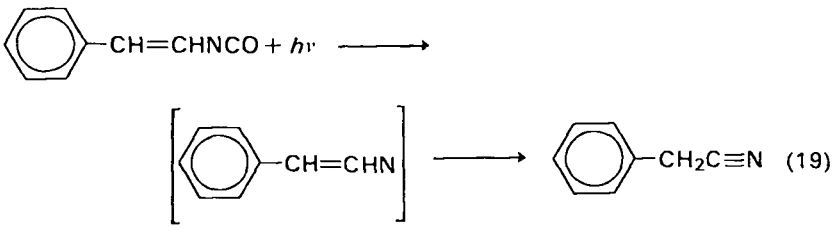


(18)

Upon irradiation of chloro isocyanate with a high-pressure mercury lamp, the formation of $COCl_2$, CO and N_2 can be observed; when using a Pyrex glass filter chlorocarbonyl isocyanate, ClCONCO, appeared as an additional product[23].

3. Aryl and styryl isocyanates

Photodecomposition of phenyl isocyanate, *o*-tolyl isocyanate and naphthyl-1-isocyanate yields aryl nitrenes. On u.v. irradiation in a hydrocarbon matrix at 70 K triplet signals were measured which were identical with those obtained from photolysed phenyl azide[24]. The reaction products from the photolysis of styryl isocyanate and biphenyl isocyanate proved to be very similar to those which were observed at their preparation from nitrene precursors (e.g., azide + $h\nu$, nitro compounds + phosphines)[25,26].



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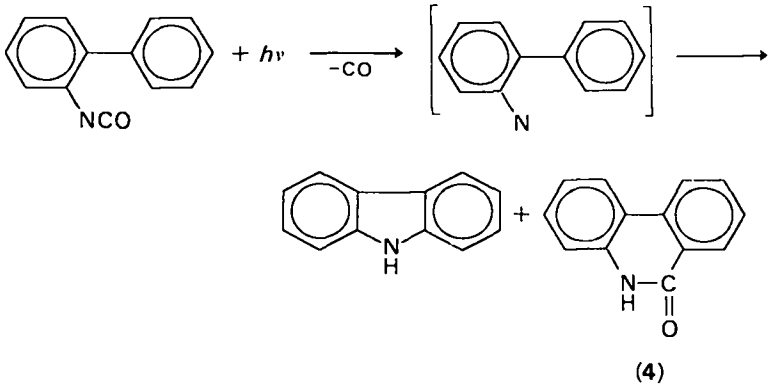


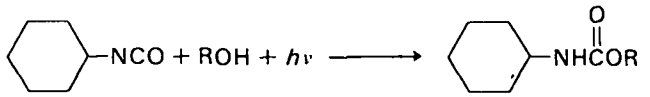
(20)

(4)

In addition phenantridone (**4**) is formed when the phenyl group reacts with the excited isocyanate.

C. Photoassisted Addition of Alcohols

The well known ionic reaction between alcohols and isocyanates, yielding urethanes, often proceeds very slowly (and gives a large amount of elimination product) when sterically hindered alcohols are used. The rate of this addition reaction may be enhanced by using a tungsten lamp, chlorinated solvents and various catalysts[27].



R = *t*-Butyl (21)

A 92% yield of *t*-butyl cyclohexylcarbamate is thus obtained by exposing a CCl_4 solution of the respective alcohol and isocyanate to light for 12 hours.

IV. PHOTOLYSIS OF CYANATES

Cyanates, ROCN, have a similar structure to the organic nitrites and hypohalogenites, whose photochemistry has been intensively investigated. However the photolysis of the cyanates has found little attention. Hara and coworkers irradiated (gaseous) *n*-butyl cyanate, which has an absorption maximum at 260 nm and a strong absorption band below 220 nm, with a high-pressure mercury lamp and obtained mainly *n*-butyl isocyanate and *n*-butyl isocyanurate (the cyclic trimer of *n*-butyl isocyanate)[1].

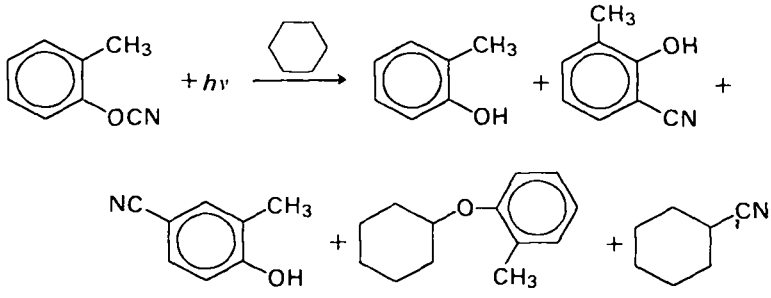
$$n\text{-}C_4H_9OCN + h\nu \longrightarrow n\text{-}C_4H_9NCO \longrightarrow (n\text{-}C_4H_9NCO)_3 \quad (22)$$

Since this is the only conversion on irradiation with light of 250 nm and the only reaction that occurs even when sensibilized with Hg or benzene, it is assumed that it proceeds via a triplet state without really producing radicals. The formation of by-products (HCN, n-C_4H_9OH, n-C_3H_7CHO etc.), however, appears to be the result of fragmentations, which assume a high energy singlet state as the excited intermediate. These radical reactions are not suppressed on addition of O_2 as is the case with the isomerization.

Likewise on irradiating aryl cyanates in cyclohexane solution a radical scission takes place[28].

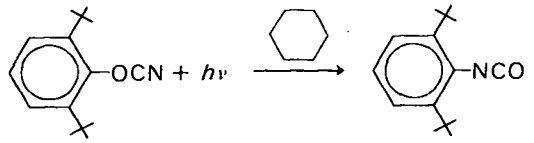
$$ArOCN + h\nu \longrightarrow ArO^{\bullet} + {}^{\bullet}CN \quad (23)$$

Aryloxy radicals are sufficiently stabilized to undergo not only dehydrogenation reactions with the solvent but also rearrangements (e.g., o-tosyl cyanate forms various phenols[28]; equation 24), whereas alkoxy radicals are too unstable and immediately abstract hydrogen from the solvent.



(24)

However, if the cyanate group is in a well-shielded position (e.g., as in the cyanate **5**) the isomerization becomes dominant again[28].



(25)

(5)

Contrary to the photolysis of nitrites and hypohalogenites in which the RO–NO and RO–X bond is split, under the same conditions cyanates are frequently isomerized to isocyanates. This corresponds to higher bond energies in the cyanate group and to its greater stability in the excited state.

V. THIOCYANATES AND ISOTHIOCYANATES—PHOTOISOMERIZATION

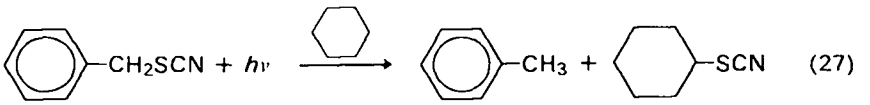
On irradiation in vacuum ultraviolet methyl thiocyanate as well as methyl isothiocyanate produce a fluorescence spectrum, which proves the generation of excited SCN radicals[7]. For the cleavage of the CH_3–NCS bond and the CH_3–SCN bond, 3·37 eV (≙ 188 ± 1 nm) and 3·04 eV (≙ 197 ± 1 nm), respectively, are required. Methyl thiocyanate, moreover, undergoes a scission of the CH_3S–CN bond with the formation of an excited CN radical.

$$CH_3SCN + h\nu \longrightarrow \begin{cases} CH_3^\bullet + {}^\bullet SCN \\ CH_3S^\bullet + {}^\bullet CN \end{cases} \qquad (26)$$

$$CH_3NCS + h\nu \longrightarrow CH_3^\bullet + {}^\bullet NCS$$

Irradiation of benzyl thiocyanate or benzyl isothiocyanate in cyclohexane leads to a photoequilibrium position of isothiocyanate:thiocyanate = 24:1[29,30].

Moreover on longer exposure to irradiation dehydrogenation of the solvent by benzyl radicals and thiocyano radicals becomes noticeable. In fact the formation of toluene, cyclohexyl thiocyanate and of their secondary reaction products dicyclohexyl sulphide and dicyclohexyl disulphide was observed.



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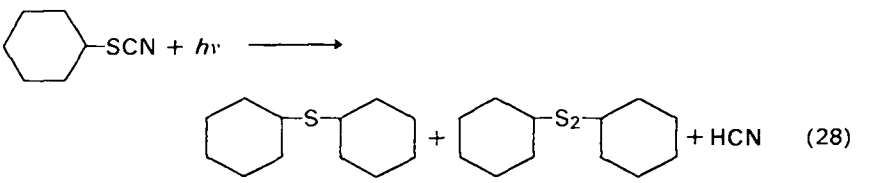


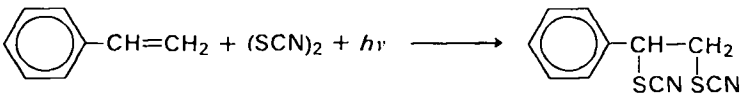
(28)

Cyclohexyl thiocyanate does not isomerize to isothiocyanate on irradiation, so that this photoisomerization cannot be regarded as a general reaction of alkyl thiocyanates and alkyl isothiocyanates.

VI. THIOCYANATION

On photolysis thiocyanogen decomposes into two thiocyano radicals, which can substitute hydrogen in the benzylic position[31,32]. Furthermore photochemical addition reactions of thiocyanogen to olefin double bonds are known[33].

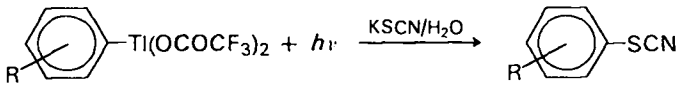
An interesting combination of an electrochemical and a photochemical process represents the thiocyanate addition to styrene[34]. A solution of KSCN in methanol is irradiated during the electrolysis, resulting in a homolytic scission of the electrochemically produced $(SCN)_2$, followed



(29)

by radical addition to the styrene in high yields.

The irradiation of an aqueous solution of KSCN gains preparative importance if it is carried out in the presence of the easily obtainable aryl-thallium bistrifluoroacetates[35].



(30)

In this way thiocyanates are obtained in moderate yields from activated as well as non-activated aromatic compounds, whereby the thiocyanate group enters the aromatic ring at the position to which thallium was originally attached.

Aromatic thiocyanates are obtained in small quantities if, instead of the thallium compounds, the corresponding halobenzenes are used[36].

VII. ELIMINATION OF ATOMIC SULPHUR FROM ISOTHIOCYANATES

For $\rangle C{=}S$ compounds, whose $\pi \rightarrow \pi^*$ transition occurs at approximately 250 nm, the low-pressure mercury lamp (almost pure emission at 253·7 nm) represents an excellent irradiation source.

Mustard oils, whose absorption maxima lie in this region, decompose to isonitriles and sulphur[37,38].

$$RNCS \overset{h\nu}{\rightleftharpoons} RNC + S(^3P) \qquad (31)$$

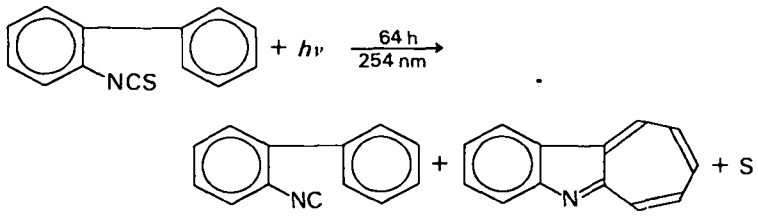
As the formed isonitrile adds the sulphur (reproducing mustard oil), the isonitrile (by Passerini reaction[37]) or the sulphur (by addition to cyclohexene) has to be removed from the equilibrium mixture in order to obtain a high conversion. Aside from the formation of cyclohexene episulphide, the sulphur undergoes no C–H insertion reaction and exists apparently in the triplet state.

(32)

In this way, after *c.* 30 hours of photolysis, cyclohexene episulphide is produced in about 40% yield from ethyl mustard oil with a tenfold excess of cyclohexene[39]. This value represents a maximum and decreases on continued irradiation, since episulphides also absorb the applied light to a slight extent and decompose[40].

The decomposition to isonitrile and atomic sulphur appears to be a general reaction of alkyl isothiocyanates and is dependent on the group R only insofar as it shifts the absorption maximum of the irradiated compound relative to the narrow emission region of the low-pressure mercury lamp.

Under very similar conditions biphenyl-1-isothiocyanate undergoes photodecomposition yielding the corresponding isonitrile and sulphur[38].



(33)

(6)

By an intramolecular ring expansion reaction the aromatic isonitrile forms the condensed heterocyclic compound, **6**, in moderate yields.

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CHAPTER 11

Radiation chemistry of organic compounds containing OCN, CNO, SCN, and CNS groups

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I. INTRODUCTION

Radiation chemistry is closely related to photochemistry. It can be considered as an extension of photochemistry to the region where the photon energies exceed the ionization potentials of the irradiated compounds.

Fundamental aspects of radiation chemistry have already been reviewed in this series[1,2] and the reader is referred to them, as well as to some excellent books and reviews[3–8]. The following brief outline is intended to provide the reader with the necessary minimum background information.

Radioactive sources of α-, β- and γ-rays are employed in radiation chemistry, as are different types of accelerators which can generate X-rays, electrons and positive ions. The spectrum of photon (X- and γ-rays) and particle (α, β, electrons, protons and neutrons) energies available from the various sources of high-energy radiation ranges from hundreds of electron volts (eV) to millions of electron volts (MeV). Sources such as linear electron accelerators can be operated in a pulsed mode while others, such as ^{60}Co gamma cells, supply a continuous beam of radiation.

According to the classification originally suggested by Platzman[9–11] the first stage of radiolysis involves the absorption of energy, its degradation to the atomic level and the formation of a great number of diversely activated molecules that are non-uniformly distributed in the irradiated medium. This stage is defined as the *physical stage*. In the *physicochemical stage* which follows, the unstable primary products formed in the first stage undergo secondary reactions which may occur either spontaneously or in collision. This stage is followed by the *chemical stage* in which thermal equilibrium is attained and the radicals present in the system react with each other and with the medium. The absorption of ionizing radiation is not selective, and every component of a system absorbs energy in proportion to its electron density and concentration. The yield of products and intermediate molecules per 100 eV of absorbed energy, known as the *G* value, indicates the efficiency of radiolysis. The ionization potentials of most compounds are in the vicinity of 10 eV. However, in gases and in the condensed phase only three to four ion pairs are formed per 100 eV of absorbed energy. Also, *G* (radicals) does not exceed 10 while the bond dissociation energies of most of the organic compounds range between 3 to 4 eV. Thus it appears that the absorbed energy in a radiolysed system is not utilized efficiently.

In many cases the energy initially absorbed by the whole system is transferred to a specific component that is present in a low concentration. Consequently the chemical change that such a component undergoes occurs at the expense of the bulk of the system. An interaction of this type is often referred to as 'radiation protection'. In systems in which redistribution of energy takes place, the apparent efficiency with which the absorbed energy is utilized increases. This is also the effect in the case of radiation-induced chain reactions.

Radiation chemistry may be subdivided, into two areas: the study of the overall chemical change induced by ionizing radiation, and the study of intermediates and their reactions. In spite of the extremely high energies of the particles and photons absorbed by a radiolysed system and in spite of the large number of states that are initially formed the final products of radiolysis are quite simple. These products are formed either by free radical or ionic reactions, and many of the chemical changes induced by decomposition of free radical initiators, photolysis, ionic catalysis and other conventional methods, also can be brought about by ionizing radiation. Unfortunately, the potential applications of radiation chemistry are reflected more in the patent literature than in production lines.

In the study of the fundamental aspects of radiation chemistry it is necessary to detect and identify transient species such as electrons, positive ions, excited molecules and radicals, and to establish the kinetics of the reactions in which these intermediates participate. Pulse radiolysis is the most widely used technique in these types of studies. A short and intense pulse of ionizing radiation produces transient species in concentrations that are sufficiently high to be detected by various means that include absorption and emission spectra, electron spin resonance spectra, electrical conductivity, etc. Nanosecond and even shorter pulses can presently be generated, thus making possible the study of the reactions of very short-lived intermediates.

An alternative (matrix isolation) technique used in the study of intermediates and their reactions is based on the fact that the lifetime of various transient species considerably increases in rigid matrices. Particularly suited for the trapping of intermediates are glasses and solids at very low temperatures.

Kinetic studies are complicated by the fact that homogeneous kinetics can be applied only in the gas phase where the reactive intermediates are not confined in the particle tracks and the effects of linear energy transfer (LET) are drastically reduced. Since liquid-phase radiolytic reactions strongly depend on the polarity of the medium, specific non-homogeneous kinetic models were developed for these systems[11–15]. In solids the possibility of long range interactions (energy and charge transfer) further complicates the situation.

Until now, systematic studies of the radiation chemistry of organic cyanates, isocyanates, thiocyanates and isothiocyanates have not been carried out. However, in the work that has been done, many of the above discussed aspects of radiation chemistry are touched upon.

II. SCHEMATIC OUTLINE OF THE RADIATION CHEMISTRY OF ORGANIC COMPOUNDS CONTAINING OCN, NCO, SCN AND NCS GROUPS

The radiation chemistry of organic cyanates has not yet been studied. Investigations of organic isocyanates, thiocyanates and isothiocyanates have been limited to the condensed phase. The radiation chemistry of this class of compounds is expected to follow the schematic outline given below. This outline applies only to condensed phase reactions; ion–molecule and unimolecular decomposition reactions that might occur in gases are not considered.

A. Pure Compounds

The primary processes in the radiolysis of organic OCN, NCO, SCN and NCS compounds (RX, where X refers to the above functional groups) are excitation and ionization which are represented as:

$$RX \rightsquigarrow RX^{*} \quad (1)$$

$$RX \rightsquigarrow [RX^{+} + e] \quad (2)$$

The electron and the parent positive ion formed in close proximity may either recombine, forming an excited molecule, or diffuse apart;

$$[RX^{+} + e] \longrightarrow RX^{*} \quad (3)$$

$$[RX^{+} + e] \longrightarrow RX^{+} + e \quad (4)$$

Electrons that succeed in escaping from the parent positive ion can attach themselves to other RX molecules. By analogy with halogen compounds and nitriles, both dissociative and non-dissociative electron capture is possible:

$$RX + e \longrightarrow RX^{-} \text{ non-dissociative capture} \quad (5)$$

$$RX + e \longrightarrow R + X^{-} \text{ dissociative capture} \quad (6)$$

The electron capture is followed by neutralization reactions (7) and (8):

$$RX^{-} + RX^{+} \longrightarrow 2RX \quad (7)$$

$$X^{-} + RX^{+} \longrightarrow X + RX \quad (8)$$

It is generally believed that although RX molecules formed in these neutralization reactions are excited, the excess energy is not sufficient to cause significant decomposition. If the molecular cation, RX^+, and the molecular anion, RX^-, are sufficiently long-lived they might initiate ionic polymerization reactions of the following type:

$$RX^+ + n\ RX \longrightarrow (RX)^+_{n+1} \text{ cationic polymerization} \quad (9)$$

$$RX^- + n\ RX \longrightarrow (RX)^-_{n+1} \text{ anionic polymerization} \quad (10)$$

The reactive site in these polymerization reactions might be X or a suitable reactive functional group present in the RX molecule.

The excited molecules formed in reactions (1) and (3) that are not collision deactivated will decompose forming stable molecules and free radicals:

$$RX^* \longrightarrow \text{Products (mainly } H_2 + MX \text{ where R = hydrocarbon radical)} \quad (11)$$

$$RX^* \longrightarrow R + X \quad (12)$$

$$RX^* \longrightarrow H + {}^\bullet R'X \quad (13)$$

Radicals formed by reactions (6), (8), (12) and (13) can react between themselves and with the RX molecules. These reactions result in the formation of all the other products of radiolysis. Telomers and polymers might be among these products and again, as in the case of ionic polymerization, X is not necessarily the active site of polymerization.

It should be noted that some of the products of the radical reactions might be identical with those formed in the unimolecular decomposition of the excited species RX*. Thus hydrogen may be formed either by reaction (11) or (14):

$$H + RX \longrightarrow H_2 + {}^\bullet R'X \quad (14)$$

In this case, addition of an appropriate scavenger might help to distinguish between the two routes of product formation. However, the use of scavengers does not allow the distinction between products that are formed by reactions of radicals that do not diffuse apart as a result of spare and cage effects, and these formed by unimolecular reactions, if these products are identical.

B. Mixtures

Many of the reactions that take place in the pure compounds can also occur in systems in which a small amount of RX is added to another

compound. Obviously, the initially-formed reactive species, i.e. excited molecules, molecular cations, electrons and radicals, will be those formed from the medium compound. However, various energy transfer reactions may result in the preferential decomposition of the added RX. Additional reactions characteristic of the medium compound to which RX has been added are also possible. Thus in aqueous systems, RX may be attacked not only by hydrogen atoms but also by the aquated electron e_{aq} and the HO and HO_2 radicals[16]. In alcohols, reactions with solvated electrons, hydrogen atoms and alkoxy radicals are expected[17] while in alkanes[18], hydrogen atoms, electrons and alkyl radicals are expected to react with RX.

III. THE RADIATION CHEMISTRY OF THIOCYANATES

A. Aliphatic Thiocyanates

The gamma radiolysis of aliphatic thiocyanates, RSCN, was investigated at 77 K mainly by electron spin resonance spectroscopy[19–21]. The following thiocyanates were studied: R = ethyl, propyl, isoamyl, hexyl and nonyl[19,20] and R = butyl, octyl, decyl and undecyl[20,21]. Alkyl radicals are formed in all the thiocyanates by dissociative electron capture:

$$RSCN \rightsquigarrow (RSCN)^+ + e \qquad (15)$$

$$RSCN + e \longrightarrow R^{\cdot} + SCN^- \qquad (16)$$

The formation of the molecular cations $(RSCN)^+$ was observed in all thiocyanates both by e.s.r. spectra and optical absorption. For example, in the case of hexyl thiocyanate an absorption band with a maximum at 510 nm was observed and attributed to $(n\text{-}C_6H_{13}SCN)^+$. Upon addition of diphenyl amine (DPA) this band is wiped out and another band with λ_{max} at 700 nm appears. This new band is characteristic of DPA^+ thus indicating that the following positive charge transfer reaction takes place:

$$(n\text{-}C_6H_{13}SCN)^+ + DPA \longrightarrow n\text{-}C_6H_{13}SCN + (DPA)^+ \qquad (17)$$

Radicals formed as result of hydrogen abstraction from the thiocyanates ($C_2H_{2n+1}SCN$) were observed for the higher homologues for which $n > 4$. It is suggested that these radicals originate from the initially formed excited thiocyanate molecules via the reaction sequence:

$$RSCN \rightsquigarrow (RSCN)^{*} \quad (18)$$

$$(RSCN)^{*} \longrightarrow R'^{\bullet}SCN + H \quad (19)$$

$$H + RSCN \longrightarrow R'^{\bullet}SCN + H_2 \quad (20)$$

The structure of the R'·SCN radicals has not been determined. It is conceivable, however, that the reactive hydrogen atoms located at the position α to the substituent will most likely be removed. This type of preferential hydrogen-atom removal has been observed in the case of other alkane substituents such as chlorine[22], hydroxyl[23] and ethoxy[24].

The initial total radical yields are the same in all the aliphatic thiocyanates and equal to 4·0 ± 0·8 while the yield of R'·SCN radicals varies with the number of carbon atoms in R. G(R·SCN) determined for the various groups are[20]: ethyl 0·65 ± 0·13, *n*-propyl 0·62 ± 0·12, *n*-butyl 0·63 ± 0·12, isoamyl 0·70 ± 0·14, *n*-hexyl 0·80 ± 0·16, *n*-octyl 0·90 ± 0·18, *n*-nonyl 0·97 ± 0·19, *n*-decyl 1·02 ± 0·20 and *n*-undecyl 1·05 ± 0·21. A linear dependence between these yields and the electron fraction of the alkyl part of the molecule, equal to $(8n + 1)/(8n + 30)$ was shown to exist for $n > 4$.

The hydrogen yields from the various aliphatic thiocyanates were determined by mass spectrometry. Except for the first three thiocyanates, where the hydrogen yield is very close to zero, the $G(H_2)$ values are half of the above radical yields. In order to account for these observations the authors suggest that in the case of ethyl, propyl and butyl thiocyanates, reactions (19) and (20) do not occur. It is suggested that in these thiocyanates R'·SCN radicals are formed as follows:

$$R + RSCN \longrightarrow R'^{\bullet}SCN + RH \quad (21)$$

analogous with similar reactions that were observed in radiolytic studies of haloalkanes[25,26]. The yields of alkanes formed in those reactions were not determined.

The linear dependence of $G(H_2)$ on the electron fraction of the hydrocarbon chain in aliphatic thiocyanates was used to estimate the hydrogen yield in alkanes, the precursors of which are electronically excited molecules. By extrapolating $G(H_2)$ in thiocyanate to $n = \infty$, a value of 0·8 was obtained. This is in reasonable agreement with other estimates of this hydrogen yield in alkanes[27–29]. However the validity of the underlying assumptions in the derivation of the above hydrogen yield from the yield in aliphatic thiocyanates can be questioned.

The gamma radiolysis of frozen *n*-heptane solutions of the thiocyanates

$C_nH_{2n+1}SCN$, with $n = 1$ to 11, was studied by Nanobashvili and coworkers[30] at 77 K. E.s.r. studies indicate that addition of all these thiocyanates to *n*-heptane considerably lowers the radical yield as compared to the radical yield in the pure solvent. However the radical yields are still higher than those in the pure thiocyanates. It is suggested that this indicates that aliphatic thiocyanates are able to protect alkanes against irradiation. The radiation protection of the alkanes is the result of some type of energy transfer reaction between the dissolved thiocyanate and the primary species formed mainly from the alkane medium. Electron capture by the thiocyanates appears to be the most likely mode of energy transfer although transfer of excitation energy from the initially formed electronically excited *n*-heptane molecules (reaction 22) is also possible.

$$(n\text{-}C_7H_{16})^* + RSCN \longrightarrow n\text{-}C_7H_{16} + (RSCN)^* \qquad (22)$$

B. Aromatic Thiocyanates

Relatively high doses of up to 3×10^8 rad (1 rad = 6×10^{13} eV/g) were used by Sugii, Kitahara and Nagai[31] in their study of the ^{60}Co gamma radiolysis of benzyl thiocyanate. Benzene, toluene, benzyl mercaptan, benzyl cyanide, dibenzyl sulphide and a trimer were found among the products of radiolysis. Probably, phenyl, benzyl, benzyl-mercapto, benzyl-cyano, cyano and thiocyanate radicals participate in the reactions that lead to the formation of these products. However, some of the products could also be formed in secondary reactions. Radiation-induced isomerization of benzyl thiocyanate to benzyl isothiocyanate was also observed by these authors. At a dose of $3{\cdot}1 \times 10^8$ rad, 8·3% of the benzyl thiocyanate is converted into benzyl isothiocyanate. Furthermore, the radiolysis of benzyl isothiocyanate at the same dose results in a 1·7% isomerization into the corresponding thiocyanate and in the formation of products similar to those observed in the radiolysis of benzyl thiocyanate. These results indicate that if dissociation and recombination are the two steps of the isomerization, then charge rearrangement in the thiocyanate anion or radical is possible.

The reaction between the aquated electron and benzyl thiocyanate:

$$e_{aq} + C_6H_5CH_2SCN \longrightarrow C_6H_5CH_2 + SCN^- \qquad (23)$$

was studied by Christensen, Sehested and Hart[32] by pulse radiolysis. The formation of the benzyl radical was detected. The rate constant k_{23} of the dissociative electron capture was found to be $2{\cdot}0 \times 10^9$ mol^{-1} sec^{-1}.

IV. THE RADIATION CHEMISTRY OF ISOTHIOCYANATES

A. Aliphatic Isothiocyanates

Trofimov and Chkheidze[33] analysed the e.s.r. spectrum of gamma irradiated methyl isothiocyanate at 77 K and identified the two radicals, $\cdot CH_2NCS$ and $CH_3NH-\dot{C}=S$. The spectrum indicates that, upon gamma irradiation, ions carrying negative or positive charge are also formed and stabilized at low temperature. It is suggested that the two radicals are formed by reactions of hydrogen atoms: $\cdot CH_2NCS$ by abstraction (24) and $CH_3NH-\dot{C}=S$ by addition (25).

$$H + CH_3NCS \longrightarrow H_2 + {}^{\bullet}CH_2NCS \quad (24)$$

$$H + CH_3NCS \longrightarrow CH_3NH-\dot{C}=S \quad (25)$$

Analysis of the e.s.r. spectrum also shows that in the latter case the hydrogen atom attaches itself to the nitrogen atom in NCS. It should be noted that reaction (24) cannot be the only source of $\cdot CH_2NCS$ radicals as suggested. The very fact that hydrogen atoms are formed is indicated by their capture and the formation of $CH_3NH-\dot{C}=S$ radicals. This shows that some or even all the $\cdot CH_2NCS$ radicals can be formed from an electronically-excited methyl isothiocyanate molecule created either directly upon irradiation (26) or as result of recombination between the initially formed anion-radical and electron (27).

$$CH_3NCS \rightsquigarrow (CH_3NCS)^{\bullet} \longrightarrow H_{hot} + {}^{\bullet}CH_2NCS \quad (26)$$

$$CH_3NCS \rightsquigarrow [CH_3NCS^{+} + e] \longrightarrow (CH_3NCS)^{\bullet} \longrightarrow H_{hot} + {}^{\bullet}CH_2NCS \quad (27)$$

It is conceivable that at least some of the hydrogen atoms thus formed are 'hot', i.e. electronically and translationally excited, and therefore very reactive chemically. Evidence for the occurrence of hot-atom and hot-radical reactions in solids and glasses was found in other systems irradiated at 77 K[34–36]. It appears that electron capture by methyl isothiocyanate is non-dissociative since methyl radicals were not detected.

Chung and Williams[37] carried out e.s.r. studies of gamma-irradiated crystalline *t*-butyl isothiocyanate in the dark at 77 K. Both the radical anion $(CH_3)_3CNCS^{\cdot -}$ and the radical anion pair $(CH_3)_3C\cdots NCS^{\cdot -}$ are formed as result of electron capture by *t*-butyl isothiocyanate. The radical anion can be photobleached irreversibly

$$(CH_3)CNCS + e \longrightarrow (CH_3)CNCS^{\bullet -} \quad (28)$$

$$(CH_3)_3CNCS + e \longrightarrow (CH_3)_3C\cdots NCS^{\bullet -} \quad (29)$$

$$(CH_3)_3CNCS^{\bullet -} \longrightarrow (CH_3)_3C\cdots NCS^{\bullet -} \quad (30)$$

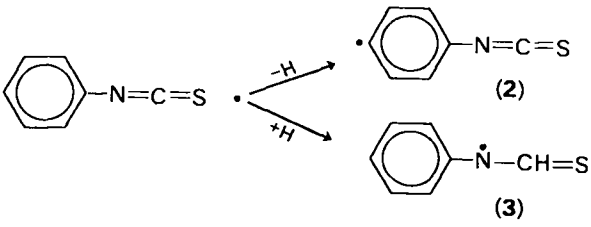
forming the radical anion pair. The two transient species can therefore be considered as intermediates in the dissociative electron capture by *t*-butyl isothiocyanate. E.s.r. studies of the radicals formed from aliphatic isothiocyanates in adamantane (**1**) matrix, upon room temperature X-ray

(1)

irradiation, were carried out by Wood, Lloyd and Lethan[38,39]. The use of adamantane offers several advantages over the widely used low temperature matrix isolation technique. It does not require the complex instrumentation necessary in the low temperature method and the results are not in the form of powder spectra, which can be rather difficult to interpret. Adamantane can be considered as a hydrocarbon matrix in which 2-adamantanyl radicals are formed upon irradiation. Analysis of the e.s.r. spectra indicates that introduction of ethyl, *n*-propyl, isopropyl and *n*-butyl isothiocyanates results in the disappearance of the 2-adamantyl radicals and concurrent formation of the radicals derived from the isothiocyanates. For all the above mentioned isothiocyanate compounds, exclusive formation of the radicals resultant from α-hydrogen removal was observed.

B. Aromatic Isothiocyanates

In gamma-irradiated phenyl isothiocyanate[33] at 77 K the formation of two radicals is deduced from the analysis of the e.s.r. spectra. As in the case of methyl isothiocyanate one of the radicals, **2**, is formed as a result of the removal of a hydrogen atom from the molecule while the other, **3**, is formed by hydrogen attachment to the isothiocyanate group. The structure of the latter radical indicates that, because a phenyl group is substituted for the methyl group in CH_3CNS, the addition of the hydrogen atom takes place at a different site. In phenyl isothiocyanate resonance stabilization of the radical with the odd electron located on the nitrogen atom, can be conceived as the reason why the hydrogen atom is attached to the carbon rather than the nitrogen atom in the CNS group.



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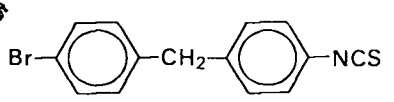
Products formed in the radiolysis of phenyl isothiocyanate at room temperature are identical with those obtained from phenyl thiocyanate (see Section III.B) because of the radiation-induced isomerization between these two compounds.

The radiation stability of solid 4-bromo-4′-isothiocyanatodiphenyl, **4**, was investigated by Uhet and coworkers[40] using the radiorelease method.



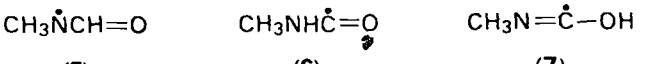
(4)

This method was used because it was assumed that radioactive krypton (^{85}Kr) incorporated in the solid carrier, **4**, would be rapidly released as a result of chemical decomposition caused by gamma irradiation. Since no enhanced release of ^{85}Kr was observed during 175 hours of irradiation at a dose rate of 0·45 Mrad/h, the authors concluded that chemical decomposition of the carrier did not occur. While the radiorelease technique is interesting it is doubtful whether the assumptions inherent in its use were justified in this particular case.

V. THE RADIATION CHEMISTRY OF ISOCYANATES

A. Aliphatic Isocyanates

E.s.r. studies of gamma irradiated crystalline methyl isocyanate at 77 K were carried out by several investigators[33,41,42]. The formation of the $\cdot CH_2NCO$ radical was observed in all these studies. However, Trofimov and Chkheidze[33] also detected the formation of another radical upon addition of hydrogen atom to the isocyanate group. In the latter case three



(5) (6) (7)

structures, 5, 6 and 7, of the resulting radical are possible. Analysis of the e.s.r. spectra indicates that only radicals having structure 6 are formed. Fujiwara and collaborators[42] also observed the radical $\cdot CH_2NCO$ at 77 K and a similar radical derived from the deuterated methyl isocyanate CD_3NCO. Rather interesting behaviour of these radicals was observed upon exposure to visible light and subsequent heating. When irradiated for 90 minutes with visible light, the $\cdot CH_2NCO$ radical completely disappeared and the e.s.r. spectrum assigned to the methylene imino radical 9 appeared. Heating the system to 150 K resulted in the complete restoration of the resonance pattern of the $\cdot CH_2NCO$ radical. This unusual behaviour can be summarized as follows:

$$\underset{(8)}{\cdot CH_2NCO} \underset{\text{heat}}{\overset{\text{visible light}}{\rightleftharpoons}} \underset{(9)}{H_2C{=}N\cdot} + CO \qquad (33)$$

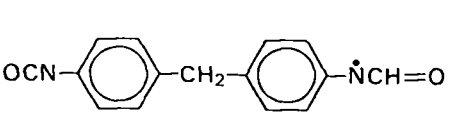
The $\cdot CH_2NCO$ radicals were also observed in X-ray irradiated CH_3NCO in adamantane matrix at room temperature[38,39]. Also observed in this matrix at room temperature was the formation of isocyanato radicals from ethyl, propyl, isopropyl and cyclopentyl isocyanates. Ethyl isocyanato radicals are also formed in gamma-irradiated ethyl isocyanate at 77 K[42]. In hexamethylene diisocyanate[33], the e.s.r. spectrum assigned to the hydrogen atom adduct radical, 10, was detected, in addition to the isocyanato radical, 11.

$$\underset{(10)}{OCN{-}(CH_2)_6{-}\dot{N}CH{=}O} \qquad \underset{(11)}{OCN{-}(CH_2)_5\dot{C}H{-}NCO}$$

B. Aromatic Isocyanates

In all the gamma irradiated aromatic isocyanates studied by the e.s.r. method at 77 K, radicals formed by hydrogen atom addition were observed[33]. Thus the corresponding 'hydrogen deficient' radicals, even if not detected, must also be formed from these compounds.

The site at which the hydrogen atom attaches itself is determined by the type of aromatic group in the molecule. In phenyl isocyanate the hydrogen atom attacks the phenyl ring while the hydrogen is bound to the NCO moiety in 4,4'-diisocyanatodiphenylmethane (12), *m*-tolyl isocyanate (13) and *p*-tolyl isocyanate (14).



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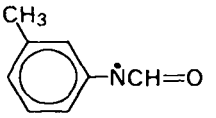

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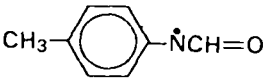
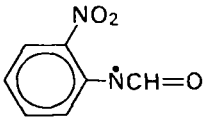


(14)

The presence of an additional reactive functional group on the phenyl ring also determines the site of hydrogen atom addition. In *m*-nitrophenyl isocyanate, the H atom is added only to the nitro group while in *o*-nitrophenyl isocyanate both the isocyanate group and the nitro group are attacked by the hydrogen atom, resulting in the formation of the corresponding radicals **15** and **16**. Of these two radicals the one in which the hydrogen atom is attached to the NO_2 group appears to be more stable.



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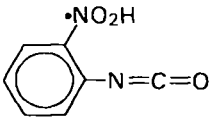


(16)

The radical resulting from removal of a hydrogen from the phenyl ring of *o*-nitrophenyl isocyanate was also observed.

VI. CHAIN REACTIONS AND RADIATION-INDUCED SYNTHESIS

A. General Aspects

The Dow radiochemical synthesis of ethyl bromide from ethylene and HBr is the only large scale industrial process in which ionizing radiation is used[43]. However, the potential applications of ionizing radiation to the synthesis of various compounds are widely recognized[44–46].

The class of compounds discussed in this review is apparently particularly suitable for synthesis by means of ionizing radiation. As an example, consider the recently reviewed case of the production of isocyanates[47]. Isocyanates are important in the production of urethane polymers, substituted ureas and carbamates and are used as crop protection agents and herbicides. It is difficult to meet the increasing demand for these compounds because complex plants are required to deal with the hazards involved in the use and handling of the raw materials and products. Production is, therefore, limited to large companies.

The conventional methods of initiating free-radical reactions include photosensitization, the use of initiators and thermal decomposition. Ionizing radiation offers several advantages over these methods: (i) The high penetrating power of gamma radiation permits the use of opaque and heavy walled pressure cylinders which cannot be used in the photosensitized reactions; (ii) the radiolytic products are free of the remnants of initiators and their products; (iii) the rate of radical formation is almost independent of phase and temperature thus allowing great flexibility in reaction conditions; (iv) the controls of ionizing radiation sources allow, if necessary, an almost instantaneous cut-off of the initiation process.

The following types of free-radical chain reactions can be envisaged as OCN and NCO compounds: condensation, substitution by addition–elimination and substitution by radical transfer. The general kinetic features of these chain reactions will be illustrated for the condensation between an aliphatic compound carrying one of the above-mentioned functional groups, denoted as X, and a terminal olefin. The various steps in this condensation reaction can be summarized schematically by the following:

Initiation

$$2\,RCH_2X \longrightarrow 2\,R\dot{C}HX + H_2 \qquad (34)$$

Propagation

$$R\dot{C}HX + \diagdown C{=}C \diagup \longrightarrow RCHX{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot \qquad (35)$$

$$RCHX{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot + RCH_2X \longrightarrow RCHX{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}H + R\dot{C}HX \qquad (36)$$

Termination

$$2R\dot{C}HX \longrightarrow \text{Products} \quad (37)$$

$$2RCHX-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \longrightarrow \text{Products} \quad (38)$$

$$R\dot{C}HX + RCHX-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \longrightarrow \text{Products} \quad (39)$$

Applying the steady state treatment to this reaction sequence, it can be shown that the rate of formation of product **17**, R_p in this system is given by expression (A). In this expression I denotes the rate at which the radiation energy is absorbed, [O] is the olefin concentration and the rate constants of all the termination reactions, k_t, are assumed to be equal.

$$R_p = \left(\frac{k_{34}I}{k_t}\right)^{1/2} k_{35}[O] \quad (A)$$

It may be immediately concluded from this equation that, in order to obtain long chains and products free from the compounds formed in the termination reactions, it is necessary to use sources with a relatively low energy output. Thus, gamma radiation sources are more suitable for radiation induced synthesis than electron accelerators. Also, RCH_2 can be replaced by other groups, such as SCN in dirhodan, Cl, etc. The reaction mechanism can easily be changed to apply to these cases.

A modification of the gamma-radiation-induced free-radical chain reaction between alkyl radicals and chloroolefins (such as 1,2-dichloroethylene, trichloroethylene, tetrachloroethylene[48,49] and fluorotrichloroethylene[50]) could possibly be employed to synthesize OCN-, NCO-, SCN- and NCS-substituted unsaturated compounds. The propagation step in this case would be expected to consist of the following reactions:

$$R\dot{C}HX + \overset{Cl}{\underset{}{}}\!\!>C=C<\!\!\overset{Cl}{\underset{}{}} \longrightarrow RCHX-\overset{Cl}{\underset{|}{C}}-\overset{Cl}{\underset{|}{C}}\cdot \quad (40)$$

$$RCHX-\overset{Cl}{\underset{|}{C}}-\overset{Cl}{\underset{|}{C}}\cdot \longrightarrow \overset{RCHX}{\underset{}{}}\!\!>C=C<\!\!\overset{Cl}{\underset{}{}} + Cl \quad (41)$$

$$Cl + RCH_2X \longrightarrow R\dot{C}HX + HCl \quad (42)$$

G values as high as 10^4 were observed for the analogous reactions of cyclohexyl radicals with the chloroolefins at 210 °C[48]. This reaction

represents the addition–elimination type of chain reaction. The hydrogen in arylalkyl hydrocarbons can be substituted by the thiocyanate group by the photochemical and peroxide-induced reaction between arylalkyl hydrocarbons and thiocyanogen chloride[51] and thiocyanogen[52]. These chain reactions can also probably be initiated by ionizing radiation. The propagation step here represents the transfer type, free-radical substitution mechanism.

$$ArCHR + XSCN \longrightarrow ArCH(SCN)R + X \quad (43)$$

$$X + ArCH_2R \longrightarrow ArCHR + HX \quad (44)$$

B. *Formation of Aliphatic Thiocyanates in Ethanol and Acetone*

The formation of aliphatic thiocyanates was observed in gamma and X-ray irradiated acetone and ethanol solutions of ammonium and potassium thiocyanates to which olefins were added[53,54]. A detailed study of this reaction was carried out by Chirakhadze and coworkers[54] to establish the optimum conditions for the radiation induced synthesis of aliphatic thiocyanates. In that study the reactions between 1-hexene, 1-heptene and 3-heptene and potassium and ammonium thiocyanates were initiated by gamma radiation at a dose rate of 10^{16} eV/ml sec and X-ray irradiations at dose rates of 0·9–1·5 × 10^{15} eV/ml sec. Acetone and ethanol were used as solvents.

The following typical results of that work are worth a detailed description. In a solution of 0·234 M-KSCN and 2·2 M-1-heptene in ethanol, a maximum yield of *n*-heptyl thiocyanate corresponding to a *G* value of 91 was observed at a total dose of 6 × 10^{19} eV/ml. Further increase of the irradiation dose lowered the *n*-heptyl thiocyanate yield indicating that it readily decomposes under irradiation. In air-saturated solutions $G(n\text{-}C_7H_{15}SCN)$ increased to 162 when the initial concentrations of the reactants were equal. Addition of water (0·22 M) further increased this yield to 426. In the NH_4SCN–1-heptene–ethanol system, a maximum yield of *n*-heptyl thiocyanate of 3200 was observed. Finally, the highest thiocyanate yield of 18,000 was observed when a solution of KSCN and 1-hexene in ethanol was irradiated in an inert gas (xenon) atmosphere.

The results of this work are of significant qualitative importance since the high values of product formation point to a long chain reaction that could be utilized for syntheses. The effect of each parameter, however, was not clearly established mainly because, instead of isolating the effects

of individual parameters, several parameters (dose, composition and atmosphere) were changed simultaneously.

It would be instructive to try to envisage the mechanism of this interesting chain reaction, as it is not given in the original work. Evidently, the reaction proceeds by a free-radical mechanism since the highest yield was observed in an oxygen-free atmosphere. In general terms, therefore, the mechanism has to include a species capable of oxidizing the thiocyanate anion to the thiocyanate radical. Also, the formation of the aliphatic thiocyanate has to be accompanied by the regeneration of the oxidizing species. It has been shown that the MeO radical formed in the radiolysis of methanol can oxidize the SCN^- anion to the SCN radical[55,56]. Also, in irradiated acetone the molecular cation $(CH_3)_2CO^+$ and the acetone triplet can oxidize SCN^-[57]. However, the regeneration of these species, as required by the chain mechanism, seems very unlikely. It appears that in ethanolic solutions the oxidizing species could be the CH_3CHOH radical. This suggestion is based on the findings of Sherman who has shown that N_2O and alkyl halides can be oxidized in 2-propanol. This reaction which proceeds by a chain mechanism that can be initiated by free radicals produced photochemically[58] or by gamma irradiation[59], involves the $(CH_3)_2CHOH$ radical as the chain carrying oxidizing intermediate. If, indeed, the CH_3CHOH radical is the oxidizing species in ethanol solutions of olefins, then the propagation step of the chain formation of aliphatic thiocyanates should be given by the following reaction scheme:

$$CH_3CHOH + NCS^- \longrightarrow CH_3CH_2O^- + NCS \qquad (45)$$

$$NCS + C_nH_{2n} \longrightarrow {}^{\bullet}C_nH_{2n}SCN \qquad (46)$$

$${}^{\bullet}C_nH_{2n}SCN + CH_3CH_2OH \longrightarrow C_nH_{2n+1}SCN + CH_3CHOH \qquad (47)$$

Presumably, the hydrogen atom migration in the first of these reactions could occur in an initially formed $(CH_3CH{-}CNS)^-$ adduct similar to that formed between CNS^- and the OH radical[60].

In acetone solutions an analogous reaction sequence could be conceived:

$$\bullet CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + NCS^- \longrightarrow \bullet CH_2{=}\overset{\overset{O^-}{|}}{C}{-}CH_3 + NCS \qquad (48)$$

$$NCS_n + C_nH_{2n} \longrightarrow {}^{\bullet}C_nH_{2n}SCN \qquad (49)$$

$$\bullet C_nH_{2n}SCN + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow C_nH_{2n+1}SCN + \bullet CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \quad (50)$$

C. Miscellaneous Reactions

The gamma-radiation-induced isomerization of ammonium thiocyanate to thiourea[61] was studied over a wide temperature range. At room temperature the reaction is very slow and a high dose of 5×10^{22} eV/g

$$NH_4CNS \longrightarrow (NH_2)_2C{=}S \quad (51)$$

is needed before any thiourea can be detected. As the temperature is increased G(thiourea) grows rapidly to 3650 at 120°C and 21,000 at 140°C. Further increase of temperature results in the pyrolytic decomposition of thiourea and an apparent decrease in the rate of its formation.

The formation of telomers containing the isocyanate group, by means of high energy radiation, has been reported[62]. The starting materials in this reaction are olefins and organic mono and polyisocyanates. The reaction probably proceeds by a free-radical mechanism since it can also be initiated by the decomposition of diazo compounds and peroxides.

Synthesis of ^{35}S-labelled methyl isocyanate was reported by Dzanitiev and coworkers[63]. Irradiation of methyl isocyanate solution in CCl_4 by a 1 to 3×10^{11} neutron/cm^2 sec flux at 50°C results in the following reactions:

$$^{35}Cl(n, p) \longrightarrow {}^{35}S \quad (52)$$

$$^{35}S + CH_3NCS \longrightarrow CH_3NC^{35}S + S \quad (53)$$

VII. RADIATION-INDUCED POLYMERIZATION

A. Isocyanic Polymers

It is well known that various organic isocyanates polymerize in the presence of anionic catalysts such as lithium and sodium alkyl compounds, forming high molecular weight linear polymers[64,65]. It is thus conceivable that ionizing radiation could replace these catalysts in initiating anionic polymerization of organic isocyanates.

Tabata and colleagues[66] have studied the gamma radiation induced polymerization of solid and liquid methyl, *n*-butyl and phenyl isocyanates at temperatures from −196–20 °C. In the case of MeNCO and PhNCO the rate of polymerization was almost unaffected by the change of temperature from 20 to −78 °C. The polymerization of *n*-butyl isocyanate was studied at three temperatures. 20 °C (liquid), −78 °C (liquid) and −196 °C (crystalline solid). The rate of polymerization was found to be considerably faster in the solid state than in the liquid state.

Recently Tabata and coworkers[67,68] reinvestigated the radiation induced polymerization of *n*-butyl isocyanate. They found that although the conclusion reached in the original work[66] as to the anionic character of the polymerization was correct, other aspects of the polymerization reaction were misinterpreted. In the more recent work[67] the polymerization was studied in various states (crystalline, glassy, supercooled and liquid) at temperatures between −196 and −78 °C. It was found that *n*-butyl isocyanate is polymerized in the supercooled state. Irradiation of the glassy monomer also resulted in polymer formation, but only when the pre-irradiated monomer was warmed, i.e. a post-irradiation polymerization reaction took place.

The anionic character of the polymerization reaction was revealed by the effect of various additives on the rate of polymerization. Radical scavengers DPPH and oxygen do not decrease the rate of polymer formation while water, triethylamine and CCl_4 inhibit the polymerization. Irradiation of ethyl and propyl isocyanates in the glassy state results in polymer formation. Rapid polymerization in a very narrow temperature range, below the melting point, was observed in ethyl isocyanate.

It is suggested that the factors that effect the polymerization are the lifetime of the anionic species and the mobility of the monomer. In the liquid phase the lifetime of the anionic species is too short while in the glassy and crystalline states the monomer is not mobile enough. Therefore, polymerization takes place only in the supercooled liquid.

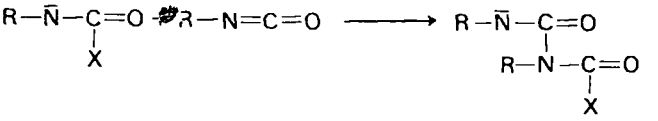
Reactions (54) to (57) represent the mechanism of the polymerization as suggested by the authors[67] with a minor correction. In the original work the polymer appeared to have *n* X units for each Y unit, a situation

Initiation

$$R-N=C=O \longrightarrow X^- + Y^+ \qquad (54)$$

$$X^- + R-N=C=O \longrightarrow R-\bar{N}-\underset{\displaystyle X}{\overset{\displaystyle |}{C}}=O \qquad (55)$$

Propagation



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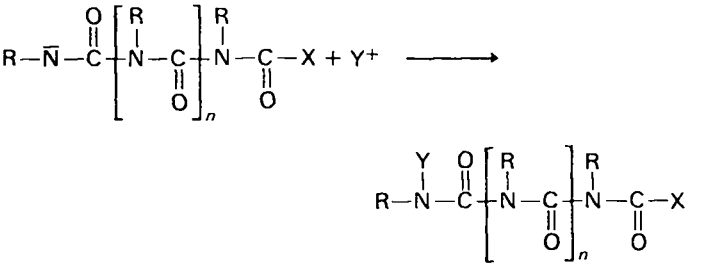
Termination



(57)

that is obviously impossible. Therefore we suggest that the structure is that given in reactions (56) and (57).

The formation of linear polymers of isocyanic acid with a high degree of polymerization has been reported[69]. The polymerization in this case occurs in the temperature range of −200 to 50 °C in the liquid and solid states in solvents. It appears that the polyisocyanic polymer obtained from isocyanic acid is formed by an anionic mechanism as in the case of the organic monomers.

B. Copolymers

The radiation-induced copolymerization of ketene and isocyanic acid[70] and the copolymerization of cyclic oligomers of formaldehyde and organic isocyanates[71–73] are described in the patent literature. Details of the polymerization mechanism and copolymer composition are not given there. Copolymerization between isocyanic acid and ketene can be carried out in the temperature range of −200 to 0 °C in the liquid and solid states. Dilution of the reactants in an appropriate inert solvent is necessary.

Oxymethylene thermostable polymers were obtained in the one-stage polymerization of cyclic oligomers of formaldehyde such as trioxane and tetraoxane in the presence of carboxylic anhydrides and organic thiocyanates[71–73]. Methyl, ethyl and phenyl thiocyanates, added in concentrations of 0·1 to 10% by weight, were probably incorporated in the

polymer. The polymerization can be initiated by α, β, γ and X-rays as well as neutron and electron beams[72]. The irradiation can be carried out prior to or after the addition of the organic thiocyanate and the polymerization takes place in solids and liquids at temperatures from 60 to 140 °C.

Polymerization of cyclic compounds such as epoxides is usually assumed to proceed by ionic mechanism[74]. However, the fact that the formation of the oxymethylene polymers in the presence of organic thiocyanates can also be initiated by u.v. radiation[72] and peroxides[75] seems to indicate that the polymerization induced by ionizing radiation proceeds by a free-radical mechanism.

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 12

Kinetics and mechanisms of reactions of cyanates and related compounds

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I. INTRODUCTION

A. General

Diverse reactions of cyanates and related compounds have been studied in varying detail and at varying stages in the development of current understanding of organic reaction mechanisms. This review does not attempt to treat all, or even most, of the ground covered, nor does the author presume to select material on any basis of importance. Instead, reactions have been chosen to provide a selection of studies in several major categories—isomerizations, nucleophilic reactions leading to bond fission, and nucleophilic reactions leading to addition. Reactions of thiocyanates and isothiocyanates have been described first and in greater detail than those of their oxygen analogues because their lower reactivity has enabled their reactions within the chosen categories to be studied more systematically and extensively, with the possible exception that the industrially-important addition reactions of isocyanates have attracted special attention.

B. Basicity and Nucleophilicity

Since the terms basicity and nucleophilicity, as used in this chapter, are not universally accepted[1], some clarification is necessary.

In 1953 Swain and Scott[2] recommended that the term 'basicity' be used for equilibrium properties of a base, and 'nucleophilicity' for its kinetic properties.

Parker[3], drawing attention to differences in relative basicity towards hydrogen and towards carbon, has suggested more specific terms such as 'carbon-basicity' and 'hydrogen-nucleophilicity'.

Basicity and nucleophilicity towards carbon may be illustrated with reference to the following bimolecular reactions:

$$RX + Y^- \underset{k_{RY}^{X^-}}{\overset{k_{RX}^{Y^-}}{\rightleftharpoons}} RY + X^- \quad (1)$$

$$RZ + Y^- \xrightarrow{k_{RZ}^{Y^-}} RY + Z^- \quad (2)$$

$$RZ + X^- \xrightarrow{k_{RZ}^{X^-}} RX + Z^- \quad (3)$$

The relative basicities of X^- and Y^- towards carbon (specifically, towards the reacting carbon atom in the chosen system R) are given by $k_{RY}^{X^-}/k_{RX}^{Y^-}$. The relative nucleophilicities towards the carbon atom are given by $k_{RZ}^{X^-}/k_{RZ}^{Y^-}$.

Since relative nucleophilicities measure reaction rates towards the one substrate, and relative basicities reflect reaction rates towards different substrates, it is not surprising that they are often not of the same value for the one pair of bases X^- and Y^-.

II. THE GROUPS –SCN AND –NCS

A. Thermal and Thiocyanate Ion-catalysed Thiocyanate–Isothiocyanate Isomerization

The nitrogen atom of the SCN group is more basic towards carbon than is the sulphur atom[4], but in most reactions the sulphur atom is more carbon nucleophilic. This enables alkyl, aryl and aryl-alkyl thiocyanates to be prepared by reaction of an appropriately active halide or a diazonium salt with thiocyanate ion in a suitable solvent, provided the product can be isolated before substantial isomerization takes place. Acyl thiocyanates usually isomerize too fast for their preparation[4] though some acyl thiocyanates of unusual stability have been prepared.

Mechanisms of the isomerization include ionization followed by return to a carbonium ion, ionization followed by addition to a free carbonium ion, intramolecular group transfer, direct S_N2 displacement, and addition–elimination involving carbonyl or aryl carbon. These will be discussed.

1. Saturated and benzylic thiocyanates

Of these compounds, those which isomerize rapidly enough in the absence of energizing irradiation to outstrip competing reactions are considered to react by ionization–recombination, ionization followed by

reaction with thiocyanate ions in solution, or nucleophilic displacement by the nitrogen end of the thiocyanate ion.

Studies of the isomerization of saturated open-chain aliphatic thiocyanates[5,6] indicate that these compounds can isomerize only under the influence of Lewis acid catalysts, with reactivity in the order tertiary (room temperature)[5] > secondary (boiling)[5] > primary (no reaction)[6].

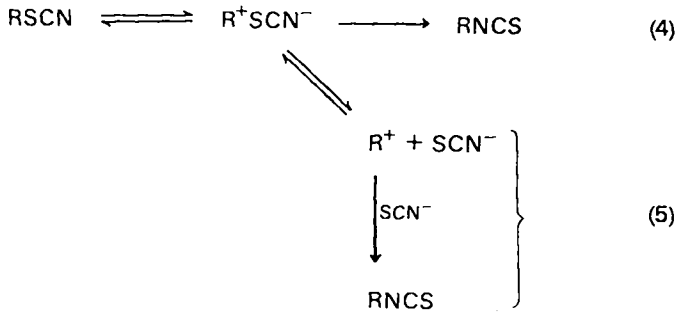
Arylmethyl and diarylmethyl thiocyanates lend themselves better to investigation than the alkyl compounds, because the aryl group accelerates the reaction and the structure precludes one troublesome side reaction—elimination[7].

a. *Ionization followed by thiocyanate ion attack.* Lewis acid catalysis and the reactivity order of thiocyanates when the structure is varied both fit a carbonium ion mechanism. After the simultaneous proposal of such a mechanism by three groups of workers in 1960[5,8,9], a detailed examination of the course of the reaction was carried out by one of these groups—Iliceto, Fava and coworkers—during the next several years.

As a prelude to a study of the detailed timing of the reaction, Iliceto, Fava and collaborators first established firmly an ionization path for isomerization of diarylmethyl thiocyanates[10]. They found the following additional evidence for this:

(i) The kinetics are first order in organic thiocyanate.
(ii) Salt effects are positive, with the rate varying linearly with salt concentration; the magnitude of the effect of sodium thiocyanate and perchlorate in methyl ethyl ketone and acetonitrile fits the general pattern of normal salt effect for ionization reactions[11].
(iii) Solvent effects on rate are typical in magnitude (220-fold increase on changing from benzene to dimethylformamide at 90 °C) and direction (faster as polarity increases) for ionization-governed reactions.
(iv) Electron-donating groups accelerate, and electron-withdrawing groups retard the reaction, giving a good fit to a Hammett plot using Brown's σ^+ constants[12] for 4-CH_3, 4-Cl and 4-NO_2 and the 4,4′-disubstituted compounds, with a slope corresponding to that observed in the solvolysis of diarylmethyl chlorides in ethanol[13,14].

With an ionic mechanism established, a further question is whether the reaction proceeds by internal return (equation 4) or by nucleophilic attack on a dissociated carbonium ion by thiocyanate ion (equation 5). The answer to this question gives us an idea of the extent to which the ions generated thermally are dissociated. The first clue came from isotopic exchange experiments[10].



These experiments established that if the isomerization of 0·1 M-diphenylmethyl thiocyanate takes place in acetonitrile at 70 °C in the presence of 0·01 M-$Na^{35}SCN$ and 0·09 M-$NaClO_4$, the first-order rate constant for *total* exchange is only 31% that for isomerization. Also, if the reaction is interrupted after about 25% isomerization and 10% total exchange, there is more labelled organic isothiocyanate present than labelled organic thiocyanate.

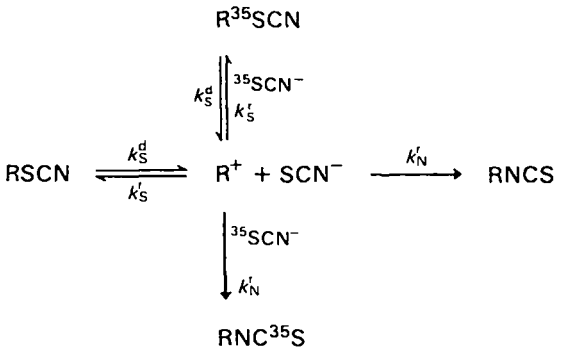
The significance of these results can be seen by comparing two notional mechanisms for isomerization and exchange, one only involving reaction via complete dissociation (Scheme 1) and the other involving isomerization by collapse of an ion pair (Scheme 2).

In Scheme 1 we have exchange and isomerization taking place by the one mechanism, with additional exchange occurring through attack on the carbonium ion by the sulphur end of the thiocyanate ion. The specific rate for total exchange would have to be equal to or greater than the isomerization rate. Since this is not so, at least some isomerization takes place without the involvement of free thiocyanate ions, that is, neither through Scheme 1 nor through a direct-displacement (S_N2) mechanism for isomerization.

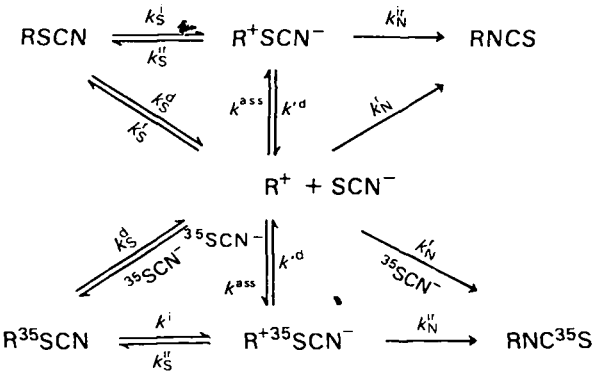
This directs attention to Scheme 2, involving isomerization through return of thiocyanate ion in an ion pair (which may or may not be solvent separated). Opportunity for isotopic exchange occurs either through dissociation and recombination of RSCN (k_S^d, k_S^r, k_N^r) or through dissociation and reassociation of the ion pair (k'^d, k^{ass}).

The result that organic isothiocyanate builds up more rapidly than organic thiocyanate in the early part of the isomerization and exchange reaction is consistent with a rapid reversible formation of dissociated ions followed by irreversible reaction to give isothiocyanate (Scheme 2), or with attack by free thiocyanate ion on the carbonium–thiocyanate ion pair.

Although it seemed clear at that stage that no more than 31% of ionic

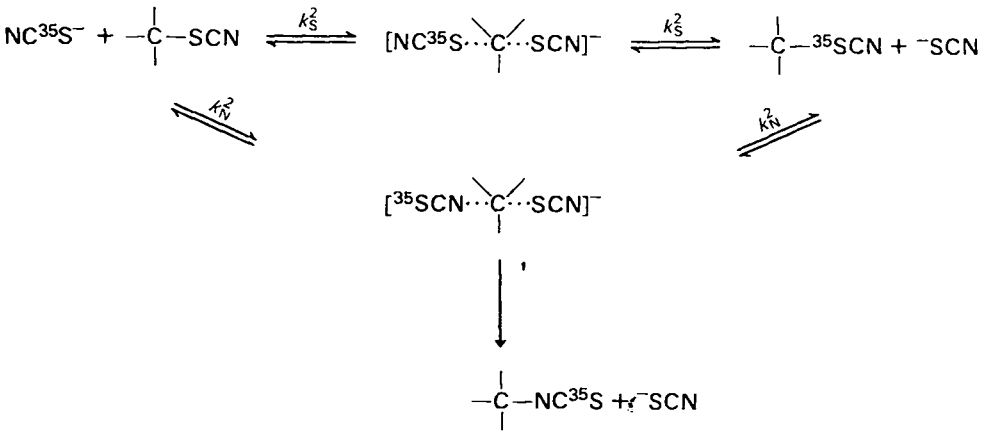


SCHEME 1.



SCHEME 2.

intermediates dissociate further, information was lacking on how much of the radioactivity enters by a non-ionic path (Scheme 3), and on what fraction of ion pairs gives isothiocyanate rather than returning to thiocyanate. Substantial non-ionic exchange and a high proportion of ion pairs giving thiocyanate would both suggest that 31% is too low a figure for further dissociation. So far an upper limit had been placed on dissociation, and substantial S_N2 isomerization had been excluded by kinetic order and salt, solvent and structural effects (i.e., it could be stated that k_N^2 in Scheme 3 is insignificant). The next step was to study the isotopic exchange reaction under conditions in which isomerization is relatively insignificant.



(k_N^2 is usually negligible. See text.)

SCHEME 3.

In a study of the isotopic exchange reactions of substituted diphenylmethyl thiocyanates[15,16] under conditions in which isomerization is negligible for a substantial part of the reaction, it was found that exchange proceeds according to a mixed rate law (equation 6).

$$\text{Rate} = k_1[\text{RSCN}] + k_2[\text{RSCN}][\text{SCN}^-] \quad (6)$$

In acetonitrile, the order ranges from first ($k_1 \gg k_2$) for thiocyanates with electron-releasing substituents to second ($k_2 \gg k_1$) for thiocyanates

TABLE 1. First and second-order rate constants for isotopic exchange between substituted diphenylmethyl thiocyanates and NaSCN in acetonitrile and acetone at constant electrolyte concentration ([NaSCN] + [$NaClO_4$] = 0·1 M) at 70 °C[a]

Substituents	Acetonitrile		Acetone
	$\log k_1$	$\log k_2$	$\log k_2$
4-NO_2, 4′-NO_2	—	−3·52	−3·11
4-NO_2	—	−3·61	−3·51
3-Cl	−6·49	−3·73	−3·80
4-Cl	−5·33	−3·24	−3·38
None	−5·15	−3·07	−3·44
4-CH_3	−3·39	—	[b]
4-CH_3, 4′-CH_3	−2·14	—	[b]

[a] From Reference 16.
[b] The kinetics were found to be complex and data are omitted.

with electron-withdrawing substituents (Table 1). In acetone the reactions are pure second order.

The first-order rate constants in acetonitrile at 70°C were found to fit a Hammett plot (using σ^+ values[13]) with a reaction coefficient $\rho = -4{\cdot}5$, compared with $-3{\cdot}4$[10] for the isomerization of the diphenylmethyl substrates. Fava and coworkers[16] attributed the high negative value of ρ to a considerably more polar transition state than the intimate ion pair involved in isomerization. This transition state, they concluded, is likely to be a dissociated carbonium ion.

The second-order rate constants do not correlate well with the Hammett equation. Arguments favouring a direct S_N2 displacement mechanism over attack on an ion pair by thiocyanate ion (the S_N2C^+ mechanism[17]) are[16]: the nature of the substituent effects, evidence that the ionization rate constant/exchange rate constant ratio is too low to agree with second-order kinetics for an S_N2C^+ mechanism; evidence[18] from experiments with 4-chlorodiphenylmethyl thiocyanate that second-order exchange involves net inversion of configuration and also that racemization through exchange occurs at a rate greater than that of ionization.

Since 4,4'-dimethyldiphenylmethyl thiocyanate exchanges in acetonitrile without a significant second-order contribution (Table 2), it was considered[19] to be a suitable system for a closer study of the isomerization reaction. This study[19] supported earlier indications[9,10,15] that the isomerization reaction occurs via an intimate ion pair and that the exchange reaction occurs via a dissociated carbonium ion. However, some formation of labelled isothiocyanate was noted, and interpreted as showing that a fraction of the total isomerization proceeds by way of the intermediate (free carbonium ion) involved in exchange. This fraction was estimated to be about 0·05. The figure of 0·05 was obtained by first noting that the partitioning of ^{35}S between organic thiocyanate and isothiocyanate gave $5{\cdot}0 \pm 0{\cdot}2$ as the relative reactivity of S to N of the thiocyanate ion towards the carbonium ion involved in exchange, and applying this to the ratio of the rate constant for exchange, k_{ex} to that for isomerization, k_{isom}:

$$\frac{k_{ex}}{k_{isom}} \times \frac{1}{1 + \text{S/N ratio}} = \frac{1{\cdot}16 \times 10^{-6}}{3{\cdot}70 \times 10^{-6}} \times \frac{1}{1 + 5{\cdot}0} = 0{\cdot}05$$

Since the ion pair is a precursor of the dissociated intermediate involved in exchange, the authors stated that the S/N reactivity ratio in internal return was also 5·0. (That is, $k_S^r/k_N^r = k_S^{ir}/k_N^{ir} = 5{\cdot}0$.)

The authors summed up their results thus: 'Of 100 intimate ion pairs,

about 5 undergo further ionization and 95 return to covalent state. Of the latter, about 79 return to thiocyanate and 16 to isothiocyanate.

Experiments with optically-active 4-chlorodiphenylmethyl thiocyanate[20] have shown that racemization occurs at a rate similar to that of isomerization, and much faster than unimolecular exchange. The maximum amount of racemization occurring by way of a free carbonium ion was calculated as about 4% and the maximum amount of isomerization by the same path was calculated as about 2%. This was shown to be consistent with the stereospecificity of the isomerization reaction (52%).

b. *Direct bimolecular displacement of thiocyanate.* Phenylmethyl (benzyl) thiocyanate, on heating with relatively concentrated sodium thiocyanate, isomerizes at a rate which is first-order each in organic substrate and in sodium thiocyanate[21]. Fava and coworkers measured rate constants for two simultaneous second-order processes—isomerization and isotopic exchange—in two solvents over a range of temperatures and sodium thiocyanate concentrations. In both acetonitrile and methyl ethyl ketone, isotopic exchange occurs much more rapidly than isomerization, allowing S/N reactivity ratios towards phenylmethyl thiocyanate to be measured directly as the ratio of exchange to isomerization rates. The ratio, at the temperatures employed (50–100 °C) varies from about 10^2 to 10^3. It is larger at lower temperatures than at higher temperatures and slightly larger in methyl ethyl ketone than in acetonitrile.

The slight suppression of the S/N nucleophilicity ratio by the more polar solvent, acetonitrile, is largely accounted for by a negative entropy of activation whose magnitude is 13 J mol^{-1} K^{-1} greater in methyl ethyl ketone than in acetonitrile. The solvent effect on S/N nucleophilicity ratios towards saturated carbon is in contrast to the solvent effect on S/N carbon–basicity ratios in which more polar solvents favour the more polar thiocyanate relative to the isothiocyanate[22], but any examination of solvent effects on the thiocyanate ion-catalysed isomerization reaction is limited by the fact that thiocyanate salts are insoluble in non-polar solvents and that protic solvents react with organic thiocyanates and isothiocyanates.

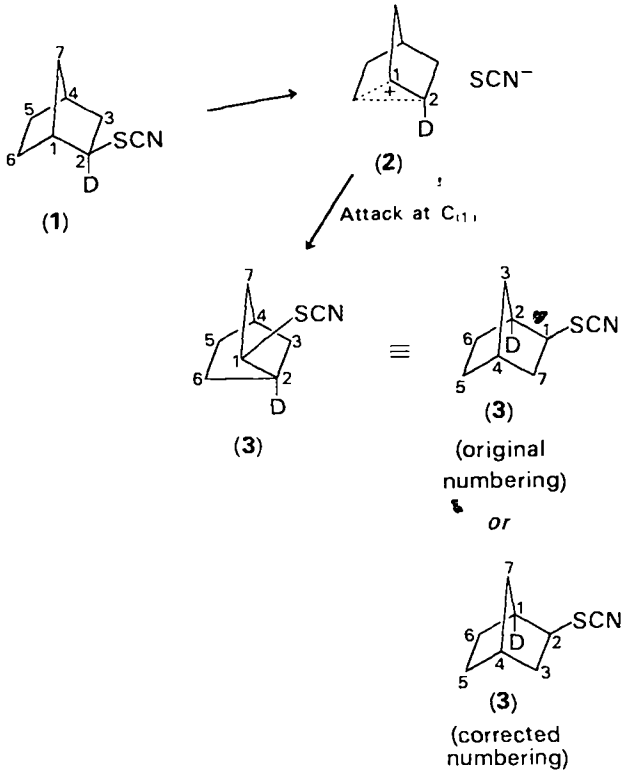
2. Cycloalkyl thiocyanates

a. *Bridged compounds.* The ionization mechanism for structurally-assisted isomerizations of thiocyanates has enabled the study of skeletal rearrangements of bridged bi- and tricyclic cations to be refined and extended[23–27]. This work is related more to carbonium ion chemistry than to thiocyanate chemistry as such, but some examples will indicate the

usefulness of the isomerization reaction in studying these rearrangements.

During solvolytic or deamination reactions of *exo*-2-bicyclo[2.2.1]-heptyl compounds, skeletal rearrangements occur involving 1,2-carbon shifts accompanied by 6,2-(and 6,1-) hydride shifts and, in solvents of low basicity, 3,2-hydride shifts[28]. N.m.r. studies[29] and tracer analysis[30] have shown that the 3,2-hydride shift is slow compared with the 6,2-hydride and 1,2-carbon shifts, and solvolysis of *exo*-2-norbornyl-2-*d*-*p*-trifluoromethylthiobenzoate gives, probably through internal return, an ester in which deuterium has equilibrated only between the 1 and 2 positions—establishing the 1,2-carbon shift as faster than the 6,2-hydride shift.[31]

Spurlock and Parks[24] found that when *exo*-2-norbornyl-2-*d*-thiocyanate (**1**, Scheme 4) is allowed to isomerize at elevated temperatures in sulpholane, deuterium again rearranges only between $C_{(1)}$ and $C_{(2)}$. The route for this rearrangement (a 1,2-carbon shift) is illustrated in Scheme 4.



SCHEME 4.

In the rearranged compound **3** deuterium has moved to $C_{(1)}$ and the configuration about the asymmetric $C_{(2)}$ has been reversed. Hence, unless SCN^- returns only to the carbon atom it left, racemization and deuterium scrambling between $C_{(1)}$ and $C_{(2)}$ will take place, at identical rates, during the return process. If the thiocyanate–isothiocyanate isomerization occurs via an ion-pair, with no 'memory' involved in recombination with a carbonium ion fully symmetrical relative to the thiocyanate ion, we expect that all isothiocyanate formed will be racemic and will have deuterium equally distributed between $C_{(1)}$ and $C_{(2)}$ (discounting kinetic isotope effects, found to be smaller than experimental error). We also expect that the thiocyanate will approach a similar equilibrated condition, with deuterium scrambling and racemization occurring so that

$$\frac{\text{Racemization rate}}{\text{Isomerization rate}} \geq \text{S/N ratio in } SCN^- \text{ combination with cations}$$

(i.e., scrambling to occur no less rapidly than ionization.)

This was shown to be so[24], indicating very rapid rearrangement of the cation into a state fully symmetrical with respect to the anion.

An estimate of the degree of dissociation of the ion pairs was made using $^{35}SCN^-$ in the equilibrating system and measuring the rate of incorporation of ^{35}S. It is only through dissociation past the intimate ion-pair stage that ^{35}S can be incorporated, and it was found that isotopic exchange occurs more slowly than isomerization. From equation (7), Spurlock and Parks[24] calculated that a maximum of 12% of ion-pairs dissociate further.

$$k_{ex}k_N/k_{isom}(k_S + k_N) = \text{Fraction of dissociated ions} \tag{7}$$

(k_{ex} is $S-^{35}S$ isotopic exchange rate constant, k_{isom} is RSCN–RNCS isomerization rate constant, and k_S and k_N are rate constants for S- and N-attack on the carbonium ion.)

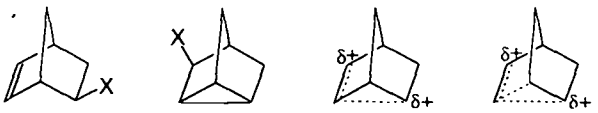
Knowledge of the k_S/k_N ratio also allowed estimation from equation (8)[19] of the ionization rate constant, k_i

$$k_i = k_{isom}(k_S + k_N)/k_N \tag{8}$$

It was found that, within experimental error, $k_i = k_r = k_{ex}^D$ (k_r = racemization rate constant, k_{ex}^D = deuterium exchange rate constant), suggesting that ion-pair formation is the rate-determining step in the 1,2-carbon shift leading to deuterium scrambling and racemization.

Other bridged carbonium ions studied by Spurlock's group using the thiocyanate isomerization include π and σ-route bicyclo[2,2,2]octyl and

bicyclo[3,2,1]octyl[25], π-route norbornyl[23], and norbornenyl and nortricyclyl[26,32] cations. In the latter work it was shown that, in contrast to solvolysis reactions, the distribution of skeletally rearranged products is strongly influenced by the polarity of the medium. In solvolyses, nortricyclyl products are strongly favoured[33–38] whether the starting material is norbornenyl (**4**) or nortricyclyl (**5**)—this is seen as a homoallyllic interaction involving the ions **6** and **7**



(**4**) (**5**) (**6**) (**7**)

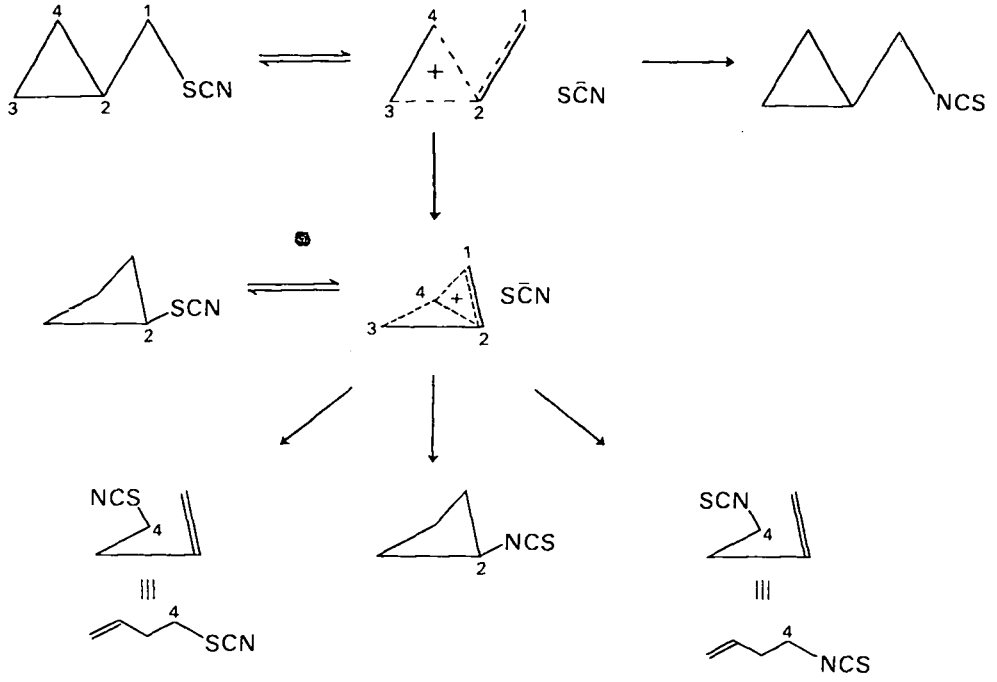
In the thiocyanate isomerization reaction, 5-*exo*-norbornenyl thiocyanate gives up to 50% 5-*exo*-norbornenyl isothiocyanate, with a greater proportion of tricyclyl product when salts or Lewis acid catalysts are introduced than in their absence. By contrast, nortricyclyl thiocyanate gives more than 80% nortricyclyl isothiocyanate. These results are attributable to a strong influence of thiocyanate ion in the ion pairs, and to a preference for a return to the ion **6** before it can rearrange to the ion **7**. High polarity or Lewis acid catalysis favours separation of the ion pairs, lengthening their average lifetime and permitting a greater amount of conversion of ion **6** into ion **7**.

A similar rapid return giving retained structure in contrast to solvolysis was observed for 2-(cyclopent-3-enyl)ethyl thiocyanate (via a π-route norbornyl cation)[23].

b. *Monocyclic compounds.* As in the bi- and tricyclic series, relative isomerization rates for cyclopropylcarbinyl, cyclobutyl, cyclopentyl and cyclooctyl thiocyanates parallel the solvolysis rates of the corresponding 4-toluenesulphonates[39], again indicating the intermediacy of carbonium ions. Cyclopentyl and cyclooctyl thiocyanate isomerizations occur without skeletal rearrangements, and at rates in keeping with the driving force of torsional I-strain in formation of carbonium ions[39]. Cyclohexyl thiocyanate does not isomerize under the reaction conditions of the other isomerizations (dipolar aprotic solvents, 130–150 °C). This is consistent with lack of strain in the six-membered ring.

Cyclopropylcarbinyl thiocyanate and cyclobutyl thiocyanate give products with rearranged skeletons analogous to those found in carbonium ion reactions of cyclopropylcarbinyl halides, sulphonate esters and amines[39,40]. However, relative product ratios in thiocyanate isomerizations were found to be different from those found in other carbonium ion

reactions, and sensitive to the reaction conditions. Spurlock and co-workers have accounted for their observations in terms of Scheme 5, in which the proximity of the anion governs the partition of the intermediate ions[39].



(Original numbering retained throughout)

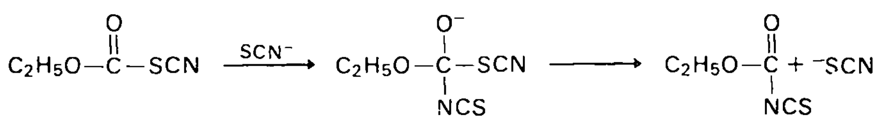
SCHEME 5.

3. Acyl thiocyanates

Most acyl thiocyanates have proved to be unobtainable, presumably because of very rapid isomerization to the isothiocyanate. Acyl chlorides almost invariably give only acyl isothiocyanates on reaction with thiocyanate ion[41–47]. It has been observed, however, that ethoxycarbonyl thiocyanate, but not ethylthiocarbonyl thiocyanate, can in fact be isolated, though excess thiocyanate ion isomerizes ethoxycarbonyl thiocyanate to the isothiocyanate[48]. (This seems at odds with Pearson's Hard and Soft Acids and Bases principle[49–51], from which one would expect the soft thioethyl sulphur atom to lessen the hardness of the carbonyl carbon and the instability of its bond with thiocyanate sulphur. However, see below.) Spurlock and Newallis[47] have explained the

stability of ethoxycarbonyl thiocyanate as due to overlap of the ether oxygen with the adjacent carbonyl π-system, delocalizing the electron deficiency of the carbonyl carbon atom and rendering it less susceptible to nucleophilic attack by thiocyanate nitrogen. The thioethyl sulphur of the thio analogue compound is less capable of a positive mesomeric effect than oxygen[52,53]. (Thus the apparent stability of the ethoxy compound relative to the ethylthio compound is probably due to kinetic factors and not necessarily a true thermodynamic stability difference—the Hard and Soft Acids and Bases principle is not necessarily violated.)

Spurlock and Newallis investigated the preparation and isomerization of carbamoyl thiocyanates (in which nitrogen–carbonyl π-overlap is expected to be even better than in ethoxycarbonyl thiocyanate)[47]. An addition–elimination path was most probable for the thiocyanate-ion-catalysed isomerization of ethoxycarbonyl thiocyanate, and on that basis it seemed that isomerization rates would be in the order $C_2H_5OCOSCN > (C_6H_5)_2NCOSCN > (CH_3)_2NCOSCN$. Surprisingly, the isomerization rates were found to be in the order $(CH_3)_2NCOSCN > C_2H_5OCOSCN > (C_6H_5)_2NCOSCN$. Thiocyanate ion was found to catalyse only the ethoxycarbonyl thiocyanate isomerization. This supports an addition–elimination mechanism for the ethoxy compound (equation 9) and a dissociation–recombination (carbonium) course for the carbamoyl compounds because of retardation of nucleophilic attack by π-overlap between nitrogen and the carbonyl carbon.

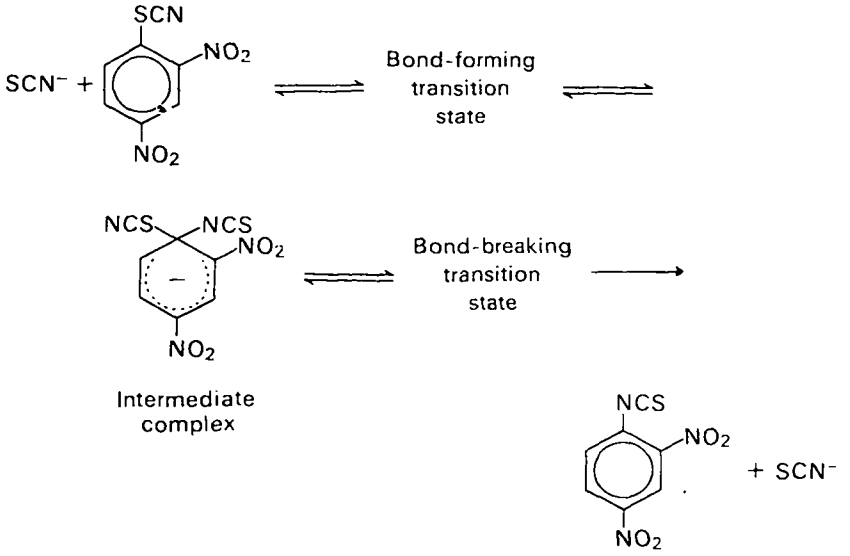

(9)

In a recent development, sulphonyl thiocyanates, RSO_2SCN have been prepared by thiocyanation of sodium sulphinates, $RSO_2^- Na^+$ by thiocyanogen at a benzene–water interface[54]. Some of these isomerize to isothiocyanates, and the isomerizations are being studied[54].

4. Aryl thiocyanates

Isomerization of aryl thiocyanates is complicated by the ease of breaking the S–CN bond, and has been studied in detail only in the case of aryl substrates activated by strong electron withdrawal[55,56]. The isomerization reaction can be followed in dipolar aprotic solvents for long enough to determine the kinetics when the substrate is 2,4-dinitrophenyl or 2,4,6-trinitrophenyl (picryl) thiocyanate.

In those cases the isomerization reaction follows second-order kinetics —first-order in aryl thiocyanate and in ionic thiocyanate. The well-established S_NAr model for nucleophilic displacements at activated aryl carbon[1,57–61] (Scheme 6) is, on the evidence available[56], fully adequate for the reaction.



SCHEME 6.

No evidence has been found for the reverse reaction in dimethylformamide or acetone. Competing reactions—especially nucleophilic reaction at the cyanide carbon atom—make it impracticable to run the isomerization to equilibrium.

Comparison of the reaction with the much faster, second-order, ^{35}S isotopic exchange reaction shows a S/N reactivity ratio towards 2,4-dinitrophenyl thiocyanate of 1×10^3 (dimethylformamide, 101·4 °C) to $1{\cdot}8 \times 10^3$ (dimethylformamide, 75·2 °C) and towards 2,4,6-trinitrophenyl thiocyanate of $1{\cdot}2 \times 10^2$ (acetone, 0 °C). This is similar to the values, and the influence of temperature, found by Fava's group for the S_N2 exchange and isomerization about phenylmethyl thiocyanate[21]. However, other features of the aromatic reaction make S_N2 mechanism unsatisfactory. In the references cited[1,57–62] a considerable body of evidence, mainly related to leaving group mobilities and relative nucleophilicities of bases, has been marshalled in support of the S_NAr mechanism. Reactions involving the thiocyanate group, and especially S/N reactivity ratios (Table 2), give further support to a mechanism other than direct displacement or ionization.

TABLE 2.[55] Sulphur/nitrogen nucleophilicity ratios towards aryl carbon in the reaction of thiocyanate ion with 1-substituted mononitro-, dinitro- and trinitrobenzenes, ArX. Abbreviations: D = dimethylformamide, A = acetone, Ts = 4-toluenesulphonyl, Py^+ = pyridinium

Ar	X	Solvent and temperature	S/N nucleophilicity ratio
2-Nitrophenyl	NO_2	D, 100 °C	> 1000
4-Nitrophenyl	NO_2	D, 100 °C	> 1000
2,4-Dinitrophenyl	NO_2	D, 0·4 °C	> 1000
2,4-Dinitrophenyl	OTs	D, 75·2 °C	> 1000
2,4-Dinitrophenyl	I	D, 75·2 °C	2000
2,4-Dinitrophenyl	SCN	D, 101·4 °C	1000
2,4-Dinitrophenyl	SCN	D, 75·2 °C	1800
2,4-Dinitrophenyl	Cl	D, 75·2 °C	480
2,4-Dinitrophenyl	F	D, 75·2 °C	2·2
2,4-Dinitrophenyl	$OC_6H_3(NO_2)_2$-2,4	D, 75·2 °C	2·2
2,4-Dinitrophenyl	Py^+	D, 75·2 °C	< 0·1
2,4,6-Trinitrophenyl	I	A, 0 °C	> 100
2,4,6-Trinitrophenyl	SCN	A, 0 °C	120
2,4,6-Trinitrophenyl	Cl	A, 0 °C	22
2,4,6-Trinitrophenyl	F	A, 0 °C	< 0·001

[a] The product of S attack on this substrate is not the thiocyanato compound but the thiophenoxide ion $2,4\text{-}(NO_2)_2C_6H_3S^-$ and the resulting diaryl sulphide and disulphide[55]. Since the precursor for the transition state for this reaction involves bonding to thiocyanate via its sulphur atom[55], the products in this and other reactions have been included as products of S attack[56]. Where this is the main S attack reaction as in the case of 1-fluoro-2,4-dinitrobenzene, however, the rate-determining transition state is very different from the 1-*X*-2,4-dinitro-1-thiocyanatocyclohexadienide ion.

S/N reactivity ratios for thiocyanate attack on alkyl carbon range from about 2 to more than 1000. Ratios in the range of 2–9 are typical of reactions with a positively charged centre, such as a carbonium[16,19,63,64] or diazonium[65] ion. When the transition state includes a partial bond to the leaving group, as in S_N2 reactions or those with a degree of S_N2 character, S/N reactivity ratios are typically at least 50 and often more than 1000[21,66].

It is immediately apparent from Table 2 that with aryl carbon there is a clear division between compounds towards which thiocyanate ion has a sulphur/nitrogen nucleophilicity ratio of 10^2 to more than 10^3, and those for which the ratio is very much lower.

Kornblum's generalization[67] that carbonium character in the transition state favours the more electronegative attacking atom (in this case

nitrogen) is consistent with the lower S/N ratios in 2,4,6-trinitrophenyl compounds than in corresponding 2,4-dinitrophenyl and 4-nitrophenyl compounds. It is also qualitatively consistent with the fact that the ratios are smaller for electron-withdrawing leaving groups. However, it does not account for some S/N ratios being as low as, or even lower than for aralkyl carbonium reactions.

In the compounds studied by Fava's group, the formation of the new compound is in one step, either from a carbonium ion[7,10] or from an aralkyl thiocyanate[21]. The S/N reactivity ratio reflects, for an S_N2 reaction, the free energies of two transition states which can differ in the degree of 'tightness' (distance along the reaction coordinate[68-73]), in the form of attachment of the thiocyanate ion, and in the degree of solvation resulting from these two factors.

Sulphur/nitrogen reactivity ratios of 2 to 3, far too low for S_N2-type reactions[19,63], and more especially the extremely low ratios for 1-fluoro-2,4,6-trinitrobenzene and 2,4-dinitrophenylpyridinium ion, could be rationalized on the other hand as reflecting a difference in free energy between a bond-breaking transition state (Scheme 6) for S-attack and a bond-forming transition state for N-attack.

Halogen mobility ratios for S and N attack by thiocyanate ion on 1-halogeno-2,4-dinitrobenzenes provide support for this view. At 75·2 °C in dimethylformamide, the mobility ratios are for S-attack F:Cl:I = 0·25:1:2·9, and for N-attack F:Cl:I = 39:1:0·5[56].

The mobility ratio in the S-attack reaction suggests kinetic dependence on bond breaking, in which the strength of the carbon–halogen bond is important[57,74,75]. In the case of N-attack, bond formation with its dependence on the electronegativity of the leaving group[76] seems to be rate determining at least for the fluoro compound.

The low S/N reactivity ratios for displacement of F, $OC_6H_3(NO_2)_2$-2,4 and the pyridinium ion provide examples of the usefulness of the addition–elimination model for aromatic nucleophilic substitution reactions, as compared with a one-step[77] mechanism.

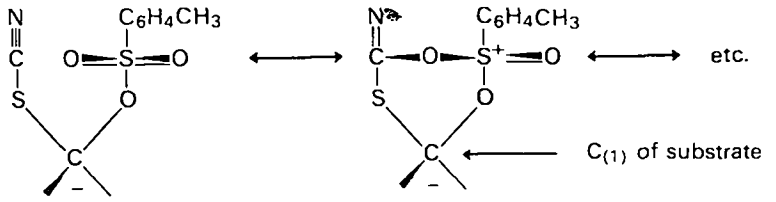
London-force interactions between entering and leaving groups[78] do not depend on whether the transition state is of bond-forming or bond-breaking type (except insofar as loss of ionic charge reduces the polarizability of the nucleophile), but rather on the distance between the groups and on their polarizability. These interactions would assist in the high S/N ratios for polarizable leaving groups $-NO_2$, –I, –SCN and (to a lesser extent) –Cl, by stabilizing the relevant transition states. Similarly, such interactions would be of less assistance to the less polarizable leaving groups, especially –F and -pyridinium. (Mutual polarizability interactions

are more important for S_NAr transition states, with entering and leaving groups arranged almost tetrahedrally about carbon[79], than in S_N2 transition states in which the separation is greater.) The S/N reactivity ratios are nearly all consistent with the principle of Hard and Soft Acids and Bases[49] if one considers the leaving group as having a symbiotic effect in the transition state[80].

5. 4-Toluenesulphonate as a leaving group

The one major exception to the above generalization is the 4-toluenesulphonate group. This group is classed by Pearson as hard[81], and is strongly electron withdrawing. The high S/N reactivity ratio for 2,4-dinitrophenyl 4-toluenesulphonate, and the high yield of thiocyanato compound reported for the reaction of 2,4-dinitrophenyl benzenesulphonate and potassium thiocyanate in ethanol[82], require special consideration.

Molecular models based on a C—S—C bond of about 120°[83] to 140°[84] on a cyclohexadienide anion indicate that the sulphonyl oxygen atom can readily approach to within bonding distance of the thiocyanate carbon atom. This allows a cyclic transition-state species as illustrated:



Models based on an isothiocyanatocyclohexadienide anion do not give the sulphonyl oxygen such ready access to the isothiocyanate carbon atom, whether the C—N—C bond angle is near to 140°[84] or 180°[85,86]. Furthermore, it is difficult to see how the isothiocyanate carbon atom could accept electrons as readily as the thiocyanate carbon atom.

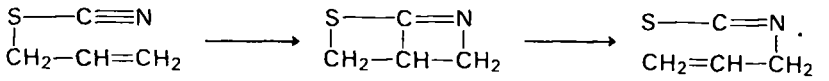
One cannot exclude London interaction between the cyanide group and the toluenesulphonate benzene ring in the transition state for S-attack. However, in contrast to the cases discussed by Bunnett[78], these centres can move apart by bond rotation. Hence each must compete with the solvent for access to the other. Partial bond formation involves forces of a different order from London-type forces and dipole–dipole interactions encountered in solvation.

Information on the mechanism of any reaction in which thiocyanate displaces group X to form an organic thiocyanate or isothiocyanate gives

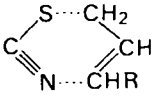
information in turn (through the principle of microscopic reversibility[87a]) on the mechanism of reactions of the organic thiocyanate or isothiocyanate with X to displace thiocyanate ion. This is of particular value when competing reactions or the equilibrium position preclude direct study of the displacement of thiocyanate ion.

6. Allyl thiocyanates

The first discussion of the mechanism of isomerization of thiocyanates was by Billeter[88], who proposed a cyclic intermediate:



Billeter suggested that the position isomerization be verified by isomerizing but-2-enyl (crotyl) thiocyanate, but it was 15 years later, in 1940, that Mumm and Richter[89] reported that this indeed gave 1-methylallyl isothiocyanate, and they proposed a similar intermediate:



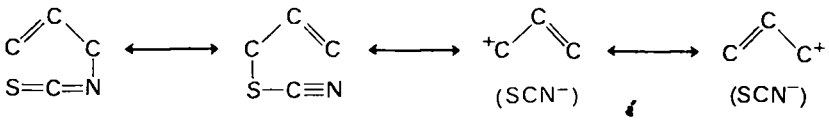
Billeter did attempt to verify his mechanism by heating 3-phenylallyl (cinnamyl) thiocyanate, but no isothiocyanate formed. This he attributed to steric hindrance, and in 1935 Bergmann[90] found that slow isomerization occurred on refluxing pure 3-phenylallyl thiocyanate, to give 3-phenylallyl isothiocyanate, i.e. no allylic shift.

In the late Fifties the investigation was extended by Smith and Emerson[5] and by Iliceto, Fava and coworkers[5,7,91].

The slow isomerization of 3-phenylallyl thiocyanate[89] was studied more closely, and found to be apparently first order, and highly sensitive to solvent changes and zinc chloride catalysis[5]. An ionization mechanism was proposed.

Allyl[5], 2-methylallyl[5], 3-methylbut-2-enyl (3,3-dimethylallyl)[91] and but-2-enyl (3-methylallyl)[91] thiocyanate isomerize at rates relatively independent of salt concentration, solvent polarity and electronic effects. Where product structure indicates whether a 1,3 shift accompanies isomerization, no trace was found of any products of isomerization about the carbon atom originally bonded to the thiocyanato group[91]. Both groups of workers proposed a non-ionic cyclic mechanism. It was noted[5]

that the entropy of activation (*c.* -38 J K^{-1} mol^{-1}) is similar to activation entropies of other rearrangements thought to proceed via a six-membered cyclic transition state[87b]. Fava[9,91] has discussed the reaction in comparison with the highly solvent and structure-sensitive rearrangements of allyl chlorides[92,93] and allylic carboxylic esters[94] and the insensitive rearrangements of allylic azides[93] and selenocyanates[7], which (unlike the chlorides) rearrange at similar rates to the thiocyanate rearrangement. The transition state is described as involving a resonance hybrid[7,92]:



This description allows for a spectrum of transition states for allylic rearrangements in which ionic structures contribute most to the chloride transition state and non-ionic structures contribute most to the thiocyanate, azide and selenocyanate transition states.

B. Photo-induced Thiocyanate–Isothiocyanate Isomerization

Parks and Spurlock[95] have investigated the isomerization of benzyl thiocyanates, $RC_6H_4CH_2SCN$, to give the isothiocyanates under the influence of light. For the parent compound (R = H), the equilibrium mixture contains mainly isothiocyanate, with about 4% thiocyanate in the non-polar solvent hexane and only 1% thiocyanate in acetonitrile. Substituent effects (R = CH_3, OCH_3, Cl, CF_3) on the isomerization rates are slight. Irradiation of benzyl thiocyanate or isothiocyanate in cyclohexane gives, in addition to the linkage isomer, dicyclohexyl sulphide and disulphide, and toluene. Earlier, Mazzucato and coworkers[96] showed by fluorescence emission measurements at 77 K that the benzyl radical is produced in the irradiation of benzyl thiocyanate or isothiocyanate in an inert solvent. Those authors suggested a radical-chain mechanism with benzyl and resonance-stabilized NCS radicals as intermediates—each able to react with the initial thio- or isothiocyanate leading to isomerization. Parks and Spurlock, however, obtained relative reaction rates after allowing for side-products unobserved by Mazzucato's group, and concluded that a radical-chain reaction was unlikely because isomerization rates decreased with increasing concentration. They proposed a homolytic cleavage of the C–S or C–N bond followed by recombination of radicals.

Cyclohexyl thiocyanate, on irradiation with light, gives only the sulphide and disulphide, with no discernible isomerization. Reaction of NCS and benzyl radicals with the solvent cyclohexane thus accounts for the toluene and the sulphide and disulphide. No cyclohexyl thiocyanate was detected.

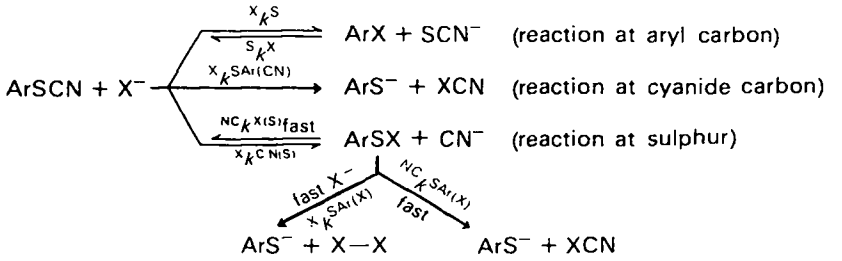
Partial isomerization of benzyl thiocyanate occurs on γ-irradiation, with production of side-products expected from $C_6H_5CH_2$ and $C_6H_5CH_2S$ radicals[97]. Low-temperature radiolysis of $CH_3(CH_2)_nSCN$ leads to primary and secondary alkyl radicals for $n > 3$[98].

C. Organic Thiocyanates as Trifunctional Electrophiles

1. Interpretation of product analyses

On the molecule RSCN there are at least three sites for nucleophilic displacements—the carbon atom on the group R bonded to thiocyanate, the sulphur[99–103], and the cyanide carbon[4]. Although detailed mechanistic studies of these reactions, with the exception of displacement of thiocyanate, have not yet been made there is some information available on the competition between the three sites in aromatic thiocyanates[56]. Scheme 7 sets out the initial products of the reactions of nucleophiles with activated aromatic thiocyanates and Scheme 8 shows some of the further reactions available. These reactions, and others such as solvolysis, certain reactions of isothiocyanates, and the Von Richter reaction[104] limit the conclusions that can be drawn from experiments on these systems. A further problem is that product analysis alone will not distinguish between attack at cyanide carbon ($^{X}k^{SAr(CN)}$) and attack at sulphur ($^{X}k^{CN(S)}$) in ArSCN (Scheme 7). However, some useful information has been obtained by product analyses in experiments designed to minimize decay of products, and by making use of known relative sulphur basicities and relative rates of substitution at carbon and sulphur to distinguish between reactions at cyanide carbon and at divalent sulphur[56].

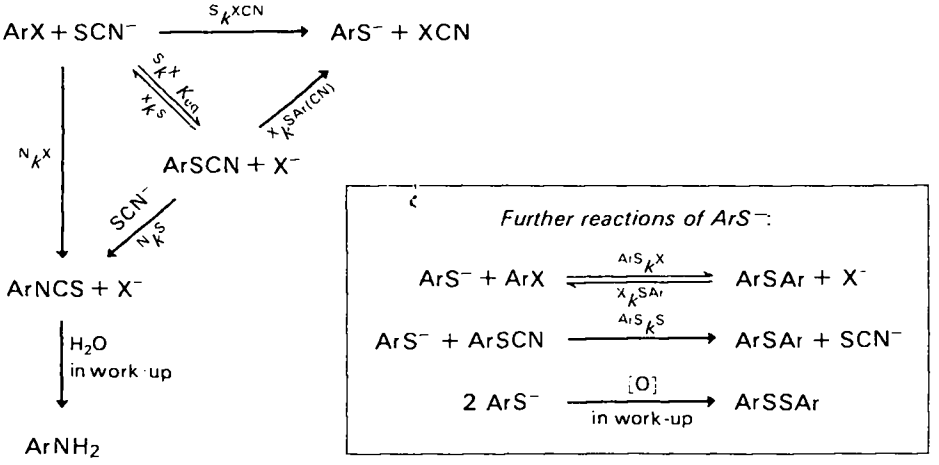
A distinction between reaction at aryl carbon on the one hand and at either cyanide carbon or sulphur on the other hand can be made by analysing for thiocyanate ion (attack at aryl carbon) and for mercaptide ion, ArS^- (attack at cyanide carbon or at sulphur). Allowance has to be made for thiocyanate ion formed by attack at sulphur or cyanide carbon followed by reaction of the resulting mercaptide with substrate ($^{ArS}k^{S}$, Scheme 8) or with a product (e.g., $^{ArS}k^{X}$ followed by $^{X}k^{S}$). This can be done in some cases by appropriate mathematical treatment of analytical



Ar is any nitroaryl group. $^{A}k^{B(C)}$ is a rate constant for, and label for, displacement of B by A at site C. N, S refer to thiocyanate N or thiocyanate S. (C) omitted if reaction is at aryl carbon.

ArS^- may also react further, as in Scheme 8. If Ar is 4-nitrophenyl and X is SPh, then the reaction $^{NC}k^{SAr(X)}$ proceeds as shown. Reaction $^{X}k^{SAr(X)}$ is likely in the presence of excess X^-, e.g. if X^- is SEt^-.

SCHEME 7. Reactions resulting from nucleophilic reactions with trifunctional aryl thiocyanates.



Attack by S—Possible products are ArSCN, ArSAr, ArS^-, ArSSAr.
Attack by N—Products are ArNCS, and $ArNH_2$ which is formed in the work-up.

SCHEME 8. Reactions resulting from aromatic nucleophilic substitution by ambident thiocyanate ion.

results, but the effect of reactions $^{ArS}k^{S}$ and $^{ArS}k^{X}$ can usually be minimized by using a large excess of the attacking nucleophile[56]. Table 3 shows the products of a series of reactions of bases with aromatic thiocyanate.

Consideration of available information on basicities and nucleophilicities of bases towards divalent sulphur enables us to distinguish further between attack at sulphur and attack at cyanide carbon.

Basicities towards divalent sulphur decrease in the order: thioalkoxides

$> CN^- \geq PhS^- > OH^-$, nitrothiophenoxides $> N_3^-$, halides, phenoxides, and alkoxides[101]. The reaction of 2,4-dinitrophenyl thiocyanate (ArSCN) with PhS^- gives quantitative yields of thiocyanate ion, and no ArS^-, in both methanol and dimethylformamide. If there were any attack by PhS^- at thiocyanate sulphur, ArS^- would be produced (Scheme 8). Displacements at divalent sulphur are very much faster than displacements at aryl carbon[101,105]—hence the failure to produce ArS^- from ArSCN must be because PhS^- is much less basic towards the sulphur atom in ArSCN than is cyanide ion. In cases where ArS^- is formed in reactions of 2,4-dinitrophenyl thiocyanate with bases which are less sulphur-basic than PhS^- and thus less sulphur-basic than CN^-, it is unlikely to be by displacement of CN^- from sulphur by those bases. Accordingly, the production of ArS^- from 2,4-dinitrophenyl thiocyanate by bases which are weaker than cyanide towards sulphur can be ascribed to reaction at cyanide carbon ($^{X}k^{SAr(CN)}$ in Scheme 7). Similar considerations apply in reactions of 2,4,6-trinitrophenyl thiocyanate to give ArS^-. In the case of 4-nitrophenyl thiocyanate, PhS^- gives a quantitative yield of ArS^- (Table 3), and this cannot as yet be assigned definitely to reaction at aryl carbon or to reaction at sulphur.

2. Mechanism of reaction at cyanide carbon atom

Some of the rate constants in Table 4 and the product proportions in Table 3 indicate the relative reactivity towards aryl carbon and cyanide carbon in ArSCN. The ratio of aryl to cyanide attack increases dramatically on changing from reaction of 4-nitrophenyl thiocyanate to reaction of 2,4-dinitrophenyl thiocyanate, with all bases studied. It seems that an extra activating nitro substituent enhances the S_NAr reactivity of aryl carbon in the usual way[1] (i.e., 10^6–10^8 increase in rate), but as shown in Table 4 for reaction with methoxide, the leaving group tendency of ArS^- from ArSCN is much less susceptible [i.e., $\log(^{MeO}k^{SAr(CN)})$ increases from +1·14 to +1·79] to a change from 4-nitroaryl to 2,4-dinitroaryl. This is expected if the displacement at cyanide carbon is a two-step process, via an intermediate such as $ArS{-}C(OMe) = N^-$ [4,106] and if bond formation is rate determining.

Also consistent with a transition state with highly localized charge is the solvent effect on the degree of preference of azide ion for cyanide carbon versus aryl carbon. When dimethylformamide is replaced by methanol as solvent in the reaction of azide ion with 2,4-dinitrophenyl thiocyanate, there is a marked swing towards attack at the cyanide carbon rather than aryl carbon (Table 3) as would be expected because of hydrogen bonding

TABLE 3. Products of reactions of aromatic thiocyanato compounds with bases in methanol and dimethylformamide[56]. The temperature was 24–30 °C unless otherwise stated. Yields are given as a percentage of aromatic thiocyanato compounds consumed. Mercaptides were determined spectrophotometrically after addition of excess NEt_3HSPh to convert diaryl sulphide and disulphide (but not ArSCN) into ArS^-. Analyses in the trinitrophenyl series have a wide margin of error because of intensely coloured solutions and the difficulty of separating the mercaptide from SCN^-

Base	Products (%)		
	from 2,4,6-$(NO_2)_3C_6H_2SCN$	from 2,4-$(NO_2)_2C_6H_3SCN$	from 4-$O_2NC_6H_4SCN$
PhS^-	100 SCN^- 100 ArSPh (DMF)	100 SCN^- 100 ArSPh (DMF, MeOH)	<0·1 SCN^- (MeOH, DMF) 100 ArS^- (DMF) some PhSCN (DMF)
EtS^-	93 SCN^- 7 ArS^- some EtSCN (DMF)	<1·2 SCN^- 97·5 ArS^- (MeOH) >95 ArS^- (DMF)	<0·1 SCN^- 91 ArS some EtSCN (DMF)
2,4-$(NO_2)_2C_6H_3S^-$	—	100 SCN^- 100 Ar_2S (DMF, MeOH)	—
2,4-$(NO_2)_2C_6H_3O^-$	—	<10 ArS^- (DMF)	—

N_3^-	95 SCN^- some ArS^- (DMF)	>99 SCN^- 0·2 ArS^- (DMF) 75 SCN^- 25 ArS^- (MeOH)	<0·1 SCN^- 100 ArS^- (DMF)
Piperidine	some ArS^- (DMF)	>99·5 ArS^- (MeOH)	100 ArS^- (MeOH)
MeO^-	—	0·1 SCN^- 100 ArS^- (MeOH)	<0·1 SCN^- 100 ArS^- (MeOH)
Cl^-	—	*c.* 99 SCN^- 1 ArS^- (DMF)[b]	—
Br^-, I^-	—	<0·1 ArS^- (DMF)[b]	—
KF	50 ArS^- (DMF)	98 ArS^- (DMF)[c]	—
Pyridine	—	*c.* 98 SCN^- <2 ArS^- (DMF)[b]	— —

[a] Thiocyanate ion is rapidly lost when potassium thiocyanate, picric acid and sodium nitrite are dissolved in dimethylformamide. ArO^- is the final product of decomposition of $ArNO_2$ when Ar is 2,4-dinitrophenyl or 2,4,6-trinitrophenyl.
[b] At 75°C.
[c] At 60°C, using a suspension of KF and $1·0 \times 10^{-5}$ M-ArSCN.

TABLE 4. Rate constants (l mol^{-1} s^{-1}) for attack by bases on aromatic thiocyanato compounds (ArSCN) at cyanide carbon ($^{X}k^{SAr(CN)}$) and at aryl carbon ($^{X}k^{S}$) in dimethylformamide (DMF) at 75·2 °C and in methanol at 30 °C[56]

Base	Solvent	log ($^{X}k^{SAr(CN)}$)	log($^{X}k^{S}$)
	2,4-Dinitrophenyl thiocyanate		
MeO^-	MeOH	+1·79	−1·16
Piperidine	MeOH	−1·04	< −3
N_3^-	MeOH	≥ −2·7	−2·2
N_3^- [a]	DMF	≥ −2·1 [a]	+0·57[a]
SCN^- [b]	DMF	≥ −5·75[c]	−5·26[b]
2,4-$(NO_2)_2C_6H_3O^-$	DMF	≥ −5·4	−4·4
Cl^-	DMF	≥ −3·1	−1·12
Br^-	DMF	< −6·7	−3·70
^-SCN[d]	DMF	< −5·7[c]	−1·99
NO_2^- [e]	DMF	< −2[e]	0·0[e]
I^-	DMF	< −7·6	−4·62
	4-Nitrophenyl thiocyanate		
MeO^-	MeOH	+1·14	< −2
Piperidine	MeOH	−1·51	< −4

[a] At −16·0 °C.
[b] Reaction at aryl carbon by N.
[c] Mode of reaction at cyanide carbon unknown but assumed to be through N.
[d] Reaction at aryl carbon by S attack.
[e] At 0·4 °C.

to stabilize a transition-state leading to an intermediate anion similar to ArS—C(OMe) = N^-. However, an alternative explanation for the solvent effect is a four-centre solute–solvent complex between the cyano group and dimethylformamide (Figure 1) similar to that proposed by Ritchie and his coworkers[107,108] for benzonitrile. Dipole moment studies[109] showing that the cyano group substantially retains its polarity when it forms part of a thiocyanato group support this. Reactions at cyanide carbon, but not at aryl carbon, would require disruption in the transition state of the substrate–dimethylformamide complex.

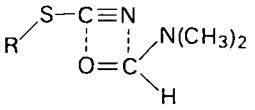


FIGURE 1. Possible complex between an organic thiocyanate and dimethylformamide.

3. Competition between aryl carbon and cyanide carbon

In the reaction between a base X^- and 2,4-dinitrophenyl thiocyanate, the degree of preference for cyanide carbon over aryl carbon can be expressed as the ratio ${}^{X}k^{SAr(CN)}/{}^{X}k^{S}$. Values of this ratio are shown in Table 5.

A generalization that can be made from Table 5 is that the selectivity of nucleophiles for aryl or cyanide follows the principle of Hard and Soft Acids and Bases[49], with the softer nucleophiles preferring the softer electrophilic centre, aryl carbon. It can also be seen, from Table 3, that activation by a single *p*-nitro group leaves aryl carbon less electrophilic than cyanide carbon, that addition of an *o*-nitro group shifts the site of attack towards the ring, and the addition of a second *o*-nitro group seems partly to reverse this shift, especially in the case when azide is the nucleophile.

The azide ion is an exception in the trend towards preference for cyanide carbon by hard bases. Pearson[50] classes azide ion as hard, yet in dimethylformamide it reacts almost exclusively at aryl carbon and even in methanol its behaviour is intermediate. This could be due to a relative advantage

TABLE 5. Reactivity ratios for reaction of 2,4-dinitrophenyl thiocyanate with nucleophiles[56]. Solvent: dimethylformamide at 75·2 °C unless otherwise stated

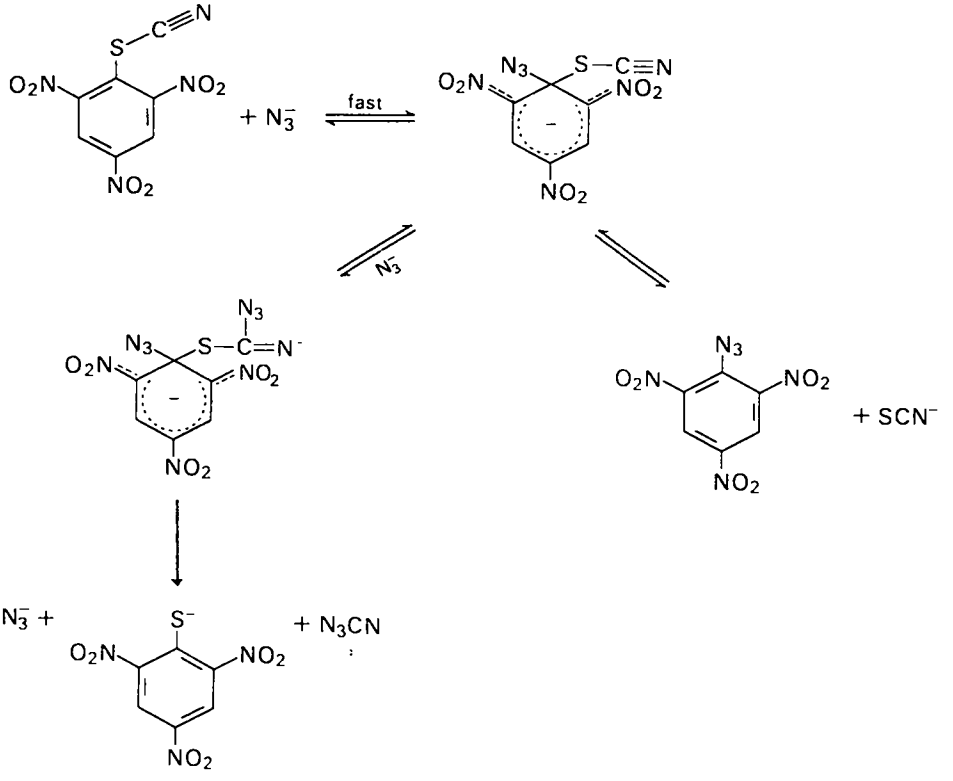
Nucleophile	$\log({}^{X}k^{SAr(CN)}/{}^{X}k^{S})$
MeO^- [a]	3·0
Piperidine[a]	> 2
$2,4\text{-}(NO_2)_2C_6H_3O^-$	< 2
F^- [b]	> 1·7
SCN^-, N-attack	> −0·5
N_3^- [a]	> −0·5
Cl^-	≥ −2
NO_2^- [c]	< −2
N_3^- [d]	≥ −3·7
Br^-	< −3
I^-	< −3
PhS^-	< −3
$2,4\text{-}(NO_2)_2C_6H_3S^-$	< −3
SCN^-, S-attack	< −3·7

[a] MeOH, 30 °C.
[b] 60 °C.
[c] 0·4 °C.
[d] −16 °C.

over other hard bases such as methoxide, 2,4-dinitrophenoxide and piperidine for reaction at the sterically-hindered aryl carbon atom[69]. Alternatively, the positively charged[110,111] central atom of the forming azido group may interact strongly with the oxygen atom of the nearby nitro group in the transition state. An interaction of this type is believed to be very strong in compounds such as 1-azido-2-nitrobenzene[111].

a. *Substituent effects.* The shift from cyanide carbon attack to ring attack when an *o*-nitro group is present in addition to a *p*-nitro group is to be expected in view of the sensitivity of S_NAr reactions in conjugative electron withdrawal[1]. Hiskey and Harpp[103] have shown that stabilization of leaving mercaptide ions is not necessarily a dominant kinetic factor—thus we can expect the influence of an *o*-nitro group in accelerating attack on aryl carbon to outweigh by far any effect in accelerating reaction at cyanide carbon and release of mercaptide.

A second *o*-nitro group appears, however, to favour formation of mercaptide ion, at least when azide is the attacking species. Cahn[112] has



SCHEME 9.

made similar observations in the reactions of 2,4-dinitro- and 2,4,6-trinitroanisoles with piperidine: displacement of methoxide ion from 2,4-dinitroanisole but reaction at the methyl carbon of 2,4,6-trinitroanisole. The observed effect of the second *o*-nitro group on product distribution need not signify a kinetic effect in favour of cyanide carbon (or of methyl carbon in Cahn's case). Meisenheimer complexes[113] can become the major species present during reactions involving picryl compounds[114], and further attack on these could give rise to the observed products (Scheme 9).

4. Reaction at thiocyanate sulphur

Thioethoxide is considerably more basic toward divalent sulphur than is cyanide[100–102], and hence the mercaptide produced by its reaction with 2,4-dinitrophenyl thiocyanate can be attributed to reaction $^{EtS}k^{CN(S)}$ (Scheme 7). Addition of a third nitro group seems to lessen the influence of attack at sulphur by thioethoxide—that is, the basicity of cyanide has moved closer to that of thioethoxide. It is already known that when there are *no* nitro groups, as in phenyl thiocyanate, even the thiophenoxide ion is more basic towards sulphur than is cyanide[99,101].

These observations fit into a picture of *increasing sulphur basicity of cyanide relative to mercaptides as electron density is withdrawn from the electrophilic sulphur atom.*

It is tempting to speculate on the reactions of thiophenoxide and thioethoxide with 4-nitrophenyl thiocyanate—if the reaction here is at sulphur and not at cyanide carbon then these results (Table 3) fit neatly into the same picture. These reactions merit closer investigation, as a distinction between the two sites of attack may be possible by employing an excess of nucleophile and analysing for disulphides from reaction $^{X}k^{SAr(X)}$ in Scheme 7.

One extremely sulphur-nucleophilic and basic class of nucleophiles is the carbanion. Products of reactions of acetylide[113], trichloromethyl, alkyl and aryl carbanions[114] with alkyl thiocyanates indicate direct displacement of cyanide ion from sulphur as in equation 10.

$$RS{-}CN + R'^{-} \longrightarrow RS{-}R' + CN^{-} \qquad (10)$$

In studying the carbanion reaction, Makosza and Fedorynski[114] used a two-phase system—aqueous and organic—so that the base used to generate the carbanion, and the displaced cyanide ion, remained outside the organic phase and could not react further with the organic thiocyanate or sulphide.

Attack by Grignard reagents or alkyl lithium at low temperatures seems to be at sulphur, especially for alkyl thiocyanates, but at cyanide carbon at higher temperatures[115], reflecting a low activation energy for attack at sulphur.

5. Reactions of organic thiocyanates with trialkyl phosphites

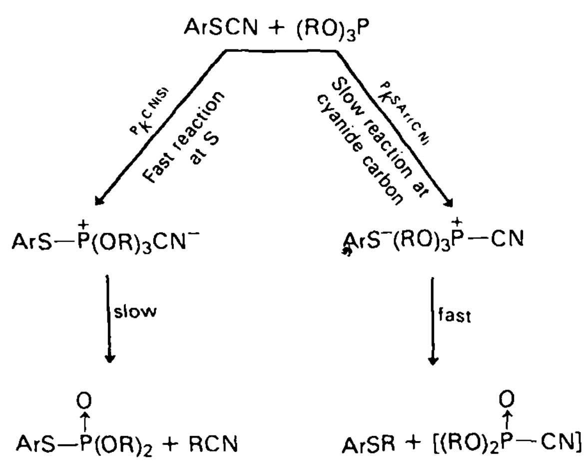
Alkyl and aryl thiocyanates react with trialkyl phosphites to give a thiophosphate and nitrile as in equation (11)[116,117]. Aryl thiocyanates, but not alkyl thiocyanates, also give an alkyl aryl sulphide (equation (12)), a reaction favoured by electron-withdrawing substituents in the ring[118,119].

$$(RO)_3P + R'SCN \longrightarrow R'S\overset{O}{\overset{\uparrow}{P}}(OR)_2 + RCN \qquad (11)$$

$$(RO)_3P + ArSCN \longrightarrow ArSR + [(RO)_2\overset{O}{\overset{\uparrow}{P}}CN] \qquad (12)$$

(The dialkyl cyanophosphate of equation 12 reacts further with dialkyl phosphite.)

Mechanisms postulated for reactions (11)[116,117] and (12)[119] are summarized in Scheme 10, due to Pilgram and Phillips[119].



SCHEME 10.

The proposed scheme is supported by studies of reactions of sulphenyl halides and dialkyl disulphides with trialkyl phosphites[100], by the absence of photocatalysis or inhibition by radical scavengers[117], and by the effect of electron-withdrawing substituents in the aryl group in accelerating both reactions and favouring displacement of mercaptide relative to displacement of cyanide[119].

D. Addition Reactions of Thiocyanates and Isothiocyanates

1. Thiocyanates

Addition reactions of thiocyanates occur in a direction governed by the polarity of the –SCN group: $-S-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$.[4] Acid-catalysed hydration or addition of alcohol, by analogy with nitriles, has been said[4] to begin with protonation, followed by addition, to give an iminothiocarbonate which rearranges to give a thiocarbamate.

2. Isothiocyanates

Addition to isothiocyanates has received considerably less detailed attention than addition to isocyanates. Isothiocyanates undergo a wide variety of addition reactions, and representative types will be considered here to illustrate general mechanistic features.

Acids add to isothiocyanates (and isocyanates) according to the general equation (13):

$$RNCS + HX \rightleftharpoons R-\overset{H}{\underset{|}{N}}-\overset{X}{\underset{|}{C}}=S \qquad (13)$$

Strong and moderately strong acids react in acidic solution, but the very weak acid, hydrogen cyanide, requires base catalysis[120,121], suggesting that the anion may be involved in the initial attack.

Addition of alcohols to isothiocyanates was investigated by Rao and Venkataraghavan[122,123] who found the reaction to be first order in alcohol and in isothiocyanate, but too slow in most instances for convenient direct study. Reactions catalysed by triethylamine (equation 14) and pseudo-first-order reactions with the alcohol as solvent were utilized to gain kinetic information.

$$ArN{=}C{=}S + NEt_3 \rightleftharpoons Ar\overset{\delta^-}{N}{\cdots}C{\cdots}\overset{\delta^-}{S} \xrightarrow{ROH} Ar{-}\overset{H}{N}{-}\overset{OR}{C}{=}S + NEt_3 \qquad (14)$$

$$\begin{array}{c} \\ | \\ \overset{+}{N}Et_3 \end{array}$$

Varying the substituent in the addition of ethanol to 4-substituted phenyl isothiocyanates showed good correlation with Hammett σ constants, and much poorer correlation with Brown's σ^+ constants[12]. Electron-withdrawing substituents were found to accelerate addition.

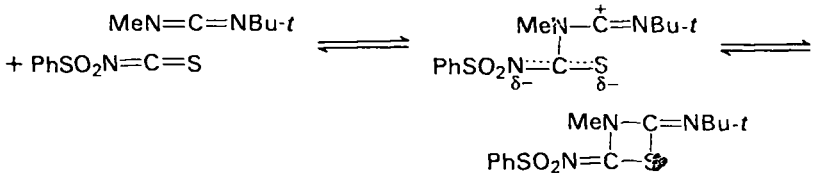
Although equation (14) shows addition across the C=N bond, tautomerism between the predominant thioamide form shown and the aryliminothiocarbonate form ($Ar{-}N{=}C\begin{array}{l}OR\\SH\end{array}$) makes the direction of initial addition undeterminable from consideration of products.

The reactivity of alcohols toward 4-bromophenyl isothiocyanate with the alcohol as solvent in each case decreases in the order $CH_3OH > C_2H_5OH > n\text{-}C_3H_7OH > i\text{-}C_3H_7OH > t\text{-}C_4H_9OH$[123]. Correlation of rate data with Taft σ^* constants[124] is poor. Ultraviolet absorption of 4-bromophenyl isothiocyanate in cyclohexane was found to depend on the concentration of added propan-2-ol, suggesting complex formation. Rao interpreted this as a steric effect which outweighs the polar effect, increasing the basicity of the alkoxide ion with increasing substitution—something which had already been noticed in some alcohol additions to isocyanates[125]. The reactivity order could, however, be rationalized on the basis of ease of cleaving the O—H bond—autoprotolysis constants decrease in the order of decreasing reactivity towards addition to 4-bromophenyl isothiocyanate[126].

In the addition reaction of substituted anilines with phenyl isothiocyanate, rates have been found to vary[123] with hydrogen basicity of the amines in much the same way as in nucleophilic substitution reactions[127,128].

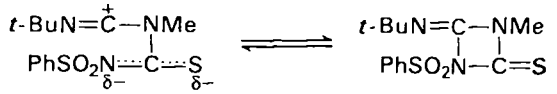
Acyl isothiocyanate–amine addition reactions were found by Brzozowski[129] to be catalysed by tertiary amines. Initial formation of a nitrogen–carbon bond involving the tertiary amine, followed by displacement by the primary or secondary amine in a manner analogous to that of equation (14), was proposed following similar proposals for isocyanates by Baker and Gaunt[125].

Ulrich, Sayigh and their coworkers[130–134], and Neidlein[135] have investigated the 1,2-cycloaddition of carbodiimides (RN=C=NR′) to isothiocyanates and isocyanates (*q.v.*). Initial problems of identifying products were overcome by fragmentation of products derived from methyl-*t*-butylcarbodiimide and isothiocyanates (and isocyanates, *q.v.*)[134], and it was shown that addition occurs across the C=S bond as in equation (15).



(15)

An alternative fate of the intermediate shown in equation (15) is rotation leading to the formation of a 1,3-diazetidine structure as in equation (16). However, in the case of

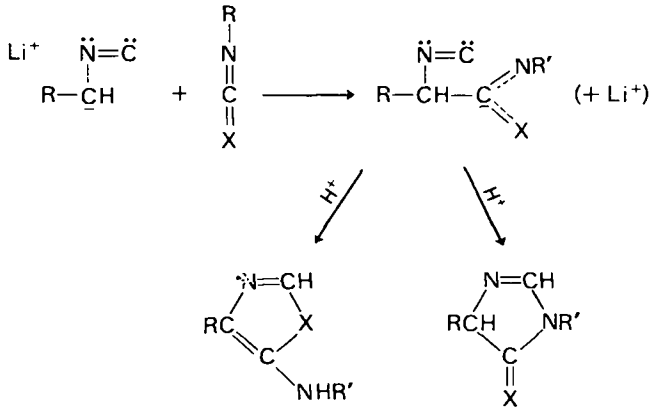


(16)

toluenesulphonyl isothiocyanate this does not take place. 1,3-Diazetidine formation does occur with isocyanates and is discussed in the relevant section. Ulrich states that the initial reaction is not necessarily donation of electrons by the carbodiimide, as donation of electrons to the carbodiimide by isothiocyanate sulphur would also give the observed product; however, in the absence of evidence to the contrary it seems reasonable to assume, with Ulrich, that the less electron-rich isothiocyanate group will provide the receptor site.

Carbothianiide anions formed from α-lithiated isocyanides and organic isothiocyanates (Scheme 11) show a similar preference for bonding to sulphur to form thiazoles and corresponding carboxamide anions give imidazoles by C–N bond formation[136].

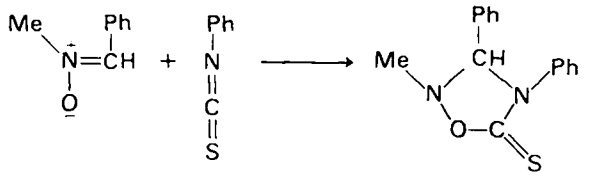
1,3-Dipolar cycloadditions, also, occur across either of the isothiocyanate double bonds depending on the 1,3-dipole under consideration[133,137]. The reaction type can be illustrated by the cycloaddition of nitrones (R · NO:CHR′) to isothiocyanates. *N*-Methyl-*C*-phenylnitrone and the cyclic nitrone 5,5-dimethyl-1-pyrroline 1-oxide (**8a**, equation 18) add across the C=N bond of phenyl isothiocyanate[138,139] but 3,3,5,5-tetramethyl-1-pyrroline 1-oxide (**8b**, equation 18) adds across the C=S bond[140]. Both cyclic nitrones give thiolactams with substituted phenyl isothiocyanates (i.e., addition across C=S) whether the substituents are



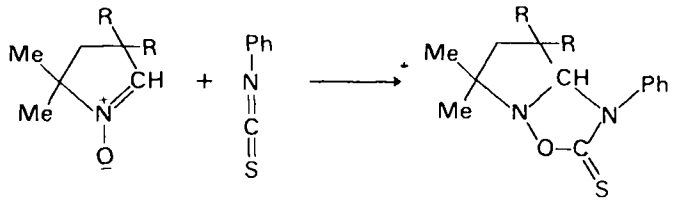
5-(*N*-Phenylamino)-1,3-thiazole 3-Phenyl-1,3-imidazolin-4-one

SCHEME 11.

electron donating or electron withdrawing (Scheme 12). Thiolactam formation is accompanied by elimination of aryl isocyanate, and product analysis indicates that nitrones add exclusively across the C=N bond of the isocyanate group.



(17)

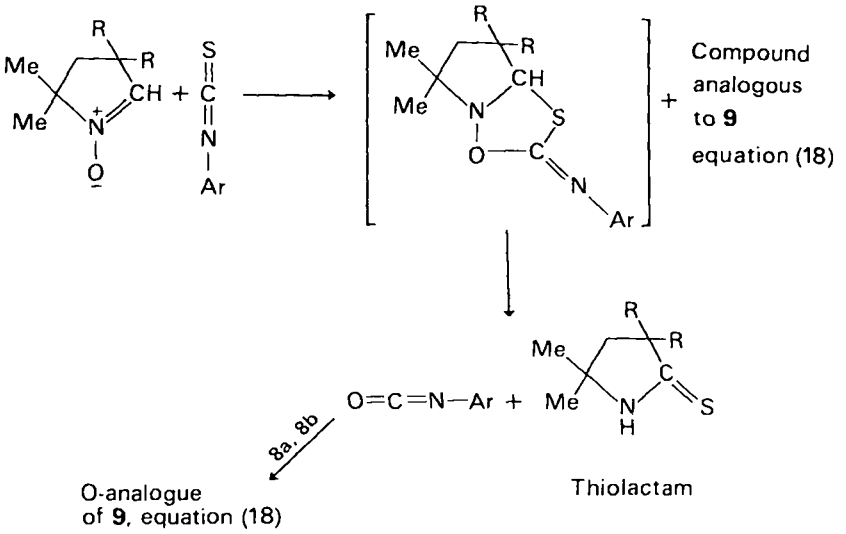


(18)

(8) (9)

a: R = H

b: R = CH_3



SCHEME 12.

Black and Watson[140] have attributed C=S addition with substituted phenyl isothiocyanates to a reduction of the C=N bond order relative to the C=S bond order by mesomeric electron donation as in 4-ethoxyphenyl isothiocyanate or withdrawal as in 4-nitrophenyl isothiocyanate. The preference of the more hindered tetramethyl cyclic nitrone for C=S addition suggests sensitivity to steric factors.

a. *Competition between addition to isothiocyanates and elimination of thiocyanate ion.* Nucleophilic substitution is relatively easy in acyl isothiocyanates, and Elmore and Ogle have published some data on the competition between this reaction and addition[141–143]. Alcohols and thiols react exclusively or almost exclusively by addition, and amines give mixed products depending on conditions. Substitution is favoured when the solvent is highly polar and the amine is strongly basic. A carboxylate ion close to the amino group also increases the proportion of substitution. Addition is favoured by steric hindrance to substitution, i.e. substitution is apparently more sterically demanding than is addition.

III. THE GROUPS –OCN AND –NCO

A. Thermal Cyanate–Isocyanate Isomerization

Cyanates are considerably more difficult to study than thiocyanates, because of the ease with which they isomerize or trimerize. The first

organic cyanate was not prepared until 1960[144]. Since then many classes of cyanates have been prepared, and their chemistry has been studied extensively[145].

Alkyl cyanates readily isomerize to form alkyl isocyanates[146–150], but aryl cyanates are stable to heat when pure and rapidly trimerize to give triaryl cyanurates in the presence of nucleophilic or electrophilic catalysts[151,152]. Martin has attributed the thermal stability of aryl cyanates to resonance[153].

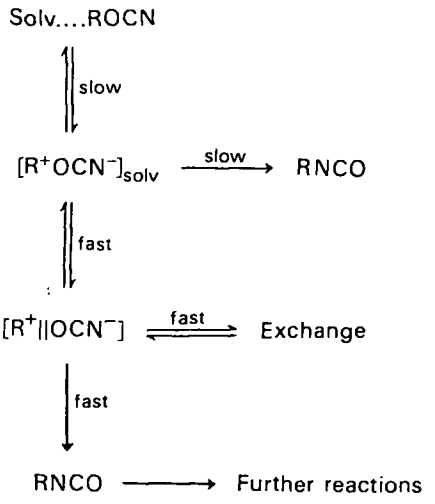
Isomerization of alkyl cyanates is promoted by elevated temperatures, high concentration (especially in polar solvents), Lewis-acid catalysis and the absence of bulky alkyl groups on the α-carbon atom[146–150, 154–156]. Martin and coworkers have investigated cyanate isomerization in some detail using ethyl cyanate as an example[150]. Despite further reactions (especially trimerization) of the product ethyl isocyanate they were able to show:

(i) The reaction is faster in polar than in non-polar solvents.
(ii) Addition of lithium perchlorate increases the rate in acetonitrile.
(iii) In solvents of low ionizing power the reaction is catalysed by the product, but when ionizing power (in particular, cation-solvating ability) is increased by solvent change or, in acetonitrile, by the addition of lithium perchlorate, the reaction is first order.
(iv) The isomerization is extremely rapid in dimethyl sulphoxide.
(v) Isomerization of ethyl cyanate-^{15}N and *n*-butyl cyanate together in nitrobenzene leads to an isocyanate mixture in which the nitrogen-15 is almost equally shared (with slightly more in the ethyl isocyanate—but further reactions of the products preclude complete equilibration).

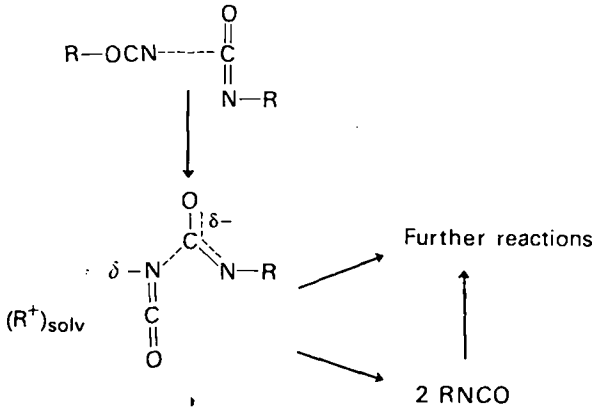
Martin rationalized these results on the basis of Scheme 13 for the first order reaction and Scheme 14 for the autocatalysed reaction.

The solvent-separated ion pair of Scheme 13 was put forward to account for the isotopic exchange in nitrobenzene, the first-order kinetics, and the unlikelihood of a solvent such as nitrobenzene supporting free ions as in a classical S_N1 reaction. The suggested autocatalytic mechanism (Scheme 14) is a special case of Lewis-acid catalysis in an S_N1 reaction.

However, the single exchange study in nitrobenzene needs to be supplemented before Scheme 13 can be well established, since the reaction in nitrobenzene is not first order and arguments relevant to that reaction cannot necessarily be applied to the first-order, uncatalysed reaction in the more-ionizing solvents (especially as one of the arguments was that the solvent nitrobenzene would not allow free ions).



SCHEME 13.



SCHEME 14.

B. Photo-induced Cyanate–Isocyanate Isomerization

Irradiation of butyl cyanate vapour with the light from a high-pressure mercury arc lamp has been found by Hara, Odaira and Tsutsumi[157] to give butyl isocyanate and its trimer, tributyl isocyanurate, as the main products. Other products, and the effects of added gases, are summarized in Table 6.

TABLE 6. Products of photolysis of gaseous butyl cyanate (BuOCN) at 35 °C, 20 mmHg pressure[157]

Added gas	Products (%)							
			HCN	$(CN)_2$	PrCHO	BuOH	BuNCO	$(BuNCO)_3$
None	3	2	8	3	9	7	38	39
Hg	trace	trace	5[b]	—	8	7	40	43
C_6H_6[a]	trace	trace	trace	trace	trace	trace	46	48
O_2[a]	2	2	4	2	6	4	20	25

[a] 10 mmHg pressure.
[b] $Hg(CN)_2$ was formed.

Three reaction paths could account for the products, one starting with reaction (19), one with reaction (20) and one with reaction (21).

$$BuOCN \xrightarrow{h\nu} BuO\bullet + \bullet CN \quad (19)$$

$$BuOCN \xrightarrow{h\nu} Bu\bullet + \bullet OCN \quad (20)$$

$$BuOCN \xrightarrow{h\nu} BuNCO \quad (21)$$

Some of the products could be formed by any of the paths, but formation of hydrogen cyanide and butan-1-ol is typical of the products following from reaction (19), butane and but-1-ene follow from reaction (20), and butyl isocyanate and its trimer are the main products of reaction (21). Butyl cyanate has an absorption maximum around 260 nm, depending on the solvent, and a strong absorption band below 220 nm. Filtering out the light above 250 nm was found to suppress the products attributed to reactions (19) and (20). From this, and the evident insensitivity of reactions (19) and (20) to oxygen, the authors deduced that Bu–OCN and BuO–CN dissociation proceeds through a high energy singlet state, and that the isomerization reaction, which is sensitized by benzene and mercury and suppressed by oxygen, may involve a triplet state without the intervention of radicals.

Similarly butyl and ethyl cyanates give mainly the isocyanate and isocyanurate on irradiation in the liquid state, but phenyl, 2-methylphenyl and 2,6-di-*t*-butylphenyl cyanates give mainly the products expected from reaction (20)[158], as would be predicted on the basis of the greater stability of phenoxy radicals than of alkoxy radicals.

C. Organic Cyanates as Trifunctional Electrophiles

Cyanates are less susceptible to nucleophilic attack at oxygen than are thiocyanates to similar reactions at sulphur. This is because oxygen has a higher electronegativity than sulphur and is unable to form intermediates by expansion of its valence shell. However, Pilgram and Korte[159], and Martin and Weise[160] obtained products from the reaction of trialkyl phosphites with aryl cyanates which indicated participation of a reaction mechanism in which initial attack is at oxygen, as in step $^{P}k^{CN(S)}$ of Scheme 10. When dialkyl phosphites are the reagents, the reaction occurs exclusively at oxygen as in equation (22)[160].

(22)

There has been no mechanistic investigation of nucleophilic replacement of cyanate ion in the aryl cyanates, a reaction which would undoubtedly require activation by very powerful electron withdrawal from the benzene ring. The usual site for nucleophilic attack is the cyanide carbon atom, with displacement of phenoxide, as shown in equation (23), or with addition across the C≡N bond (Section III.D). This topic has been reviewed[145,161].

$$Y^- + ArO{-}CN \longrightarrow ArO^- + Y{-}CN \qquad (23)$$

(Y^- is, e.g., RO^-, RS^-)

With alkyl cyanates, however, competition for the nucleophile arises between the alkyl carbon atom and the cyanide carbon atom. Martin's group has made a wide-ranging study of this competitive reaction[162]. The primary products of reactions at the alkyl carbon atom are shown in equation (24), and those of reaction at the acyl carbon atom are shown in equations (23) (replacing Ar with R) and (25).

$$R{-}OCN + Y^- \text{ or } HY \text{ or } (Y^-/\text{Protic solvent}) \longrightarrow RY + OCN^- \text{ or } HOCN \qquad (24)$$

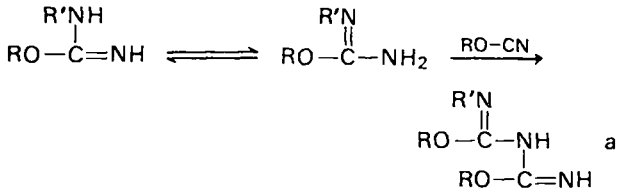
$$RO{-}C{\equiv}N + HY \text{ or } (Y^-/\text{Protic solvent}) \rightleftharpoons RO{-}\overset{\displaystyle Y}{\underset{|}{C}}{=}NH \text{ or } RO{-}\overset{\displaystyle Y}{\underset{|}{C}}{=}N^-_{(solv)} \qquad (25)$$

Cyanic acid immediately reacts further to give such products as cyamelide, cyanuric acid, (in the presence of alcohols) allophanic acid esters or (in the presence of amines) substituted ureas.

The product of equation (25) can dissociate to reform the alkyl cyanate (reverse of equation 25) or to give YCN as in equation (26). Alternatively

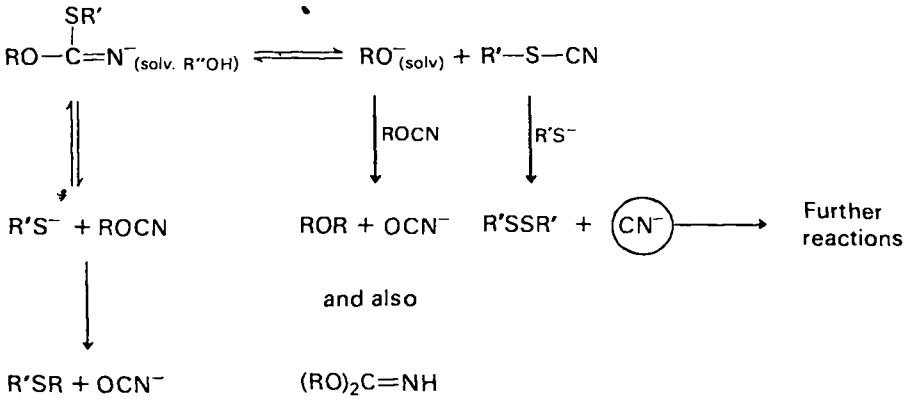
$$RO{-}\overset{\displaystyle Y}{\underset{|}{C}}{=}NH \longrightarrow ROH + YCN \qquad (26)$$

$$RO{-}\overset{\displaystyle OCOR'}{\underset{|}{C}}{=}NH + R'COOH \longrightarrow RO{-}\overset{\displaystyle OCOR'}{\underset{|}{\overset{|}{C}}}{-}NH_2 \longrightarrow RO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2 + R'COOCOR' \qquad (27)$$



(28)

it can react with further reagent as in equations (27) and (28) and in Scheme 15.



SCHEME 15.

Fortunately the reverse reaction of equation (25) and further reactions of products shown in equations (23), (26), (27) and (28) and Scheme 15 are slow enough at the temperatures of Martin's study (mostly in the range 0 to 20 °C) to allow a product analysis to give some information on relative rates of nucleophilic reactions at the alkyl and cyanide carbon atoms. This information, for a selection of nucleophiles, is summarized in Table 7. (It is of interest that Scheme 15 also accounts for the formation of dialkyl sulphide in the reaction of alkyl thiocyanate with alcohol[106,163].)

The role of dipolar aprotic solvents in determining the product distribution can be rationalized in terms of their strong solvation of S_N2-type transition states, in which charge is well distributed, relative to transition states such as RO—C(Y)=N⁻, which are more suited to systems in which protonation or hydrogen-bonding solvation is possible.

The product distribution in the other solvent classes is, however, difficult to explain. Martin has proposed that the stronger nucleophiles react more readily at the more electrophilic cyanide carbon atom and the less reactive nucleophiles prefer the less electrophilic alkyl carbon atom[162]. It is not clear why this should be so, and in any event there are some notable exceptions such as phenol in ether or the highly nucleophilic

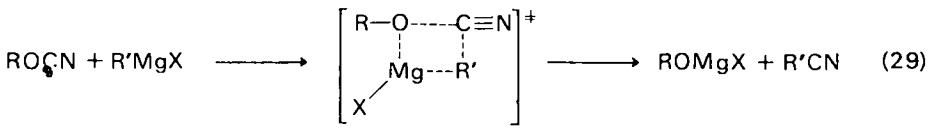
TABLE 7. Reactions of nucleophiles with alkyl cyanates[a]

Solvent type	Nucleophiles reacting mainly at alkyl C	Nucleophiles reacting mainly or appreciably at cyanide C
Protic[b]	I^-, OCN^-, SCN^-, NO_2^-, ROH	CN^-, N_3^-, RO^-, RS^-
Non-polar aprotic[c]	$PhNH_2$, ROH, RCOOH, HCL, R_3N	PhOH, RSH, PhCOSH, R_2NH, carbanion-active systems[d]
Dipolar aprotic[e]	I^-, OCN, SCN^-, NO_2^-, $NO_3^-(Ag^+)$, CN^-, N_3^-, RO^-, PhO^-, RS^-, PhCOSH, RNH_2, R_2NH, carbanion-active systems	

[a] Data from References 154, 162, 164 and 165.
[b] Water, alcohol or water-saturated ether.
[c] Ether, hydrocarbons.
[d] E.g. NCCHNaCOOEt, NCCHNaCN, $CH_3COCHNaCOCH_3$, Grignard reagents.
[e] Dimethylformamide, dimethylsulphoxide.

anion–dipolar aprotic solvent systems. Neither can the data for protic and non-polar solvents be readily explained in terms of polarizability, hardness and softness, or even by the availability of protons to reduce the high charge density on the nitrogen atom in the transition state for reaction at cyanide carbon (for example, alcohols, carboxylic acids and hydrogen chloride react at alkyl carbon).

Some kinetic evidence has recently been obtained suggesting that the second-order reaction between alkyl or aryl cyanates and alkyl or aryl Grignard reagents may be by way of a four-centre transition state in which the magnesium bonds to oxygen synchronously with nitrile formation, thus by-passing any imido-ester type intermediate[166–168] (equation 29). It is not claimed[166–168], however, that the evidence is yet strong enough for definite exclusion of an imido ester.



(29)

(X=halogen alkyl or aryl)

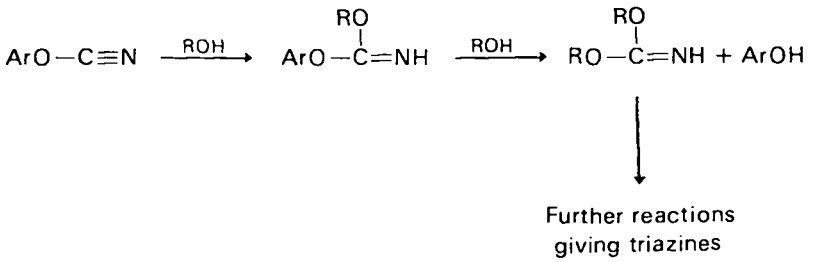
Much detailed investigation remains to be done before the product distributions in the reactions of nucleophiles with alkyl cyanates can be adequately accounted for.

D. Addition Reactions of Cyanates and Isocyanates

1. Cyanates

Addition to cyanates can follow nucleophilic attack at the cyanide carbon atom as discussed in Section III.C. A detailed examination of some addition reactions of aryl cyanates has recently been made by Martin's group[169–171].

The reaction of aryl cyanates with alcohols is slow in the absence of acid or base catalysis, and leads first to alkyl aryl imidocarbonate and then to dialkyl imidocarbonate, followed by further reactions leading to triazines (Scheme 16)[170]. The formation of triazines in the reaction of



SCHEME 16.

methanol with aryl cyanates could be suppressed by the use of a large excess of methanol, and the formation of each imidocarbonate diester and phenol was followed spectrophotometrically and matched to a computer model based on equations (30) and (31)[160].

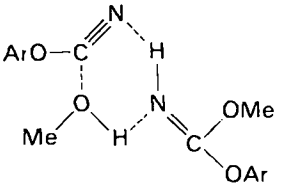
$$\mathrm{ArOCN + MeOH\ (excess) + Autocatalyst} \xrightarrow{k} \mathrm{ArOC(OMe){:}NH + Autocatalyst} \tag{30}$$

$$\mathrm{ArOC(OMe){:}NH + MeOH\ (excess)} \xrightarrow{k'} \mathrm{(MeO)_2C{:}NH + ArOH} \tag{31}$$

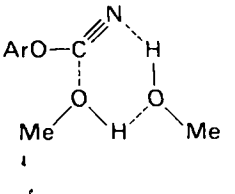
The autocatalyst was taken to be the methyl aryl imidocarbonate, since the dimethyl imidocarbonate concentration was negligible during the

part of the reaction course studied. The strongly negative activation entropy (-162 J K^{-1} mol^{-1}) and low activation energy (30·5 kJ mol^{-1}) for the reaction of methanol with phenyl cyanate in methanol (equation 30), and the negative Hammett ρ value[169,172], support Martin's assignment of a trimolecular transition state (**I**) for the reaction. (Since the ρ value for other addition reactions is positive, the overall negative ρ value was taken to signify a strongly negative value for the autocatalysis, i.e. electron-withdrawal decreases the ability of the catalyst to contribute to structure **I**.)

Before the concentration of imidocarbonate becomes significant, the alcohol itself can contribute (less effectively) to a similar cyclic transition state (**II**)—in keeping with the observation that the addition of methanol to methylphenylketene is second order in methanol[173].



(I)



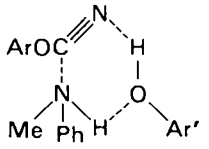
(II)

Since structure **I** involves an N–H group and an O–H group, it is predictable that hydroxylic compounds would catalyse the addition of an amine to a cyanate, and the amine would catalyse the addition of a hydroxylic compound. Martin found this to be the case: *N*-methylaniline and phenols separately add only very slowly to aryl cyanates, but together they both react rapidly, forming an isourea from amine addition and an imidocarbonate from phenol addition. The kinetics follow the integrated form of equations (32) and (33) well, the presence of substituents in either the phenol or the cyanate influence both addition reactions in the one direction (acceleration by electron-withdrawing groups), and in all cases studied by Martin the ratio k'/k (equations 32 and 33) was found to be close to a constant value of 2. Hence it was proposed that one-third of the aryl cyanate reacts through transition state **III** and two-thirds react through transition state **IV**.

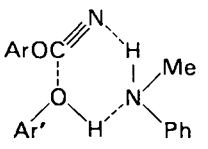
$$dx/dt = k(a - x - y)(b - x)(c - y) \tag{32}$$

$$dy/dt = k'(a - x - y)(b - x)(c - y) \tag{33}$$

(x = [isourea], y = [imidocarbonate], $a = [\text{ArOCN}]_0$, $b = [\text{amine}]_0$, $c = [\text{phenol}]_0$)



(III)



(IV)

2. Isocyanates

Isocyanates are more reactive to addition than cyanates, thiocyanates or isothiocyanates. Their addition reactions have been extensively reviewed over the years[121,173–181], and in this chapter we shall direct our attention to the addition reactions which have been most exhaustively studied (especially addition of alcohols and amines to alkyl and acyl isocyanates and the dimerization and trimerization of isocyanates), and to some studies whose interest lies in their relationship to isothiocyanate reactions or in their importance in typifying major trends in current or recent research.

a. *Addition of alcohols, amines, water and phenols.* For a number of years, thinking on the mechanism of the addition of alcohols to isocyanates (equation 34) was dominated by the pioneering work of Baker and Gaunt[125,182–185].

$$R{-}N{=}C{=}O + R'OH \longrightarrow R{-}NH{-}\overset{\displaystyle OR'}{\overset{|}{C}}{=}O \qquad (34)$$

Baker and Gaunt measured the kinetics of the reaction, with and without the assistance of tertiary amine catalysts, between a range of aryl isocyanates and a range of alcohols. In the absence of tertiary amine catalysis, the addition reaction appeared to be second-order, but the second-order rate constant was found to increase with increasing initial [ROH]/[RNCO] ratios. This was ascribed to the stepwise mechanism shown in equation (35). Assumption of a steady state in the concentration of the intermediate complex leads to equation (36), and this equation and the mechanistic scheme leading to it were supported by the linearity of plots of $[ROH]/k_{obs}$ against [ROH], for several alcohols with phenyl isocyanate in dibutyl ether[125].

$$Ar{-}N{=}C{=}O + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar{-}N{=}\overset{\displaystyle \overset{+}{R}OH}{\overset{|}{C}}{-}O^- \xrightarrow[ROH]{k_2} Ar{-}\underset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{\displaystyle OR}{\overset{|}{O}} + ROH \qquad (35)$$

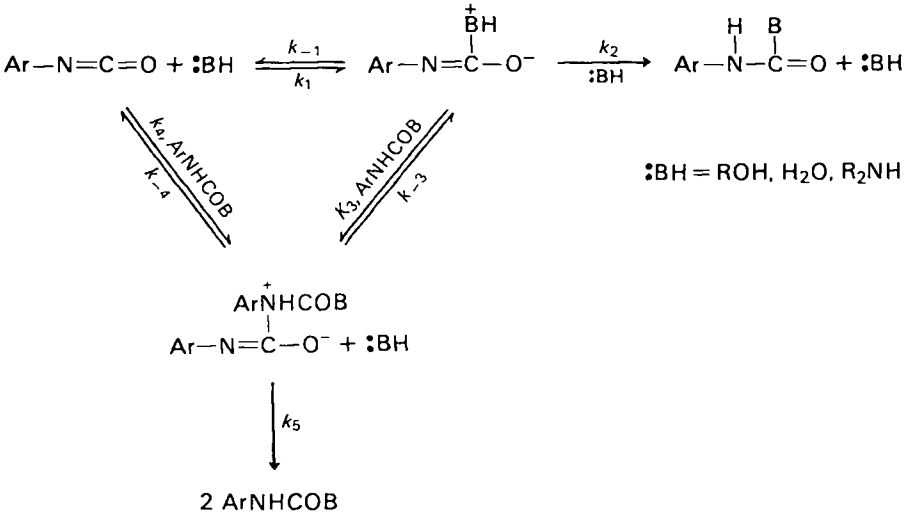
$$[ROH]/k_{obs} = k_{-1}/k_1k_2 + [ROH]/k_1 \quad (36)$$

(k_{obs} is the observed second-order rate constant)

$$ArN{=}C{=}O + NR_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar{-}N{=}\overset{\overset{+}{N}R_3}{\overset{|}{C}}{-}O^- \xrightarrow[ROH]{k_2} Ar{-}\underset{H}{\overset{|}{N}}{-}\underset{OR}{\overset{|}{C}}{=}O + NR_3 \quad (37)$$

$$[NR_3]/k_{obs} = k_{-1}/k_1k_2 + [ROH]/k_1 \quad (38)$$

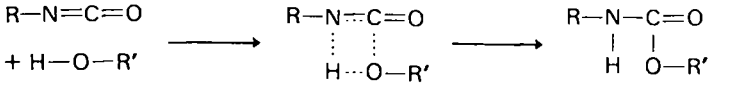
The *N*-arylurethane formed by addition of an alcohol to an aryl isocyanate is itself a catalyst, though a weak one. The kinetics would be complicated if the catalytic action of the product were strong or its concentration relative to the alcohol grew high. In the addition of amines to isocyanates, the substituted urea formed is a strong catalyst[186], and Scheme 17, due in part to Arnold, Nelson and Verbanc[174], summarizes the application of Baker and Gaunt's mechanism to the addition of alcohols, water[187] and amines to aryl isocyanates.



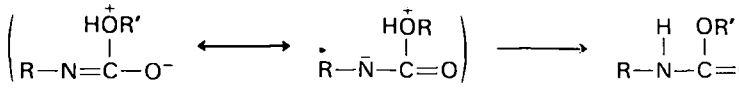
SCHEME 17.

However, it later became apparent that the kinetics and mechanism of the addition reactions might not always be as Baker and Gaunt described. Large negative entropies of activation and low activation energies in the non-catalytic reactions of isocyanates with alcohols[188,189] support the possibility of a four-centre transition state as in equation (39)[177], and large positive values of ρ in the Hammett equation, observed for reactions

of isothiocyanates as well as isocyanates, could be accounted for if the intermediate adduct of equation (35) were to undergo prototropic rearrangement as in equation (40)[190].



(39)



(40)

These mechanisms are not separable on kinetic grounds and may provide energetically-comparable alternative paths depending on conditions. Both imply second-order kinetics (first order each in alcohol and in isocyanate) and neither in itself accounts for base catalysis or the increase in second-order rate constant with increasing alcohol concentration. However, Robertson and Stutchbury found that the linear change of $[ROH]/k_{obs}$ with [ROH], noted by Baker and Gaunt, depended on the reaction conditions and the nature of the alcohol[191]. In a number of instances they found that this ratio *falls* with increasing alcohol concentration[191].

Entelis and Nesterov have suggested that the variation in rate constant as alcohol concentration is changed is due to the change in the properties of the medium[177]. Kinetic experiments[192–194] support the conclusion[177] that the addition reaction is retarded by solvation of the reactants by polar components in the medium.

More recently, Lammiman and Satchell[195] have made a thorough investigation of suggestions[196,197] that alcohol polymers are the reactive species in the addition of alcohols to isocyanates. It had been shown that polymers are likely to be significant in other reactions of alcohols in solvents of low polarity[198–200], and Satchell combined a spectrophotometric study of the self-association of alcohols in diethyl ether with measurements on the kinetics of their addition reactions with 4-chlorophenyl isocyanate in the same solvent. He found that the reaction follows rate equation (41), in which [M] is the alcohol monomer concentration rather than stoichiometric alcohol concentration, and n has the value 3 for secondary alcohols and 2 for primary alcohols.

$$d[\text{product}]/dt = (k_2[M]^2 + k_n[M]^n)[RNCO] \qquad (41)$$

The significance of the terms in $[M]^2$, $[M]^3$ and $[M]^4$ is that it is readily shown from equilibrium considerations that they would be generated by dimer, trimer and tetramer contributions to the observed rate constant.

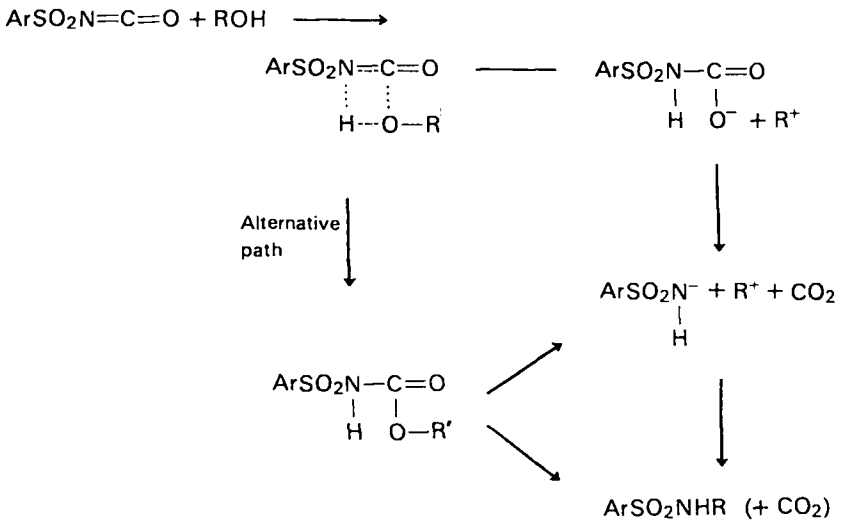
The contribution of a term for the monomer itself was found to be negligible.

Analogous to the alcohol dimer is the notion of an amine–alcohol complex (rather than an amine isocyanate complex) in the amine catalysis of the alcohol addition[201–203], though this is not kinetically distinguishable from the Baker and Gaunt mechanism of equation (37). The linearity of plots based on equation (38) has been taken to support the amine–isocyanate complex mechanism[125,182–185,204], but the slope is not independent of the nature of the alcohol. The amine–alcohol complex mechanism depends on the ability of amines to polarize the alcohol by formation of hydrogen bonds to the –OH group. Attempts to correlate the catalytic strength of amines with their hydrogen basicity have been only partly successful, because hydrogen basicities in water are greatly different from those in the solvents used, and catalytic activity is more subject to steric hindrance than is hydrogen basicity[177].

McFarland and coworkers have measured the kinetics of the reactions of arylsulphonyl isocyanates with triarylmethanols[205–208], and with phenols[209], in toluene. In the case of triarylmethanols, the reaction was found to be second order—first order in alcohol and first order in isocyanate—and strongly catalysed by pyridine. Electron-withdrawing substituents in the triarylmethanol retard the reaction (Hammett ρ constant *c.* $-0{\cdot}65$). The products were *N*-alkylsulphonamides and CO_2 in all instances studied except one—tri(4-nitrophenyl)methanol with 4-methylphenyl isocyanate. The authors suggested a mechanism involving a four-centre adduct as in Scheme 18, leading to a urethane in the case of tri(4-nitrophenyl)methanol or to sulphonamide and CO_2 in the instances in which there is less electron withdrawal and a more stable carbonium ion. The catalytic effect of pyridine was attributed to addition of the amine followed by displacement as in equation (37). The authors could not establish whether urethane was an intermediate in all cases—attempts to detect it failed, yet the ρ value was thought to be too small for a carbonium reaction[208]. Addition of the alcohol to the cyanide carbon atom as in equation (40), in place of the four-centre transition state shown in Scheme 18, cannot be excluded.

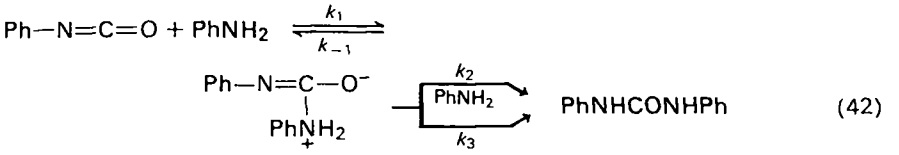
The reaction with phenols[209] is also second order, and the probable mechanism is similar to that of the triarylmethanol reaction except that carbonium ions are not available. The product is a urethane.

In the addition of amines to isocyanates, the kinetics are complicated by strong product catalysis, but some kinetic studies which have been made have not been inconsistent with Scheme 17[129,210,211]. Briody and Narinesingh[211] found that much of the kinetic complexity was avoided by



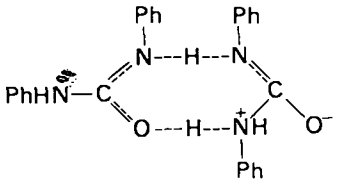
SCHEME 18.

use of the polar solvent acetonitrile. Their mechanism for the addition of aniline to phenyl isocyanate (equation 42) is similar to Scheme 17.



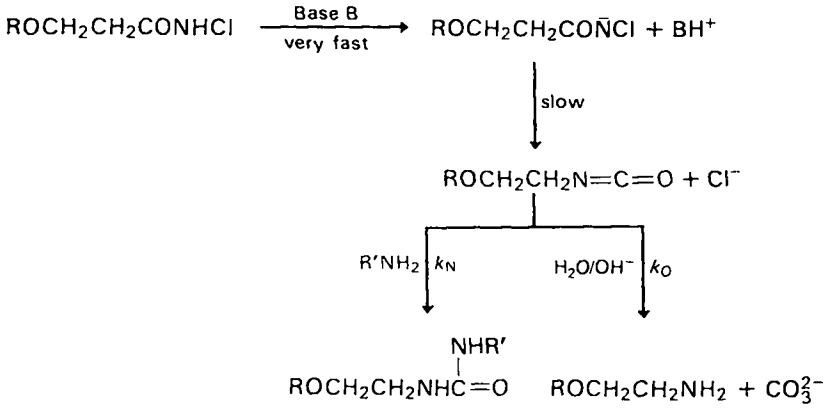
(42)

This reaction scheme was consistent with the observed kinetics provided $k_2 \simeq k_3$, and k_1 and $k_{-1} \gg k_2$ or k_3. In solvents other than acetonitrile they argued, k_2 and k_3 are very dissimilar, leading to complex kinetics. Using deuterated amines, they found a primary isotope effect (k_H/k_D) of 1·3–2·0, consistent with proton transfer as the rate-determining step. Since the product urea is a much weaker base and is more hindered than the amine, its catalysis must operate in a different manner for its effectiveness to be comparable ($k_2 \simeq k_3$). Briody and Narinesingh attributed the effect to bi-functional catalysis:



Carboxylic acids were found to be highly effective catalysts in the same systems, and little sensitive to polar substituents.

Recently Higuchi, Takeshita and Senju investigated the competing reactions of an isocyanate group with amine and with hydroxide ions in water by carrying out a Hofmann degradation of *N*-carbamoylethyl starch in the presence of both bases and analysing for the products (Scheme 19)[212]. Preliminary experiments established that the rate of



SCHEME 19.

formation of isocyanate is almost independent of the nature and concentration of the base used in the decomposition of the *N*-chloroamide group when the pH is over 11, and that in the absence of added hydroxide ion, water does not compete appreciably with amines for reaction with the isocyanate group. When the concentrations of amine and hydroxide were neither too low nor too high, the authors observed a linear relationship between the ratio of product formation rates and the ratio of base concentrations, consistent with simple second-order kinetics with no catalytic effects (equations 43–45).

$$\text{d[urea derivative]}/\text{d}t = k_N[\text{isocyanate}][\text{amine}] \tag{43}$$

$$\text{d[aminoethyl group]}/\text{d}t = k_O[\text{isocyanate}][\text{OH}^-] \tag{44}$$

$$\frac{\text{d[urea derivative]}}{\text{d[aminoethyl group]}} = \frac{k_N\,[\text{amine}]}{k\ [\text{OH}^-]} \tag{45}$$

Reactivities of a series of amines indicated that the presence of branching on the carbon atom bonded to the amino group retards the amine addition. Arrhenius activation parameters were determined by plotting $\log(k_N/k_O)$ against $1/T$, and in all those cases studied, both $(\Delta H_N^{\neq} - \Delta H^{\neq})$ and $(\Delta S_N^{\neq} - \Delta S^{\neq})$ were negative, pointing to an important role for

hydration, especially the high degree of hydration of the hydroxide ion.

In another recent study[213], McManus and coworkers discovered that the addition of alcohols to isocyanates can be photocatalysed in carbon tetrachloride solvent but not in benzene or heptane—suggesting an isocyanate–carbon tetrachloride complex. One effect of light is to accelerate the addition of *t*-butyl alcohol to isocyanates enough to avoid the extensive elimination which occurs in the thermal addition.

b. *Metallic catalysis in addition reactions of isocyanates.* Organometallic catalysts have been found to be up to 10^4 times as effective as amines in promoting addition reactions of isocyanates. The subject has been well reviewed[177,214,215]. Although there is a wide variety of catalyst types, tin(IV) compounds have attracted the most interest.

Entelis' group has made a detailed kinetic study of the addition of methanol to 4-chlorophenyl isocyanate in heptane in the presence of tin(IV) catalysts[216–220]. A methanol–catalyst complex was determined spectrophotometrically, and the rate of catalytic action was found to be proportional to the concentration of the complex. The scheme outlined in equation (46) leads to equation (47), in which the quantities in square brackets are stoichiometric concentrations. The equilibrium constant for complex formation, k_1/k_{-1} (equation (47),

$$\text{Catalyst} + \text{ROH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Catalyst}\cdot\text{ROH} \xrightarrow[\text{R'NCO}]{k_2} \text{R'NHCOOR} \qquad (46)$$

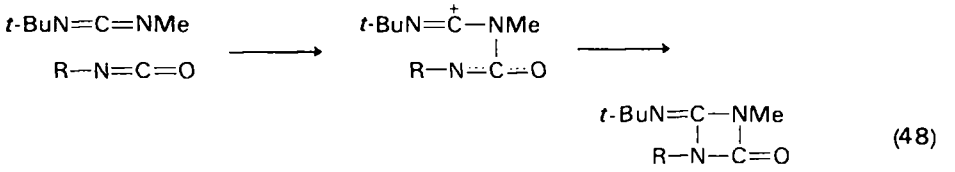
$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = \frac{(k_2k_1/k_{-1})[\mathrm{ROH}][\mathrm{R'NCO}][\mathrm{catalyst}]}{1 + (k_1/k_{-1})[\mathrm{ROH}]} \qquad (47)$$

was measured separately by spectrophotometry. The reaction was found to follow the kinetics of equation (47) to within the experimental accuracy. A further clue to the mechanism is obtainable from the activation parameters: $E_A = 34\ \mathrm{kJ\ mol^{-1}}$ for the uncatalysed reaction and $26\ \mathrm{kJ\ mol^{-1}}$ for the catalysed reaction, giving a *c.* 10-fold rate increase, and $\Delta S^{\neq}$ changes in the presence of catalyst from $-186\ \mathrm{J\ K^{-1}\ mol^{-1}}$ to $-99\ \mathrm{J\ K^{-1}\ mol^{-1}}$, giving a 10^5-fold rate increase. Two possibilities suggested by Entelis and Nesterov to account for the effect of tin(IV) catalysts on the entropy of the reaction were (i) that the catalyst–methanol complex has a lengthened O–H bond, bringing it close to the length of the N=C bond in the isocyanate and facilitating a four-centre reaction as in equation (39), and (ii) that the addition takes place by way of a linear adduct. If the reaction follows either of these paths we can expect that the influence of catalyst–methanol complex stability on reaction rate will reflect two conflicting factors: increasing stability will mean increasing reactivity of the alcoholic

hydrogen atom but diminishing nucleophilicity of the alcoholic oxygen atom. In fact, Entelis and Nesterov found, on changing the catalyst, that positive catalysis occurs only when the complex stability constant lies between about 4 and 150, with the greatest activity in catalysts such as diethyltin dichloride, dibutyltin diacetate and dibutyltin dilaurate, whose complex stability constants in heptane are between 10 and 20.

As the proposed reaction mechanism implies a change from a nucleophilic addition of alcohol without a catalyst towards one in the presence of tin(IV) catalysts involving increased electrophilic character in the catalyst-alcohol complex, Entelis' group measured Hammett ρ constants for the reaction of methanol with substituted phenyl isocyanates in heptane, with and without the presence of dibutyltin dilaurate[221]. The value of ρ (at 25 °C) was found to decrease from 3·3 to 0·9 under the influence of the catalyst, reflecting the decreased importance of assistance to nucleophilic addition by electron withdrawal in the isocyanate.

c. *Cycloaddition to isocyanates.* Where comparisons have been made, 1,2-cycloadditions to isocyanates appear to favour the C=N bond more than in similar additions to isothiocyanates. For example, methyl-*t*-butylcarbodiimide and aryl and arenesulphonyl isocyanates give a 1,3-diazetidine as in equation (48) rather than the 1,3-oxazetidine which would follow addition across the C=O bond[131–135] (cf. equations 15 and 16, Section II.D.2).



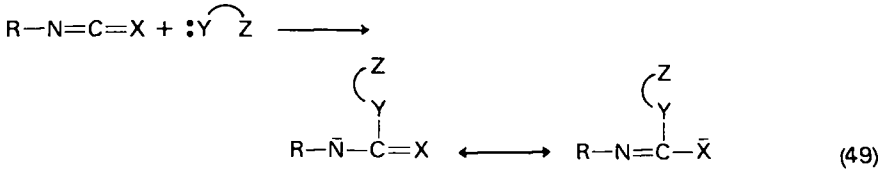
(48)

(R = aryl, alkyl or arylsulphonyl)

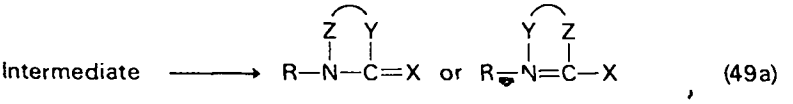
Electron withdrawal in R favours addition across the C=O bond[134].

A similar situation arises in the 1,2-addition of α-lithiated isocyanides[136] (Scheme 11, Section II.D.2) and the 1,3-dipolar addition of nitrones[133, 137–139] (equations 17 and 18, Section II.D.2)—addition across the C=N bond is favoured more in the case of isocyanates than in the case of isothiocyanates. Black and Watson have related the direction of addition to C=N bond order (with bond order close to 2 favouring C=N addition) and to steric factors[140]. It must be remembered, however, that if the initial bond formation is by nucleophilic reaction at the isocyanate carbon atom (equations 15, 16 and 48) the factors deciding the direction of further reaction will be related to the intermediate, not to the ground-state

iso(thio)cyanate (equations 49, 49a). Sulphur is more polarizable than oxygen, more capable of *mesomeric* electron withdrawal, and more nucleophilic[1].



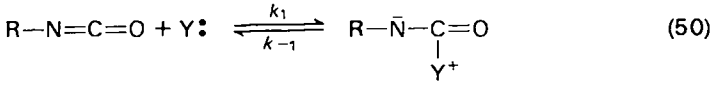
(49)



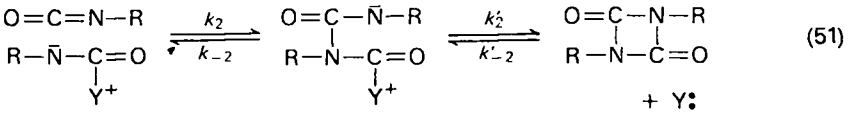
(49a)

When R is aryl or acyl, it can assist in the stabilization of the negative charge on the nitrogen atom. It is interesting that a change from aryl to alkyl isocyanate can change the mode of cycloaddition from C=N to C=O[222].

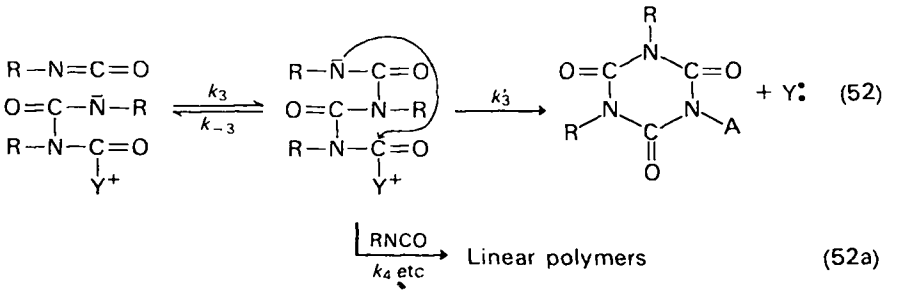
An important class of cycloadditions to isocyanates consists of self-addition to give dimers and trimers. These reactions have been known since before the turn of the century[174,223–225]. Dimer formation is brought about by a variety of catalysts, and is reversible; formation of trimer, on the other hand, is irreversible[174]. Catalysts for these reactions are nucleophiles and include trialkylphosphines, aryldialkylphosphines, pyridine and methylpyridines, and trialkylamines. Certain anionic initiators, such as sodium cyanide in dimethylformamide, can lead to dimers, trimers or linear polymers. Shashoua, Sweeny and Tietz[226] proposed a mechanism which can be described by equations (50) to (52a) (:Y neutral or anionic), but presented no kinetic evidence beyond the observation that linear polymerization rather than cyclization is favoured by low temperatures, high monomer concentrations and low catalyst concentrations.



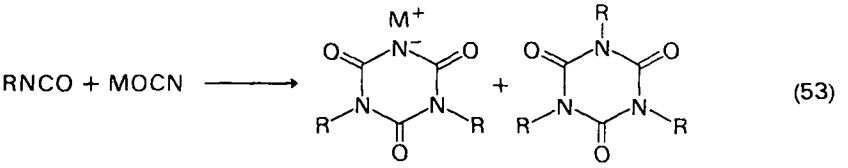
(50)



(51)



More recently Argabright and coworkers[227], in seeking to optimize conditions for synthesis of disubstituted isocyanuric acids from organic isocyanates and isocyanate salts, obtained some semiquantitative data which gives some support to the mechanism of Shashoua and coworkers. Argabright reported that the reaction gives a single side-product, the cyclic trimer of the isocyanate (equation 53, not balanced).



The side reaction was attributed to catalysis of the trimerization by the disubstituted isocyanurate salt, since separate experiments established its effectiveness. Argabright showed that equations (50)–(52) (:Y≡⁻NCO), together with either a one- or two-step rate-controlling path from RN⁻CONCO to the isocyanurate salt, can lead to equation (54) for the selectivity to isocyanurate salt rather than trimer.

$$\left.\begin{array}{l}\text{Fraction of RNCO}\\ \text{converted into}\\ \text{isocyanurate salt}\end{array}\right\} = \frac{k_S[\text{NCO}^-]}{k_S[\text{NCO}] + k_T[\text{isocyanurate salt}][\text{RNCO}]} \qquad (54)$$

(k_S = overall rate constant for salt formation, and k_T = overall rate constant for trimer formation)

It was found that selectivity to isocyanurate salt is an inverse function of initial organic isocyanate concentration and increases with increasing concentration of inorganic isocyanate, consistent with equation (54).

Selectivity to the isocyanurate salt was also found to increase with decreasing ionic strength and with electron-withdrawing groups in ROCN, indicating that charge dispersal changes more in the generation of the rate-determining transition state for salt formation than for trimer formation.

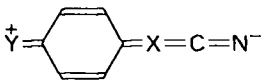
Cycloadditions to the reactive isocyanate group of acyl isocyanates have recently been reviewed by Arbuzov and Zobova[181].

Use of isocyanates in the formation of polyurethanes, polythiolcarbamates, polyureas and related high polymers has been studied in great detail and forms a large subject in its own right[228].

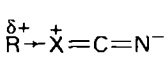
IV. POLAR SUBSTITUENT EFFECTS OF –OCN AND RELATED GROUPS

A. –OCN and –SCN

In the group –XCN, factors favouring electron withdrawal include the electronegativity of X, the ability of X to transmit the electron-withdrawing effect of the CN group, the ability of X to expand its octet to accommodate conjugative electron-withdrawal as in structure **10**, and the ability of X to lose electrons conjugatively to nitrogen as in structure **11**.

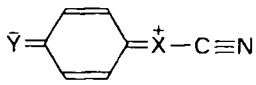


(10)



(11)

If R is aryl, and especially if –XCN is *ortho* or *para* to a group capable of conjugative electron withdrawal, the ability of X to lose electrons can contribute to electron *donation* (structure **12**).



(12)

Sulphur is more polarizable and less electronegative than oxygen. It is less able than oxygen to form a double bond to carbon, because of the difficulty of 2p–3d overlap relative to 2p–2p overlap. Thus the donor strength of sulphur towards aromatic carbon has been reported to be only about one-fifth that of oxygen (σ_R for –SH is $-0{\cdot}10$ and σ_R for –OH is $-0{\cdot}49$)[229]. The poor overlap between sulphur and carbon is also reflected in the calculated π bond orders for the cyanate and thiocyanate ions[230]:

In a study based on dipole moment measurements, LCAO—MO calculations, ^{19}F magnetic resonance and infrared absorptions, Martin and Brause[231] have shown evidence that the oxygen of cyanates, but not the sulphur of thiocyanates or the selenium of selenocyanates, is capable of mesomeric donation into an aromatic nucleus (structure **12**). Their measurements indicated that all three atoms can donate electrons to the cyano group (structure **11**), and that in the case of cyanates the donation of electrons from oxygen to the ring is slightly greater than to the cyano group.

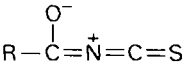
Conjugative withdrawal of electrons (structure **10**) is possible for sulphur but not for oxygen, because of the available 3d orbitals in sulphur. Dipole moment measurements indicate, for example, that there is some withdrawal by the thiocyanato group in *N*,*N*-dimethyl-4-thiocyanatoaniline[231] (structure **10**, $Y \equiv N(CH_3)_2$).

The thiocyanato group has a Hammett σ_p value of $+0{\cdot}52$[229], most of which is due to inductive electron withdrawal[231,231]. The pattern of inductive and conjugative effects in the cyanato group is quite different[231], as would be expected from the above considerations. The contributions of inductive (σ_I) and resonance (σ_R) effects to σ_p are (in carbon tetrachloride)[231]:

$$-SCN: \sigma_I = +0{\cdot}42,\ \sigma_R = +0{\cdot}10,\ \sigma_p = +0{\cdot}52$$
$$-OCN: \sigma_I = +0{\cdot}79,\ \sigma_R = -0{\cdot}31,\ \sigma_p = +0{\cdot}48$$

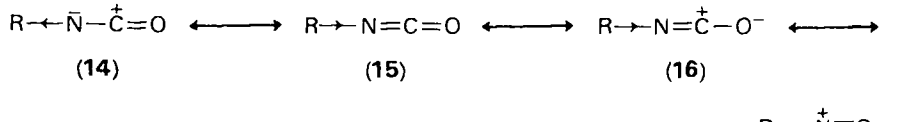
B. –NCO and –NCS

There seems to be very little conjugative interaction between the group –NCO and other groups formally capable of conjugation. Thus the conjugation energy of phenyl isocyanate is close to zero[177], and spectroscopic data indicate no conjugation between isocyanato groups and adjacent acyl or sulphonyl groups[178]. Molar refraction studies suggest some conjugative release from isocyanato groups to ring systems with electron-withdrawing substituents[233]. Isothiocyanates are apparently more polarizable than cyanates, and there is evidence for a slight conjugative donation in the case of acyl isothiocyanates (contributing structure **13**)[48,176,178,234]

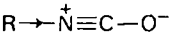


(13)

Internal conjugation within the –NCX groups leads to charge separation between the nitrogen, carbon and chalcogen atoms, and the nature of this separation is different in isocyanates and isothiocyanates. Dipole moment studies[235], microwave[236,237] and electron diffraction[238] determinations of dimensions, molecular orbital theory[239], and chemical properties[177] lead to conclusions [74,177,240] which can be summarized in structures **14–17**, with structure **17** contributing little if anything, and structure **14** contributing more than structure **16**.



(14) **(15)** **(16)**



(17)

In the case of isothiocyanates, however, dipole moments and Raman spectra[85], and bond lengths and angles[84,86,241], indicate that structure **17a** is a significant contributor to the electron distribution[240]. A slight contribution has also been indicated for structure **18**[240]. With its greater electronegativity, the oxygen atom in the corresponding cyanates does not appear to lose any control of its lone pair.

(17a) **(18)**

We would expect the chemical outcome of the above considerations to be that the polar effects of both the –NCO and the –NCS groups will be due mainly to inductive withdrawal by the electronegative nitrogen atom. We would also expect that the effects of sulphur having a lower electronegativity than oxygen will act in the opposite direction to the effects of its greater polarizability, leading to very little difference in the polar substituent effects of the two groups. Thus the measured Hammett σ_p values for –NCO (e.g., 0·24[242]–0·38[243]) and for –NCS (e.g., 0·32–0·48[244]) differ little.

Also consistent with a primarily inductive effect, the σ_m value (e.g., 0·30[242]–0·43[243] for –NCO) is slightly greater than the σ_p value.

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CHAPTER 13

Acyl and thioacyl derivatives of isocyanates, thiocyanates and isothiocyanates

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I. INTRODUCTION

Although no studies on acyl and thioacyl cyanates seem to have been reported up to date, a great deal of interesting information on acyl and thioacyl derivatives of isocyanates, which are one of the most reactive systems among analogous compounds, have been obtained and convenient methods for the preparation of these have been reported. The chemistry of acyl[1-3] and thioacyl isocyanates[3] has been partially reviewed. Some acyl and thioacyl thiocyanates have been prepared in recent years, but little attention has been paid to their chemistry. On the other hand, acyl and thioacyl isothiocyanates, especially acyl derivatives, are familiar compounds and a great number of studies have been reported. This review covers the contributions to the chemistry of the title compounds which have been reported in recent years.

II. METHODS OF PREPARATION

A. Acyl Isocyanates

Acyl cyanates, RCO—OCN, are possibly formed when acyl halides react with metallic cyanates, but the product which can be isolated is the acyl isocyanate.

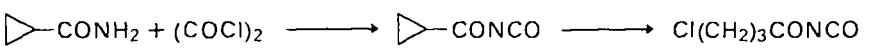
Acyl isocyanates, RCONCO (R = Me, Ph), were first obtained by reaction of the corresponding acyl chlorides with silver cyanate[4,5]. This reaction was used later by several workers[6-9] to prepare acyl isocyanates. More recently, it has been reported that reactions of isocyanic acid with acyl chlorides in the presence of pyridine[10,11] and with perfluorinated carboxylic anhydrides[12] afford acyl isocyanates respectively (equation 1).

$$RCOCl + HNCO \xrightarrow{\text{Pyridine}} RCONCO$$

$$[F_3C(CF_2)_nCO]_2O + HNCO \longrightarrow F_3C(CF_2)_nCONCO \quad (1)$$

Although it is well known that alkyl or aryl isocyanates are obtained by reaction of amines with phosgene, this method is not applicable to the preparation of acyl isocyanates since phosgenation of primary amides leads to the formation of nitriles or complex mixtures[13]. However, the phosgenation in the presence of lime gives acyl isocyanates[14]. The above methods suffer the disadvantages of either low yields or complex procedures.

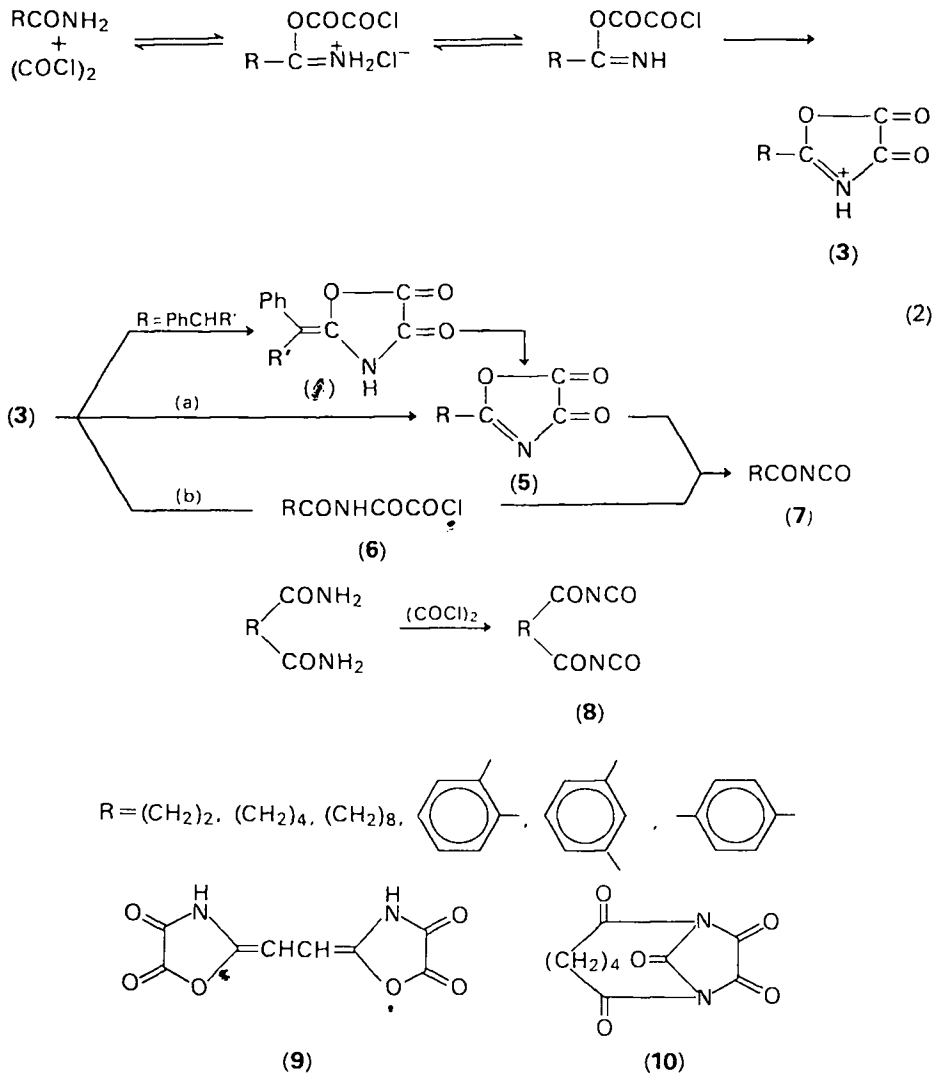
In 1962, a facile method for the preparation of acyl isocyanates was found by Speziale and his coworkers[15–17]. It consists of the reaction of primary amides with oxalyl chloride and many aliphatic and aromatic acyl isocyanates can be prepared. Aromatic amides give excellent results regardless of substitution but yields with aliphatic amides are not very satisfactory unless an electron-withdrawing group is present on the α-carbon atom or there are no α-hydrogen atoms. Carbamates undergo the reaction quite readily to give isocyanato formates. The reaction of cyclopropanecarboxamide with oxalyl chloride does not give the expected isocyanate **1**, but rather γ-chlorobutyroyl isocyanate (**2**)[17].



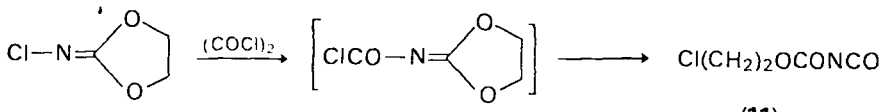
(**1**) (**2**)

The formation of acyl isocyanates from amides and oxalyl chloride is envisaged as illustrated in equation (2)[15,16]. *O*-Acylation of the amide with oxalyl chloride followed by rearrangement yields a cyclic intermediate **3**. With α-phenyl- and α,α-diphenylacetamides, the α-hydrogen atom is acidic enough to be lost as hydrogen chloride yielding benzylideneoxazolidinediones (**4**), which on pyrolysis give the isocyanates **7**. In the case of derivatives other than the α-phenylacetamides, (a) the hydrogen atom attached to nitrogen may be lost directly giving **7** by way of the oxazoline **5** or, alternatively, (b) attack of chloride ion could open the ring giving the acyloxamic acid chloride (**6**) which can decompose to yield **7**.

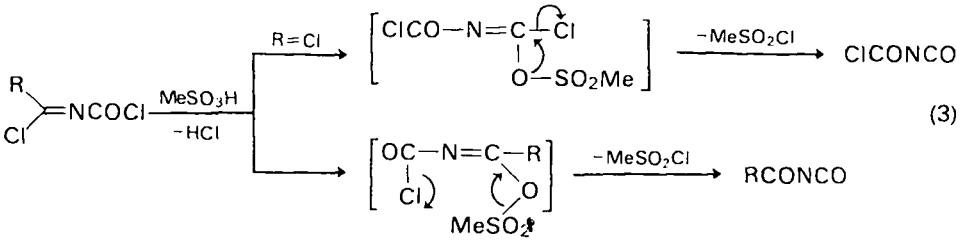
This method can be also used to prepare dioyl diisocyanates. Reactions of sebacamide[18], phthalamide[18], isophthalamide[18], and terephthalamide[18,19] with oxalyl chloride proceed smoothly, forming the corresponding dioyl diisocyanates **8**. With succinamide or adipamide, however, the amide requires an excess of the chloride, and bis(oxazolidinedione)-ethanediylidene (**9**) or adipoylimidazolinetrione (**10**) is formed in addition to the expected isocyanate respectively[18].



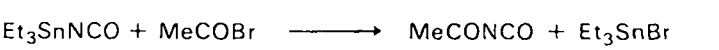
Recently, several preparative methods have been developed. For instance, 2-chloroethoxycarbonyl isocyanate (**11**) is prepared from 2-chloroimino-1,3-dioxolane and oxalyl chloride[20]. The reaction of *N*-chlorocarbonylimidoyl chloride[21,22] with methanesulphonic acid gives the corresponding acyl isocyanates in good yields. The reaction path is illustrated in equation (3)[23]. Triethylstannyl isocyanate reacts with acetyl bromide to give a 58% yield of acetyl isocyanate (equation 4)[24]. Thermolysis of trihaloisocyanuric acids gives carbonyl diisocyanate (**12**)[25,26].



(11)



(3)



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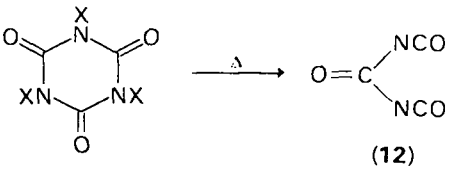
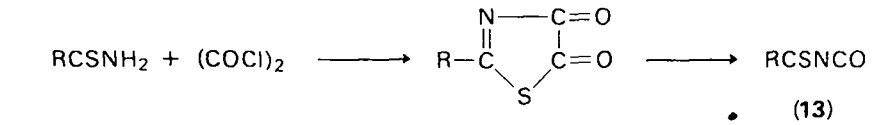


(12)

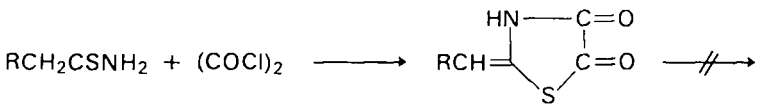
X = Cl, I

B. Thioacyl Isocyanates

In 1963[27], aromatic thioacyl isocyanates (**13**. R = Ar) have been first prepared by thermolysis of the corresponding thiazolinediones[28] which are obtained from thioamides and oxalyl chloride. Similarly, alkyl- and aryl-mercaptothiocarbonyl isocyanates[29,30] thiocarbamoyl isocyanates[30], and oxythiocarbonyl isocyanates[30] are prepared from the thiazolinediones. However, thioacetamide and phenylthioacetamide react with oxalyl chloride to form



(13)



RCH_2CSNCO (5)

2-alkylidenethiazolidinediones which on heating do not yield thioacyl isocyanates (equation 5)[31].

Thioacyl isocyanates are liable to thermally change to other compounds. The optimum conditions to obtain thioacyl isocyanate from the thiazolinedione depend upon the properties of the dione as well as of the isocyanate. The optimum conditions for 2-arylthiazolinediones are given in Table 1[31].

TABLE 1. Optimum conditions for thermal decomposition of 2-arylthiazoline-4,5-diones to thioacyl isocyanates

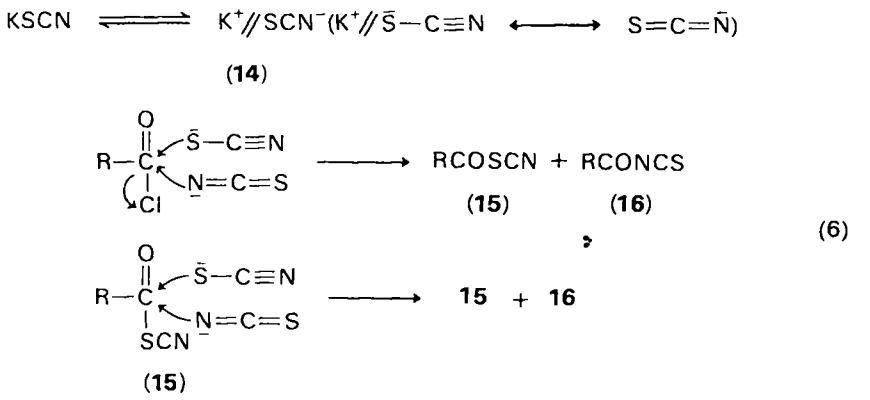
Aryl	Solvent	Decomposition beginning temperature (°C)	Optimum decomposition temperature (°C)
C_6H_5	Methylcyclohexane	65–70	91–93
α-$C_{10}H_7$	Decalin	93	109
p-$MeOC_6H_4$	Methylcyclohexane	70–75	94–96
p-ClC_6H_4	Methylcyclohexane	63–65	85–89
p-$O_2NC_6H_4$	Methylcyclohexane	60–65	85–90
p-$Me_2NC_6H_4$	Decalin	97	145

C. *Acyl and Thioacyl Derivatives of Thiocyanates and Isothiocyanates*

The reaction of an acyl chloride with thiocyanate ion produces, with a few exceptions, exclusively the acyl isothiocyanate. Aliphatic and aromatic acyl isothiocyanates are easily accessible by reactions of acyl halides with lead thiocyanate[32], potassium thiocyanate[33,34], and ammonium thiocyanate[35,36]. The solvents used in the reactions are generally benzene, toluene, acetone, and acetonitrile. Dimethylformamide is a good solvent for metallic thiocyanates, but it cannot be used for the preparation of acyl isothiocyanates. For instance, benzoyl chloride reacts with lead thiocyanate in dimethylformamide to give *N*,*N*-dimethyl-*N'*-benzoylformamidine obtained from the reaction of benzoyl isothiocyanate with the solvent, in addition to other products[37]. Perfluorinated acyl chlorides such as trifluoroacetyl chloride are reported to react with silver thiocyanate without solvent to afford thiocyanates. However, evidence is not given to distinguish between the thiocyanate and isothiocyanate[38].

In 1963, acyl derivatives of thiocyanates were first obtained by Takamizawa and his coworkers[39]. When potassium thiocyanate is allowed to react with excess of ethyl or butyl chloroformate, the thiocyanate is and

the isothiocyanate **16** are obtained. Under similar conditions, however, thioethoxycarbonyl, benzoyl, and acetyl chlorides afford isothiocyanates **16** respectively. The addition–elimination mechanism has been proposed for the reaction (equation 6). In an acetone solution the thiocyanate ion takes the form of an ion pair **14**, and the S site or N site of this ion attacks the carbonyl carbon atom to give **15** or **16** as the respective products. Since aliphatic and aromatic acyl, and alkylthiocarbonyl thiocyanates (**15**) are powerful acylating agents, they react with thiocyanate ion



(6)

to yield stable isothiocyanates **16**. As alkoxycarbonyl thiocyanate (**15**, R = alkoxy) is a rather weak acylation agent, the excess of alkyl chloroformate consumes the thiocyanate ion and the thiocyanate **15** is not able to participate in the reaction with the thiocyanate ion.

Surprisingly, ethoxycarbonyl thiocyanate is thermally stable and does not change upon being boiled in ethanol in the presence of acetic acid. When small amounts of potassium thiocyanate or acetate are added, however, the thiocyanate is readily converted into the isothiocyanate[39].

Diphenylcarbamoyl chloride reacts with potassium thiocyanate in acetonitrile to afford a carbamoyl thiocyanate **17** which on heating at 140 °C changes to the isothiocyanate **18**[40]. Although ethyl dimethylcarbamoyl hydrothiocyanate (**19**) is formed from the reaction of dimethylcarbamoyl chloride with potassium thiocyanate in ethanol[40,41], lead dimethylthiocarbamate reacts with cyanogen bromide to give a mixture of the corresponding thiocyanate **20** and isothiocyanate **21**. Thiocyanate **20** easily isomerizes to **21**[40].

Similarly, thiocarbamoyl isothiocyanates (**22**) are prepared by reaction between thiocarbamoyl chlorides with sodium[42] or potassium thiocyanate[43].

$$Ph_2NCOCl + KSCN \xrightarrow{\text{in MeCN}} Ph_2NCOSCN \longrightarrow Ph_2NCONCS$$

(17) (18)

$$Me_2NCOCl + KSCN \xrightarrow{\text{in EtOH}} Me_2NCOEt$$

$$\overset{\delta^-}{O}\cdots H\cdots \overset{\delta}{N}CS$$

(19)

$$[Me_2NCOS]_2Pb + BrCN \longrightarrow Me_2NCOSCN + Me_2NCONCS$$

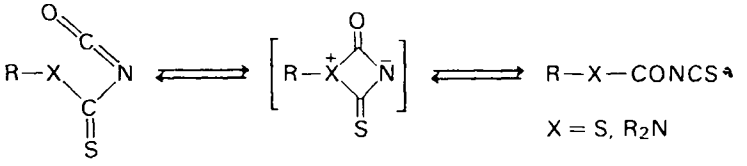
(20) (21)

$$R_2NCSCl + MSCN \longrightarrow R_2NCSNCS$$

M = Na, K (22) R = Me, Et, $PhCH_2$, $-(CH_2)_5-$

An elegant method for the preparation of acyl isothiocyanates by reaction of silyl isothiocyanates with acid chlorides is reported[44]. Alkyl- and arylsilyl isothiocyanates may be used, especially trialkylsilyl isothiocyanates with C_1–C_6 alkyls. For instance, trimethylsilyl isothiocyanate reacts with benzoyl chloride and phosgene to give benzoyl isothiocyanate and carbonyl diisothiocyanate respectively. The sole by-product is a chlorosilane, which may be treated with an alkali thiocyanate to give silyl isothiocyanate for re-use (equation 7).

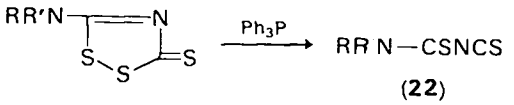
$$Me_3SiNCS \begin{cases} \xrightarrow{PhCOCl} PhCONCS + Me_3SiCl \\ \xrightarrow{COCl_2} CO(NCS)_2 + Me_3SiCl \end{cases} \quad (7)$$



(8)

If the thioacyl isocyanato group is attached to sulphur[29] or nitrogen[30], rapid rearrangement to the corresponding isothiocyanate occurs. Thus the mercaptothiocarbonyl and carbamoyl isocyanates rearrange quantitatively to the isothiocyanates. The reaction proceeds by an intramolecular 1,3-rearrangement, as evidenced by carbon tracer studies (equation 8)[29].

Recently, it has been reported that elimination of sulphur from 5-amino-1,2,4-dithiazole-3-thiones with the aid of triphenylphosphine affords thiocarbamoyl isothiocyanates (22)[45].



(22)

R = R′ = Et; R = Et, R′ = Ph
R = R′ = Ph

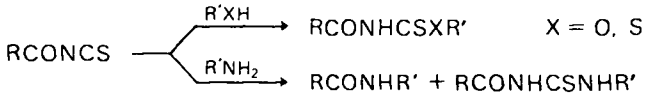
III. REACTIONS WITH ACTIVE HYDROGEN COMPOUNDS

A. General

Electron-withdrawing acyl and thioacyl groups may enhance the reactivities of the isocyanato and isothiocyanato groups.

Nucleophilic additions to acyl and thioacyl isocyanates are popular and widely used reactions. For instance, benzoyl isocyanate reacts with ammonia, aniline, benzamide, and benzenesulphonamide to yield the corresponding ureas[5], and with benzyl, isopropyl, and *t*-butyl alcohols to give the respective carbamates[46]. Similarly, thiobenzoyl isocyanate gives the ureas by interaction with primary and secondary amines[47].

Reactions of acyl isothiocyanates with nucleophilic reagents are complex, since addition to the isothiocyanato system and nucleophilic substitution at the carbonyl carbon atom may compete with one another. The rates of these reactions depend on factors such as basic strength of nucleophile, solvent polarity, nature of isothiocyanate, and temperature. Acyl isothiocyanates react additively with compounds such as alcohols[48] and mercaptans[49], to give *N*-acylthio- and *N*-acyldithiocarbamates, often in excellent yields. A competing reaction with stronger nucleophiles such as alkylamines, is that of direct nucleophilic substitution leading to the formation of *N*-alkylamides in addition to *N*-acylthioureas (equation 9). This tendency to substitution occurs more readily in highly polar solvents[50].

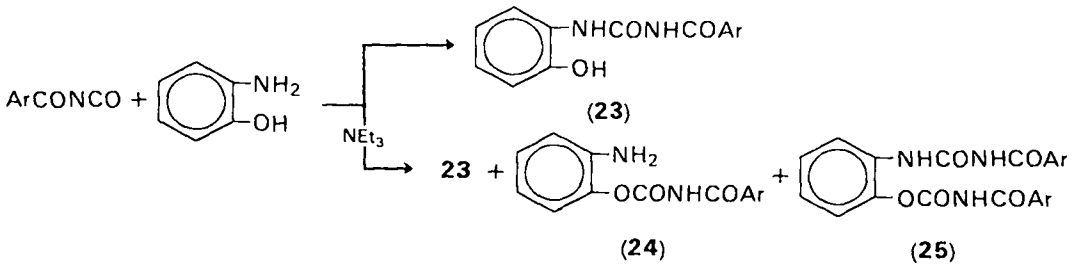


(9)

New and selected reports will be mentioned in this section.

B. Reactions with Amines, Alcohols, and Related Compounds

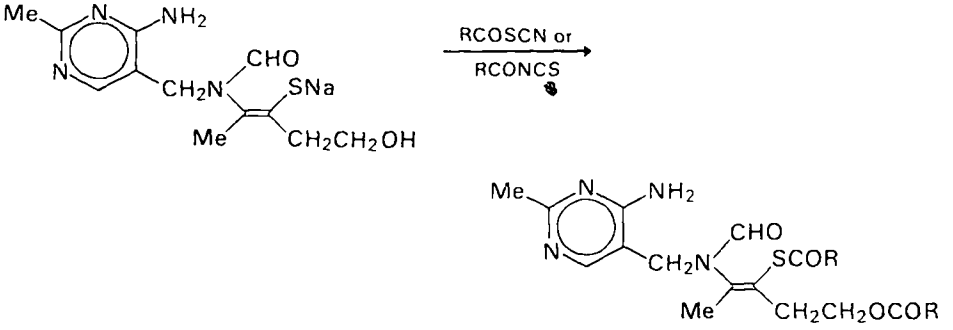
Benzoyl isocyanates react with *o*-aminophenol to give the corresponding urea **23**, while a mixture of **23**, urethane(**24**) and 1:2 adduct(**25**) is obtained from the reaction in the presence of triethylamine[51].



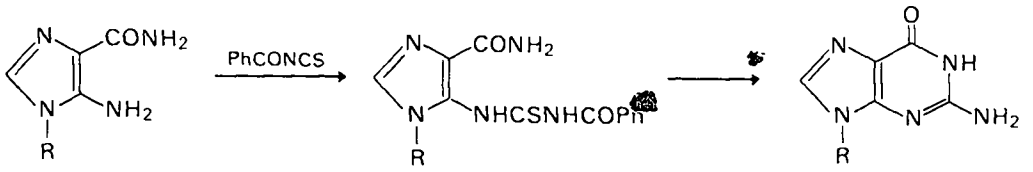
Trichloroacetyl isocyanate (TAI) reacts quickly and quantitatively with primary, secondary, and tertiary alcohols. A quantitative analysis (TAI-method) is based on following the reaction by n.m.r. spectroscopy[52]. The TAI method can be applied to the classification of steroid alcohols[53], but the isocyanate reacts with not only the hydroxyl group but also the α-hydrogen of the furan ring in sesquiterpenic alcohols of furoeremophilane type[54].

In the reaction with thiamine sodium salt, alkoxycarbonyl thiocyanate and acyl isothiocyanates act as acylating agents, giving *O,S*-diacylthiamines (**26**)[39]. Guanosines (**27**) are obtained by reaction of 5-amino-4-imidazolecarboxamides with benzoyl isothiocyanate, followed by methylation and ring closure[55].

3-Aminopyrazole adds ethoxycarbonyl or benzoyl isocyanate and isothiocyanate at the cyclic or exocyclic nitrogen to give adducts **28**



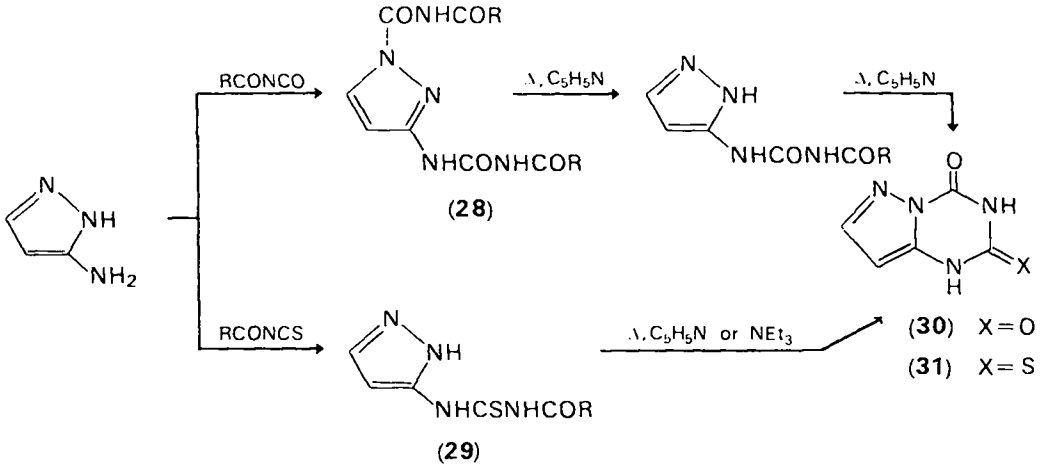
(**26**)



(27)

or **29**, which on heating with pyridine or triethylamine are converted into pyrazolotriazines **30** and **31**. The reaction of ethoxycarbonyl or benzoyl isothiocyanate with aminoazoles such as 3-amino-1,2,4-triazole, 5-aminotetrazole and 2-aminobenzimidazole results in the elimination of HSCN and formation of the corresponding acylamino derivatives **32**[56]. The reaction proceeds by an intramolecular N–N transacylation, as evidenced by using ^{15}N-isothiocyanates[57].

The reaction of ethoxycarbonyl isothiocyanate with 2-amino-5-phenyl-1,3,4-oxadiazole in ethyl acetate yields thiourea derivative **33**, whereas the

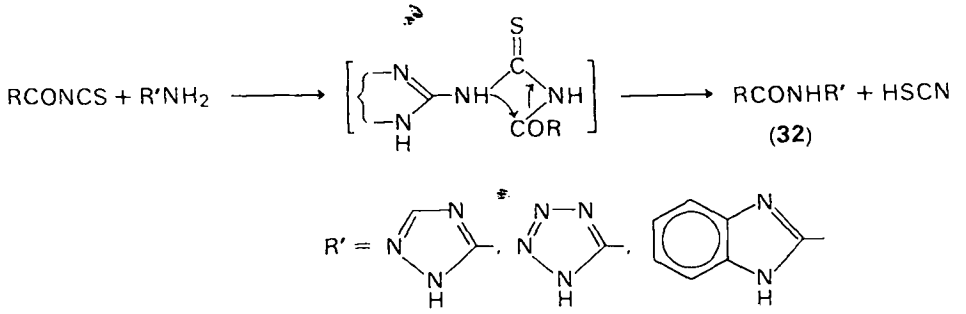


(28)

(29)

(30) X=O

(31) X=S



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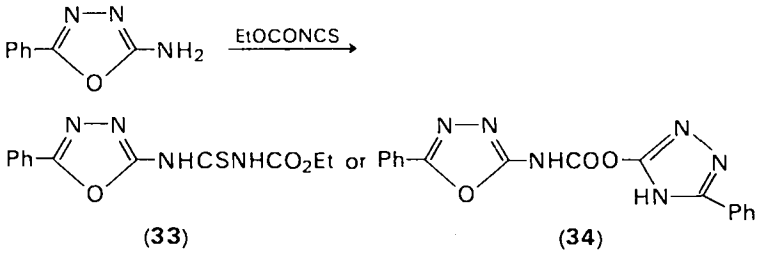


(33) (34)

same reaction in *o*-dichlorobenzene gives triazolylurethane **34**[58]. Trichloroacetyl isocyanate adds to 2-bromomethylacrylamide to afford a urea, which on treatment with an alkaline catalyst undergoes ring closure to 5-methylenehexahydroprimidinedione[59].

C. Reactions with Hydrazines and Related Compounds

The reactions of acyl and thioacyl isocyanates and isothiocyanates with hydrazine derivatives provide useful methods for the preparation of triazole derivatives.

1. With hydrazines

Benzoyl isocyanate reacts with hydrazine to yield 1,2-bisbenzoylcarbamoylhydrazine (**35**)[46], while thiobenzoyl isocyanate gives the triazolone compound **37**, which has arisen from 4-thiobenzoylsemicarbazide (**36**) by the evolution of hydrogen sulphide[60]. Even when 2 moles of the isocyanate are used, no 1:2 adduct is formed except **37**. The reaction of benzoyl isothiocyanate with an excess of hydrazine gives a mixture of the triazolinethione (**38**) and benzoylhydrazine (**39**). With equimolar quantities of reactants, dibenzoylthiosemicarbazide (**40**) is formed[61].

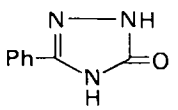
Acyl isocyanates easily add to arylhydrazines to give the corresponding

$$PhCONCO + N_2H_4 \longrightarrow (PhCONHCONH)_2$$

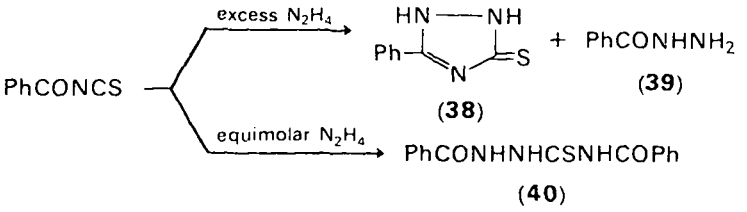
(**35**)

$$PhCSNCO + N_2H_4 \longrightarrow [PhCSNHCONHNH_2] \longrightarrow$$

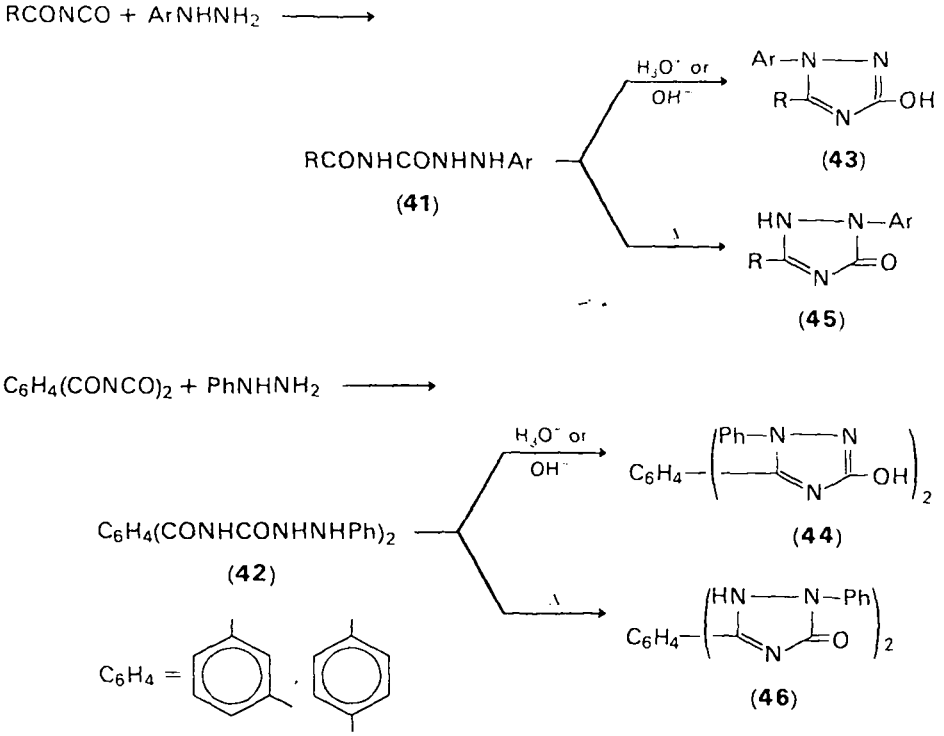
(**36**)



(**37**)

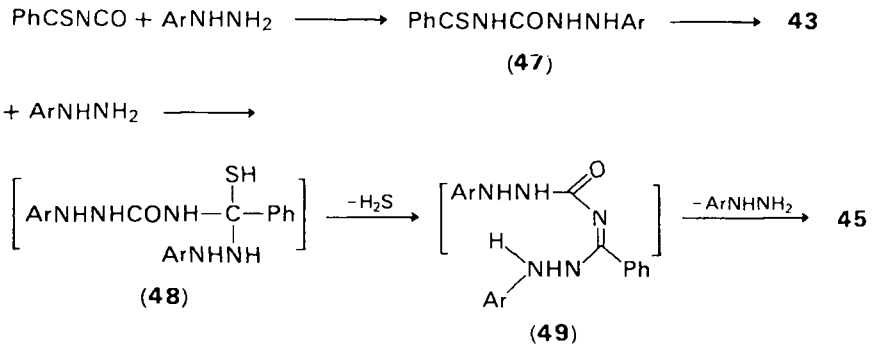


semicarbazides **41** quantitatively[46,62]. Similarly, dioyl diisocyanates such as isophthaloyl and terephthaloyl diisocyanates afford the semicarbazides **42**[62]. On treatment with aqueous hydrochloric acid or potassium hydroxide, semicarbazides **41** and **42** are converted to the 3-hydroxytriazoles **43** and **44**, whereas thermal ring closure produces the Δ^3-1,2,4-triazolin-5-ones **45** and **46** respectively[62].



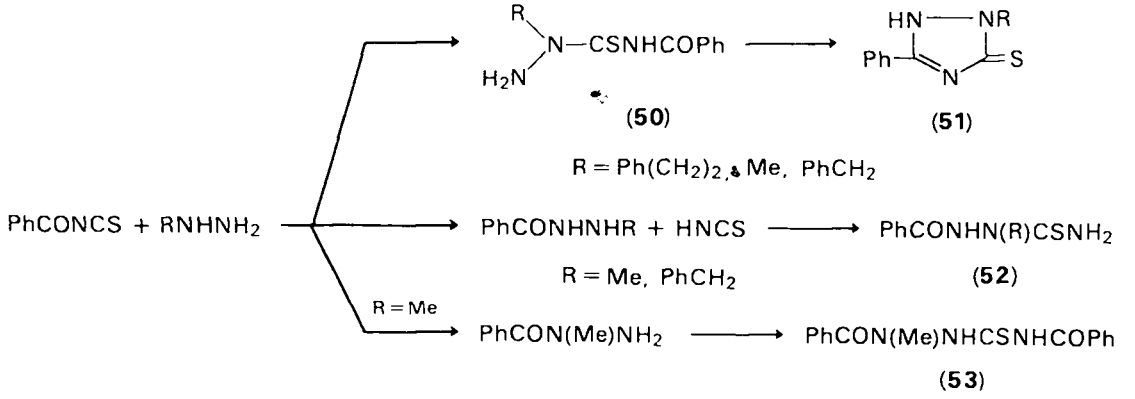
The reaction of thiobenzoyl isocyanate with an arylhydrazine at low temperature yields an unstable thiobenzoylsemicarbazide **47**, which is easily converted to triazole **43**. However, the isocyanate reacts with a

slight excess of arylhydrazine at room temperature to give directly triazolinone **45** by the evolution of hydrogen sulphide. The reaction can be understood in terms of the further reaction of the hydrazine with the thiobenzoyl carbon of **47** to form an intermediate **48**, followed by the elimination of hydrogen sulphide to



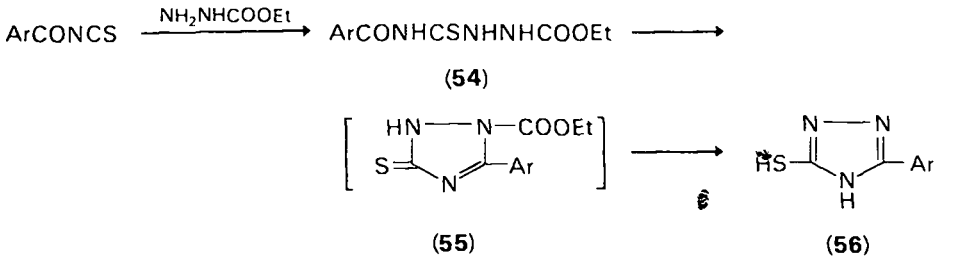
yield **49**. The loss of the hydrazine gives the triazolinone **45**[63].

Although benzoyl isothiocyanate reacts with phenylhydrazine to afford 4-benzoyl-1-phenylthiosemicarbazide as a main product[64], the reaction with alkylhydrazines is complex. The isothiocyanate reacts with phenethylhydrazine to give the corresponding Δ^3-1,2,4-triazoline-5-thione (**51**) which is obtained from the thiosemicarbazide **50**, while methyl- and benzylhydrazines form additional products as the result of a competing benzoylation reaction[65]. For instance, methylhydrazine gives 1-benzoyl-2-methylthiosemicarbazide (**52**) and 1,4-dibenzoyl-1-methylthiosemicarbazide (**53**), along with a 20% yield of the triazolinethione **51**. The formation of **52** probably occurs via initial benzoylation

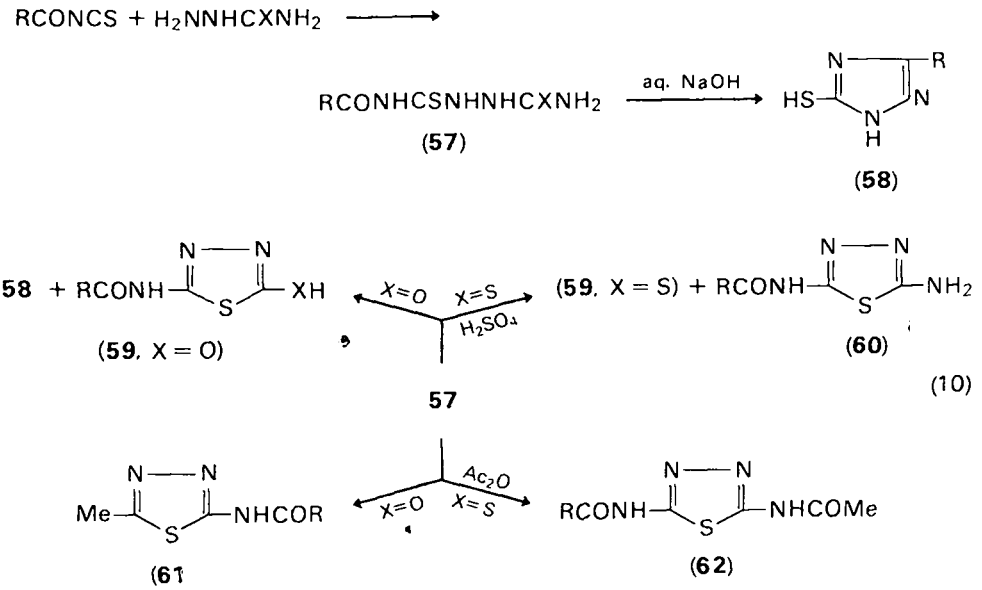


at the primary amino function, followed by reaction with the thiocyanic acid liberated in the process. The formation of **53** indicates partial benzoylation of methylhydrazine at the secondary nitrogen atom, followed by further reaction with the isothiocyanate.

Addition of aroyl isothiocyanates to ethoxycarbonylhydrazine yields 4-aroyl-1-ethoxycarbonyl-3-thiosemicarbazides (**54**), which are ring-closed in alkaline media, with loss of carbon dioxide and ethanol, to triazoles **56** via triazolinethiones **55**[66].

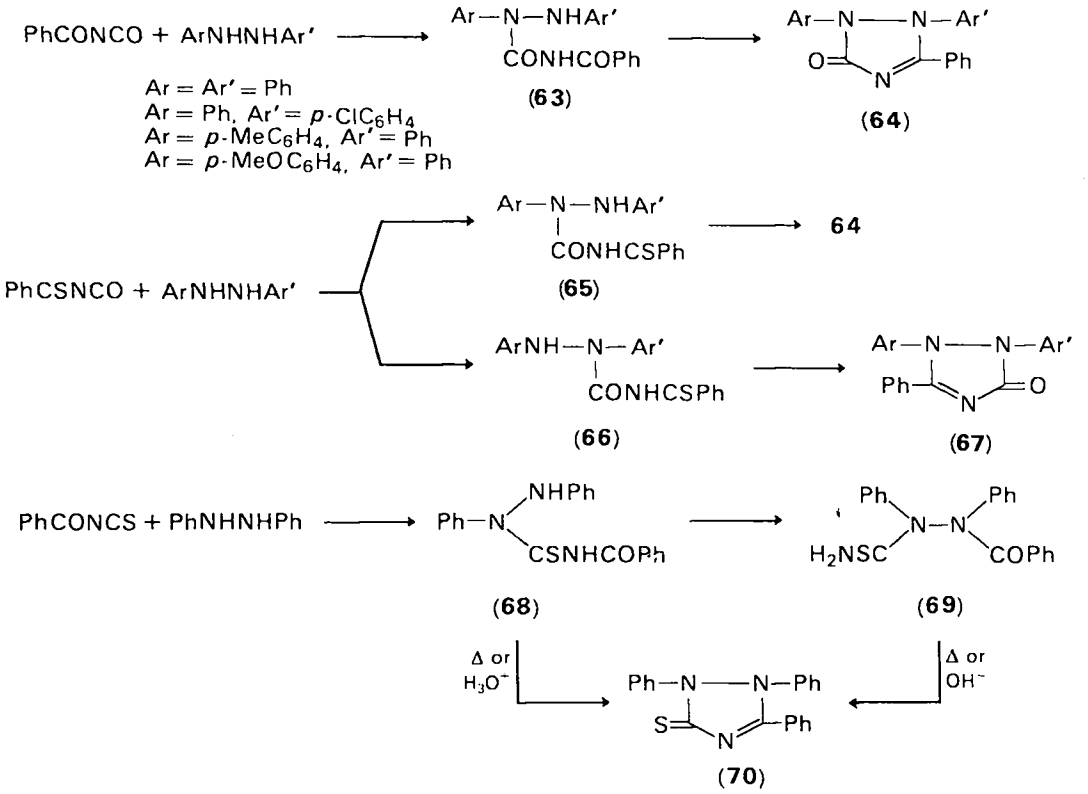


Acyl isothiocyanates react with semicarbazide[67] and thiosemicarbazide[68] to yield the corresponding 1-acyl-4-(thio)carbamoylthiosemicarbazides (**57**). Treatment of **57** with aqueous sodium hydroxide affords 1,2,4-triazoles **58**, while 1,3,4-thiadiazole derivatives **59–62** are formed in acids (equation 10).



2. With hydrazobenzenes

Benzoyl isocyanate reacts exclusively with the more basic nitrogen atom of hydrazobenzenes to give 1,2-diaryl-4-benzoylsemicarbazides (**63**), which on treatment with hydrochloric acid undergo ring closure to the triazolinones **64** by loss of water. Although thiobenzoyl isocyanate reacts preferentially with the more basic nitrogen atom in hydrazobenzenes, it attacks both nitrogen atoms to afford a mixture of semicarbazides **65** and **66**, which on heating are easily converted to two isomeric triazolinones **64** and **67** with the elimination of hydrogen sulphide[63].

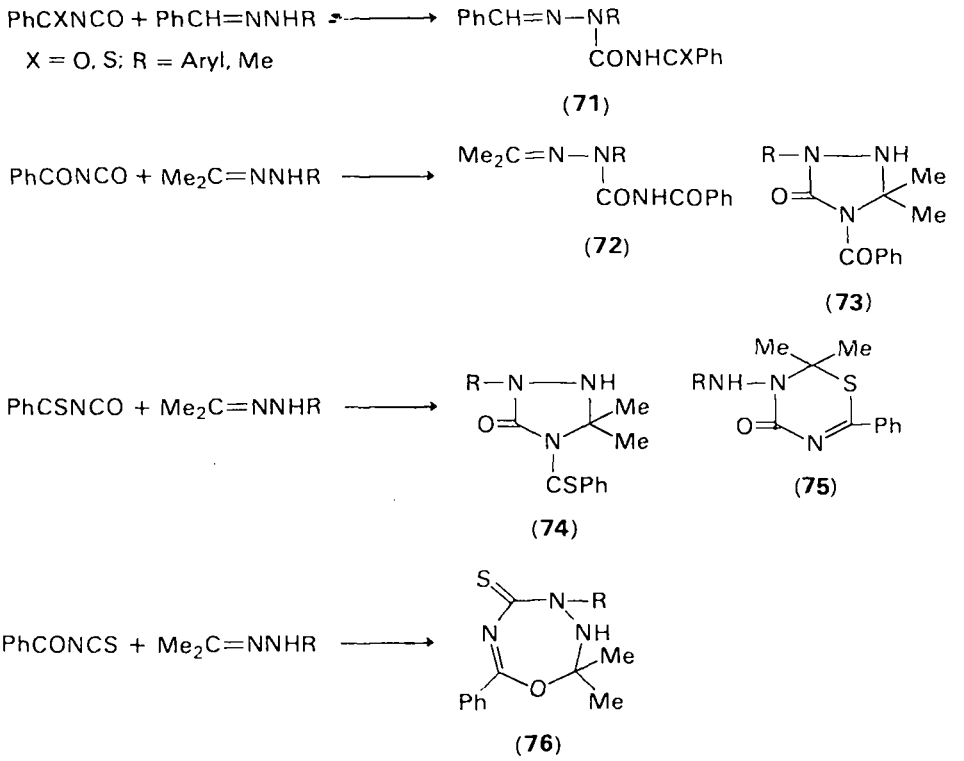


Benzoyl isothiocyanate easily reacts with hydrazobenzene at room temperature to yield 1,2-diphenyl-4-benzoylthiosemicarbazide (**68**), which on warming in ethanol or benzene is transformed into 1,2-diphenyl-1-benzoylthiosemicarbazide (**69**). On heating or treatment with hydrochloric acid, **68** is converted to Δ^3-1,2,4-triazolinethione **70**, which is also obtained from **69** by heating or action with aqueous sodium hydroxide solution[63].

3. With hydrazones

Hydrazones, $R^1R^2C{=}NNH_2$ (R^1 = H, Me; R^2 = Me, Ar), react with an equivalent of acyl isocyanates, RCONCO, to give $R^1R^2C{=}NNHCONHCOR$, and with 2 moles of the isocyanate to produce $R^1R^2C{=}NN(CONHCOR)_2$[69].

Benzoyl and thiobenzoyl isocyanates react with benzaldehyde arylhydrazones and methylhydrazone to give the corresponding semicarbazones **71** as isolated products respectively. In the reactions with acetone arylhydrazones and methylhydrazone, however, the *s*-triazolidinones **73** whose structures correspond to the ring tautomers of semicarbazones **72**, are isolated as sole products from the reaction of benzoyl isocyanate. In some cases the isomerization of **72** into ring tautomer **73** is observed by n.m.r. spectroscopy. On the other hand, thiobenzoyl isocyanate affords *s*-triazolidinones **74** and/or 1,4-cycloadducts **75** (see Section V.C.3)[70].

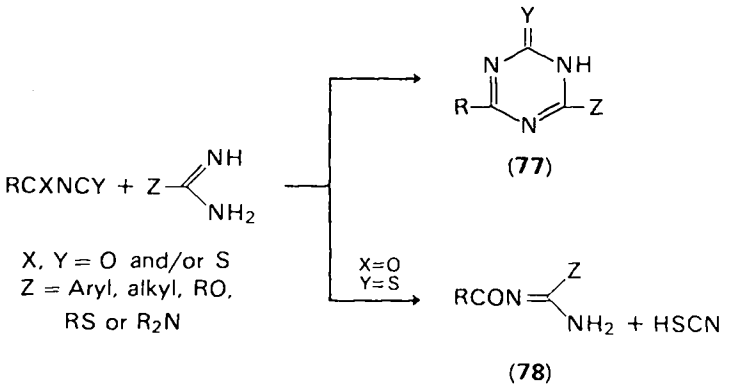


The reaction of benzoyl isothiocyanate with alkyl hydrazones such as acetone methyl-, phenethyl-, and 2,6-xylyloxyethylhydrazones leads to

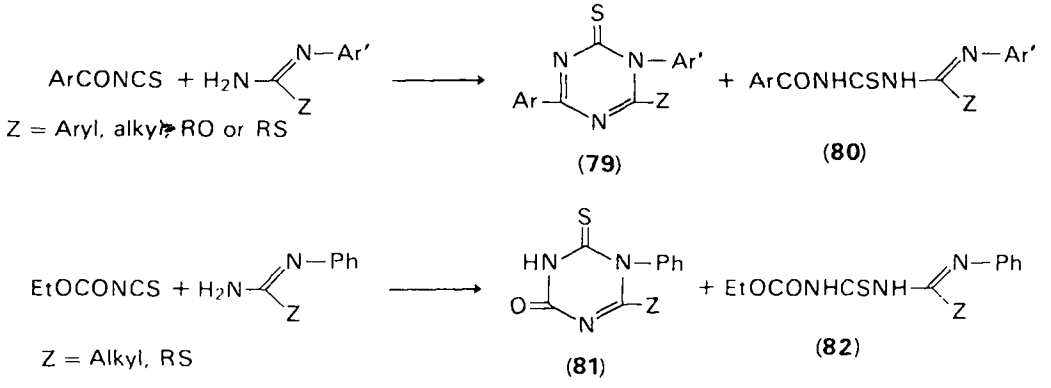
the formation of oxatriazepinethione derivatives **76**. However, benzaldehyde methylhydrazone gives an open-chain thiosemicarbazone[71].

D. Amidines and Related Compounds

The reactions of acyl and thioacyl derivatives of isocyanates and isothiocyanates with amidino compounds provide useful methods for the preparation of *s*-triazine derivatives. For instance, isocyanates and isothiocyanates of these classes react with *N*-unsubstituted amidino compounds, giving the corresponding *s*-triazinones and -thiones **77**[47,72,73] However, the reaction of acyl isothiocyanates is accompanied by acylation leading to the formation of *N*-acylamines (**78**). Combination of weakly basic amidino compounds with weakly electrophilic isothiocyanates is favourable to the formation of triazinethiones **77** (Y = S)[73].

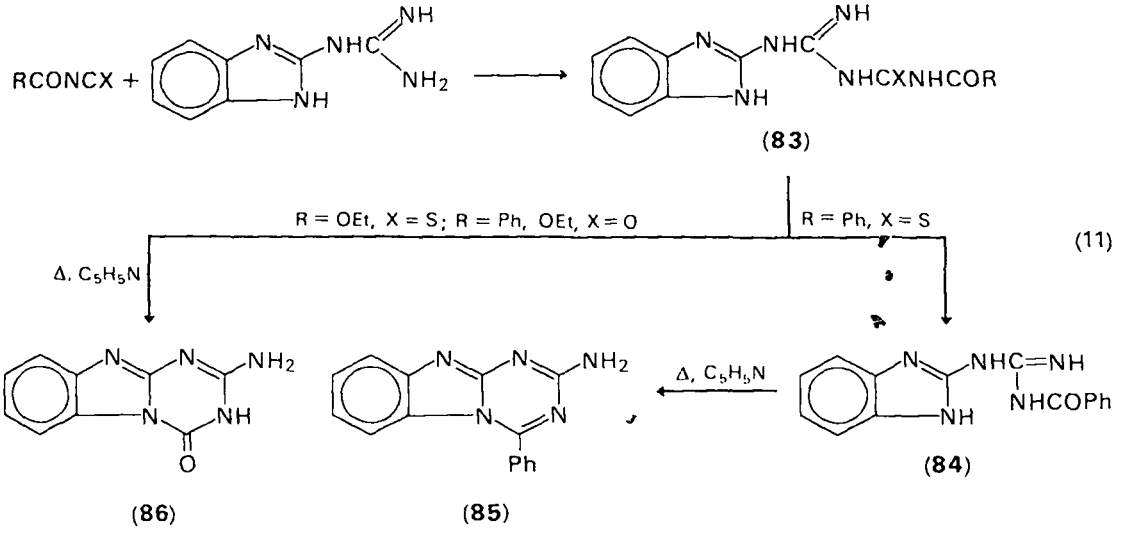


The reactions of aroyl and ethoxycarbonyl isothiocyanates with *N*-phenylamidino compounds in many cases afford mixtures of triazinethiones, **79** and **81**, and imidoylthioureas, **80** and **82**[74]. The triazines **79**



and **81** originate by reaction of the substituted nitrogen atom of amidines, and the thioureas **80** and **82** by addition to the NH_2 group of the bases. The latter reaction is the more general one. However, the reaction of *S*-alkyl-*N*-phenylisothioureas is an exception in that it results in preferential formation of the triazine[75–77]. Similarly, aroyl isocyanates and isothiocyanates react with 2-amino-5,6-dihydro-4*H*-1,3-thiazine to afford the corresponding *s*-triazinones and *s*-triazinethiones respectively[78].

The base-catalysed reaction of 2-guanidinobenzimidazole with acyl isothiocyanates leads via the formation of unstable intermediates **83** and **84** by the elimination of thiocyanic acid from the side chain, to benzimidazotriazine compounds **85** and **86**. The compound **86** is also formed by



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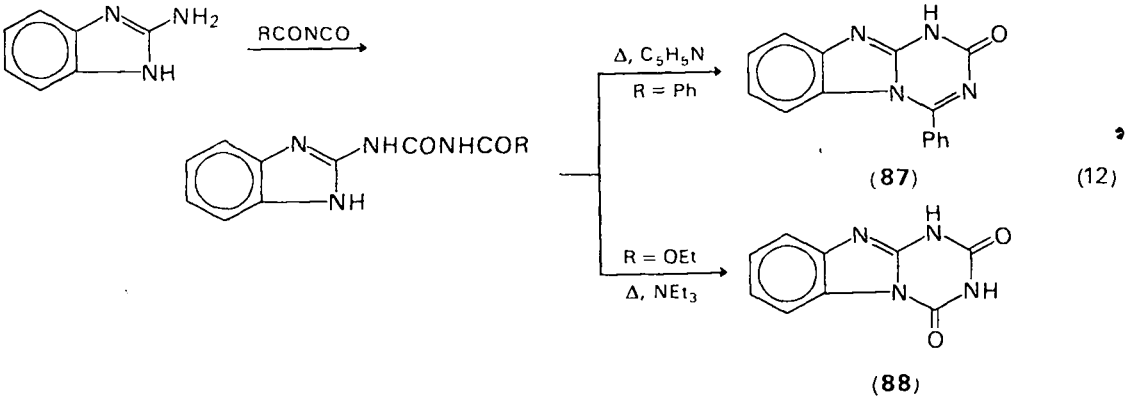
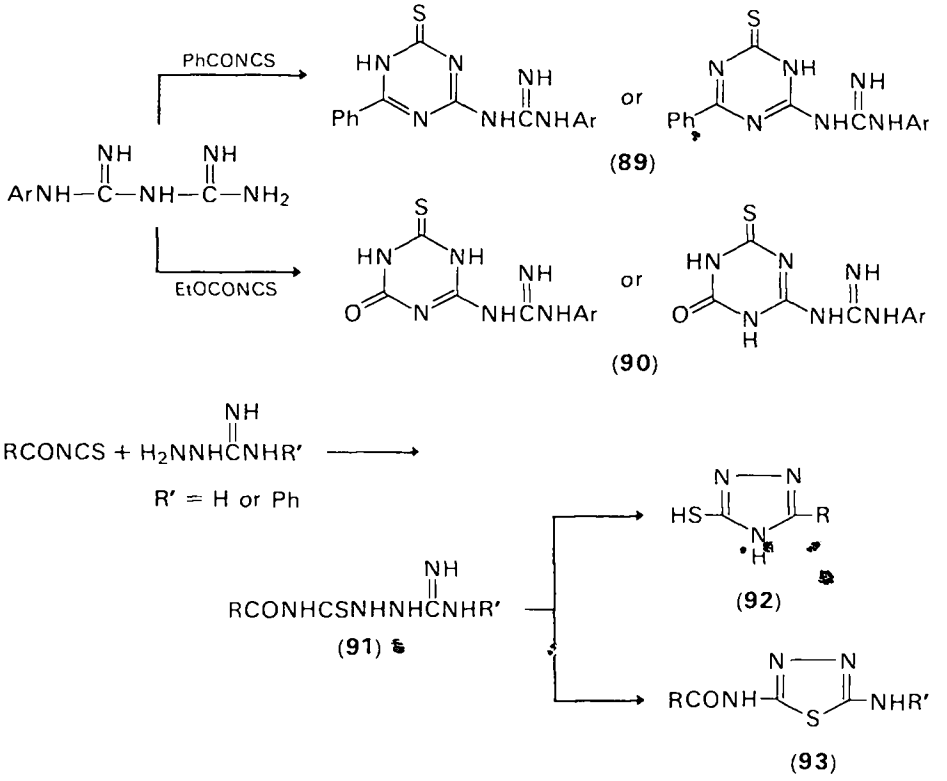


(12)

reaction with benzoyl or ethoxycarbonyl isocyanate via the adducts **83** with the formal elimination of benzamide or ethyl carbamate respectively. Under similar conditions, acyl isocyanates react with 2-aminobenzimidazole to give benzimidazotriazine compounds **87** and **88** (equations 11 and 12)[79].

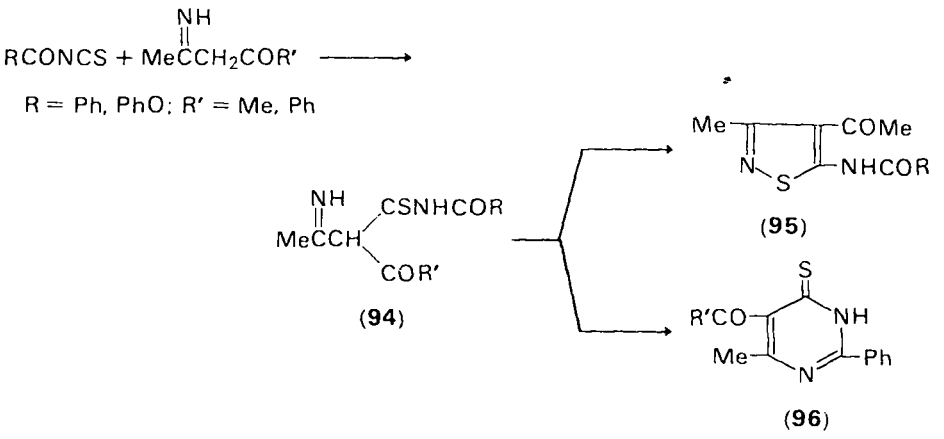
The reaction of benzoyl and ethoxycarbonyl isothiocyanates with arylbiguanides leads to the formation of *s*-triazines **89** and **90** respectively[80]. On the other hand, equimolar quantities of aroyl isothiocyanates and aminoguanidine react additively to afford excellent yields of amidinothiosemicarbazides (**91**): the addition occurs at the more reactive hydrazino group. The adducts **91** are cyclizable to *s*-triazoles **92** in alkaline, and to 1,3,4-thiadiazoles **93** in acidic media[81].



E. CH-Acidic Compounds

Addition of acyl isothiocyanates to CH-acidic compounds such as β-iminoketones, β-iminonitriles and benzoylacetamidine, leads to the formation of the corresponding 1:1 adducts[82,83]. For instance, the reaction with

β-iminoketones affords α-acyl-β-iminothiocrotonoylamides (**94**), which on dehydrogenation are cyclized to the isothiazoles **95**. Upon an intramolecular dehydration the adducts **94** (R = Ph) are transformed into the pyrimidines **96**.

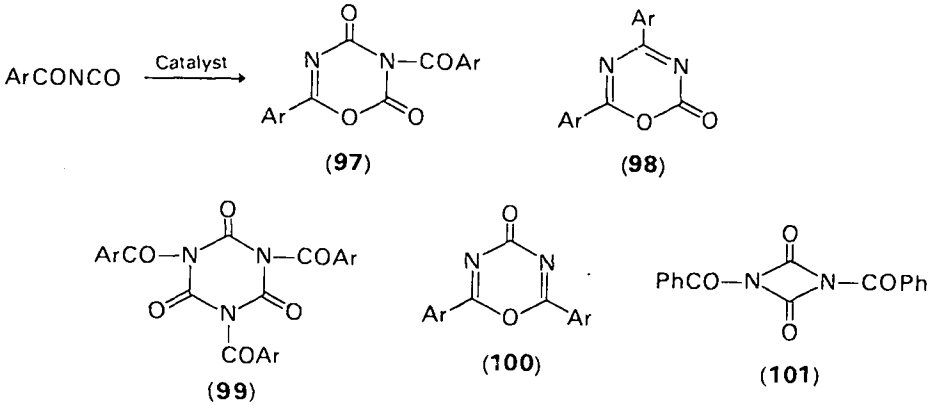


IV. DI- AND TRIMERIZATION REACTIONS

It is well known that aryl isocyanates form dimers (uretidiones) and trimers (isocyanurates) when treated with appropriate catalysts, whereas aliphatic isocyanates do not dimerize, although trimers have been made[84,85]. The conversion of aryl isocyanates to carbodiimides through the use of phospholene oxide catalysts has been also reported[86].

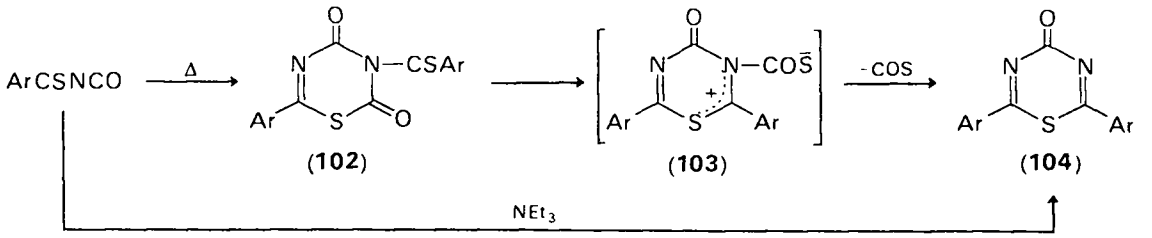
Para-substituted benzoyl isocyanates give dimers, trimers and/or related compounds, depending on the nature of catalysts and substituents as well as on the reaction conditions[87,88]. With triethylamine as the catalyst, benzoyl isocyanate affords mainly the dimer, oxadiazinedione **97**, at 50 °C, and the 1,3,5-oxadiazin-6-one **98** at 80 °C. From *p*-chloro- and *p*-nitrobenzoyl isocyanates, the corresponding oxadiazinones **98** are formed in good yields. However, *p*-methoxybenzoyl isocyanate gives the trimer, isocyanurate **99**, at 50 or 80 °C.

In the presence of benzylpyridinium chloride, isocyanates give the corresponding 1,3,5-oxadiazin-4-ones (**100**) which are isomers of **98**. It has been reported that the reaction of benzoyl isocyanate with benzoyl chloride, pyridine and water affords the compound **100** (Ar = Ph)[9]. The trimer **99** (Ar = Ph) and dimer **97** (Ar = *p*-$MeOC_6H_4$) are obtained from benzoyl and *p*-methoxybenzoyl isocyanates in the presence of



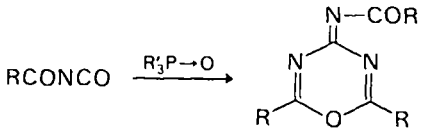
pyridine 1-oxide, whereas *p*-chlorobenzoyl and *p*-nitrobenzoyl isocyanates give the corresponding tribenzamides as main products, accompanied by small amounts of **100**. When treated with stannic chloride, benzoyl and *p*-methoxybenzoyl isocyanates afford the trimers **99**, although *p*-chlorobenzoyl and *p*-nitrobenzoyl isocyanates do not react in this way. The 1,3-uretidione structure **101** assigned to the dimer by Neidlein[89], is in error.

Thiobenzoyl isocyanate dimerizes readily without a catalyst to form the 1,3,5-thiadiazinedione **102** by a 1,4-cycloaddition sequence in which the isocyanate reacts both as the diene and the dienophile[27,31]. On further heating, dimer **102** is converted to the 1,3,5-thiadiazin-4-one **104** (Ar = Ph) via a zwitterion intermediate **103** with the elimination of carbonyl sulphide[31]. The reaction of thiobenzoyl isocyanates with triethylamine at room temperature affords **104** directly in good yields[90].



Benzoyl[91] and trichloroacetyl isocyanates[92] react with a phospholene oxide catalyst to give the corresponding 4-acylimino-1,3,5-oxadiazines **105**, whose structures correspond to the compound derived from trimer with the elimination of two molecules of carbon dioxide. Triacetyl

isocyanurate is obtained when acetyl isocyanate is treated with tributylphosphine, while benzoyl isocyanate gives **100** (Ar = Ph)[93]. Trichloroacetyl isocyanate reacts with quinoline to yield a 1,3,5-oxadiazinoquinoline derivative **107**. It is supposed that quinoline causes a dimerization of



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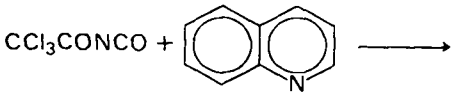
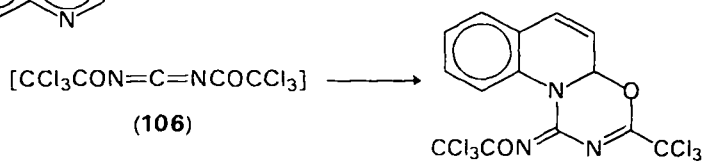
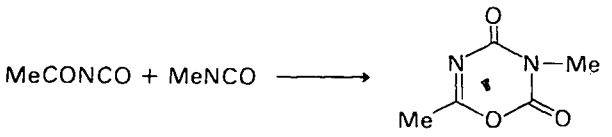




(106) **(107)**

the isocyanate, followed by the elimination of carbon dioxide to produce the carbodiimide **106**, which adds to the C=N bond of quinoline[92]. This result is somewhat surprising since benzoyl isocyanate reacts with quinoline to afford the dimer **97**.

Acetyl isocyanate reacts with methyl isocyanate to yield a mixed dimer **108** quantitatively[94]. When carbamoyl isothiocyanates are allowed to stand in an ampoule, dimers **109** are formed. The dimer **109** corresponds to the 1,4-cycloadduct of the isomeric thiocarbamoyl isocyanate (see Section II.C, equation 8) to the isothiocyanato group of carbamoyl isothiocyanate[95].



(108)

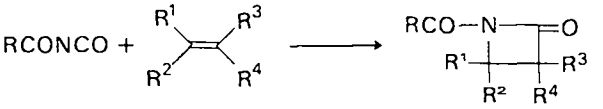
(109)

V. CYCLOADDITIONS AND RELATED REACTIONS

A. Addition to C=C Bonds

1. Addition to olefins

Acyl isocyanates react with some alkyl- and aryl-substituted olefins by a 1,2-cycloaddition process, giving the corresponding azetidinones

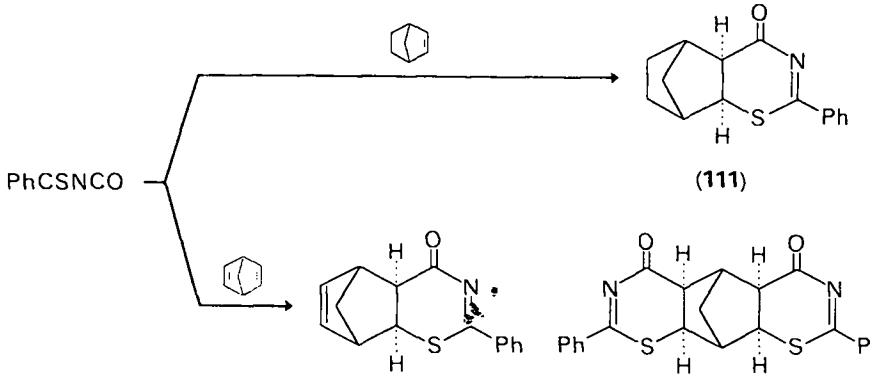


R = CCl_3, Ph $R^1 = R^2 = Me$, $R^3 = R^4 = H$
$R^1 = R^2 = R^3 = R^4 = Me$
$R^1 = R^3 = H$, $R^2R^4 = -(CH_2)_4-$
$R^1 = Ph$, $R^2 = R^3 = R^4 = H$

(110)

110[96–98]. When trichloroacetyl isocyanate reacts with norbornene[96] or 4-vinylpyridine[99], however, the corresponding [4 + 2] cycloadducts are formed.

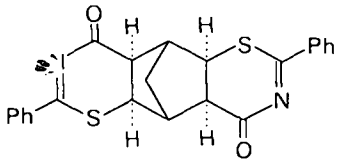
The reaction of thiobenzoyl isocyanate with norbornene proceeds by a 1,4-cycloaddition to give an exo-1:1 adduct **111**. Similarly, with norbornadiene, a mixture of exo-1:1 adduct **112** and two isomeric 1:2 cycloadducts **113** and **114** are formed[100].



(111)

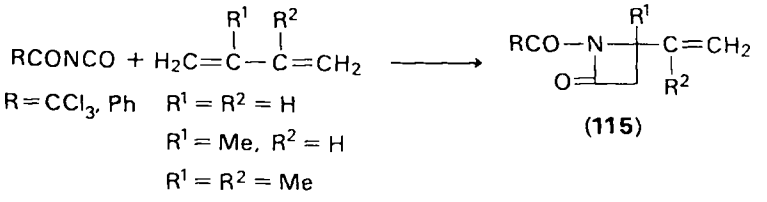
(112)

(113)



(114)

Benzoyl isocyanate adds to *p*-benzoquinone and α-naphthoquinone by a 1,2-cycloaddition process to give 1:1 adducts of azetidinone type, while the reaction of trichloroacetyl isocyanate with *p*-benzoquinone affords a [4 + 2] cycloadduct[101]. When benzoyl and trichloroacetyl isocyanates react with acyclic and cyclic 1,3-dienes, the corresponding 1:1 adducts **115** and **116** of azetidinone type are obtained in moderate yields[98,102,103].



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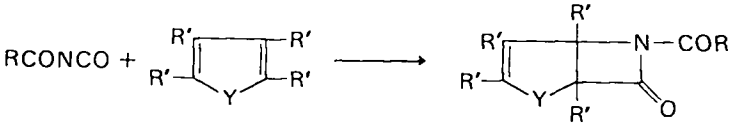
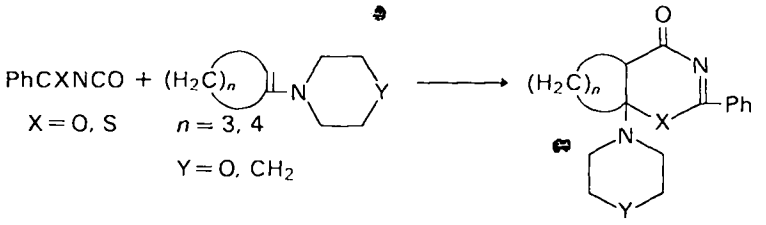


(116)

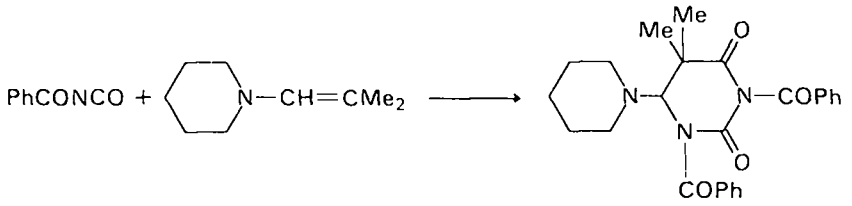
2. Addition to enamines

Acyl and thioacyl derivatives of isocyanates and isothiocyanates react readily with enamines in several manners. The reaction of benzoyl isocyanate with some cyclic enamines under mild conditions gives the [4 + 2] cycloadducts **117** in rather good yields[104]. Interactions between benzoyl isocyanate and morpholinoisobutene[96], and between trichloroacetyl isocyanate and morpholinocyclopentene[104] proceed analogously. Thiobenzoyl isocyanate adds to morpholinocyclohexene with the formation of the [4 + 2] cycloadduct **117**[105]. However, trichloroacetyl isocyanate affords generally [2 + 2] cycloadducts with cyclic



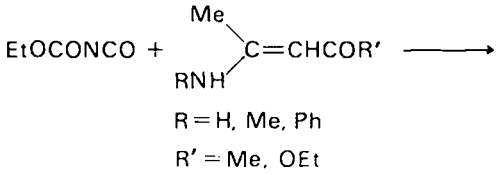
(117)

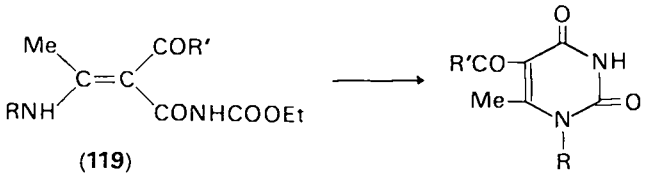
enamines[104]. The reaction of *p*-chlorobenzoyl isocyanate with morpholinocyclohexene similarly yields the [2 + 2] cycloadduct[96]. On the other hand, piperidinoisobutene reacts with 2 moles of benzoyl isocyanate to afford a hexahydropyrimidine derivative **118**[106,107]



(118)

The introduction of an electron-withdrawing substituent to the β-carbon atom of enamine decreases the nucleophilicity of the C=C bond, and makes its hydrogen atom more labile. Therefore conjugated addition takes place in reactions of benzoyl isocyanate with 1-dimethylamino-2-nitroethylene[108] and of ethoxycarbonyl isocyanate with enaminoketones[109] and 6-aminouracils[110]. In the reaction of ethoxycarbonyl isocyanate with ethyl 3-aminocrotonate, however, the product of reaction at the enamine nitrogen is also obtained[109]. Upon treating with amines or heating, the conjugated adducts afford pyrimidine derivatives. For instance, treatment of the adducts **119** with aqueous trimethylamine gives 5-acetyl- or 5-ethoxycarbonyl-6-methyluracils (**120**) in yields of 62–99%[109].

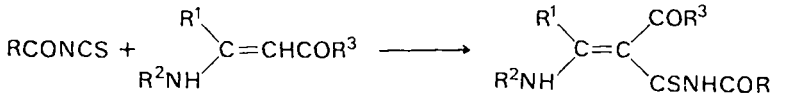




(119) **(120)**

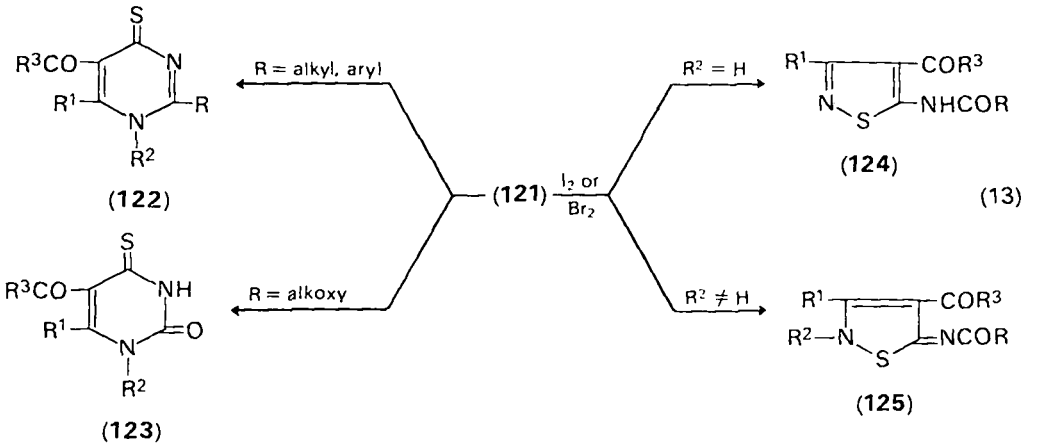
In general, acyl isothiocyanates react with enamines to yield acyclic 1:1 adducts. For instance, acyl isothiocyanates add to enaminoketones or

enaminoesters, giving conjugated adducts **121**[111–117], which afford thiopyrimidine compounds **122** and **123** by dehydration[114–117], or isothiazole compounds **124** and **125** by oxidation[111–114] (equation 13).



R = Alkyl, aryl, alkoxy; R^1, R^2 = H, Me, Ph
R^3 = Me, OEt

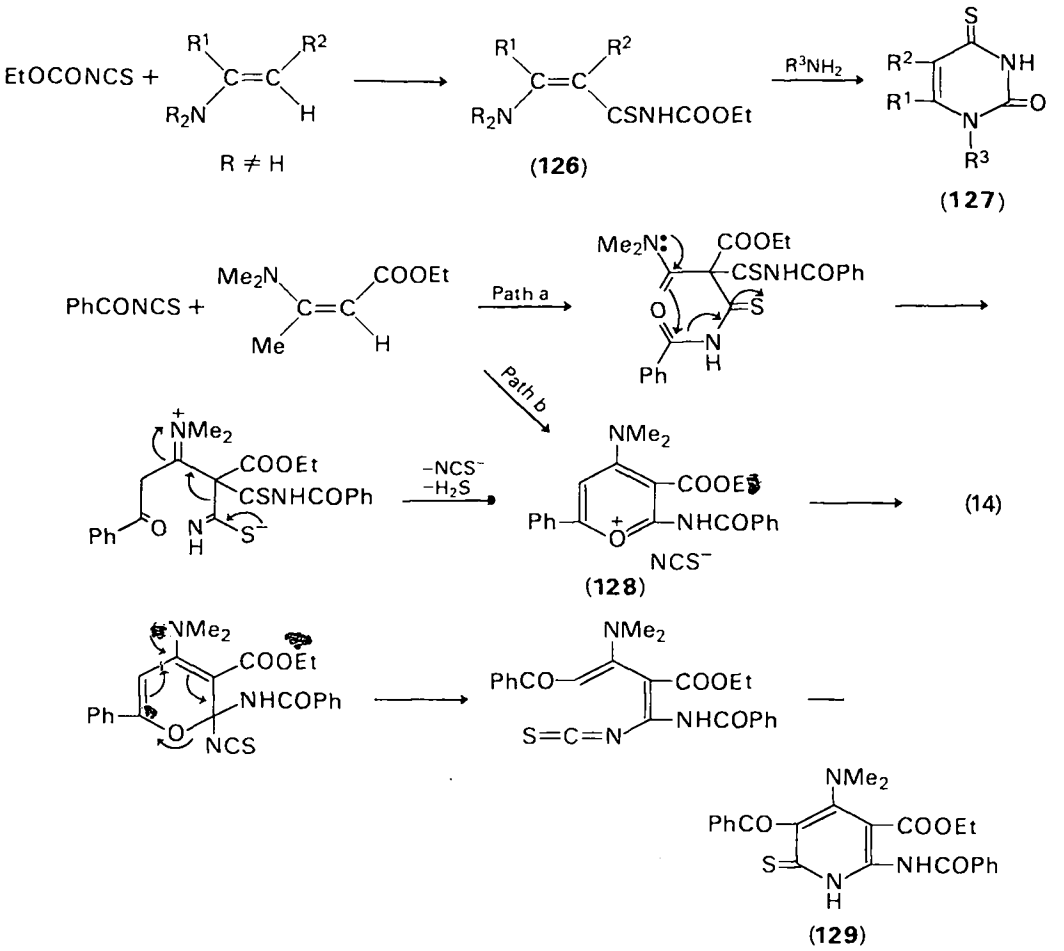
(121)



(13)

On treatment with primary amines or ammonia, adducts **126** undergo apparent amine exchange and cyclization to 4-thiouracil derivatives **127**[118]. However, the reaction of benzoyl isothiocyanate with ethyl β-dimethylaminocrotonate yields the 6-thioxonicotinate derivative **129**. The reaction pathway proceeds most likely through the addition of 2 moles of the isothiocyanate to the α-carbon atom of the crotonate with subsequent internal benzoyl displacement with loss of isothiocyanate (path a) or by the addition of 1 mole of the isothiocyanate to the α-carbon atom with direct nucleophilic addition of benzoyl to the carbon atom at 4-position (path b). Cyclization with loss of hydrogen sulphide gives **128** which adds thiocyanate with ring opening and then enamine undergoes ring closure to give **129**[119] (equation 14).

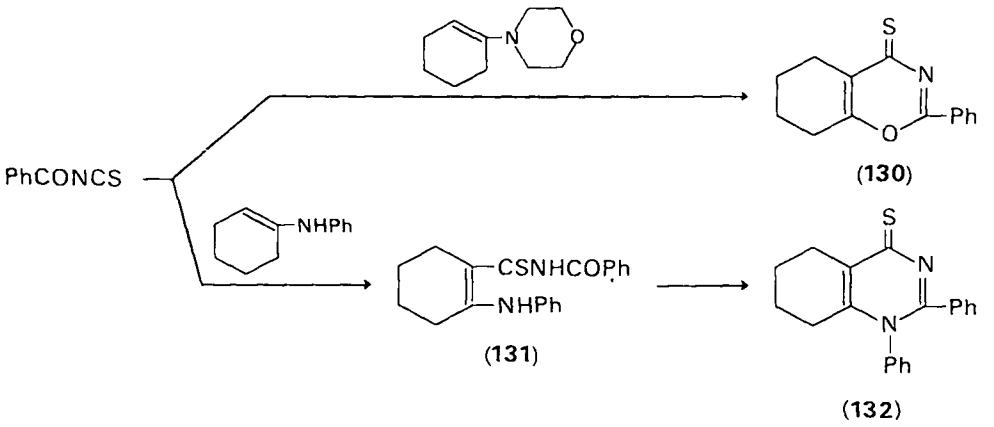
The reaction of benzoyl isothiocyanate with morpholinocyclopentene affords an acyclic 1:1 adduct[120], while direct ring closure to benzoxazinethione derivative **130** is observed in the reaction with morpholinocyclohexene[121]. Upon reacting anilinocyclohexene with benzoyl isothiocyanate



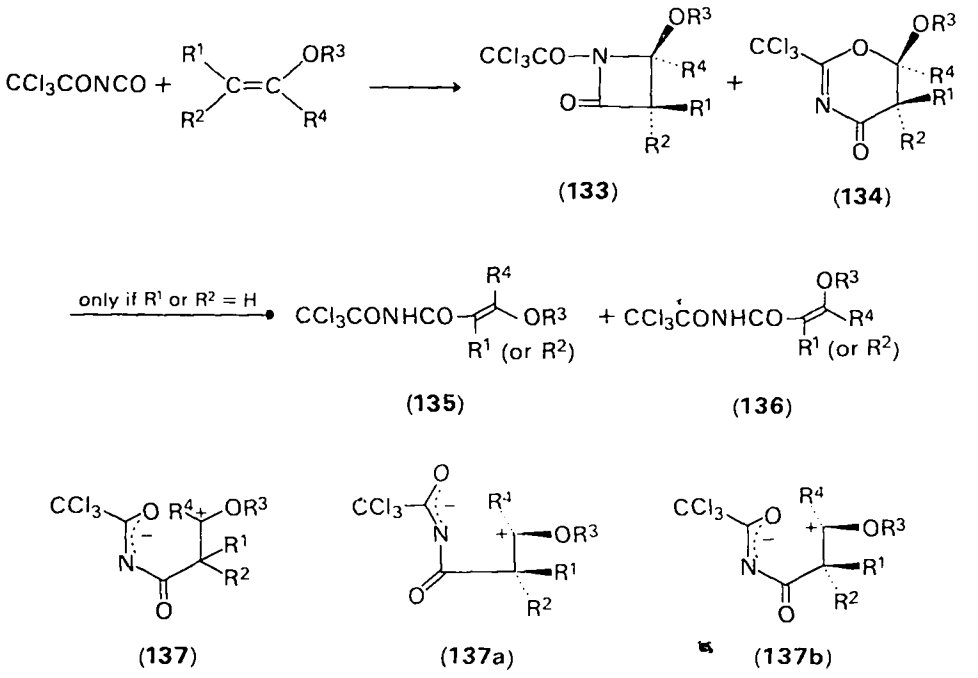
in diethyl ether an adduct **131** is obtained, which cyclized in refluxing tetrahydrofuran to form **132**. If the reaction is conducted in tetrahydrofuran, **132** is directly formed[122].

3. Addition to enol ethers and their related compounds

Although the reactivity of benzoyl isocyanate toward enol ethers is weak[123,124], trichloroacetyl isocyanate reacts readily with enol ethers to give 3-alkoxy-*N*-(trichloroacetyl)acrylamides **135** and **136**, by way of the four- and six-membered cyclic intermediates **133** and **134**[125]. The cyclic intermediates appear to be formed stereospecifically. At the first stage of the reaction both **133** and **134** are formed, but later **134** becomes

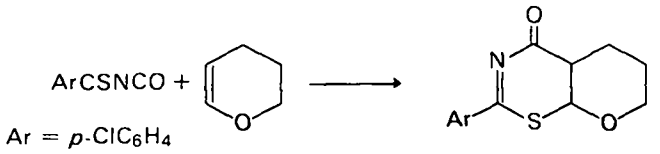


the main product in the mixture. In the cases where R^1 or R^2 = H the cyclic isomers undergo conversion into linear products **135** and **136**. The addition rate enhancement with increasing solvent polarity suggests a zwitterion **137** for the formation of both cyclic intermediates and linear



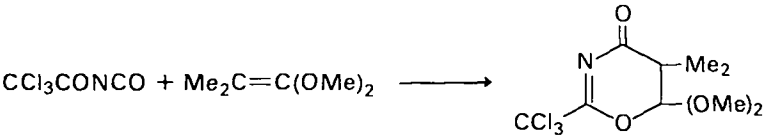
products. The initial ratio of **133** to **134** is probably determined largely by the initial conformation of the zwitterion, with orientation **137a** leading to **133** and **137b** to **134**.

On the other hand, *p*-chlorothiobenzoyl isocyanate adds to dihydropyrane with the formation of a [4 + 2] cycloadduct **138**[105].



(138)

Trichloroacetyl[125] and benzoyl isocyanates[126] react quite easily with ketene diethylacetal to give linear 1 : 1 adducts. However, if hydrogen atoms at the β-carbon atom of the ketene acetal are replaced by alkyl groups, 1,4-cycloaddition occurs (equation 15)[125]. The latter predominates or occurs exclusively in reactions of acyl isocyanates with 1,2-dialkyl-1-alkenes (equation 16)[96].



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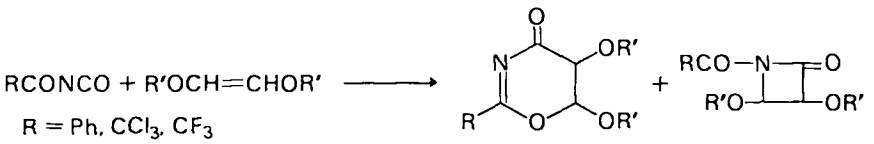
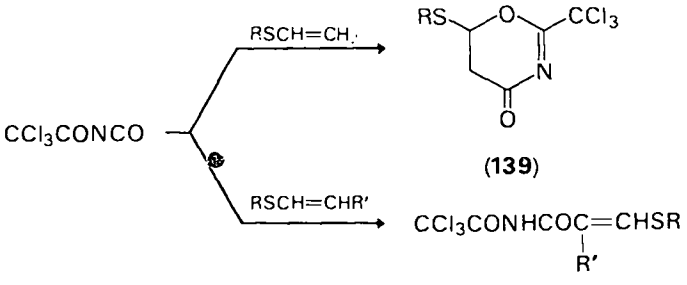


(16)

Benzoyl isocyanate does not react with alkenyl sulphides. However, trichloroacetyl isocyanate reacts with the sulphides to afford [4 + 2] cycloadducts or linear 1 : 1 adducts, depending on the nature of the sulphides. For instance, the reaction with vinyl sulphides gives [4 + 2] cycloadducts **139**[124,127], but linear adducts **140** are obtained from the



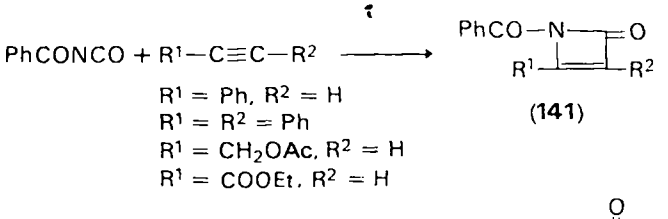
(139)

(140)

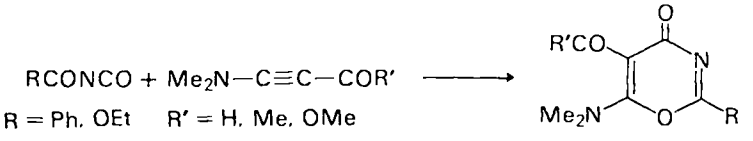
reaction with 2-substituted alkenyl sulphides[124]. 2-Vinylthioethyl acetate reacts with the isocyanate to afford a linear 1:1 adduct[125].

B. Addition to C≡C Bonds

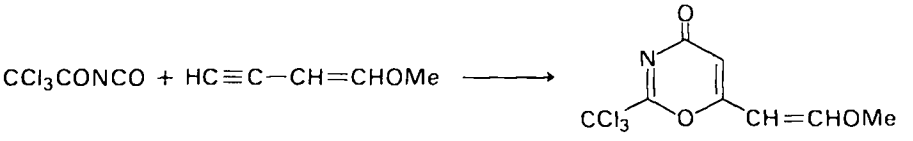
The reaction of benzoyl isocyanate with acetylenes such as phenylacetylene[97], tolane[99], propargyl acetate[97], and ethyl propiolate[128] gives the corresponding [2 + 2] cycloadducts (**141**) in rather low yields. In the reaction with ynamino-ketones and -esters, however, benzoyl and ethoxycarbonyl isocyanates afford the [4 + 2] cycloadducts (**142**) in good yields[129]. Similarly, benzoyl isocyanate adds to ethyl ethynyl ether with the formation of a [4 + 2] cycloadduct[125].



(141)



(142)



(143)

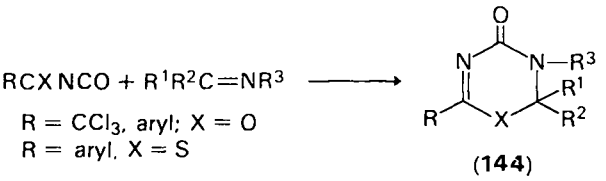
The reaction of trichloroacetyl isocyanate with acetylenic compounds results usually in the formation of [4 + 2] cycloadducts[99,125,130]. In the reaction with 1-butene-3-ynyl methyl ether, a cycloaddition involving only the acetylenic bond takes place and a [4 + 2] cycloadduct **143** is obtained[125].

C. Addition to C=N or C≡N Bonds

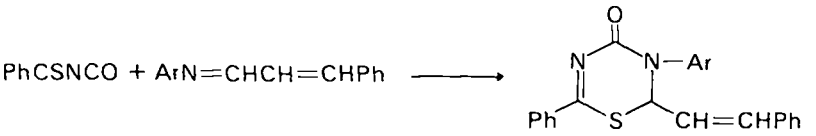
1. Reaction with Schiff bases

The reactions of acyl isocyanates with benzylidenealkylamines[90,131–133] and of thioacyl isocyanates with benzylidenealkyl- and arylamines[90,105,131,134] under mild conditions result in the formation of

[4 + 2] cycloadducts **144**. Furthermore, benzoyl and thiobenzoyl isocyanates add to dianils such as dibenzylidenethylenediamine and hydrobenzamide, giving bis[4 + 2] cycloadducts[131]. Thiobenzoyl isocyanate does not add to the C=C bond of cinnamylideneanilines, but it reacts with the C=N bond by a 1,4-cycloaddition process to give adducts **145**[131].



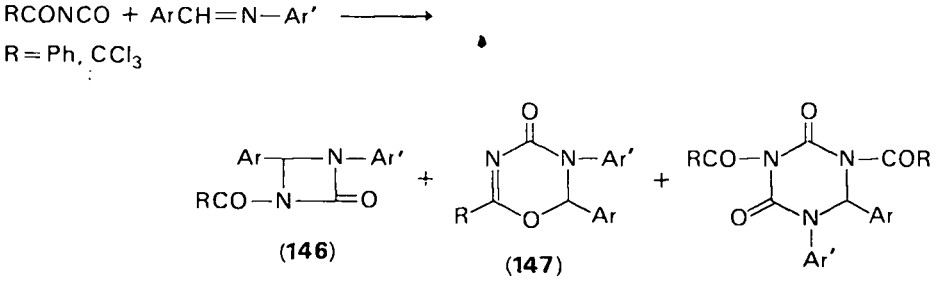
(144)



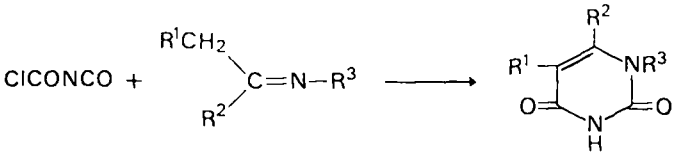
(145)

In the reaction of benzoyl and trichloroacetyl isocyanates with benzylideneanilines, diazetidinones **146**, oxadiazinones **147** and 2:1 adducts **148** are formed[135,136]. Electron-donating groups in the *para* position of the bases increase the overall rate of reaction and shift the product composition toward the formation of **146**, but electron-withdrawing groups favour the formation of **147**.

The reaction of chlorocarbonyl isocyanate with Schiff bases affords uracil compounds **149**, useful as plant protecting agents or their intermediates, with the elimination of hydrogen chloride[137].

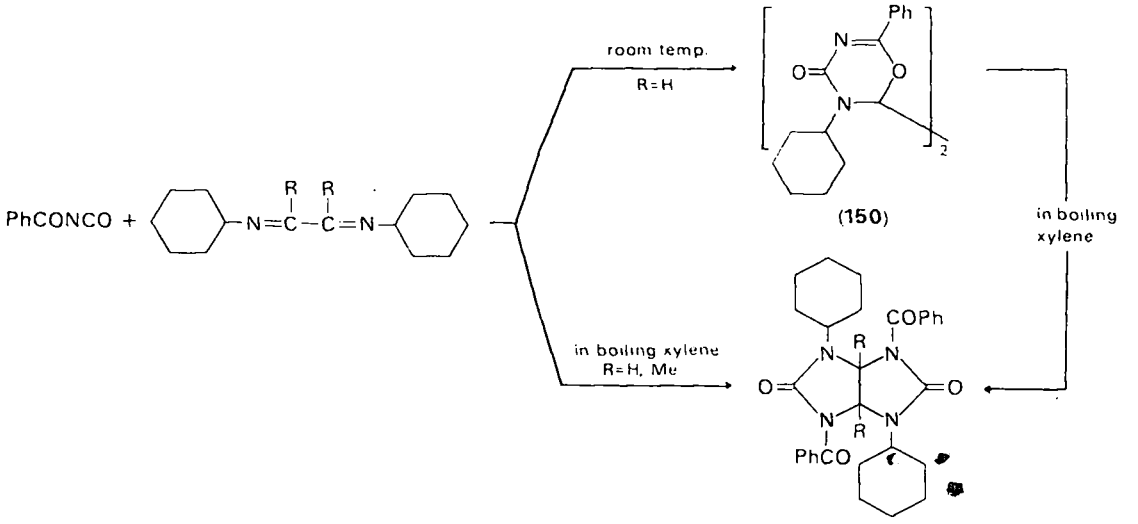


(146) (147) (148)



(149)

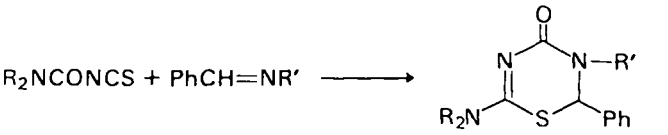
As the result of interaction of benzoyl isocyanate with bis-cyclohexylethylenediimine at room temperature, a 2:1 adduct **150** is formed through a 1,4-cycloaddition to the C=N bonds of diimine, whereas a criss-cross adduct **151** (R = H) is obtained in boiling xylene. Similarly, the isocyanate reacts with the butylenediimine in boiling xylene to give a criss-cross adduct **151** (R = Me)[138].



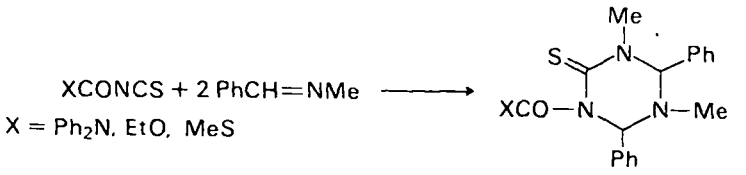
(150)

(151)

Benzoyl isothiocyanate adds to benzylidenemethylamine to form a [4 + 2] cycloadduct[139]. When aliphatic carbamoyl isothiocyanates are allowed to react with Schiff bases, 1,3,5-thiadiazinones (**152**) whose structures correspond to the 1,4-cycloadducts of thiocarbamoyl isocyanates to the bases, are obtained. However, diphenylcarbamoyl, ethoxycarbonyl, and methylmercaptocarbonyl isothiocyanates react with benzylidenemethylamine to give 1:2 adducts, triazinethiones **153**[95].



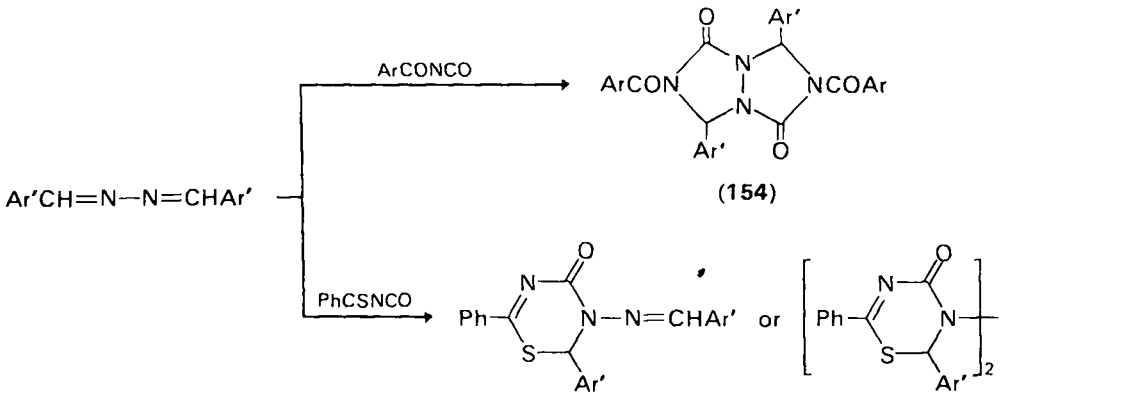
(152)



(153)

2. Reaction with azines

Benzoyl and thiobenzoyl isocyanates react with aldazines. While benzoyl isocyanates do not react with benzaldazines at room temperature, criss-cross adducts **154** are formed if the reaction is conducted in xylene under reflux. On the other hand, thiobenzoyl isocyanate reacts easily with azines at room temperature to afford mono[4 + 2] **155** or bis[4 + 2] cycloadducts **156** depending on the nature of the substituent of the azine[140].



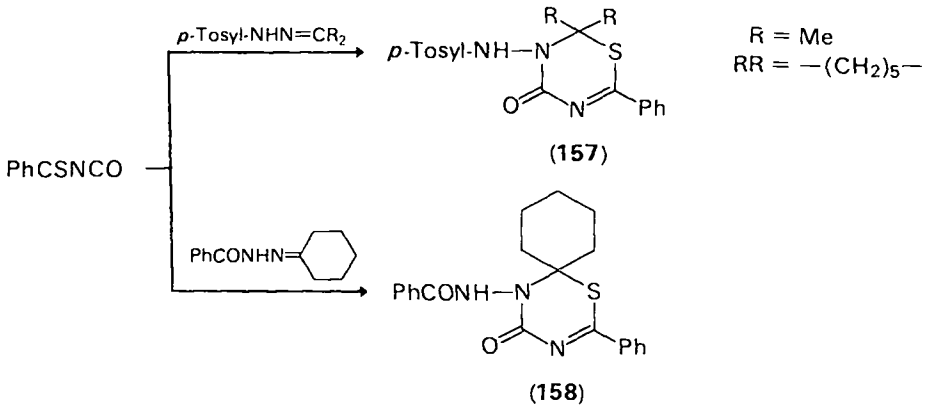
(154)

Ar' = Ph, *p*-ClC$_6$H$_4$ (155)

Ar' = *p*-MeC$_6$H$_4$, *p*-MeOC$_6$H$_4$ (156)

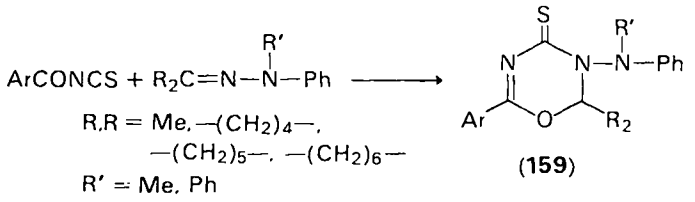
3. Reaction with C=N bonds of hydrazones

As described in Section III.C.3, benzoyl isocyanate reacts with acetone arylhydrazones to form the corresponding semicarbazones and their ring tautomers, *s*-triazolidinones and/or [4 + 2] cycloadducts to the C=N bond of the hydrazone. Thiobenzoyl isocyanate reacts with *p*-tosyl- and benzoyl-hydrazones to give exclusively [4 + 2] cycloadducts **157** and **158**, although benzoyl isocyanate does not react with the hydrazones[70].



(157)

(158)



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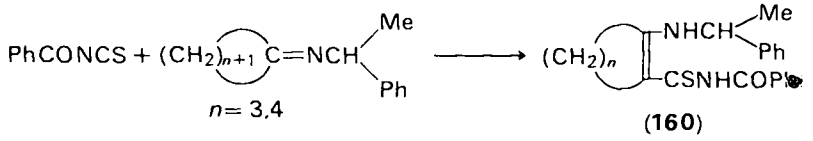
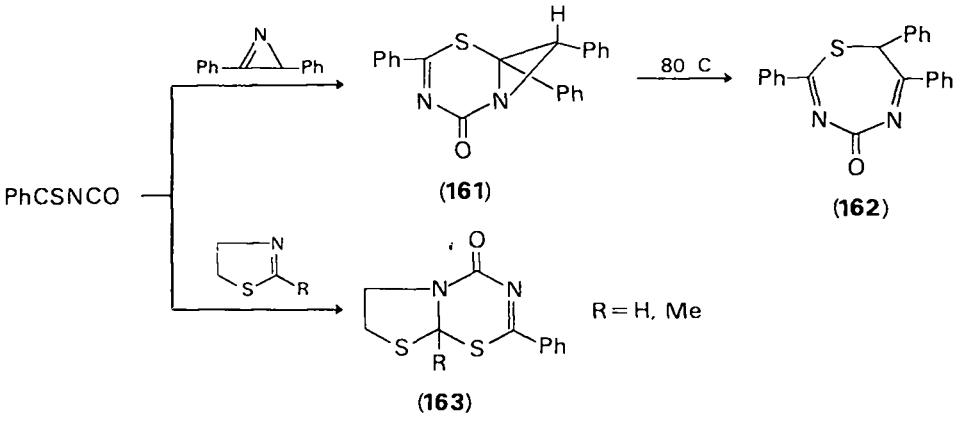


(160)

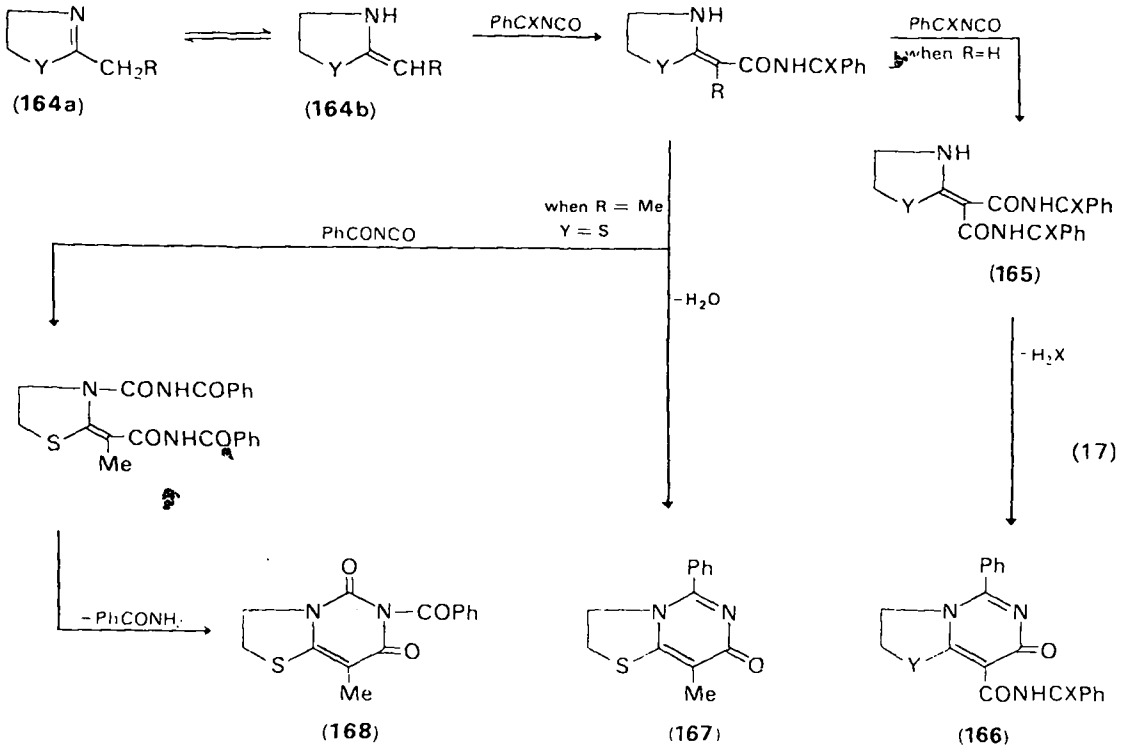
Aroyl isothiocyanates react with some *N,N*-disubstituted hydrazones, especially of cyclanones, by a 1,4-cycloaddition to yield unstable 1,3,5-oxadiazines **159**. The corresponding cycloalkanoneimines, however, afford vinylogous thioureas **160**[141].

4. Reaction with cyclic C=N bonds

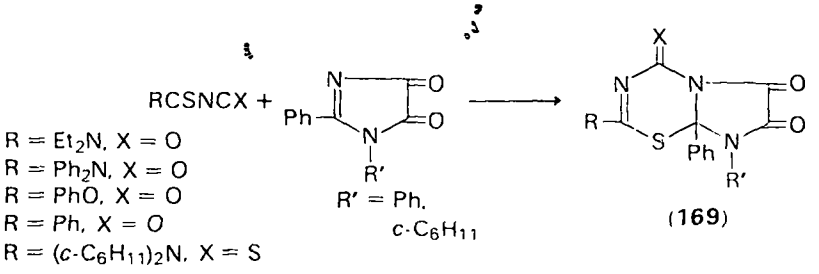
Thioacyl isocyanates add easily to a cyclic C=N bond. When thiobenzoyl isocyanate is treated with 2,3-diphenyl-1-azirine at room temperature, the [4 + 2] cycloadduct **161**, which at higher temperature is transformed into thiadiazepinone compound **162**, is obtained in an 85% yield[142,143]. Similarly, thiobenzoyl isocyanate adds to 2-thiazoline and its 2-methyl derivative at low temperature, affording [4 + 2] cycloadducts **163**[144].

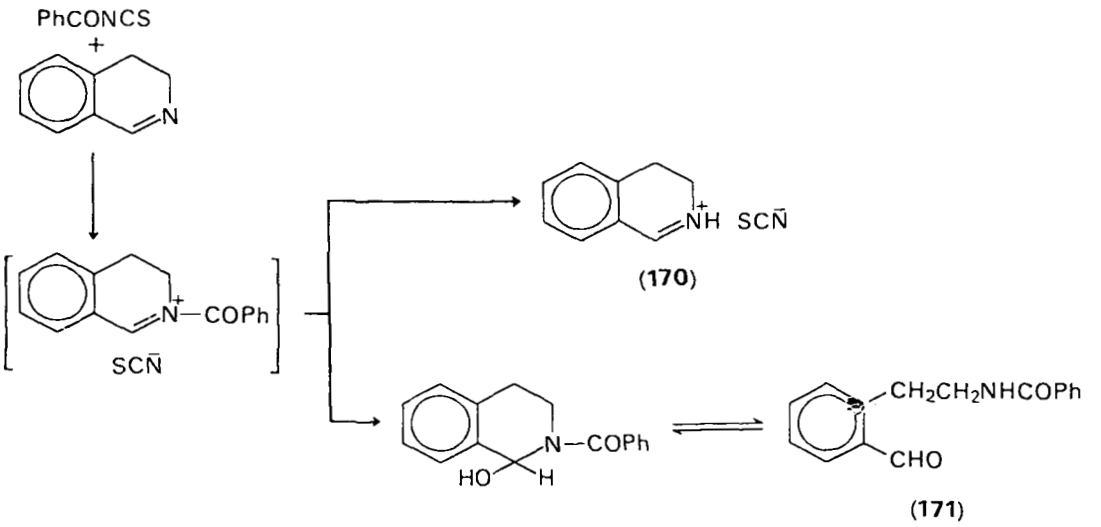


However, reactions of 2-methyl-2-thiazoline with benzoyl isocyanate at room temperature and with thiobenzoyl isocyanate at 90 °C afford thiazolo[3,2-*c*]pyrimidin-7-ones **166** (X = O, S; Y = S) respectively. Thiobenzoyl isocyanate reacts with 2-methyl-2-oxazoline to form directly the oxazolo[3,2-*c*]pyrimidin-7-one **166** (X = S, Y = O), while benzoyl isocyanate affords a 2:1 adduct **165** (X = Y = O), which with acetic acid gives **166** (X = Y = O). On the other hand, benzoyl isocyanate reacts with 2-ethyl-2-thiazoline to afford 8-methylthiazolo[3,2-*c*]pyrimidin-7-one (**167**) and thiazolo[3,2-*c*]pyrimidine-5,7-dione (**168**). These reactions can be understood by initial attack of the isocyanate on the β-carbon atom of the tautomeric enamine **164b** of 2-alkyl-2 thia(oxa)-zoline **164a**, as illustrated opposite[144].



Thioacyl iso(thio)cyanates react with the C=N bond of imidazoline-4,5-dione to form the [4 + 2] cycloadducts **169**[145]. However, the reaction of benzoyl isothiocyanate with 3,4-dihydroisoquinoline forms *N*-benzoyl-3,4-dihydroisoquinolinium thiocyanate (**170**) and 2-(2-benzamidoethyl)-benzaldehyde (**171**)[139].

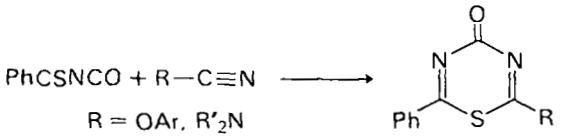




5. Addition to C≡N bonds

Trichloroacetyl isocyanate reacts with trichloroacetonitrile to afford a [2 + 2] cycloadduct **172** in a 35% yield[146]. On the other hand, thiobenzoyl isocyanate adds to aryl cyanates and disubstituted cyanamides by a 1,4-cycloaddition to give 1,3,5-thiadiazin-4-ones **173**[134].

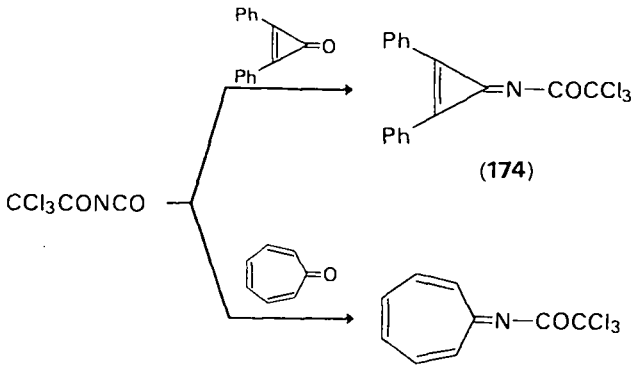
(172)



(173)

D. Addition to C=O Bonds

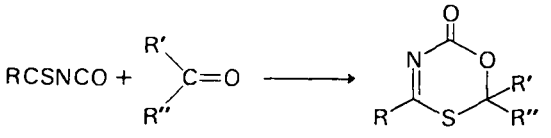
Acyl and thioacyl isocyanates are capable of addition to carbonyl compounds. Trichloroacetyl isocyanate reacts easily with diphenylcyclopropenone[147] and tropone[148] to give iminocyclopropenone **174** and troponimine **175** with the evolution of carbon dioxide. On treatment with dimethylformamide in the presence of lithium chloride as a catalyst,



(174)

(175)

benzoyl and trichloroacetyl isocyanates give the corresponding dimethylformamidines[149]. These reactions proceed via a 1,2-cycloaddition process. On the other hand, ethoxythiocarbonyl and thiobenzoyl isocyanates react with aliphatic and aromatic aldehydes and acetone tc form the corresponding [4 + 2] cycloadducts **176**[150].

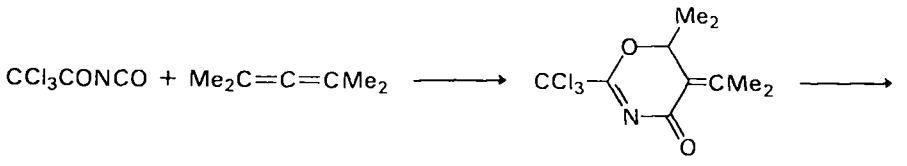


R'' = H (aldehydes):
R' = CCl_3, Et, Ph,
p-$MeOC_6H_4$, p-$O_2NC_6H_4$,
α-furyl
R' = R'' = Me

(176)

E. Reaction with Cumulated Compounds

Trichloroacetyl isocyanate reacts with tetramethylallene to give a [4 + 2] cycloadduct **177**, which rearranges to the acyclic product **178**[151]. Acyl isocyanates and dimethylketene undergo a 1,4-cycloaddition across the C=C bond to give oxazinediones **179**. Benzoyl isocyanate reacts with ketene to afford an adduct **180**, presumably formed via a 1,4-cycloaddition followed by enolization. In cold diethyl ether, **180** is formed in a 62% yield, but in benzene at 30–40 °C the acetylated product **181** is obtained[152].



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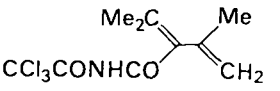
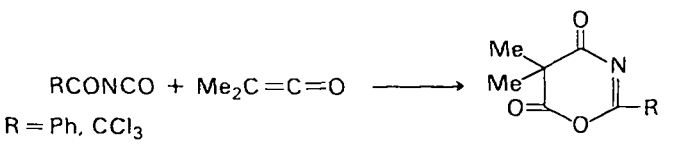
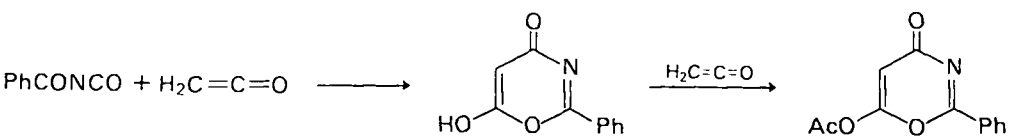


(178)



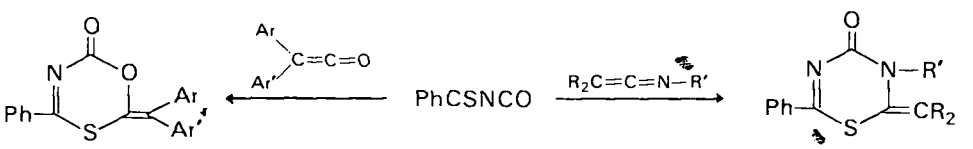
(179)



(180) (181)

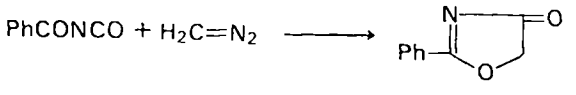
On the contrary, thiobenzoyl isocyanate adds to the C=O bond of aromatic ketenes and to the C=N bond of aromatic keteneimines, giving oxathiazinones **182** and thiadiazinones **183** respectively[153].

Since diazo compounds such as diazoalkanes and diazoketones may be justified as cumulated compounds by regarding the contribution structure $RR'C{=}N^{+}{=}N^{-}$, the reactions with diazo compounds are discussed in this section.

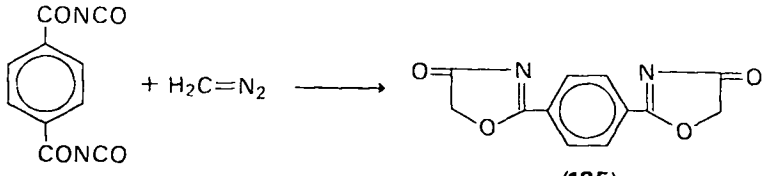


(182) (183)

Unlike the formation of the β-lactam in the case of phenyl isocyanate[154], benzoyl isocyanate reacts readily with diazomethane to form oxazolone **184** in 68–70% yields[155]. Similarly, the reaction of terephthaloyl diisocyanate with diazomethane leads to the formation of oxazolone **185**[19].

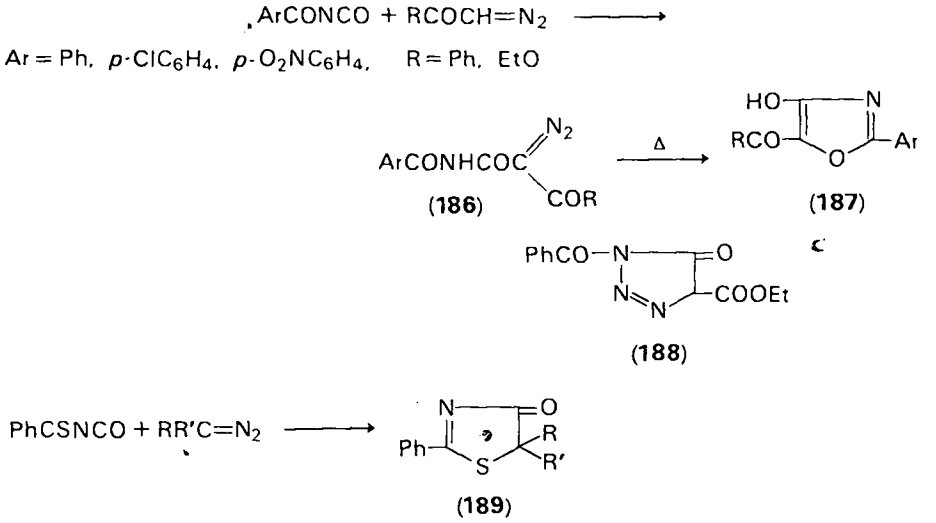


(184)



(185)

When ethyl diazoacetate and diazoacetophenone are allowed to react with benzoyl isocyanates, the corresponding benzoylcarbamoyldiazo compounds **186**, which are thermally decomposed to oxazoles **187**, are obtained[156]. The product from benzoyl isocyanate and ethyl diazoacetate is not the 1,2,3-triazolone **188** as reported by Neidlein[157], but is **186** (Ar = Ph, R = OEt). Thiobenzoyl isocyanate reacts with diazoalkanes such as phenyl-, methylphenyl-, diphenyldiazomethane and diazofluorene to give directly the corresponding thiazolones **189**[158].

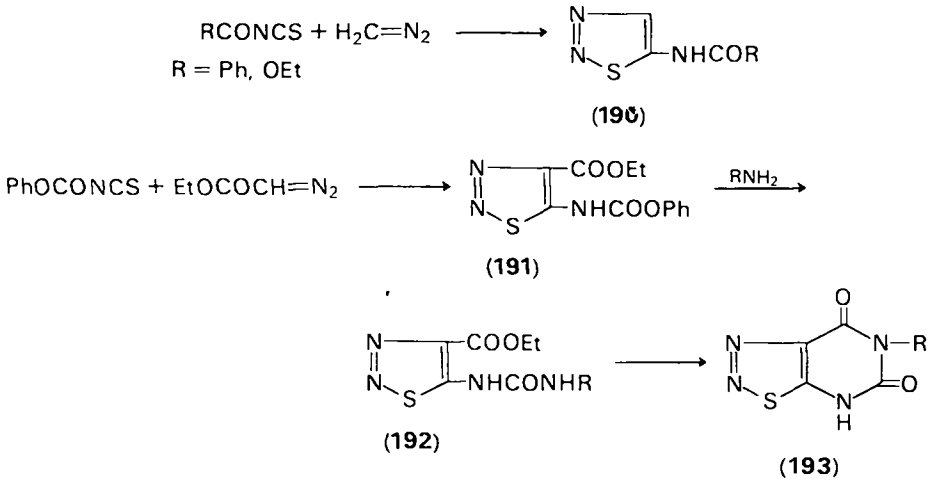


(186) (187) (188)

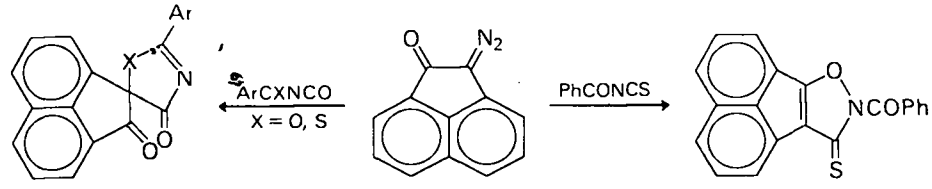
(189)

In the reaction of diazo compounds with isothiocyanates, thiadiazole derivatives are formed, apparently by a 1,3-cycloaddition across the C=S bond. Acyl isothiocyanates react with diazo compounds more easily than alkyl and aryl isothiocyanates. Benzoyl and ethoxycarbonyl iso-

thiocyanates react with diazomethane to give the corresponding 5-amino-1,2,3-thiadiazoles **190**[159]. The adduct **191** obtained from phenoxycarbonyl isothiocyanate and ethyl diazoacetate reacts with amines to afford the urea **192** which is readily cyclized to 1,2,3-thiadiazolo[5,4-*d*]pyrimidines **193**[159].



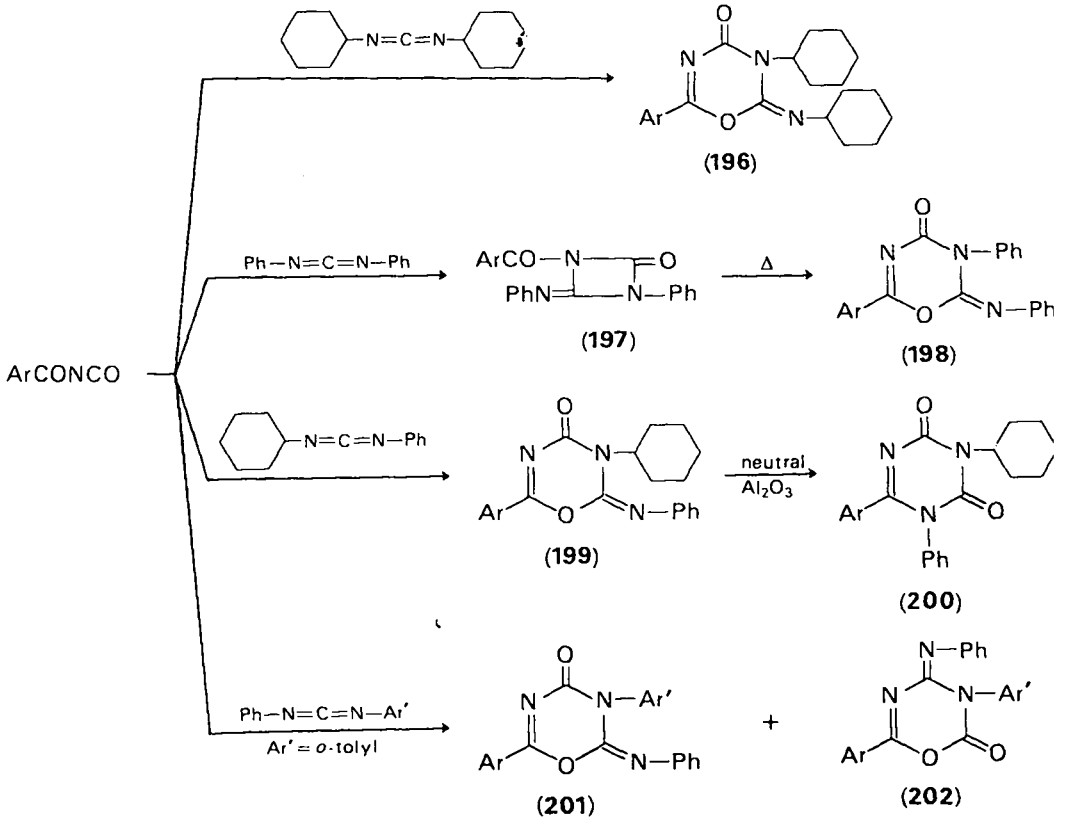
Although a cyclic diazoketone, 2-diazoacenaphthenone, does not react with phenyl isocyanate or isothiocyanate on prolonged reflux in toluene, the diazoketone reacts with benzoyl and thiobenzoyl isocyanates to give the corresponding spiro[acenaphthenone-2,5'-oxa(or thia)zolin-4'-ones] **194** in good yields. The reaction of benzoyl isothiocyanate gives acenaphtho[1,2-*d*]isoxazolinethione derivative **195**[160].



Reactivities of diazo compounds toward benzoyl isothiocyanate decrease as follows[161,162]: CH_2N_2, $C_2H_4N_2$ > $PhCHN_2$ > $H_2NCOCHN_2$ > $EtOCOCNH_2$ > $PhCOCHN_2$.

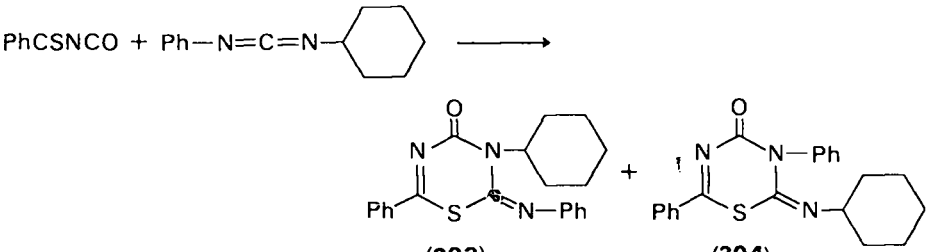
Benzoyl isocyanates add to dicyclohexylcarbodiimide, giving the corresponding [4 + 2] cycloadducts (**196**)[163], and not the [2 + 2] cycloadducts

proposed by Neidlein[89]. The reaction of benzoyl isocyanates with diphenylcarbodiimide at 0 °C affords [2 + 2] cycloadducts (**197**), which are thermally isomerized into the [4 + 2]cycloadducts (**198**). The isocyanates add across the cyclohexyl–N=C bond of *N*-cyclohexyl-*N'*-phenylcarbodiimide to form [4 + 2] cycloadducts (**199**) which on treatment with neutral alumina are easily isomerized into 1,3,5-triazines (**200**). Similarly, the isocyanates react with *N*-phenyl-*N'*-*o*-tolylcarbodiimide to yield the corresponding [4 + 2] cycloadducts **201** to the *o*-tolyl–N=C bond and/or the isomeric 1,3,5-oxadiazin-6-ones **202**, depending on the nature of the substituent in the isocyanate[163].

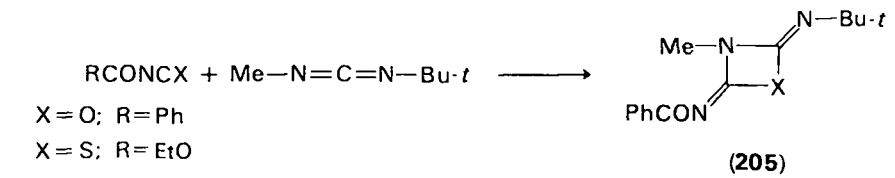


As a result of the reaction of thiobenzoyl isocyanate with carbodiimides, 1,3,5-thiadiazin-4-ones are formed, apparently by a 1,4-cycloaddition across the N=C bond in the carbodiimide[105,163]. For instance, the isocyanate reacts with both the N=C bonds of *N*-cyclohexyl-*N'*-phenylcarbodiimide to afford two isomeric [4 + 2] cycloadducts **203** and **204**[163].

In the reactions of benzoyl isocyanate and of ethoxycarbonyl isothiocyanate with methyl-*t*-butylcarbodiimide, the cycloaddition of the sterically unhindered N=C bond of carbodiimide to the C=O bond of the isocyanate and C=S bond of the isothiocyanate takes place and the oxa- or thiazetidine compound **205** is formed[164].

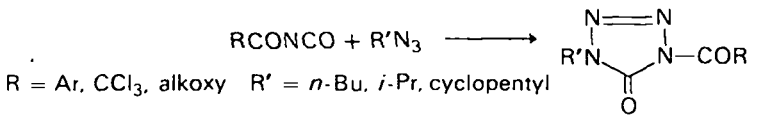


(203) **(204)**



(205)

Although efforts to obtain cycloadducts from the reaction of acyl isocyanates with aryl azides are unsuccessful, the reaction of the isocyanates with alkyl azides provides a convenient method for the preparation of Δ^2-tetrazolin-5-ones **206**[165].

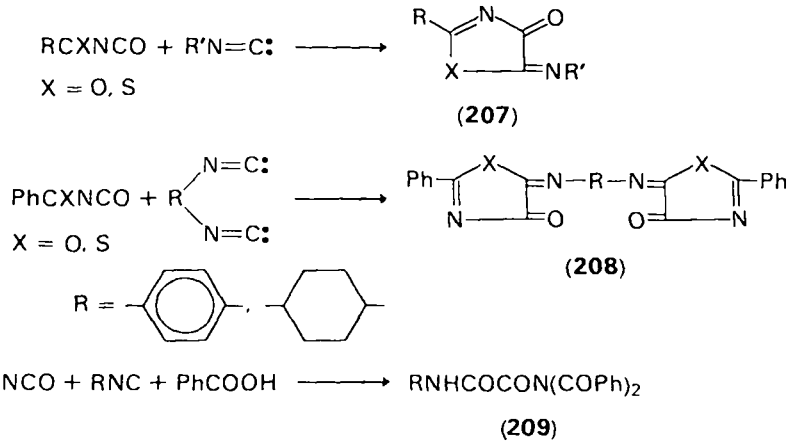


(206)

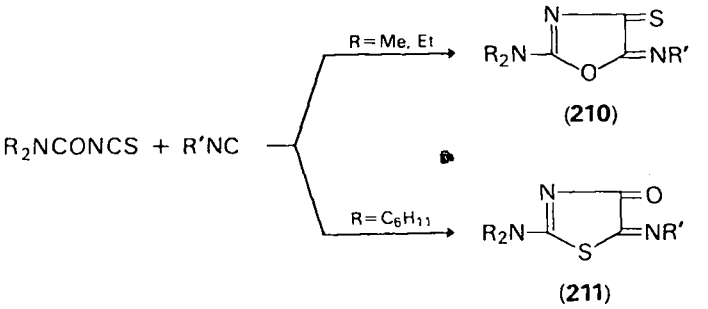
F. Reaction with Isonitriles

In the reactions with isonitriles, acyl and thioacyl isocyanates act as 1,4-dipoles, while isonitriles act as 1,1-dipoles. Additions to isonitriles occur quite readily, and 5-iminooxa- or thiazolinone compounds **207** are formed[105,157,166]. Both functional groups of *p*-phenylene- and 1,4-cyclohexylene-diisonitrile take part in the reaction with benzoyl and thiobenzoyl isocyanates, bis-5-imino- or thiazolinone derivatives (**208**) being formed, respectively[167]. The reaction of benzoyl isocyanate with

isonitriles in the presence of benzoic acid gives mixed amides (**209**) which are rather difficult to obtain by other routes[168].

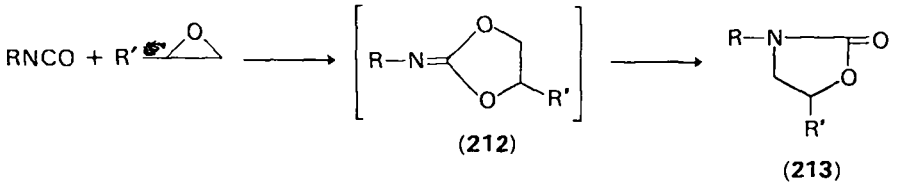


As described earlier (Section V.C.1), carbamoyl isothiocyanates react as themselves and sometimes as thiocarbamoyl isocyanates. Dimethyl- and diethylcarbamoyl isothiocyanates react with isonitriles to give iminoxazolinethiones (**210**), while dicylohexylcarbamoyl isothiocyanate behaves as the thiocarbamoyl isocyanate and gives iminothiazolinones (**211**)[95].



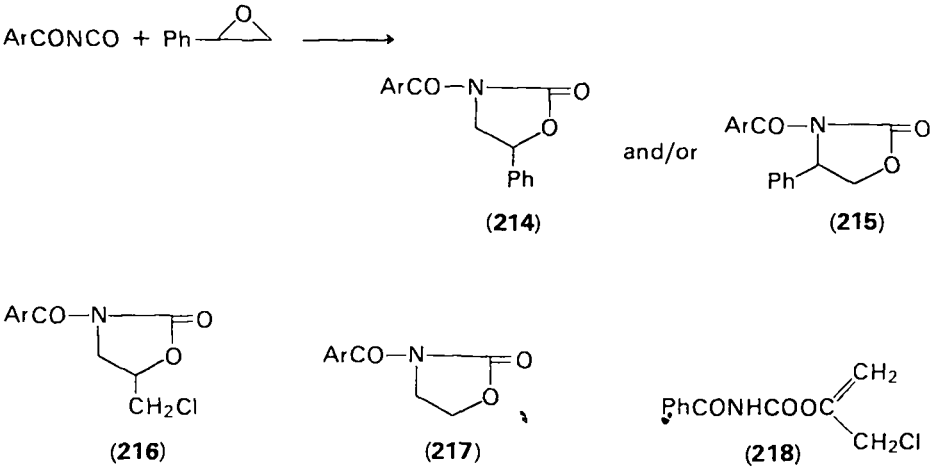
G. *Reaction with Oxygen-, Sulphur-, or Nitrogen-containing Three-membered Heterocycles*

Alkyl and aryl isocyanates react with oxiranes in the presence of lithium chloride[169] or tetraethylammonium iodide[170] to afford 3-substituted oxazolidin-2-ones (**213**) through the initial 2-imino-1,3-dioxolanes **212**[171].



(212) (213)

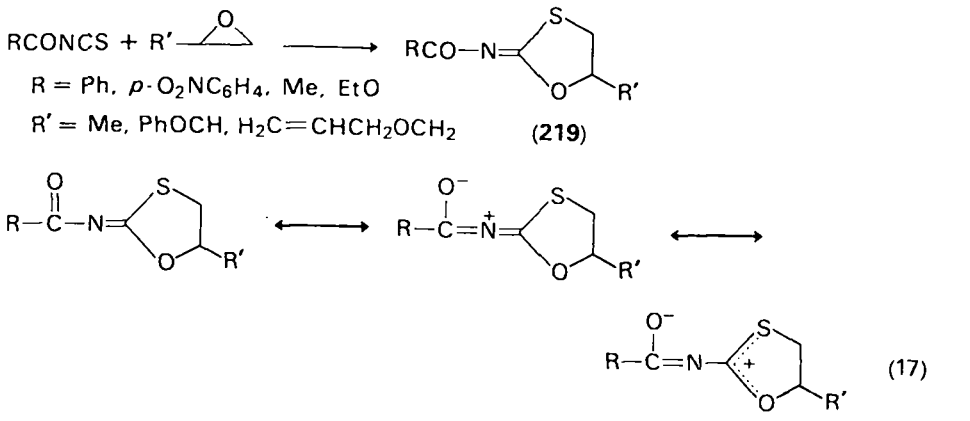
Benzoyl and *p*-chlorobenzoyl isocyanates react with styrene oxide in the presence of tetraethylammonium iodide to afford two isomeric oxazolidinones, **214** and **215**, in almost equal yields, while the 4-phenyl-oxazolidinones (**215**) can be only isolated from reactions with *p*-methoxy-benzoyl and *p*-nitrobenzoyl isocyanates. Similarly, reactions with epichlorohydrin and with ethylene carbonate give the corresponding oxazolidinones **216** and **217**[172]. Considering these results, it is somewhat surprising that benzoyl isocyanate reacts with epichlorohydrin to give an open-chain product **218**, and oxiranes derived from ethylene, propylene and cyclohexene can only induce dimerization of the isocyanate[173].



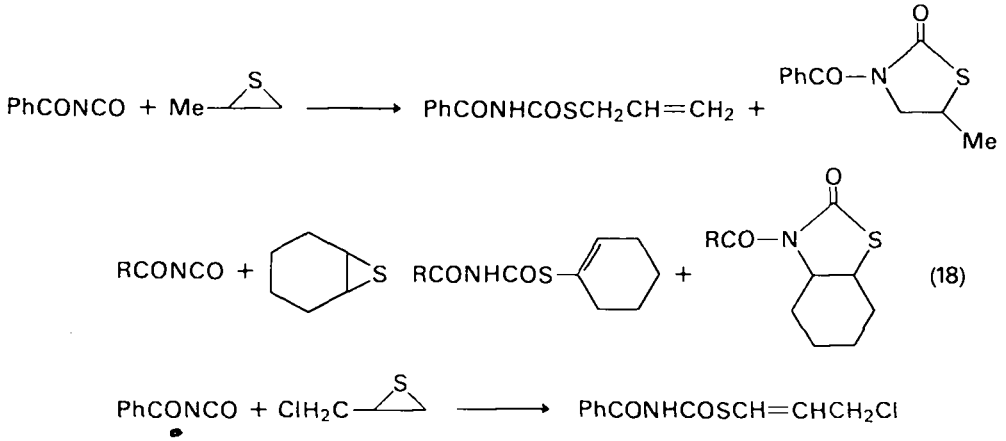
(214) (215)

(216) (217) (218)

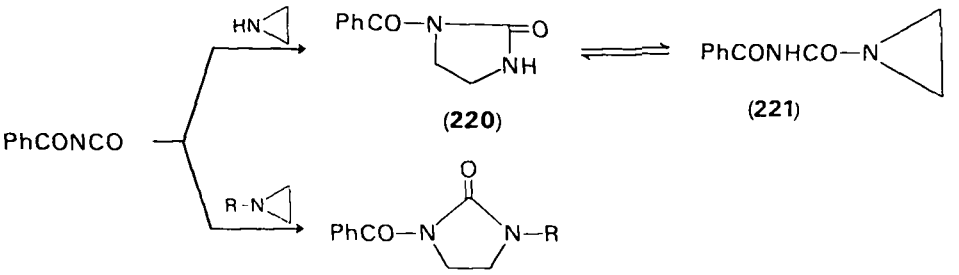
While the reaction of phenyl isothiocyanate with oxiranes in the presence of lithium chloride is accompanied by exchange of sulphur by oxygen and results in the formation of oxazolidinones **213** acyl isothiocyanates react with oxiranes to give 2-acylimino-1,3-oxathiolanes **219** via addition across the C=S bond[174]. Even on being heated, 1,3-oxathiolanes **219** do not isomerize to oxazolidinethiones, and their stability is attributed to the contribution of their mesomeric structures (equation 17).



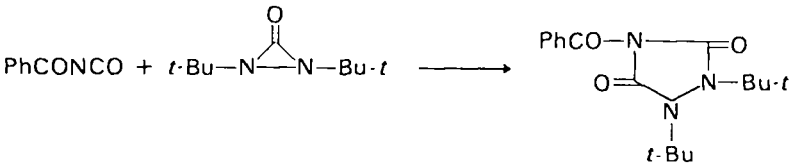
In the reaction of acyl isocyanates with thiiranes, a mixture of linear and/or cyclic products is obtained, with the former being usually predominant (equation 18)[173,175].



Benzoyl isocyanate reacts with aziridine at low temperature in diethylether to give 1-benzoylimidazolin-2-one (**220**), and the same reaction in carbon tetrachloride affords the urea **221**[175]. On dissolution in acetonitrile or deuteriochloroform, urea **221** rearranges rapidly into **220**. The back transformation of **220** into **221** can be brought about in carbon tetrachloride or even in the solid state but proceeds more slowly. The reaction of *N*-substituted aziridines with benzoyl isocyanate occurs at high temperature in the presence of lithium bromide as a catalyst and gives imidazolinones **222**[176].



(220) (221) (222)

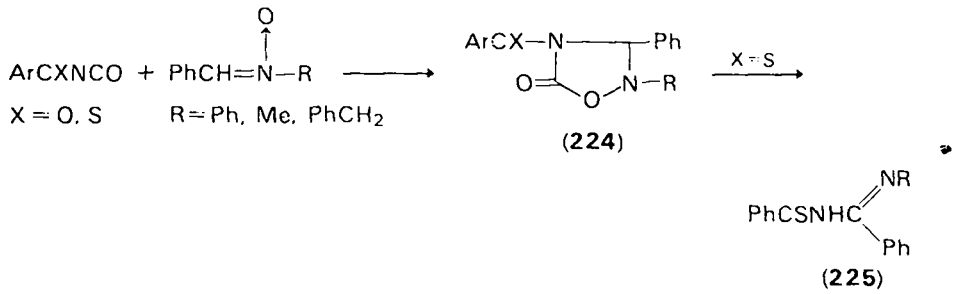


(223)

Recently, it has been reported that benzoyl isocyanate reacts with di-*t*-butyldiaziridinone to afford 1,2-di-*t*-butyl-4-benzoyl-1,2,4-triazolidine-3,5-dione (**223**)[177].

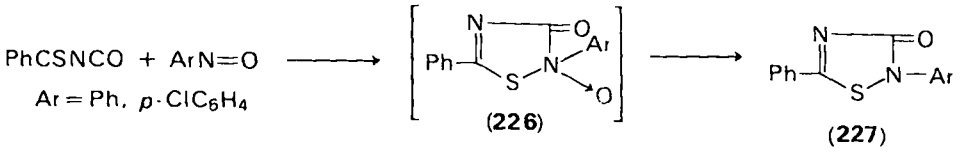
H. Reaction with Nitrones and Nitrosobenzenes

Benzoyl[89,90] and thiobenzoyl isocyanates[158] react with nitrones via a 1,3-cycloaddition, giving 1,2,4-oxadiazolines **224** respectively. However, the oxadiazolines **224**(X = S) are labile and easily change into the amidines **225** with the elimination of carbon dioxide[158].



(224) (225)

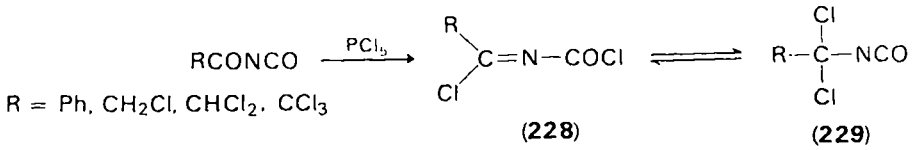
Thiobenzoyl isocyanate affords thiadiazole derivatives **227** by reaction with nitrosobenzenes, probably via the initial 1,4-cycloadduct **226**, followed by the exclusion of oxygen atom[158].

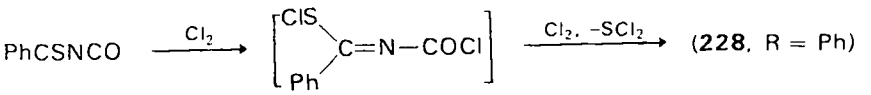


VI. MISCELLANEOUS REACTIONS

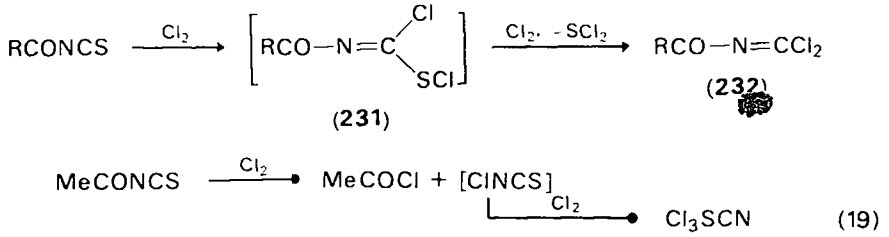
A. Chlorination

The chlorination of acyl and thioacyl derivatives of isocyanates and isothiocyanates affords dichlorides which are useful precursors for the synthesis of heterocyclic compounds. Benzoyl isocyanate is treated with phosphorus(v) chloride in refluxing chlorobenzene to give *N*-(α-chlorobenzylidene)carbamoyl chloride (**228**, R = Ph), while a mixture of *N*-(α-chloroalkylidene)carbamoyl chloride (**228**, R = alkyl) and α,α-dichloro alkyl isocyanate (**229**) is obtained from the same reaction of aliphatic acyl isocyanate[178]. The chlorination of thiobenzoyl isocyanate with chlorine gas at room temperature gives dichloride **228** (R = Ph) in good yield[179]. This reaction proceeds via an initial formation of *N*-(α-chlorosulphinylbenzylidene)carbamoyl chloride (**230**), followed by further chlorination with the concurrent elimination of sulphinyl chloride.





On the other hand, acyl isothiocyanates yield the corresponding acyl isocyanide dichlorides. For instance, chlorination of acyl isothiocyanate with chlorine gas at 0–50 °C affords the corresponding acyl isocyanide dichloride **232** in good yield[178,180,181]. Aluminium chloride or titanium tetrachloride can be used as a catalyst in the chlorination[182]. The reaction pathway for the formation of dichloride **232** can be viewed as proceeding



(231)

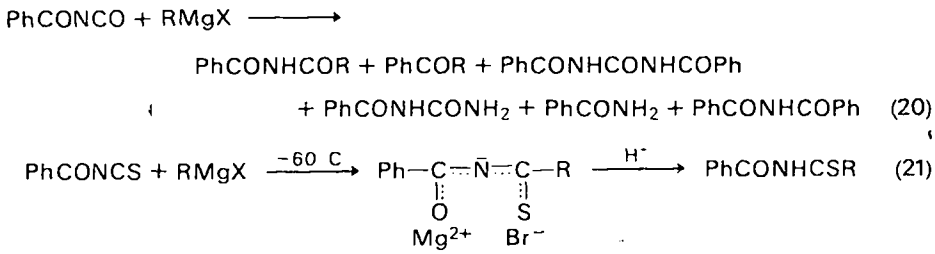
(232)

(19)

via an initial formation of *N*-(chloro-chlorosulphinylmethylene)carbonamide (**231**), followed by further chlorination with the elimination of sulphinyl chloride. In the case of acetyl isothiocyanate, acetyl chloride and trichlorothiocyanate are obtained as main products, together with a poor yield of dichloride **232** (R = Me) (equation 19).

B. Reaction with Organometallic Compounds

Benzoyl isocyanate reacts with Grignard reagents to give many kinds of products (equation 20), and the amount of each product depends on the type of Grignard reagent used, the sequence of reagent addition, and the ratio of isocyanate to Grignard reagent[183]. The reaction of benzoyl isothiocyanate with Grignard reagents affords *N*-benzoylthioamide (equation 21)[184].

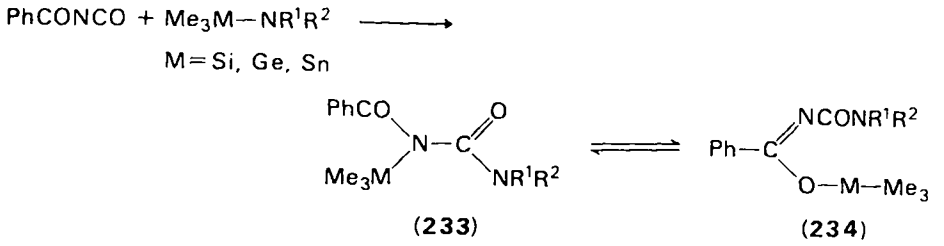


(20)

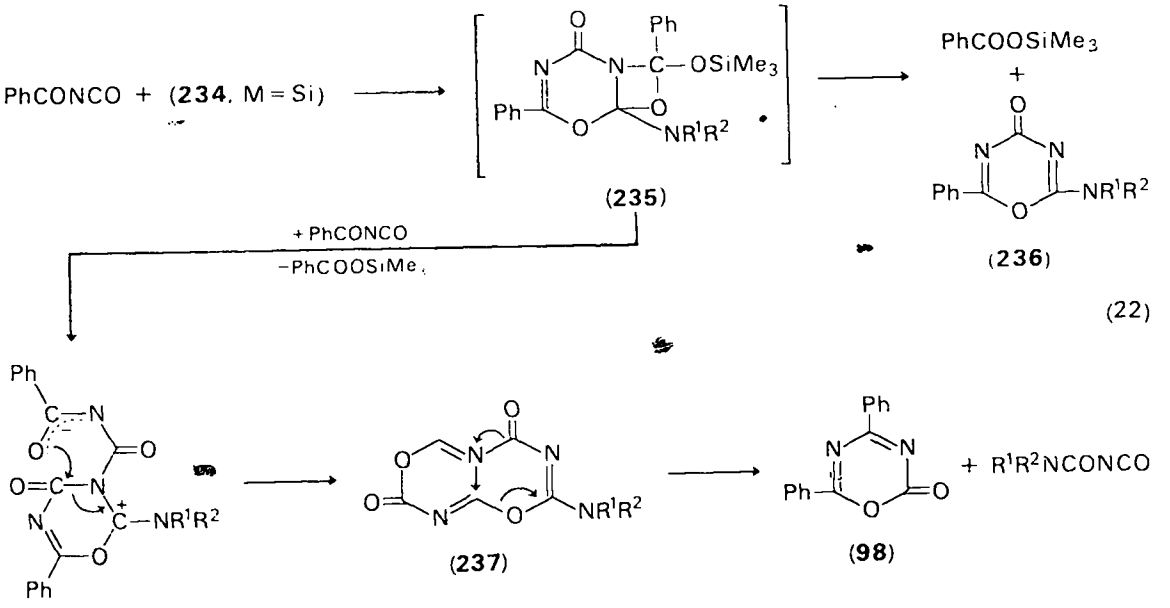
(21)

Benzoyl isocyanate can be inserted into the metal–nitrogen bond of *N*-trimethylmetal(IV)dialkylamines[185,186]. Thus the reaction of the isocyanate with equimolar amounts of *N*-trimethylmetal(IV)dialkylamines affords the insertion products **233**. It has been established by n.m.r. spectroscopy that the equilibrium between *N*-silylated **233** (M = Si) and *O*-silylated structures **234** (M = Si) exists in the adducts.

When the isocyanate is treated with *N*-trimethylsilyldialkylamines in a



2:1 molar ratio, trimethylsilyl benzoate is eliminated and 2-dialkylamino-6-phenyl-1,3,5-oxadiazin-4-one (**236**) and/or 2,4-diphenyl-1,3,5-oxadiazin-6-one (**98**) are formed. The relative yields of **236** and **98** are greatly affected by the nature of the alkyl substituents on the nitrogen atom. In all cases when **98** is isolated, the corresponding *N,N*-dialkylcarbamoyl isocyanates are identified in yields which correspond to those of **98**. The reaction pathway is illustrated in equation (22). The first step of the reaction is the addition of **234** to benzoyl isocyanate acting as a 1,4-dipole, giving the unstable intermediate **235**. A direct elimination of trimethylsilyl benzoate from **235** gives **236**. Further incorporation of the isocyanate, subsequent elimination of trimethylsilyl benzoate, and further liberation of *N,N*-dialkylcarbamoyl isocyanate from **237** results in the formation of **98**.



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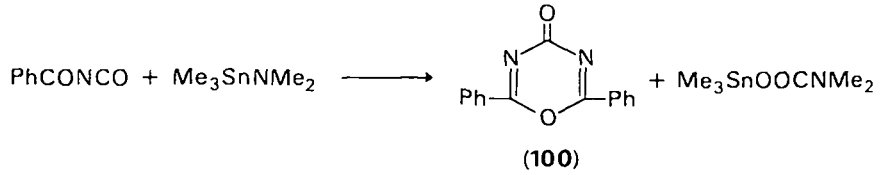


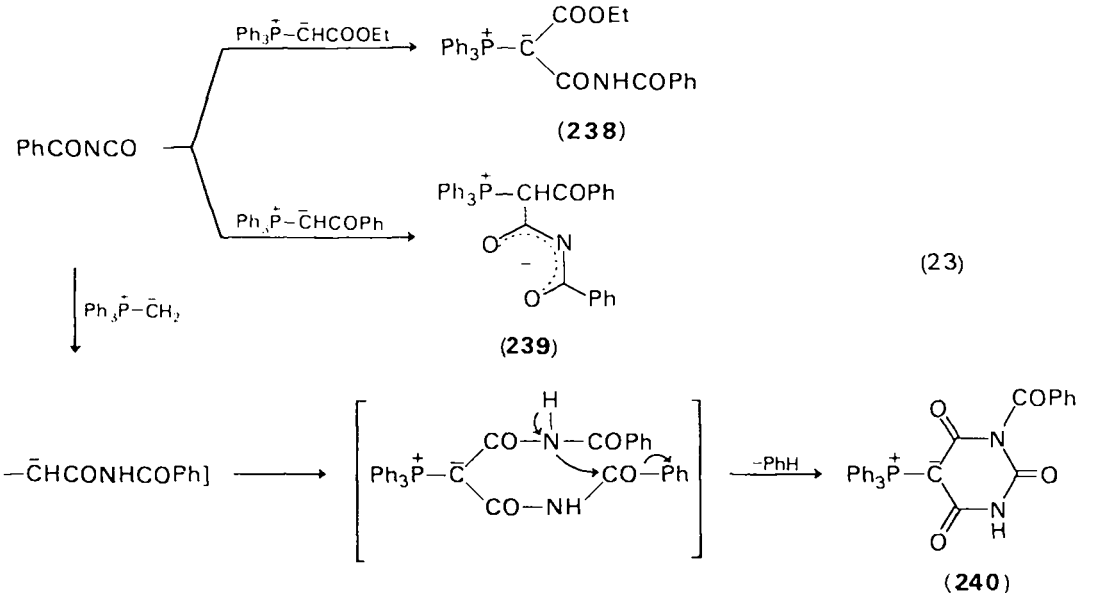
(100)

However, *N*-trimethylstannyldimethylamine reacts with an excess of the isocyanate to give 2,6-diphenyl-1,3,5-oxadiazin-4-one (**190**)[185].

C. Reaction with Ylides

The reaction of benzoyl isocyanate with phosphonium ylides gives products of different types, whose structures depend on the nature of the ylides used[187]. For instance, benzoyl isocyanate reacts with ethoxycarbonylmethylenephosphorane to give the stable benzoylcarbamoyl phosphonium ylide **238**, whereas the betaine **239** is formed by reaction with phenacylide. In the reaction with methylenephosphorane, however, 2 moles of the isocyanate react with the ylide to afford the cyclic ylide **240**, whose structure corresponds to that of the compound derived from bisbenzoylcarbamoyl ylide by the elimination of benzene (equation 23).

Benzoyl isocyanates react with ethyl (dimethylsulphuranilidene)acetate and dimethylsulphonium phenacylide to give the corresponding stable



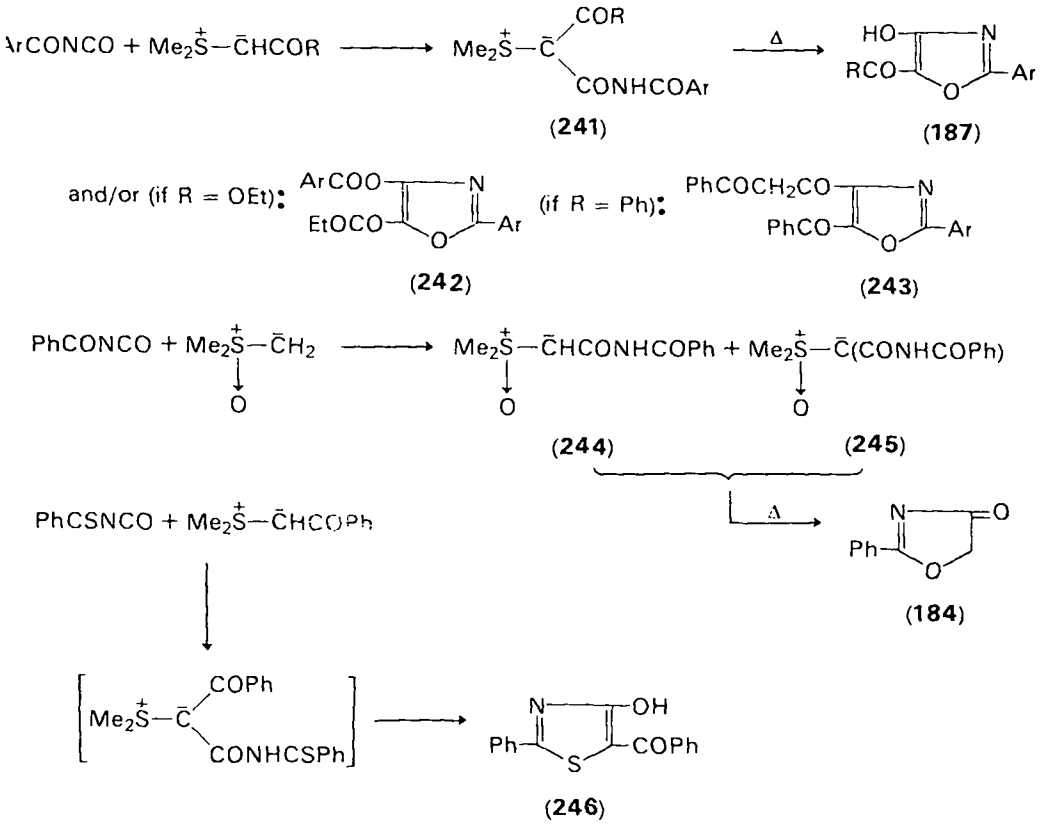
(238)

(239)

(23)

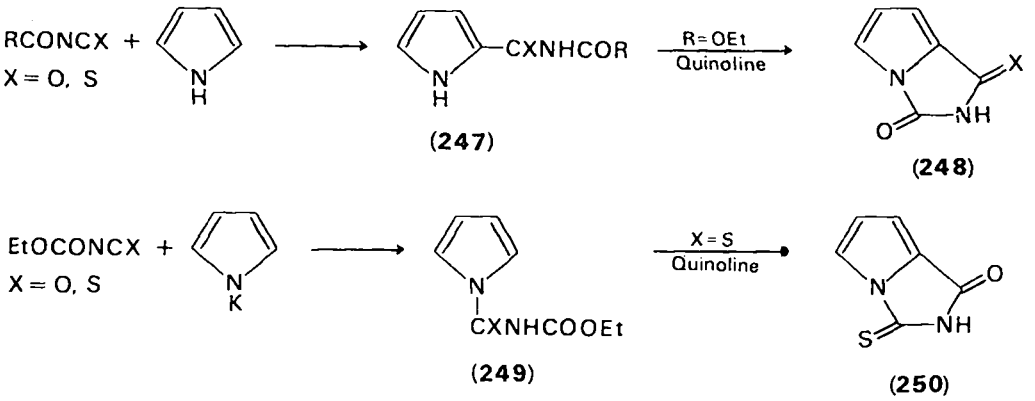
(240)

benzoylcarbamoylsulphonium ylides **241** which on pyrolysis, are converted into oxazoles **187** and/or **242** or **243**. Similarly, the reaction of the isocyanate with dimethyloxosulphonium methylide affords 1:1 adduct **244** and 2:1 adduct **245**. Pyrolysis of both the adducts **244** and **245** gives oxazolone **184**[156]. However, with dimethylsulphonium phenacylide, thiobenzoyl isocyanate affords the thiazole compound **246**[156].



D. Reaction with Pyrrole

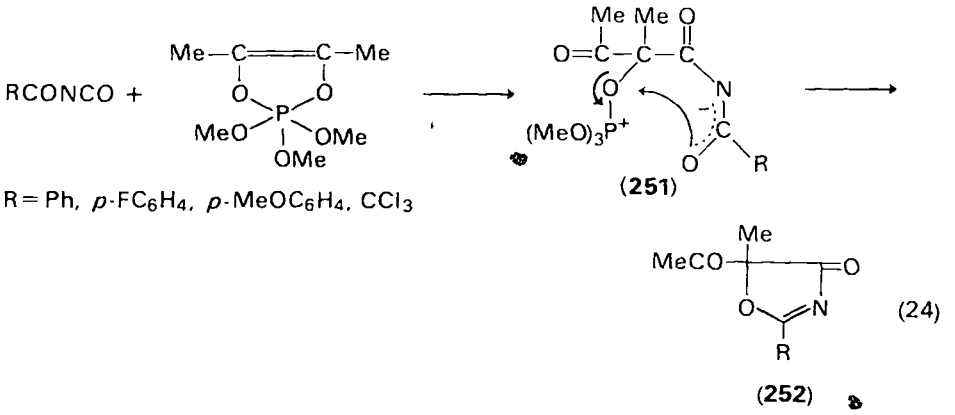
The reactions of pyrrole with trichloroacetyl isocyanate[188], ethoxycarbonyl isocyanate[189], and isothiocyanate[190] are known to yield the corresponding derivatives of pyrrole-2-carbox- and -thiocarboxamides **247**. *N*-Ethoxycarbonylpyrrole-2-carbox- and -thiocarboxamides **247** (R = OEt) are converted to the pyrrole-1,2-dicarboximides **248** by treatment with hot quinoline[189,190].



Pyrrolylpotassium reacts with ethoxycarbonyl isocyanate in tetrahydrofuran to form, after acidification, *N*-ethoxycarbonylpyrrole-1-carboxamide (**249**)[189]. Similarly, ethoxycarbonyl isothiocyanate affords the 1-thiocarboxamide **249** which on treatment with quinoline is converted to 1-thiopyrrole-1,2-dicarboximide (**250**)[190].

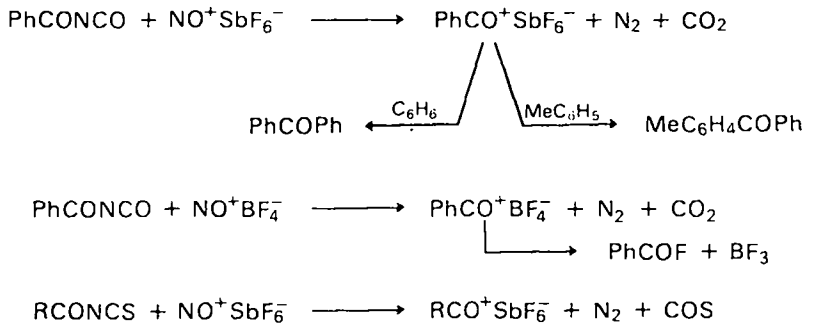
E. Reaction of Acyl Isocyanates with 2,2,2-Trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene[191]

Acyl isocyanates react with the dioxaphospholene to give the 2-oxazolin-4-ones **252**. The reaction proceeds probably via the addition of the dioxaphospholene to the isocyanate to form a dipolar adduct **251**, which undergoes an intramolecular displacement of trimethylphosphate by the acyl oxygen to yield **252** (equation 24).



F. Reaction with Nitrosonium Salts[192]

Acyl isocyanates and isothiocyanates react with nitrosonium salts to give oxocarbonium ions. For instance, the reaction of benzoyl isocyanate with $NO^+SbF_6^-$ in the presence of benzene in nitrobenzene affords benzophenone. Similarly, the benzoylation of toluene with benzoyl isocyanate and $NO^+SbF_6^-$ gives a 32% yield with an isomer distribution of 10·5% *o*-, 0·7% *m*-, and 88·8% *p*-methylbenzophenone, a typical electrophilic isomer distribution. When the reaction of the isocyanate is carried out with $NO^+BF_4^-$ at room temperature



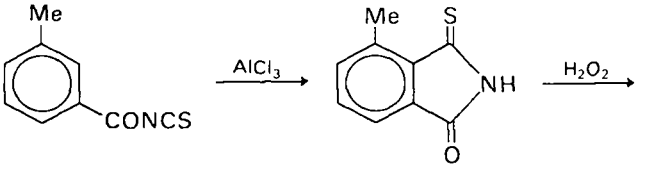
(25)

in the absence of aromatics, benzoyl fluoride is obtained through the decomposition of the relatively unstable oxocarbonium tetrafluoroborate. Acyl isothiocyanates react similarly to the isocyanates in the reaction with nitrosonium salts (equation 25).

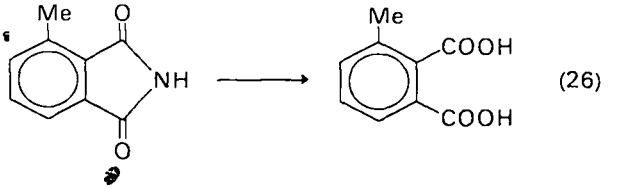
G. Cyclization of Acyl Isothiocyanates with Aluminium Chloride[193]

Under Friedel–Crafts conditions, benzoyl isothiocyanates undergo cyclization to monothiophthalimides, and phenylacetyl isothiocyanates give monothiohomophthalimides. The thioimides may be converted to their oxygen analogues, reduced to isoquinoline derivatives, or hydrolysed to the dicarboxylic acids.

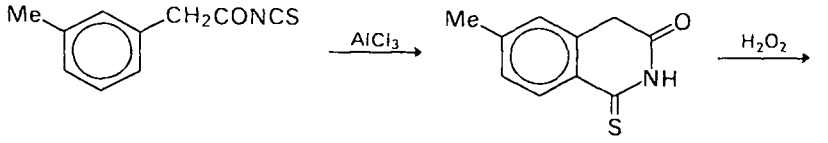
The cyclization shows great selectivity when two different *ortho* positions are open for ring closure. For instance, *m*-toluyl isothiocyanate gives exclusively the monothiophthalimide **253** resulting from carbonylation in the position *ortho* to the methyl group, thus providing a facile route to 3-methylphthalic acid and its derivative (equation 26). *m*-Tolylacetyl isothiocyanate, on the other hand, cyclizes to the opposite side, *para* to the methyl group, to give the monothiohomophthalimide **254**,



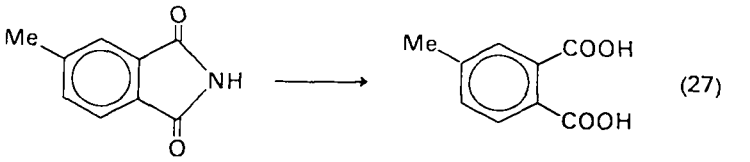
(253)



(26)



(254)

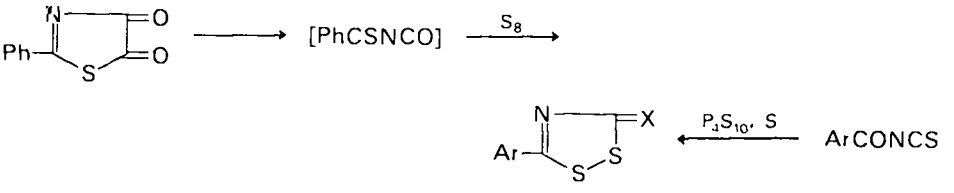


(27)

which gives 4-methylphthalic acid by ring contraction (equation 27). The reaction provides a general route to aromatic *ortho* dicarboxylic acids hitherto available only with difficulty or not at all.

H. Reaction with Sulphur

The reaction of aroyl isocyanate or isothiocyanate with sulphur provides a route to 5-aryl-3*H*-1,2,4-dithiazol-3-one or -3-thione. When



(255)

2-phenylthiazoline-4,5-dione which is a precursor of thiobenzoyl isocyanate (Section II.B), is heated with excess of sulphur at 120 °C, 5-phenyl-3*H*-1,2,4-dithiazol-3-one (**255**, Ar = Ph, X = O) is obtained in a 72% yield[134]. The reaction of aroyl isothiocyanates with P_4S_{10} in boiling xylene affords the 3-thione analogues **255** (X = S) in good yields[194].

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The Chemistry of Cyanates and Their Thio Derivatives
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CHAPTER 14

Syntheses and uses of isotopically labelled cyanates and related groups

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I. INTRODUCTION

Cyanates, thiocyanates and their *iso* isomers can be labelled on the functional group as well as elsewhere in the molecule. Although some examples of isotopic labelling on the chain will be given, this chapter presents a review of the methods by which labelling on the functional group with isotopic C, N, O or S, most frequently ^{14}C and ^{35}S, is achieved. In most instances the compounds are prepared as intermediates for further synthetic purposes and therefore the clear-cut distinction between syntheses and uses in treating the matter, rather than being real, is justified by its convenience. For the same reason, the synthetic subjects have been classified according to the nature of the final step in which the functional group is formed. We must point out, however, that the synthesis of the labelled precursors, although reported only in some cases, is as important as the final step because the recovery of the radioactive material depends on the overall process in which it is involved. The steps of the sequence are often classical synthetic organic reactions. They are modified and repeatedly checked for the best experimental conditions in order to work on a millimolar scale and to avoid contamination.

Cyanates and related groups and the compounds synthesized from them find, in most cases, practical use as tracers. The uses include applications in widely different fields ranging from biological and physiological to more technological research.

II. LABELLED INORGANIC IONS

The methods of obtaining labelled OCN^- and SCN^- ions are reported here since very often the two ions, particularly SCN^-, are important intermediates in the syntheses of products which can also be prepared starting from organic labelled isocyanates, thio- and isothiocyanates. The general procedures have been established by several workers in the

early Fifties, but many are now commercially available at high specific activity.

A. Alkali Cyanates: ^{14}C, ^{13}C, ^{15}N or ^{18}O

Oxidation of cyanide can, in principle, afford any labelled cyanate ion. The availability of differently labelled cyanide ions allows the corresponding cyanates to be obtained using a semimicro procedure which gives almost quantitative conversion. Oxidation by potassium permanganate in alkaline solution is carried out in the presence of cupric hydroxide (equation 1).

$$CN^- \xrightarrow[OH^-,\ Cu(OH)_2]{KMnO_4} OCN^- \qquad (1)$$

According to the method chosen, $KO^{14}CN$ [1,2,3], $KO^{14}C^{15}N$ [4] and $KO^{13}CN$ were obtained with only slight modifications of the procedure.

Molecular oxygen can also be used to carry out the oxidation. $K^{13}CN$ and $KC^{15}N$ have been oxidized by heating the cyanide in air or in an enclosed system under reduced oxygen pressure (100–200 torr)[5]. Under the last conditions the preparation of $K^{18}OCN$ was performed using oxygen with enrichment in the ^{18}O isotope in the 5% to 10% range[5].

Labelled cyanate has been prepared from labelled urea by melting with potassium carbonate (equation 2). The cyanate resulting

$$K_2CO_3 + 2^{14}CO(NH_2)_2 \longrightarrow 2\ KO^{14}CN + CO_2 + H_2O + 2\ NH_3 \qquad (2)$$

from this reaction possesses the entire radioactivity of the starting urea[6]. The procedure has been adopted with good yields by various authors[6,7,8] for the preparation of potassium [^{14}C]cyanate, of silver [^{14}C]cyanate (74%) and of [^{15}N]ammonium [^{14}C]cyanate[6]. More recently a similar method starting from barium [^{14}C]cyanamide has been described. According to this, barium cyanamide was heated at 700 °C with K_2CO_3 and SiO_2 to give 64% yield of $KO^{14}CN$[9]. The synthesis appears to be convenient since barium carbonate, the usual source of carbon isotopes, can be directly converted into barium cyanamide in an ammonia atmosphere with very good yield (96%).

The laborious procedures which are usually required to isolate the product are avoided in the method devised by Ratusky and Tykva[10], in which the exchange reaction is carried out in a sealed ampoule between molten potassium cyanate and $^{14}CO_2$. The exchange occurs without the

incursion of side reactions giving rise to random distribution of ^{14}C-radioactivity between cyanate and CO_2 molecules. On the other hand, in aqueous solution exchange does not occur between cyanate ion and sodium [^{14}C]carbonate, whereas it takes place between [^{14}C]urea and cyanate ion at 80 °C[11].

B. Alkali Thiocyanates: ^{14}C or ^{35}S

Though commercially available at present, labelled inorganic thiocyanates are still often synthesized starting with less expensive or more highly active radiochemical sources. The reaction between alkali cyanide and elemental sulphur has been favoured by most workers (equation 3).

$$KCN + S \longrightarrow KSCN \qquad (3)$$

Heating of potassium cyanide and sulphur in acetone under reflux appears to be the most favourable operative condition since the heterogeneous reaction takes place very rapidly[12]. By this method $KS^{14}CN$ [13] and $K^{35}SCN$ [14,15] were prepared. The last was also obtained in 85% yield running the reaction in boiling water[16], while the ^{14}C compound was recovered almost quantitatively when the reaction was carried out in ethanol[17]. Finally, the preparation of $K^{35}SCN$ was achieved by heating[18] or melting together the reactants[19]. Beside the possibility of obtaining $K^{35}SCN$ by digesting a mixture of $K_2{}^{35}S$, KCN and S[20], the method of labelling the thiocyanate ion by synthesis does not seem to offer efficient alternatives since generally the exchange reaction between SCN^- and radiochemical sources such as $^{14}CN^-$ [21,22], $^{35}S^{2-}$ [20,22], and $^{35}S_8$[23] fails to occur.

As far as the sources of radioactivity are concerned, the methods of obtaining alkali cyanides labelled with ^{14}C or ^{13}C and ^{15}N have been reviewed by Pichat[24]. Elemental ^{35}S is easily available commercially or from the oxidation (with acid iodine solutions) of barium sulphide which is prepared by reduction of barium sulphate with hydrogen at 900 °C[15].

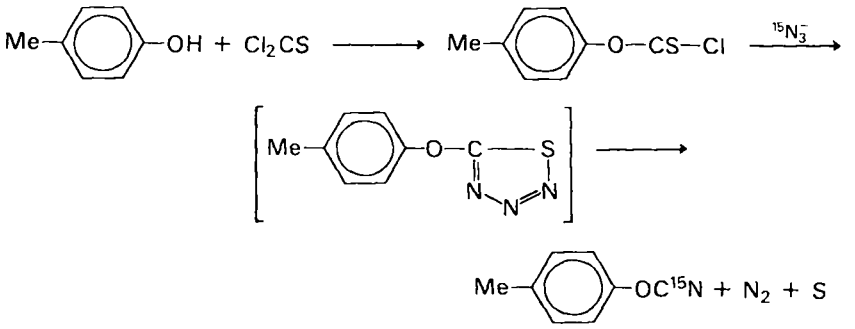
III. SYNTHESES OF LABELLED ORGANIC CYANATES, ISOCYANATES, THIOCYANATES AND ISOTHIOCYANATES

Introduction of labelled OCN and SCN groups into an organic moiety is accomplished both by exchange and by classical methods of organic synthesis. There is, however, a clear prevalence in labelling of the cyanate

function through synthesis while exchange is widely used for the thiocyanate group.

A. Cyanates

The preparation of aryl and of alkyl cyanates dates back not more than 10 years. Reich and Martin[25] reported the synthesis of the 4-tolyl[^{15}N]-compound through equation (4)



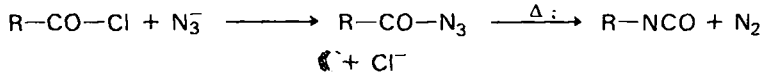
(4)

B. Isocyanates

14-Carbon isotopic substitution on the functional group is by far the predominant one in the labelling of isocyanates (see Table 1). Most workers adapt the Curtius rearrangement starting from a labelled carboxylic acid. Less frequently the reaction between amines and phosgene has been used.

1. Curtius rearrangement of acyl azides

The Curtius rearrangement of acyl azides appears to be the most popular way of obtaining labelled isocyanates. It is efficient, simple to carry out and can easily be adapted to label the isocyanate group on C, N or O starting from easily available radiochemical sources. In most cases the reaction involves the preliminary formation of the acyl chloride, its conversion by reaction with azide ion to an acyl azide and finally thermal rearrangement of the latter to isocyanate (equation 5)



(5)

The known labelled isocyanates are usually ^{14}C-tagged on the carbonyl carbon. The synthesis involves the conversion of $^{14}CO_2$ to the acyl chloride via Grignard carbonation (equation 6).

$$RMgX \xrightarrow{^{14}CO_2} R-{}^{14}COOH \xrightarrow{SOCl_2} R-{}^{14}COCl \qquad (6)$$

Obviously the same procedure allows the labelling of isocyanate at oxygen and nitrogen if $C^{18}O_2$ or [^{15}N]azide ion respectively is used.

The method was used by Keglevic and Leonhard[26] to convert 1-naphthoic[^{14}C]acid into 1-naphthyl[^{14}C]isocyanate in 80–85% yield (based on 1-naphthoic acid) and by Logan and Odel[27] to obtain 4-chlorophenyl[^{14}C]isocyanate in anhydrous toluene by successive steps carried out without isolation of the intermediates.

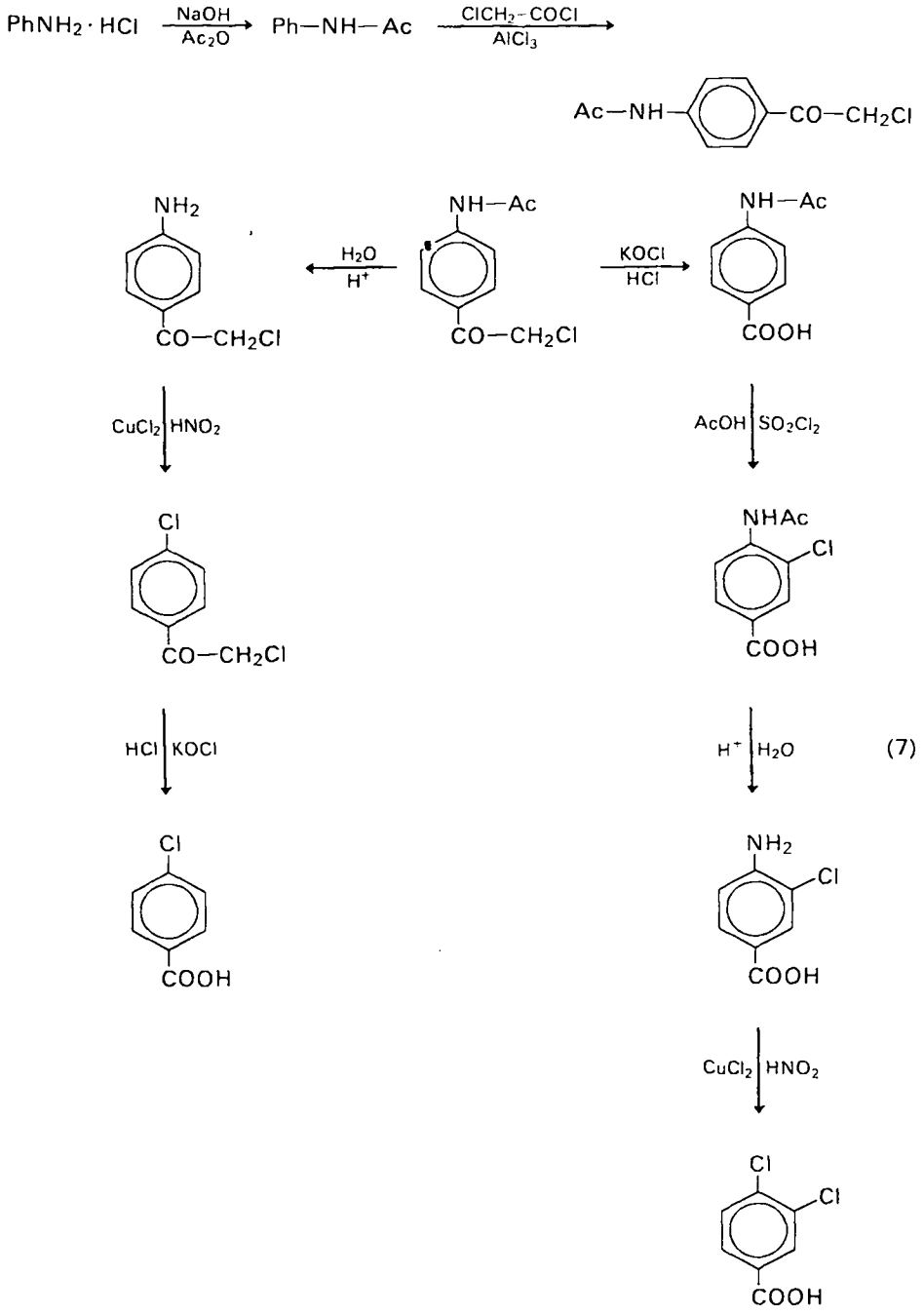
In most cases isocyanates are not isolated but are used without purification for further syntheses. For example methyl [^{14}C]isocyanate was prepared from [^{14}C]acetyl chloride in benzene at 140 °C and then converted to *N*-methylcarbamates on a 0·5 mmol scale in overall yields of 40–70%[28].

Yields of higher than 80% have been reported for the preparation of [^{14}C]carbonyl-labelled phenyl isocyanate starting from [^{14}C]benzoic acid[29] or [^{13}C]benzoic acid[30]. Besides slight differences in obtaining the azide intermediate, the Curtius rearrangement was again carried out by heating in benzene under anhydrous conditions.

Substituted ureas labelled in different positions have been prepared from 3,4-dichlorophenyl and 4-chlorophenyl isocyanates ^{14}C-labelled in both ring and carbonyl group[31]. The complete radiochemical syntheses of the four isocyanates have been developed. Starting from the corresponding [^{14}C]carbonyl acids, the 3,4-dichloro and the 4-chloro compounds were obtained by the usual three-step procedure (equation 5) in at least 78 and 80% yields respectively. The ring-labelled compounds were similarly synthesized from the corresponding acids which, in turn, were obtained from the ring-labelled aniline hydrochloride in accordance with equation (7).

The eight- and nine-step processes to get the two isocyanates gave yields of 53 and 22%, respectively. The entire synthesis is carefully described and the individual reactions may be useful in the synthesis of other radiochemical compounds.

Besides chlorides, other acid derivatives can be used for the radiochemical synthesis of acyl azide intermediate. Thus the synthesis via azide of phenyl [^{14}C]isocyanate was accomplished starting from methyl [^{14}C]benzoate[32] (equation 8).


PhNH2 · HCl
NaOH
Ac2O
Ph—NH—Ac
ClCH2—COCl
AlCl3
Ac—NH—CO—CH2Cl
NH2
CO—CH2Cl
H2O
H+
NH—Ac
CO—CH2Cl
KOCl
HCl
NH—Ac
COOH
CuCl2 HNO2
Cl
CO—CH2Cl
HCl KOCl
Cl
COOH
AcOH SO2Cl2
NHAc
Cl
COOH
H+ H2O
NH2
Cl
COOH
CuCl2 HNO2
Cl
Cl
COOH

(7)

$$Ph-{}^{14}COOMe \xrightarrow{NH_2-NH_2} Ph-{}^{14}CONH-NH_2 \xrightarrow{HNO_2}$$

$$Ph-{}^{14}CO-N_3 \xrightarrow{\Delta} Ph-N{}^{14}CO \qquad (8)$$

and that of methyl [^{14}C]isocyanate starting from [1,1-^{14}C]acetic anhydride. In the last case, the radioactive recovery was 35%[33] (equation 9).

$$Me-{}^{14}CO-O-{}^{14}CO-Me + NaN_3 \longrightarrow$$

$$Me-N{}^{14}CO + N_2 + Me{}^{14}COONa \qquad (9)$$

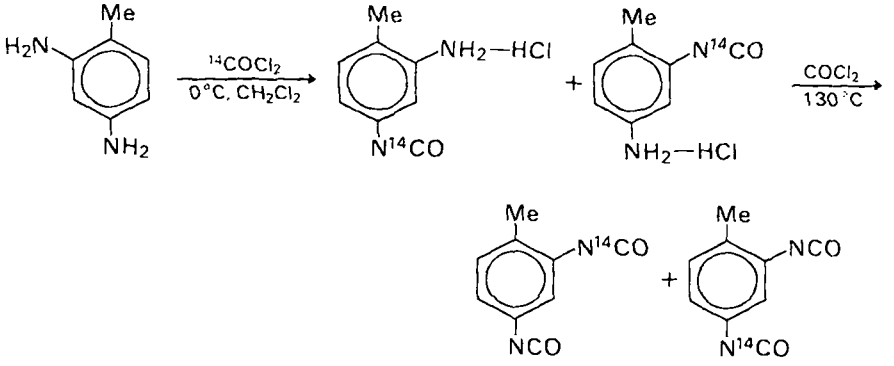
2. From amines by reaction with phosgene or related reagents

The general method for preparation of isocyanates from amines and phosgene can be modified to meet the special requirements in synthesizing specific labelled compounds. The commercial availability of [^{14}C]-phosgene allows use to be made of this one-step synthesis (equation 10).

$$R-NH_2 + \begin{matrix} Cl \\ {}^{14}CO \\ Cl \end{matrix} \longrightarrow RN{}^{14}CO + 2\,HCl \qquad (10)$$

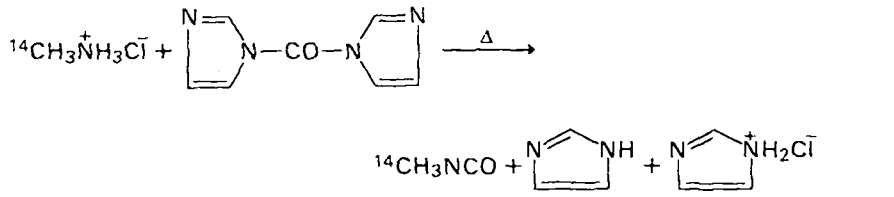
According to equation (10), 2-tolyl and 4-tolyl isocyanates were prepared from the corresponding toluidine hydrochloride in benzene. The reaction was conducted by heating in a closed system at moderate pressure obtaining the two compounds in 62 and 74% radioactive yield, respectively[34]. No mention of the yield and experimental conditions, however, was given for the preparation of 3,4-dichlorophenyl [^{14}C]isocyanate from the 3,4-dichloroanilinium salt[35].

Two different procedures have been reported in detail for the preparation of 2,4-tolylene [^{14}C]diisocyanate (TDI). By using 2,4-tolylene diamine dihydrochloride in dry toluene, 41% radioactive yield was reached but with a different radioactivity distribution in the two isocyanate groups[34]. It was suggested that this phenomenon arises from the different basicity of the two amino groups combined with the different timing in the addition of unlabelled and labelled phosgene. On the other hand, [^{14}C]TDI labelled at only one of the isocyanate groups was obtained in 57% yield (44% radiochemical) by Wilkniss and Levine[36] who applied a two-step procedure (equation 11) starting from free diamine.



(11)

Besides phosgene the direct carbonylation of amines can be satisfactorily achieved with other reagents. Thus methyl [^{14}C]isocyanate was prepared by pyrolysis of a mixture of [^{14}C]methylamine hydrochloride and *N,N'*-carbonyldiimidazole[37,38] with about 75% yield (equation 12).



(12)

A different sequence for the synthesis of the same isocyanate has been reported with an overall yield of 84% starting from [^{14}C]methylamine hydrochloride[39] (equation 13).

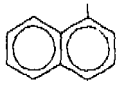
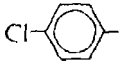
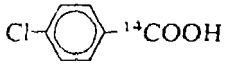
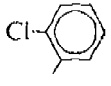
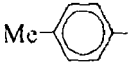
$$^{14}CH_3\overset{+}{N}H_3Cl^- + Ph_2N{-}CO{-}Cl \xrightarrow[40\text{-}50\ C]{NaOH}$$

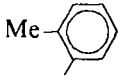
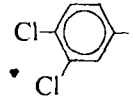
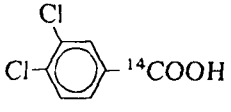
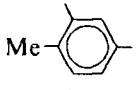
$$Ph_2N{-}CO{-}NH{-}{}^{14}CH_3 \xrightarrow{\Delta} {}^{14}CH_3{-}NCO + Ph_2NH \qquad (13)$$

3. By exchange with phenyl [^{14}C]isocyanate

The known tendency of isocyanates to dimerize in the presence of a suitable catalyst and the thermal dissociation of the formed dimer allows the ^{14}C scrambling between different isocyanates (equation 14). Ötvös and coworkers[32] found that labelled phenyl isocyanate equilibrates with inactive alkyl isocyanates both in the presence and in the absence of dimethyl phenyl phosphine as catalyst, suggesting for the intermediate dimer the structure 1,3-diaryl-1,3-diazacyclobutane-2,4-dione.

TABLE 1. Labelled isocyanates

Alkyl or aryl group	Source of isotope	Procedure of labelling	Position of labelling	Reference
	$^{14}CO_2$	Azide	$-N^{14}CO$	26
Ph	Ph—^{14}COOH	Azide	$-N^{14}CO$	29
	Ph—^{14}COOMe	Azide	$-N^{14}CO$	32
	Ph—^{13}CNO	Isomerization	$-N^{13}CO$	40
	Ph—^{13}COOH	Azide	$-N^{13}CO$	30
		Azide	$-N^{14}CO$	27, 31
	[^{14}C]PhNH$_2$	Azide	Ring	31
	$^{14}COCl_2$	Amine	$-N^{14}CO$	34

	$^{14}COCl_2$	Amine	$-N^{14}CO$	34
	$[^{14}C]PhNH_2$	Azide	Ring	31
		Azide	$-N^{14}CO$	31
	$^{14}COCl_2$	Amine	$-N^{14}CO$	35
 (TDI)	$^{14}COCl_2$	Amine	$-N^{14}CO$	34, 36
Me	$Me^{14}COCl$	Azide	$-N^{14}CO$	28
	$(Me^{14}CO)_2O$	Azide	$-N^{14}CO$	33
	$[^{14}C]MeNH_2$	Carbodiimidazole	$[^{14}C]MeNCO$	37, 38
	$[^{14}C]MeNH_2$	$Ph_2N-COCl$	$[^{14}C]MeNCO$	39
	$PhN^{14}CO$	Exchange	$-N^{14}CO$	32
Et	$PhN^{14}CO$	Exchange	$-N^{14}CO$	32
i-Pr	$PhN^{14}CO$	Exchange	$-N^{14}CO$	32

$$R{-}NCO + Ph{-}N^{14}CO \longrightarrow R{-}N^{14}CO + Ph{-}NCO \qquad (14)$$

Thermal reaction at 140 °C without solvent afforded the labelling of methyl, ethyl and isopropyl isocyanates in over 80% yield while milder conditions (room temperature, solvent anisole) were required when the reaction was run in presence of the catalyst, giving an almost quantitative recovery of alkyl isocyanates.

4. By isomerization of nitrile oxides

The thermal rearrangement of nitrile oxides to isocyanates (equation 15)

$$R{-}CNO \xrightarrow{\Delta} R{-}NCO \qquad (15)$$

is a process which, in principle, could be applied to the synthesis of labelled isocyanates. However, the longer procedure while starting from the same reagents (labelled acids), seldom has high yield of the rearrangement and is scarcely competitive. Recently, phenyl [^{13}C]isocyanate and 4-deuterophenyl isocyanate have been formed via this method[40].

C. Thiocyanates

There are few papers in the literature devoted to the preparation of labelled thiocyanates. Some of them mention the substitution of a halide or ester group by thiocyanate ion as a method which appears to be the most useful route for thiocyanates but not for isothiocyanates. The general features of the reaction are well known since much work has been devoted to this subject. In this section the peculiar aspects concerning the possibility of a successful labelling of thiocyanates and isothiocyanates are discussed.

1. By replacement reaction with labelled thiocyanate ion

a. *Substitution reaction.* The nucleophilic reaction of alkali thiocyanates with halides or similar substrates is a widely used method for synthesizing labelled organic thiocyanates. However, the bidentate character of this ion may also give rise to the formation of the isomeric isothiocyanate as a consequence of the attack by the nitrogen end of the SCN^- ion (equation 16).

$$R{-}X + SCN^- \begin{cases} \longrightarrow R{-}SCN \\ \longrightarrow R{-}NCS \end{cases} + X^- \qquad (16)$$

The main feature of this phenomenon is the increase in the isothiocyanate yield as the carbonium ion character of the electrophilic centre increases. The matter has been reviewed by Fava[41]. The displacement at saturated primary and secondary halides in dipolar protic and aprotic solvents gives the corresponding thiocyanates in very good yield. This appears from the results obtained in experiments carried out both with labelled and unlabelled[42] ionic thiocyanate. Thus from the corresponding bromides, γ-methyl allyl[^{35}S]thiocyanate in dimethylformamide[43], 1-benzoylamino-2-[^{35}S]thiocyanoethane in ethanol (90% yield)[44], and 2-[^{35}S]-thiocyano-3-bromopropylamine hydrobromide in water (77%)[16] were obtained by reaction with K^{35}SCN. On changing the organic moiety, in going from primary to secondary and tertiary alkyl to aryl alkyl substrates, the relative amount of isothiocyanate progressively increases since the structural effect increases both the rate of substitution by the nitrogen end of the ion and the rate of isomerization of the initially-obtained thiocyanate (equation 17).

$$R{-}SCN \longrightarrow R{-}NCS \qquad (17)$$

Table 2 reports the relative nucleophilicities of the N and S ends obtained for the reaction between K^{35}SCN and benzyl and isopropyl halides[45] in acetonitrile at 50 °C.

Less satisfactory yields of thiocyanate are obtained in the reaction of diphenylmethyl[46,47] and allyl substrates[46], as shown in Tables 3 and 4 which report the yield of isothiocyanate in the two classes of compounds.

The formation of the isomeric product becomes predominant or exclusive in the case of tertiary substrates. Thus the reaction of *t*-butyl chloride with alkali thiocyanate gives a yield of 22% isothiocyanate[48] whereas with triphenylmethyl halides the yield of trityl isothiocyanate depends upon the nature of substituents in the ring; for example, with tris-*p*-nitrophenylmethyl bromide, isothiocyanate is formed in 33% yield[49] while the corresponding isomer is the only product in the reaction of trityl chloride[50]. Thus, the displacement reaction on trityl halides by SCN^- is a good method for obtaining the trityl isothiocyanate instead of the corresponding isomer.

b. *Exchange reaction.* The isotopic exchange between ionic labelled thiocyanate and organic thiocyanates has been found to be generally useful for the labelling of thio- and isothiocyanates, since the exchange is a particular case of a substitution reaction where the leaving-group, SCN, behaves very like a halide ion. Therefore the ratio of thio–isothio isomers in the 'product' mixture depends on the same factors which govern the displacement reaction of halides.

TABLE 2. Relative rate of formation of thio- and isothiocyanates in the reaction between benzyl and isopropyl halides, R—X, and potassium [^{35}S]thiocyanate in acetonitrile at 50 °C

R	$PhCH_2$—	$PhCH_2$—	$PhCH_2$—	4-$MeC_6H_4CH_2$—	4-$NO_2C_6H_4CH_2$—	*i*-Pr
X	Cl	Br	I	Br	Br	I
$\frac{k_S}{k_N}$	415	840 950[a]	1300	220	730	85

[a] Solvents: ethanol and acetic acid (separately).

TABLE 3. Yields of isothiocyanate from diphenylmethyl bromides and KSCN in acetone at room temperature

Substrate	Ph_2CH—	(4-MeC_6H_4)$_2$CH—	(4-ClC_6H_4)$_2$CH—	(4-$NO_2C_6H_4$)PhCH—	(4-MeC_6H_4)PhCH—
% iso	5	17	<2	Trace	10

The isotopic exchange has been shown to be an important tool for investigating the mechanism of the isomerization and ionization of organic thiocyanates, and therefore the kinetic data available allow estimation of the yields of radioactivity intake in comparison with other processes which may occur simultaneously (isomerization, solvolysis, etc.). Thus methyl, ethyl, isopropyl, *n*-butyl, benzyl and allyl thiocyanates exchange with potassium [^{35}S]thiocyanate in cyclohexanone at moderate rates at 100–130 °C[19]. *n*-Butyl thiocyanate has been studied also in DMF at 145 °C and gave exchange with some solvolysis and isomerization[51]. Under the same conditions[19] phenyl thiocyanate does not exchange appreciably, while the more activated 2,4-dinitrophenyl thiocyanate is labelled at the carbon atom by the exchange reaction with $S^{14}CN^-$ in dimethylformamide at room temperature[52].

Benzyl [^{35}S]thiocyanate can be prepared by exchange with $^{35}SCN^-$ in methyl ethyl ketone and acetonitrile between 50 and 70 °C, with almost exclusive formation of the thio isomer which is kinetically favoured by a factor of 10^2–10^3 [53]. Exchange reactions of benzhydryl thiocyanate have been extensively studied and in this case the thiocyanate is clearly the less favoured isomer. Thus the 4,4'-dimethyl compound shows at 0 °C k_S/k_N ratios of 5 and 4·2–7·8 in acetonitrile[54,55] and acetone[55], respectively, values which are close to that (3·8) of a carbonium ion reaction such as the deamination of 4-chlorobenzhydryl amine in presence of $^{35}SCN^-$ [56]. In the triphenylmethyl series a ratio k_S/k_N of 9 has been found for the exchange of tris-*p*-nitrophenyl methyl thiocyanate with $^{35}SCN^-$ in acetone[57].

In those cases where the labelled thiocyanate is formed together with some isothiocyanate, a careful choice among the usual separation methods must be made in order to minimize isomerization. In a few cases a chemical method of separation suitable for micro or semimicro synthesis has been devised in order to get isomer-free thiocyanate; isothiocyanate is converted into the corresponding thiourea by reaction with a difunctional amine (3-dimethylamino-1-propylamine), the perchlorate of which is separated by filtration and/or aqueous extraction. 4,4-Dimethylbenzhydryl, 4-chlorobenzhydryl, benzhydryl and tris-*p*-nitrophenylmethyl compounds have been obtained by this procedure[58].

2. By replacement reaction with labelled cyanide ion

Substitution reaction at the sulphur atom by cyanide ion can be used to prepare thiocyanates labelled on carbon and nitrogen. The labelling of methyl, ethyl, isopropyl, *t*-butyl, benzyl and phenyl [^{14}C]thiocyanates

TABLE 4. Yields of isothiocyanate from substituted allyl halides and alkali thiocyanates in acetone at room temperature

Substituent	None	α-Me	γ-Me	γ-Me	γ-Me	α,α-diMe
Halide	Br	Br	Br	Br	Cl	Cl
% iso	≃2	≃2	5	4[a,b]	67[b]	65 + 18[b]

[a] In acetonitrile at 0 °C.
[b] S_Ni product.

has been accomplished by the exchange reaction with $^{14}CN^-$ (K and Hg) in methanol at 25 °C[21] (equation 18)

$$R—S—CN + {}^{14}CN^- \longrightarrow R—S^{14}CN + CN^- \quad (18)$$

The displacement of the sulphite ion from organic thiosulphates (Bünte salts) has been used to obtain 2-aminoethyl [^{15}N]thiocyanate[59] (equation 19).

$$R—S—SO_3^- + C^{15}N^- \longrightarrow R—SC^{15}N + SO_3^{2-} \quad (19)$$

D. Isothiocyanates

1. By exchange on isothiocyanates

The stability of isothiocyanates under rather drastic thermal conditions allows the exchange to be carried out with several labelled reagents. This reaction is of general use in labelling with ^{35}S since it offers a synthetic route for preparing compounds of widely different structure.

a. *Exchange with elemental 35-sulphur.* The exchange with $^{35}S_8$ has been used successfully to prepare labelled isothiocyanates of aryl, aryl–alkyl and alkyl structure (equation 20)

$$R—NCS + {}^{35}S \longrightarrow R—NC^{35}S + S \quad (20)$$

Phenyl and ethyl isothiocyanates have been labelled by this procedure using decalin as solvent[60]. Under the same conditions (180–190 °C) or in the absence of solvent, Augustin and Drobnica[18,61] were able to obtain phenyl, 4-bromophenyl, benzyl, 4-bromobenzyl, 4-diphenyl, 1- and 2-naphthyl isothiocyanates. Moreover, the same authors carried out some kinetic experiments in order to determine the optimal conditions under which exchange occurs at sufficient rate with negligible decomposition. They claim that the great advantage of this method is that it is possible to prepare compounds having high specific activity directly. The same procedure allowed Moye[62] to obtain *n*-dodecyl isothiocyanate in the

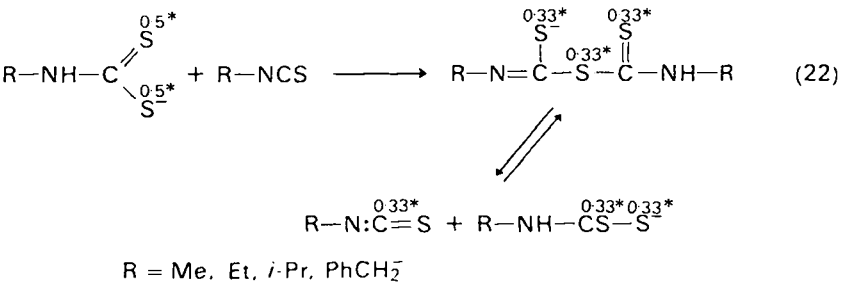
absence of solvent at ~165 °C. After the exchange had been completed, the reaction mixture was passed through a copper column in order to remove elemental sulphur. Although the column chromatography purification of thiocyanates must be used with care because they can in some cases undergo isomerization, the separation of isothiocyanates from reagents and eventual decomposition products can be satisfactorily carried out by this method. Distillation, too, can be confidently used to obtain pure products.

A particular case of exchange reaction with radioactive elemental sulphur is the formation of labelled methyl [^{35}S]isothiocyanate by direct irradiation of solutions of unlabelled compound in carbon tetrachloride in a nuclear reactor[63]. This is probably the result of the hot reaction of replacement of a sulphur atom in the CH_3—NCS molecule by ^{35}S recoil atom generated *in situ* by the nuclear reaction $^{35}Cl(n, p)^{35}S$, the chlorine source being carbon tetrachloride used as solvent.

b. *Reaction with* $H^{35}S^-$ *and* $H_2{}^{35}S$. Methods have been proposed to prepare [^{35}S]isothiocyanates through their reaction with labelled HS^- to form dithiocarbamate intermediates (equation 21).

$$R{-}NCS + H^{35}S^- \longrightarrow R{-}NH{-}CS{-}{}^{35}S^- \qquad (21)$$

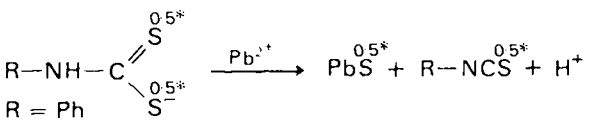
From this intermediate two different procedures have been devised to obtain labelled isothiocyanates: the first entails equilibration of this intermediate with another isothiocyanate (equation 22),



(22)

R = Me, Et, *i*-Pr, $PhCH_2^-$

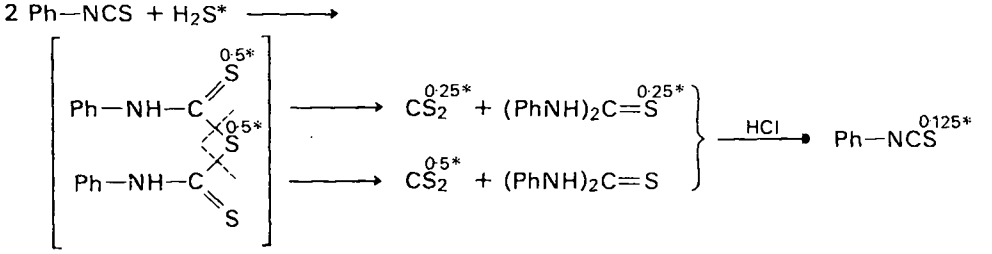
a reaction which has been found to occur very rapidly[64]; the second, which makes use of ammonium instead of sodium hydrosulphide, is based upon the decomposition of the dithiocarbamate intermediate with Pb^{2+} to recover isothiocyanate[65] (equation 23).



(23)

From (22) and (23) it appears that the last method offers a better isotopic yield unless a very large excess of isothiocyanate is used.

An alternative way of synthesizing phenyl isothiocyanate by reaction with $H_2{}^{35}S$ was also accomplished[65]. Through the dithiocarbamic acid and diphenyl thiourea, phenyl isothiocyanate containing one-eighth of the original activity was obtained (equation 24).



c. *Exchange with [^{35}S]thiocyanate ion.* Owing to the relatively high stability of the C–N bond, the importance of this method of labelling (equation 25) is almost negligible with respect to that concerning thiocyanate substrates.

$$R{-}NCS + {}^{35}SCN^- \longrightarrow RNC^{35}S + SCN^- \qquad (25)$$

The data of radioactivity intake reported by Fava and Iliceto[19,53,66] are instructive. The half-life times of exchange of primary as well as tertiary isothiocyanates are very long in acetone, whereas in cyclohexanone they show appreciable exchange only at temperatures at which considerable decomposition takes place. Table 5 reports the approximate half-life

TABLE 5. Isotopic exchange between alkyl isothiocyanates and $K^{35}SCN$ in cyclohexanone[a]

R	T(°C)	$t_{0.5}$(min)
Me	170	≃300
Et	180	≃1300
	120	$>3.7 \times 10^4$[b]
i-Pr	180	≃800
n-Bu	170	≃700
t-Bu	170	≃130
	120	$>3.7 \times 10^4$[b]
$PhCH_2$—	170	49
Allyl	110	32

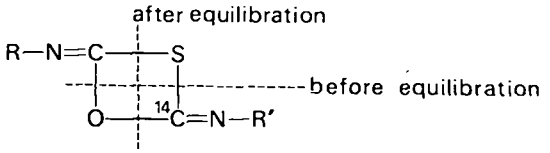
[a] [R—NCS] = [$K^{35}SCN$] = 0·23 M (Reference 66).
[b] Acetone. [RNCS] = [$K^{35}SCN$] = 0·1 M (Reference 19).

times for such reactions. It appears that intake of radioactivity occurs at convenient rates only for benzyl and allyl compounds.

d. *Exchange with phenyl [^{14}C]isocyanate.* A successful attempt to prepare phenyl [^{14}C]isothiocyanate by reaction of inactive compound with phenyl [^{14}C]isocyanate was reported by Ötvös and coworkers[32] (equation 26).

$$R'—N^{14}CO + R—NCS \rightleftharpoons R'—NCO + R—N^{14}CS \qquad (26)$$

By heating at 180 °C for several hours, equilibration of radioactivity was achieved and [^{14}C]isothiocyanate could be isolated. A mechanism has been postulated involving the intervention of the dimer of structure:



If this mechanism is correct, the method should be applicable also for the sulphur and carbon labelling of isothiocyanates.

2. From amines

Both alkyl and aryl amines react with carbon disulphide or thiophosgene to give isothiocyanates. This general method of synthesis has been used to prepare alkyl and aryl isothiocyanates labelled at the thiocyanate group with 14-carbon, 15-nitrogen and 35-sulphur.

a. *By reaction with carbon disulphide.* Reaction of primary amines with CS_2 in the presence of bases produces dithiocarbamate salts (equation 27).

$$RNH_2 + CS_2 \xrightarrow{\text{Base}} R—NH—CS—S^- + H^+ \qquad (27)$$

Two different pathways have been proposed for the decomposition of this intermediate to give isothiocyanate:

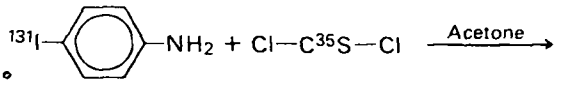
(i) Reaction with chlorocarbonate (equation 28):

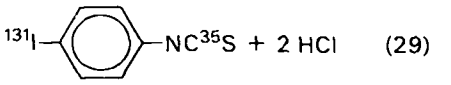
$$RNH—CS—S^- + EtO—CO—Cl \longrightarrow \left[R—NH—\overset{\overset{S}{\|}}{C}—S—\overset{\overset{O}{\|}}{C}—O—Et\right] + Cl^- \xrightarrow{\Delta} R—NCS + COS + EtOH \qquad (28)$$

n-Butyl [^{15}N]isothiocyanate has been prepared in 95% yield by this method starting from *n*-butyl[^{15}N]amine prepared by Gabriel reaction between *n*-butyl bromide and potassium [^{15}N]phthalimide[67]. By a similar procedure [^{13}C]methyl [^{15}N]isothiocyanate[68] and phenyl [^{35}S]isothiocyanate[62] have been obtained.

(ii) Reaction with heavy metal salts (equation 23): Preparation of *n*-butyl [^{35}S]isothiocyanate by this route[67] showed that it is less convenient than that using carbonate. 5-Fluorescein [^{14}C]isothiocyanate was similarly obtained starting from 5-aminofluorescein, $^{14}CS_2$ and iron trichloride[69].

b. *By reaction with thiophosgene.* [^{35}S]Thiophosgene was used for preparing *p*-iodo phenyl [^{35}S]isothiocyanate in high yield (95%)[70] (equation 29).

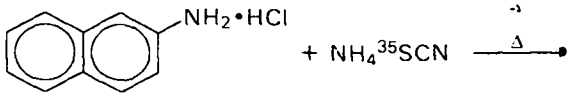


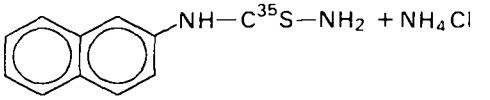


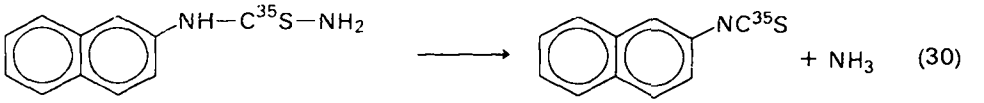
(29)

The required iodination of aniline using Na^{131}I as the source of iodine occurs with favourable yield (56%) and both the reactions carried out in solution are described as easily accomplished.

c. *By reaction with ammonium thiocyanate.* The method was used for the preparation of 2-naphthyl [^{35}S]isothiocyanate[18,71]. By heating of 2-naphthylamine with ammonium [^{35}S]thiocyanate 2-naphthylthiourea is formed, which is then decomposed by heating in chlorobenzene to 2-naphthyl isothiocyanate and ammonia (equation 30).







(30)

The same compound was obtained by the same authors by isotopic exchange with elemental sulphur. Their experience in the preparation of [^{35}S]isothiocyanates suggests that use could be made of the last method, at least for the preparation of ^{35}S-labelled compounds.

d. *By reaction with benzoyl isothiocyanate.* The synthesis of 2,6-dichloro- and 2,6-dimethylphenyl [^{14}C]isothiocyanates starting from K^{14}CN has been recently reported[13] to occur with an overall yield of 75% calculated on K^{14}CN. The reaction is based on the thermal decomposition of the corresponding thioureas, a process which occurs with yields exceeding 95% (equation 31).

$$ArNH-{}^{14}CSNH_2 \xrightarrow{180\,^{\circ}C} Ar-N^{14}CS + NH_3 \qquad (31)$$

The thioureas were prepared in 81% yield through the following multistep reaction without isolating the intermediates (equation 32).

$$K^{14}CN \xrightarrow{S} KS^{14}CN \xrightarrow{PhCOCl} PhCO-N^{14}CS \xrightarrow{ArNH_2}$$

$$ArNH-{}^{14}CS-NHCOPh \xrightarrow{OH^-} ArNH-{}^{14}CSNH_2 \qquad (32)$$

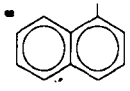
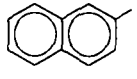
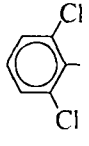
3. By isomerization of thiocyanates

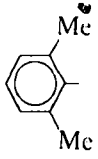
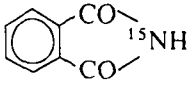
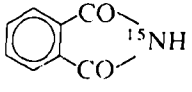
The isomerization of thiocyanates to the thermodynamically more stable isothiocyanates (equation 17) is a useful reaction for obtaining the labelled isothiocyanates. However, the process in the majority of cases requires rather drastic conditions, and a variety of side-reactions may take place simultaneously. Therefore, the synthetic use is restricted to those substrates which undergo isomerization in mild conditions. At the present time different mechanisms have been recognized as being responsible for the isomerization, the most important of which involves ionization pathways. When these are favoured by the structure or other factors (solvent, salt or Lewis acids) the thermal reaction represents a clean route for the rearrangement. On the other hand, a non-ionic cyclic mechanism is implicated in the isomerization of allylic substrates, an equilibrium reaction which involves the simultaneous rearrangement of the allylic moiety[41] (equation 33).

$$\begin{matrix} R \\ \diagdown \\ \quad C=CH-CH_2-SCN \\ \diagup \\ R \end{matrix} \rightleftharpoons \begin{matrix} \quad\quad R \\ \quad\quad | \\ SCN-C-CH=CH_2 \\ \quad\quad | \\ \quad\quad R \end{matrix} \qquad (33)$$

According to this behaviour, α-methylallyl [^{14}C]isothiocyanate has been obtained from γ-methylallyl thiocyanate which was formed, *in situ*, by

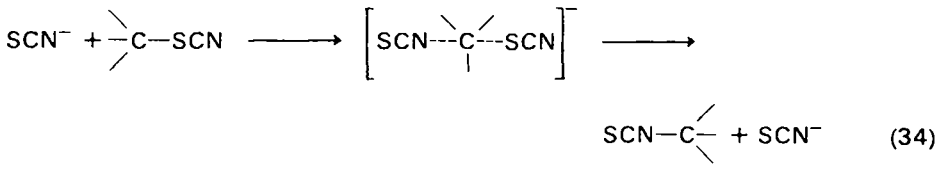
TABLE 6. Labelled isothiocyanates

Alkyl or aryl group	Source of isotope	Procedure of labelling	Position of labelling	Reference
	$^{35}S_8$	Exchange	$-NC^{35}S$	18, 61
	$^{35}S_8$	Exchange	$-NC^{35}S$	18, 61
	$NH_4{}^{35}SCN$	Decomposition of thiourea	$-NC^{35}S$	71
Ph 	$^{35}S_8$	Exchange	$-NC^{35}S$	18, 61
Ph	$^{35}S_8$	Exchange	$-NC^{35}S$	18, 60, 61
	$NH_4{}^{35}S^-$	Exchange	$-NC^{35}S$	65
	$H_2{}^{35}S$	Exchange	$-NC^{35}S$	65
	$C^{35}S_2$	Reaction with amine	$-NC^{35}S$	62
	$[^{14}C]PhNH_2$	Reaction with CS_2	ring ^{14}C	74
	$PhN^{14}CO$	Exchange	$-N^{14}CS$	32
Br 	$^{35}S_8$	Exchange	$-NC^{35}S$	18,61
^{131}I 	$C^{35}SCl_2$	Reaction with amine	$-NC^{35}S$	70
	$K^{14}CN$	Decomposition of thiourea	$-N^{14}CS$	13

	$K^{14}CN$	Decomposition of thiourea	$-N^{14}CS$	13
Me	$H^{35}S^-$	Exchange	$-NC^{35}S$	64
	^{14}MeI and 	Reaction between amine and CS_2	$^{13}Me-^{15}NCS$	68
	^{35}S recoil	Exchange	$-NC^{35}S$	63
Et	$^{35}S_8$	Exchange	$-NC^{35}S$	60
	$H^{35}S^-$	Exchange	$-NC^{35}S$	64
i-Pr	$H^{35}S^-$	Exchange	$-NC^{35}S$	64
n-Bu		Reaction between amine and CS_2	$-^{15}NCS$	67
n-Dodecyl	$^{35}S_8$	Exchange	$-NC^{35}S$	62
$PhCH_2-$	$^{35}S_8$	Exchange	$-NC^{35}S$	18, 61
	$H^{35}S^-$	Exchange	$-NC^{35}S$	64
	$K^{35}SCN$	Exchange	$-NC^{35}S$	66
Allyl	$K^{35}SCN$	Exchange	$-NC^{35}S$	66
α-Methyl allyl	$KS^{14}CN$	Exchange and isomerization	$-N^{14}CS$	43
5-Fluorescenyl	$^{14}CS_2$	Reaction with amine	$-N^{14}CS$	69
PhCO—	$KS^{14}CN$	Reaction with halide	$-N^{14}CS$	73, 13
	$K^{35}SCN$	Reaction with halide	$-NC^{35}S$	73
EtO—CO—	$K^{35}SCN$	Reaction with halide	$-NC^{35}S$	72
	$KS^{14}CN$	Reaction with halide	$-N^{14}CS$	72

reaction between the corresponding chloride and $KS^{14}CN$ in DMF[43].

The procedure of preparing *in situ* thiocyanates from labelled SCN^- offers the advantage of the specific catalytic effect of this ion when used in excess on the isomerization reaction, beside that of using an easy and general source of radioactivity without isolating the intermediates. This arises from a direct nucleophilic displacement carried out by the N-end of SCN^- (equation 34).



(34)

As a consequence, this route can be successfully applied for those substrates which undergo easy nucleophilic S_N2 attack, i.e. primary and secondary alkyl thiocyanates, which would require drastic conditions for thermal isomerization. In any case, the method of starting from the halides or esters and labelled SCN works for all substrates which undergo S_N substitution. In fact, in the presence of excess SCN^-, whenever ionization or direct substitution is involved, both halide substitution and isomerization of the intermediate thiocyanate can occur efficiently. According to this method some ^{35}S-labelled benzyl and benzydryl isothiocyanates have been obtained[58].

4. From halides by displacement with SCN^-

The reaction between an alkyl halide and labelled SCN^- produces a mixture of thio- and isothiocyanate the composition of which depends mainly on the structure of the organic moiety. The subject has already been treated in Section C.1. The mixture, as pointed out in the last section, can be converted in most cases to isothiocyanate.

It is known that the reaction between acyl halides and thiocyanate ion gives exclusively the isothio isomer. The reaction carried out in acetone has been used to prepare some acyl isothiocyanates which, however, were not isolated but converted to other compounds. Thus, ethyl chlorocarbonate was converted into carboxyethyl [^{14}C] and [^{35}S]isothiocyanates (yield 40%)[72] and benzoyl chloride into benzoyl [^{14}C]-isothiocyanate[13,73] (yield > 80%) and [^{35}S]isothiocyanate[73]. In Table 6 some isothiocyanates of different structure together with procedures and position of labelling are reported.

IV. USES OF LABELLED ISOCYANATES, ISOTHIOCYANATES AND THIOCYANATES

Organic isocyanates and isothiocyanates are rather reactive compounds. Therefore, when labelled, they find use as intermediates in the syntheses of labelled derivatives and as a tool to introduce a tag into a molecule, the fate of which is required to be followed.

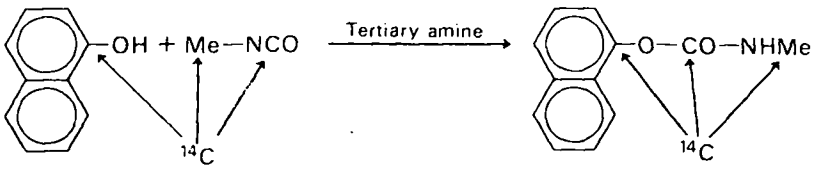
This concerns a large number of products of great technical, biochemical or biological interest. Labelling is useful to follow the chemical and biochemical transformations of molecules and their metabolites, including their translocations in plants, animals and soil.

A. Conversion of Isocyanates into Carbamates and Ureas

Most of the synthetic work in the field of labelled isocyanates has been carried out in relation to their conversion into labelled carbamates or urea derivatives. Many studies in this area concern commercial or experimental chemicals which are used in agriculture as herbicides or insecticides. The tracer technique is an analytical tool often applied to these compounds to study their mechanism of action and their metabolism. For the purpose of evaluating the potential hazard in the use of radioactive tracers on a variety of agricultural crops, including food crops, it is necessary to know their fate in soil, in plants and in the animal body. In particular, the research has been directed mainly towards the resistance to leaching, to the persistence in soil and on plants and to the fate of metabolites and degradation products in plants and animals.

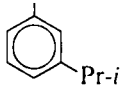
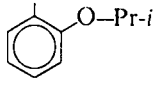
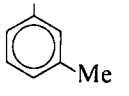
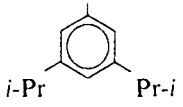
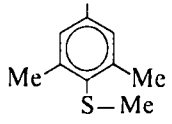
This kind of interest prompted Skraba and Young[75] to provide a convenient synthesis of the insecticide 'Sevin' labelled with radioactive carbon. They started from commercial 1-[1-^{14}C]naphthol which reacted with methyl isocyanate to give almost quantitatively [1-^{14}C]naphthyl-*N*-[^{14}C]methylcarbamate (equation 35).

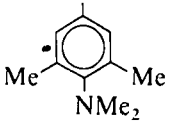
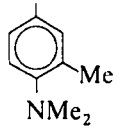
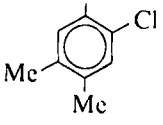
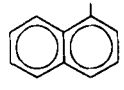
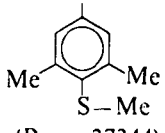
The same compound was prepared and extensively studied by other authors[76–80]. Labelling of 'Sevin' with ^{14}C at two further different sites



(35)

TABLE 7. Aryl-*N*-methyl carbamates, ArOCONHMe, prepared from methyl isocyanate, [^{14}C]methyl or [^{14}C]carbonyl, and the appropriate phenol

Aryl	Position of labelling, references		Aryl	Position of labelling, references	
	Carbonyl	Methyl		Carbonyl	Methyl
 (UCC 10854) (Hercules 5727)	28, 81	28	 (Baygon) (Bayer 39007)	28, 81	28, 81
	—	39		—	39
	—	81		28, 81	28
(HRS 1422)			(Mesurol)		

 (Zectran)	28, 33, 81	28	 (Matacil)	81	—
 (Banol)	81	—	 (Carbaryl) (Sevin)	28, 79, 81	28, 79, 81
			 (Bayer 37344)	28	—

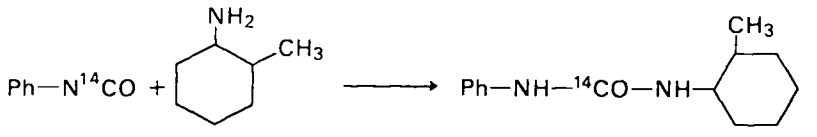
of the molecule, i.e. at carbonyl and at *N*-methyl carbon, has been accomplished[28,79,81] making use of the appropriate methyl isocyanate synthesized for this purpose.

The labelling in different positions allows the fate of different fragments to be followed. Together with its rate of excretion via urine, faeces and expiration this gives a rough idea of the path of a fragment through the animal body. Table 7 reports some *N*-methyl carbamates obtained from methyl isocyanate, [^{14}C]methyl or [^{14}C]carbonyl and phenols of different structure, the yields ranging between 40% and 90%. Besides the carbonyl and methyl positions, *N*-methyl carbamates have frequently been labelled in other sites, cf. the above-mentioned 1-[1-^{14}C]naphthyl compound. For this purpose the availability of the appropriately labelled phenols (or alcohols) was required. They were in some cases obtained through a complete radiochemical synthesis. For example, 3,4-dichlorobenzyl-*N*-methyl carbamate was obtained labelled at the methyl position by reaction of methyl[^{14}C]isocyanate with 3,4-dichlorobenzyl alcohol, and the [^{14}C]benzyl label was achieved via a four-step synthesis starting with 3,4-dichlorophenylmagnesium bromide and [^{14}C]carbon dioxide[37]. 4-Dimethylamino-3,5-xylyl methyl carbamate was also labelled in the 1-position of the ring by using the 4-dimethylamino-3,5-[1-^{14}C]xylenol prepared by a four-step synthesis starting from $^{14}CO_2$[33]. The same carbamate labelled both at the 3-position in the ring and the 3-methyl group is reported to be synthesized by a ten-step procedure in 10% yield[33]. [^{14}C]Methyl isocyanate was used to obtain (78% yield) 2-methyl-2-(methylthio)propionaldehyde *O*-([^{14}C]methyl carbamoyl) oxime (Temik) (equation 36),

$$^{14}CH_3{-}NCO + CH_3S{-}C(Me)_2{-}CH{=}NOH \longrightarrow CH_3S{-}C(Me)_2{-}CH{=}N{-}O{-}CO{-}NH^{14}CH_3 \quad (36)$$

a product which has been also prepared with the label at the 2- and methylthio carbon atoms[38]. The 2-carbon labelled oxime required a six-step synthesis from $^{14}CO_2$.

Amines react with isocyanates to form substituted ureas. The reaction is widely used to obtain labelled ureas, a large number of which is reported in the literature. Phenyl [*carbonyl*-^{14}C]isocyanate was reacted with 2-methyl cyclohexylamine to yield 1-(2-methylcyclohexyl)-3-phenyl-[2-^{14}C]urea[29] (equation 37).



(37)

The reaction which was run in boiling benzene gave an overall yield of 80% based on [*carboxyl*-^{14}C]benzoic acid from which the phenyl isocyanate was synthesized.

Among the ureas a great deal of interest has been devoted to 'Monouron' and 'Diuron', the 3-(4-chlorophenyl)- and 3-(3,4-dichlorophenyl)-1,1-dimethyl ureas, respectively. As shown in Table 8, these compounds have been labelled at carbonyl, methyl and ring by reaction of aryl isocyanates and dimethylamine with the label in the appropriate position.

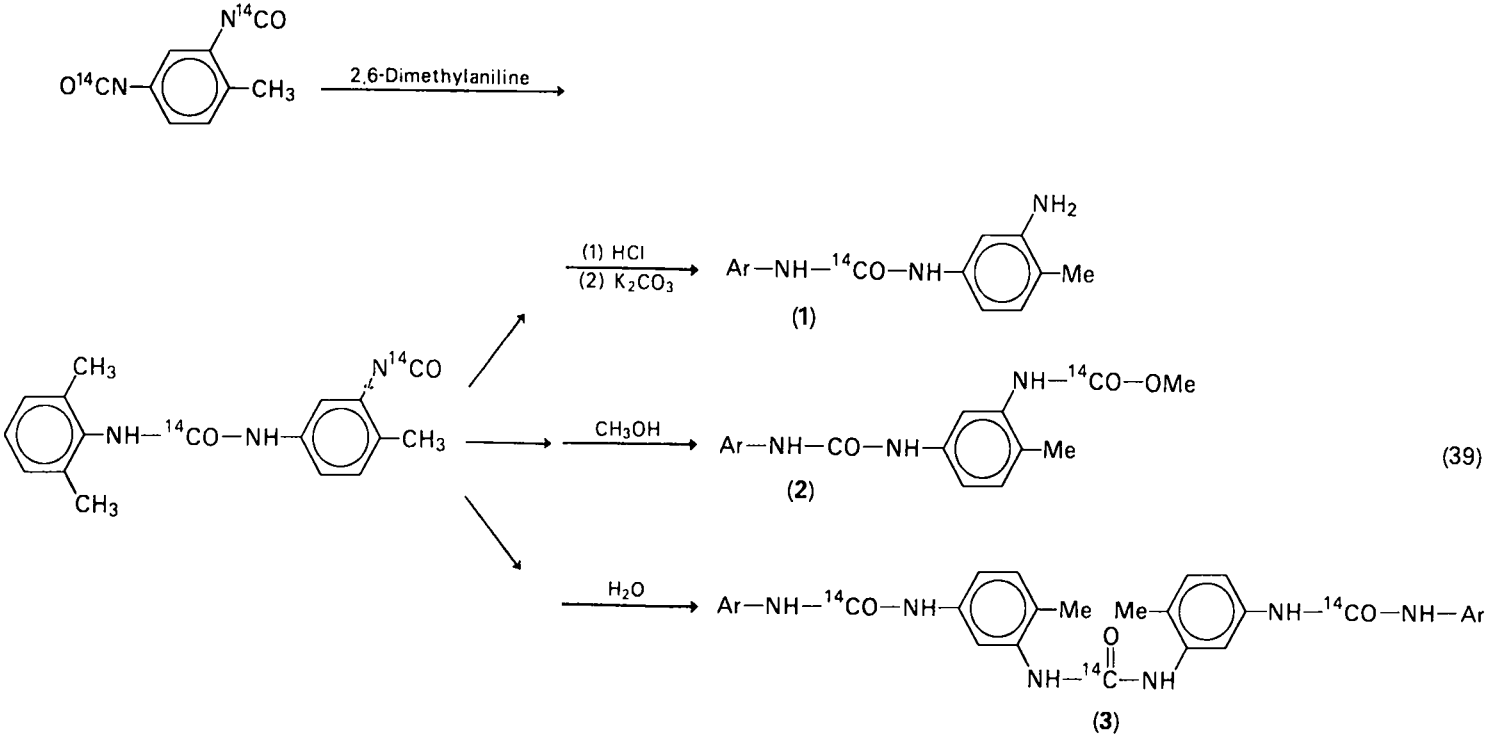
Isocyanates have been also reacted with the amino group of amino acids. Keglevic and Leonard prepared ethyl β-{3-(1'-naphthyl)-[2-^{14}C]-ureido} butyrate from 1-naphthyl[^{14}C]isocyanate and ethyl β-amino-butyrate (62%)[26]. An example of a cyclic urea, 1-(5-nitro-2-thiazolyl)-2-[4-^{14}C]imidazolidone is also reported. The 2-imidazolidone ring labelled in the 4-position is obtained from the bifunctional reagent 2-chloro-1-[1-^{14}C]isocyanatoethane and 2-amino-5-nitrothiazole[83]. To this purpose the interesting synthesis of the α-labelled isocyanate was accomplished by the following reaction sequence (equation 38).

$$K^{14}CN \xrightarrow[(2)\ PhCOCl]{(1)\ HCHO} Ph{-}CO{-}O{-}CH_2{}^{14}CN \xrightarrow[(2)\ H_2O,\ HCl]{(1)\ LiAlH_4} HO{-}CH_2{-}{}^{14}CH_2{-}NH_2{\bullet}HCl \xrightarrow{SO_2Cl_2} Cl{-}CH_2{-}{}^{14}CH_2{-}NH_2{-}HCl \xrightarrow{COCl_2} Cl{-}CH_2{-}{}^{14}CH_2{-}NCO \qquad (38)$$

The problem of the different intake of radioactivity in the synthesis of 2,4-tolylene [^{14}C]diisocyanate ([^{14}C]TDI) from 2,4-tolylene diamine and [^{14}C]phosgene[34] has been solved by using the reaction with the sterically-hindered 2,6-dimethylaniline, the first step of a sequence of reactions in which the carbon atom of one of the isocyanate groups is removed exclusively to form compound **1** (equation 39). The ^{14}C distribution was established by comparison of specific radioactivity of compound **1** with respect to compound **2** or **3**.

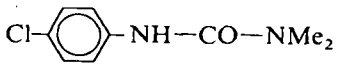
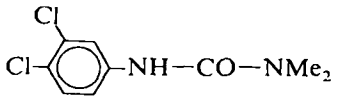
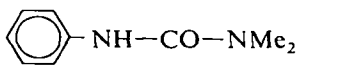
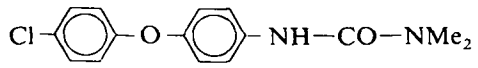
[^{14}C]TDI has been used by the same authors to prepare TDI–polyoxypropylenglycol copolymer in order to follow the fate of labelled isocyanate in the thermal degradation process of the polymer[84].

The isotopic labelling of isocyanates sometimes plays an indispensable role in the field of reaction mechanisms. An example is the isomerization of nitrile oxides to isocyanates previously mentioned as a synthetic method[40]. The question arises as to whether or not the reaction is intramolecular. Labelling of molecules allows the performance of crossover experiments which gave a clear-cut response. Phenyl nitrile oxides, 4-^{2}H


N14CO
O14CN
CH3
2,6-Dimethylaniline
(1) HCl
(2) K2CO3
NH2
Ar—NH—14CO—NH
Me
(1)
CH3
N14CO
NH—14CO—NH
CH3
CH3OH
NH—14CO—OMe
Ar—NH—CO—NH
Me
(2)
H2O
Ar—NH—14CO—NH
Me
Me
NH—14CO—NH—Ar
O
NH—14C—NH
(3)

(39)

TABLE 8. 1,1-Dimethyl-3-arylureas from aryl isocyanates and dimethylamine

Compound	Percentage yield (Reference) Position of labelling		
	Carbonyl	*N*-Methyl	Ring
	78(31)	94(31)	53(31)
(Monouron)	(27)	92(82)	
	80(31)	92(31)	22(31)
	(35)	(35)	(35)
(Diuron)		85(82)	
	—	98(82)	—
(Fenuron)			
	—	72(82)	—
(Chloroxuron)			

and α-^{13}C, respectively, were isomerized to isocyanates, which were isolated as ureas by reaction with *o*-toluidine. No cross-product corresponding to the [4-^{2}H,α-^{13}C] phenyl isocyanate was formed, showing that the intramolecularity of aryl migration exceeds 97%.

The intermediacy of isocyanates is implicated in some decomposition reactions of organic substances. The labelling of the reactants and the formation of labelled isocyanates or their derivatives allows distinction to be made between different reaction paths[85,86].

B. Conversion of Isothiocyanates into Thiourea Derivatives

In the reaction with amines, isothiocyanates introduce a thiocarbamoyl function in the molecule giving rise to thiourea derivatives.

Table 9 reports a number of differently-labelled thioureas obtained from the reaction of [^{14}C]- or [^{35}S]isothiocyanate with amines. Some of them have been synthesized in order to determine their movements in plants[62], others in order to determine their metabolism in plants and animals[72,73]. To this end autoradiography (a technique used also in

TABLE 9. Labelled thioureas and related compounds from isothiocyanates

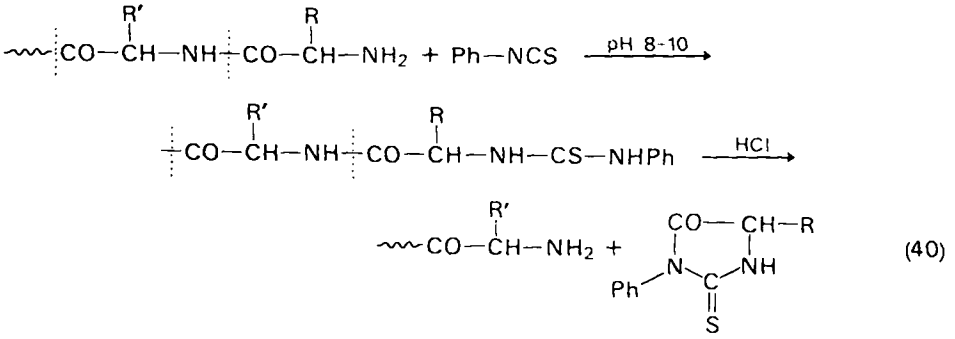
Compound	Radioactivity source	Reference
1-Phenyl-3-(2-hydroxyethyl)[^{35}S]thiourea	Ph—NC^{35}S	62
1-Phenyl-3-di-(2-hydroxyethyl)[^{35}S]thiourea	Ph—NC^{35}S	62
1-Phenyl-3-(2′-ethylhexyl)[^{35}S]thiourea	Ph—NC^{35}S	62
1-Phenyl-3-cyclohexyl[^{35}S]thiourea	Ph—NC^{35}S	62
1,3-Diphenyl[^{35}S]thiourea	Ph—NC^{35}S	62
N-(*N*′-Phenyl)[^{35}S]thiocarbamoylmorpholine	Ph—NC^{35}S	62
n-Dodecyl[^{35}S]thiourea	*n*-Dodecyl-NC^{35}S	62
1-Benzoyl-3-phenyl-2-[2-^{14}C]thiourea	PhCON^{14}CS	73
Phenyl[2-^{14}C]thiourea	PhCON^{14}CS	73
Phenyl[^{35}S]thiourea	PhCONC^{35}S	73
[^{14}C]Phenylthiourea	[^{14}C]Aniline	73
1-α-Methylallyl [^{14}C]thiocarbamoyl-2-methylthiocarbamoyl hydrazine	γ-Methyl allyl-N^{14}CS	43

1-Benzoyl-3-(2,6-dichlorophenyl)-[2-^{14}C]-thiourea	$PhCON^{14}CS$	13
1-Benzoyl-3-(2,6-dimethylphenyl)-[2-^{14}C]-thiourea	$PhCON^{14}CS$	13
2,6-Dichlorophenyl [2-^{14}C]thiourea	$PhCON^{14}CS$	13
2,6-Dimethylphenyl [2-^{14}C]thiourea	$PhCON^{14}CS$	13
1-(2,6-Dichlorophenyl)-3-methyl [2-^{14}C]-thiourea	$PhCON^{14}CS$	13
2-Methylimino-3-(2,6-dichlorophenyl)-4-methyl-[2-^{14}C]thiazolidine	$2,6\text{-}Cl_2C_6H_3{-}N^{14}CS$	13
2-(2,6-Dimethylphenyl)-imino-3-methyl-[2-^{14}C]thiazolidine	$2,6\text{-}Me_2C_6H_3{-}N^{14}CS$	13
Dimethyl or diethyl 4,4′-*o*-phenylenbis (3-thioallophanate) [^{14}C]thiocarbonyl	$MeOCON^{14}CS$	72
[^{35}S]thiocarbonyl	$MeOCONC^{35}S$	72
[^{14}C]methyl	[^{14}C]MeOCONCS	72
[*U*-^{14}C]phenyl	[*U*-^{14}C]aniline	72

penetration studies of 4-chlorophenyl [^{35}S]isothiocyanate[87]) and/or paper chromatography are largely utilized.

Physiological studies prompted the preparation of labelled [2-^{14}C]-thiazolidines[13] and of 1-α-methylallyl[^{14}C]thiocarbamoyl-2-methylthio-carbamoyl hydrazine (MATCH^{14}C), a compound which inhibits the pituitary gonadotropic function[43]. The conversion to thioureas of amino groups by ^{14}C ring-labelled Ph—NCS allowed evaluation to be made of the difference in protonation at pH 8 among the different amino groups of insulin[74].

A specific case of thiocarbamoylation on the amino group of peptides or proteins is that carried out by phenyl isothiocyanate, the well known Edman degradation[88]. By this procedure the phenylthiocarbamoyl peptide is obtained at pH 8–10 and in subsequent acid conditions it splits into a substituted phenyl thiohydantoin and a polypeptidic fragment (equation 40)



(40)

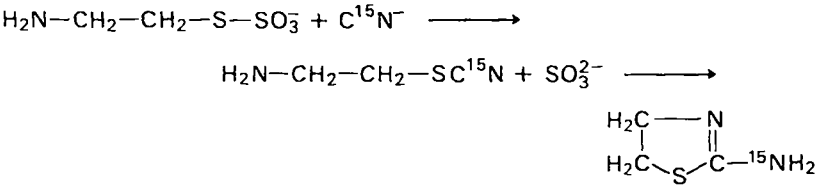
The shorter peptide is then degraded step by step through successive reactions on the N-terminal amino acid. Paper chromatography of the thiohydantoins containing the N-terminal amino acid allows the sequence of amino acids in the peptide to be determined.

The use of phenyl [^{35}S]isothiocyanate for the determination of the sequence of amino acids in a di- or tripeptide was suggested by Rabino-witz[89–91]. A 10- to 20-fold increase in sensitivity of the method was achieved. The Edman degradation with phenyl [^{14}C]isothiocyanate as tracer has been applied also to the resin-bound peptide in order to control the best conditions for the solid phase peptide synthesis, namely the condensation and the amino group deprotection steps[92].

In antibody studies, fluorescein isothiocyanate (FITC) is a commonly used fluorochrome as it can supply the linkage between the protein and the fluorescent moiety through the reaction of the isothiocyanate group with

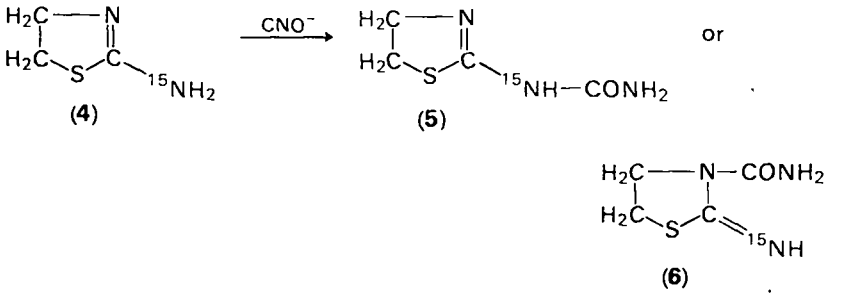
the amino groups. The amount of fluorochrome present in a protein molecule is determined by spectrophotometry. Since the absorption of FITC changes on bonding with protein, [^{14}C]FITC can be used to couple the absorption with radiochemical analysis in order to allow a more accurate measurement of fluorescein–protein ratios[69]. In view of obtaining a model compound of the peptide bond to study the structure of proteins by infrared analysis, *n*-butyl [^{15}N]isothiocyanate was used to prepare *N*-butyl[^{15}N]acetamide[67] by reaction with acetic acid.

Organic thiocyanates, too, find some uses as intermediates in the syntheses of labelled compounds. Thus besides isothiocyanates as reported in Table 9, the thiazole skeleton can also be formed starting from thiocyanates. The synthesis of 2-amino-[^{15}N]-Δ^2-thiazoline has been carried out from 2-aminoethane 1-thiosulphate and K^{15}CN through the intermediate 2-amino-1-thiocyanatoethane[59] (equation 41).



(41)

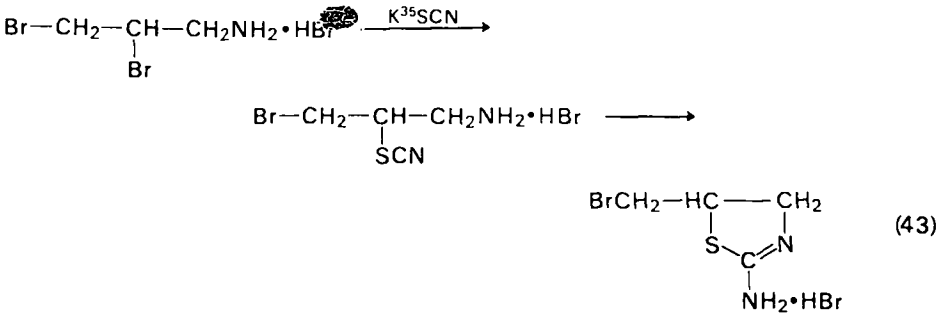
The labelling allowed evidence to be presented in favour of one of the two possible structures which may be written depending on the site of attack in the reaction of thiazoline with cyanate ion (equation 42)



(42)

Raney nickel desulphurization led to the formation of urea which was found by mass spectrometry to contain the ^{15}N label. It was concluded that structure **6** was untenable, showing that the addition of cyanate to **4** does not follow the general pattern observed when the amino groups are involved.

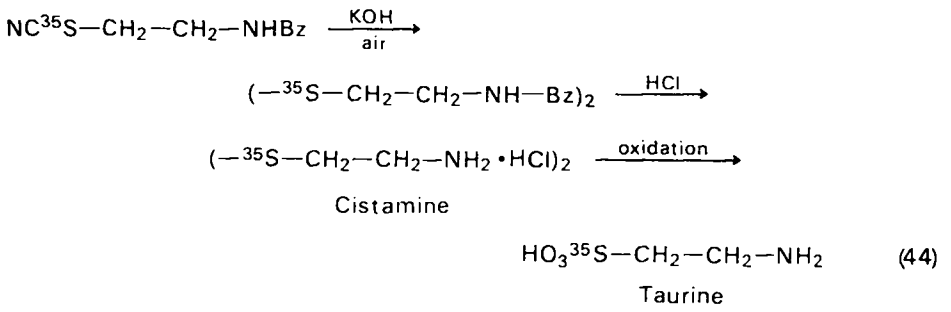
Cyclization of 1-bromo-2-[^{35}S]thiocyano-3-propylamine hydrobromide also occurs to form 2-amino-5-bromomethylthiazoline (equation 43)



(43)

The course of the reaction was monitored by radiochromatography[16].

In order to investigate the metabolism of taurine, the synthesis of the ^{35}S-labelled compound has been accomplished through a reaction sequence which involves a [^{35}S]thiocyanate as intermediate[44] (equation 44).



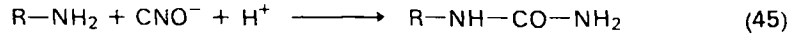
(44)

The overall yield of taurine is approximately 50% based on the sulphur of thiocyanate.

C. *Some Uses of Labelled Inorganic Cyanates and Thiocyanates*

Although not strictly within the scope of this chapter, we mention here some uses of labelled inorganic cyanates and thiocyanates.

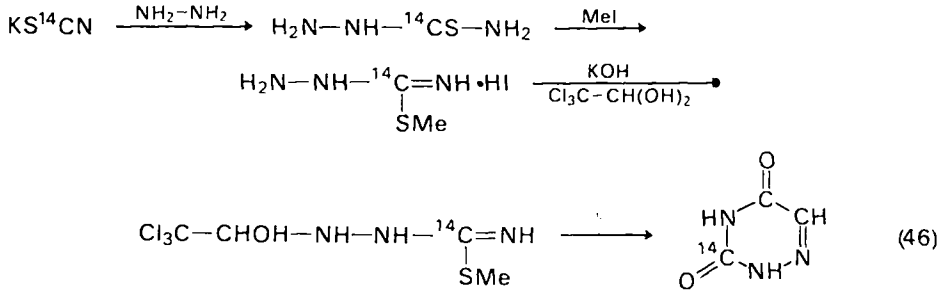
Cyanates react with compounds containing amino groups according to the well known Wöhler reaction to form urea derivatives (equation 45).



(45)

This reaction is closely related to the use of organic labelled isocyanates which form the same class of compounds (Section IV.A). Table 10 summarizes some examples and reports the further synthetic use of the urea derivatives.

Thiocyanate ion undergoes the same reaction to give thiourea derivatives. An example is the reaction with hydrazine to give [2-^{14}C]thiosemicarbazide which is an intermediate in the synthesis of 6-[2-^{14}C]-azauracil[17] (equation 46).



(46)

The use of $NH_4{}^{35}SCN$ has been also suggested instead of the unlabelled compound to improve the Schlanck–Kumpf method for determining the C-terminal groups in proteins[97]. As known the method consists in the condensation of the C-terminal residues with ammonium thiocyanate. The 2-thiohydantoin formed from the intermediate isocyano derivative of the C-terminal amino acid is detached by alkaline or acid cleavage, identified and determined.

Wide use of inorganic labelled thiocyanates has been made in mechanistic studies of reactions involving organic thiocyanates. The 2,4-dinitrophenyl-^{35}S derivative was prepared as having the scope to investigate the mobility of the SCN group in nucleophilic aromatic substitution[52]. The exchange reaction starting from alkaline-[^{35}S]thiocyanate and organic thiocyanate has been largely applied in the study of nucleophilic substitution at saturated carbon. The main topics concern the ionization–dissociation process of benzhydryl thiocyanates[54,55], the borderline behaviour of the same[98–100] as well as of triphenylmethyl substrates in dipolar aprotic solvents, and, finally, the mechanism of isomerization to isothiocyanates[46,47]. The synthetic aspects of this subject have been reported in the previous sections of this chapter. The mechanistic aspects, on the other hand, have been previously reviewed[41] and they are included in another chapter of this Volume.

TABLE 10. Labelled urea derivatives from inorganic labelled cyanates

Compound	Yield (%)	Product of further reaction	Reference
[^{14}C]Urea	—	[2-^{14}C]Barbituric acid	2
[^{14}C,^{15}N]Urea	42	—	4
[^{14}C]Urea	80	D-[2-^{14}C]Riboflavin	3
[2-^{14}C]Methylurea	95–98	[2-^{14}C]Barbituric acid derivatives	93
Carbamoyl-[^{14}C]-aspartic acid	—	4-[2-^{14}C]Carboxyuracil	8
s-[2-^{14}C]Butylurea	75	5-Bromo-3-*s*-butyl-6-methyl [2-^{14}C]uracil	94
t-[2-^{14}C]Butylurea	—	5-Bromo-3-*t*-butyl-6-methyl [2-^{14}C]uracil	94
Carbamoyl[^{14}C]aminocyanoacetamide	69	4-Amino-2(3*H*)-oxo-5-imidazole [2-^{14}C]carboxamide	96
δ-Carbamoyl[^{14}C]ornithine	60	—	7
ϵ-Carbamoyl[^{14}C]lysine	60	—	7
α-Amino γ-carbamoyl[^{14}C]butyric acid	26	—	7
Carbamoyl[^{14}C]valine of haemoglobin	—	—	95

Finally, we mention some spectroscopic studies involving isotopic substitution in cyanate and related groups. The interest of the investigators has been dedicated more to the linear ions X—Y—Z and to the corresponding acids than to the organic derivatives. The isotopic substitution of the NCO group is currently used to obtain the molecular parameters from microwave spectra, e.g. silyl isocyanates[101] and isocyanic acid[102]. The rotational constants of five isotopic species of the methyl thiocyanate molecule allowed a complete r_S-structure of the molecule to be determined[103].

In infrared spectroscopy the anharmonicity constants, the harmonic frequencies and the force constants obtained from the study of the isotopic species of the cyanate ion have given an exceptionally solid basis to interpret the vibrational behaviour of the OCN^- species as a free ion or as contained in a solid host matrix[104]. The mean square amplitudes of vibration were evaluated for $SCN^-[^{13}C]$ and $[^{34}S]$ from the vibrational frequencies[105]. Moreover ^{15}N isotope substitution in OCN group has been considered in the i.r. and Raman studies of a series of alkyl and aryl cyanates[25].

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CHAPTER 15

Pyrolytic reactions of cyanates and related compounds

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I. INTRODUCTION AND SCOPE

In this chapter we deal mainly with the gas phase pyrolytic reactions of esters derived from the tautomeric forms of cyanic and thiocyanic acids. We cannot fail, however, to mention the work of Ravinovitch and collaborators[1,2] and Casanova and collaborators[3] on the isonitrile–nitrile isomerization, and that of Fava and collaborators[4,5] on the isomerization of thiocyanates in solutions, since these investigations greatly motivated our own work in this field. Moreover, Section IV discusses a variety of reactions which, while not being truly gas phase pyrolyses, appear to be relevant to the main subject here.

Linear triatomic pseudohalides, including fulminic acid derivatives and selenium compounds, have been known for a long time. Nevertheless, their gas phase chemistry has only been subject to research very recently and consequently the number of references found in the literature is relatively

small. The case is extreme with the cyanates, ROCN, which were prepared for the first time just over 10 years ago[6]. Because of their great instability in the pure state they are difficult subjects for kinetic studies in the gas phase and have withstood all our attempts to get meaningful results. The thermal stability of the other compounds in the group decreases in the order RNCO > RNCS > RSCN; the relative rates of decomposition being 1:2900:5900 respectively for the isopropyl derivatives at 440·8 °C. The similarity of these compounds to the organic halides in many of their reactions in solution is again verified by gas phase pyrolysis, where in all circumstances the functional group —XYZ maintains its unity. The most obvious differences are in the polarity of the transition states and the tendency to enter into free radical chain reactions. In those cases in which detailed kinetic studies have been carried out, the mechanism of the olefin-forming reaction has been found to fit in nicely with the general pattern of pyrolytic eliminations recently reviewed by Maccoll[7,8].

It is of special interest to note that if one accepts the idea of a spectrum of polarities for the transition states of these reactions, then the relative positions of the compounds within the scope of our interest are as follows: RX(X) = Cl, Br, I) $\ggg$ $ROCOCH_3$ > RNCS ~ RNCO > RSCN > cyclobutanes where the reaction of alkyl halides has been termed quasi-heterolytic[7]. The relative reactivities which have given rise to the sequence above are shown in Table 1.

II. CYANIC AND THIOCYANIC ACIDS

Although in principle the title compounds can exist in two tautomeric isomers according to the equation

$$H{-}N{=}C{=}X \underset{}{\overset{K_1}{\rightleftharpoons}} H{-}X{-}C{\equiv}N \qquad (X = S, O) \qquad (1)$$

the fact is that only the so-called 'iso' form, that is, the one with the cumulative double bonds, has been detected in the gas phase. This is so irrespective of the mode of preparation which can either be by pyrolysis of isocyanates, thio- or isothiocyanates or by displacement from metallic salts with strong mineral acids[9-12]. This is in sharp contrast with the sulphur-containing parent compound, thiocyanogen, which has been proved[13] to have the structure $N{\equiv}C{-}S{-}S{-}C{\equiv}N$. On the other hand, there is definite spectroscopic[14] and chemical evidence[15-18] that the equilibrium (1) is indeed established in solution. While both acids are extremely unstable in the pure liquid state, their vapour is stable at the temperatures at which the pyrolysis of the corresponding esters occurs. Back and Childs[19] found that isocyanic acid decomposes into CO_2, CO, N_2, HCN and H_2 between

TABLE 1. Relative rates for the reaction RX → Olefin + HX at 307 °C

R	X = Cl—[a,b]	X = CH_3COO—[b]	X = —NCS[c]	X = —SCN[c]	X = Cyclobutanes[d]
Ethyl	1	1	1	1	1·5
i-Propyl	190	36	34	9	1·0
s-Butyl	500	18	39	15	—
t-Butyl	55,000	3000	700	49	0·3
n-Propyl	—	0·8	—	1·6	2·2
3-Butenyl	—	—	1·32	3·6	—
2-Phenylethyl	—	5·8	—	3·3	—
i-Propenyl	—	—	—	—	1072

[a] Other halides behave similarly.

[b] Data for acetates and chlorides are 'preferred' values in the compilation of S. Benson and H. O'Neal, U.S. Department of Commerce NSDRS-NBS-21, U.S.A., 1970.

[c] From data reported in Table 4 below.

[d] Reference 39, relative rates for the olefin-forming reaction taking the unsubstituted cyclobutane as the parent compound.

550 and 700°C through a complex and partially heterogeneous reaction. On the other hand, cyanic acid is formed in good yield in the pyrolysis of cyanuric acid[20] above 400°C, under a stream of nitrogen.

The molecular structure[21,22] dipole moments[23,24], ionization constant[25], electron impact phenomena[26] and atomic charge distribution[27] of the acids, all of which are useful when discussing the nature of the transition state of the pyrolytic eliminations undergone by their esters, are well known. If not written in italics, the names 'cyanic' and 'thiocyanic' acid are used here to imply the actually occurring equilibrium mixture, whatever the value of K_1 may be for each set of conditions, while names in italics signify the single form, as named.

III. KINETICS AND MECHANISM OF HIGH TEMPERATURE PYROLYSIS

A. General Stoichiometry of Pyrolysis

Contrary to what has been found in solution, and in the gaseous phase for the related isonitriles[3], cyanates[6] and the sulphur analogues[4] do not undergo group isomerization by direct migration of the hydrocarbon moiety when their vapours are subject to elevated temperatures, but instead they eliminate acid to form olefins according to the general Scheme 1 below

$$C_nH_{2n+1}XCN \underset{k_{-x}}{\overset{k_x}{\rightleftharpoons}} HNCX + C_nH_{2n} \underset{k_{-n}}{\overset{k_n}{\rightleftharpoons}} C_nH_{n+1}NCX$$

$$K_1 = \frac{k_x}{k_{-x}}, K_2 = \frac{k_n}{k_{-n}}$$

SCHEME 1.

where X = O,S. This scheme implies that when an isomer is pyrolysed, finite amounts of the other isomers are formed, although it has been demonstrated in the case of thiocyanates that these come from the back addition of thiocyanic acid to the corresponding olefins[28,29,30]. A typical near-equilibrium distribution of products is shown in Table 2 for the *i*-propyl isothiocyanate decomposition[28,31]. From these data, two important facts emerge: in the first place the positional distribution of products is that of the Markownikoff mode of addition and secondly, although not detected by normal i.r. techniques, the nitrile tautomer of thiocyanic acid must be present, as small amounts of thiocyanates are produced.

In Scheme 1 both equilibria are endothermic by about 16 to 20 kcal/mol, the thermodynamics[32,33] being such that a value near to 4 kcal/mol is

obtained for the enthalpy change of the thiocyanate–isothiocyanate isomerization. Whenever the possibility exists of several olefins being produced, as is the case of the 2-butyl derivatives, their proportions change with time as shown in Figure 1. Nevertheless, extrapolation to zero time allows the real distribution to be found. These are given in Table 3 along with those obtained from other classes of substances for comparison.

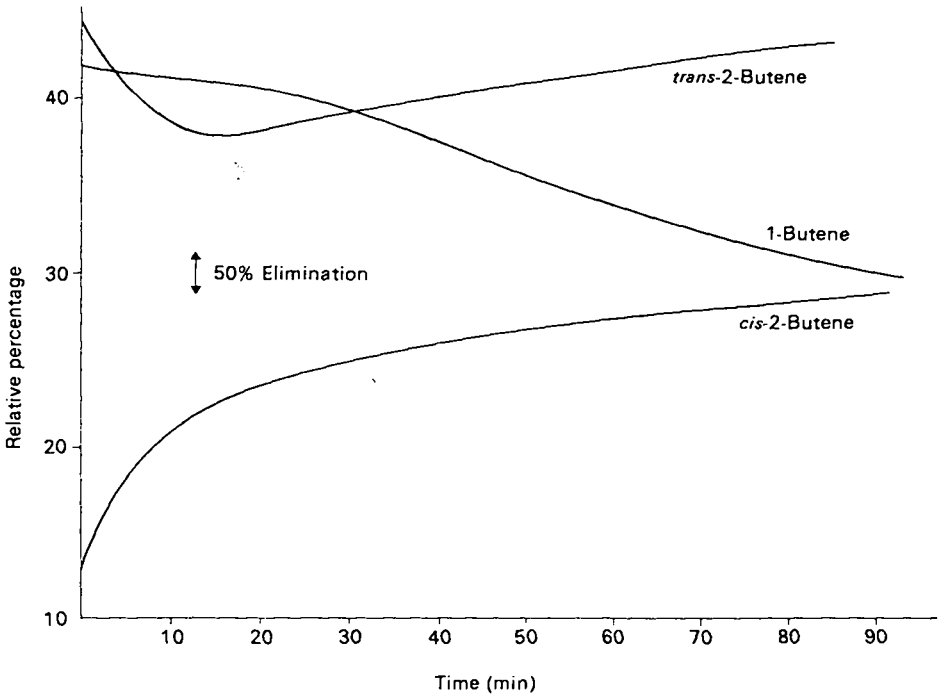

FIGURE 1. Relative percentage of *n*-butenes.

Although care has not always been taken to account for the time dependent isomerization of the initially formed butenes, these results are interesting in that they reveal a trend toward higher *trans/cis* ratios as the concerted nature of the transition state increases. Thus the thiocyanate reaction shows the highest value and at the same time appears to be the least polar of them all (*vide infra*). This may be understood by referring to Figure 2 where it can be seen that the more concerted the reaction is (or, in other words, the higher the double bond character of the transition state), the smaller is the mean amplitude of the out-of-plane vibration as measured by the angle θ and the smaller the space to accommodate the methyl groups in the configuration leading to the *cis* olefin.

TABLE 2. The products of the back addition of HNCS in the pyrolysis of isopropyl isothiocyanate[a]

Temperature (°C)	Conversion (%)	*i*-PrNCS calculated for no addition	Total C_3H_7NCS	*i*-PrNCS	*i*-PrSCN	*n*-PrNCS	*n*-PrSCN
276	66·9	8·30	33·14	31·28	1·14	0·36	0·36
280	71·7	4·40	28·28	25·60	1·75	0·51	0·42
290	86·2	1·65	13·83	12·35	0·74	0·45	0·29
320	91·1	0·04	8·93	7·57	0·53	0·53	0·30
320	55·2	40·66	44·80	44·7	0·10	0·00	0·00
320	82·6	10·23	17·45	16·86	0·33	0·14	0·12

[a] All pressures in mmHg adjusted for an initial pressure of 100 mmHg of reactant.

TABLE 3. Proportions of olefins (%) from several *s*-butyl compounds

Substance	Temperature (°C)	1-Butene	*trans*-2-Butene	*cis*-2-Butene	*trans*/*cis*
Thiocyanate[a]	325	41	46	13	3·53
Isothiocyanate[b]	310	41	45	14	3·21
Chloride[c]	350	41	38	21	1·81
Xanthate[d]	350	41	40	19	2·10
Acetate[d]	450	57	28	15	1·86
Methanesulphinate[e]	260	42	35	23	1·52
Thionacetate[f]	287	38	41	21	1·95
Equilibrium	330	21	45	34	1·32

[a] See Reference 29.
[b] See Reference 37.
[c] H. Heydtmann and G. Rinck, *Z. Phys. Chem.*, **36**, 75 (1963).
[d] C. H. De Puy, C. A. Bishop, and C. N. Goeders, *J. Amer. Chem. Soc.*, **83**, 2151 (1961).
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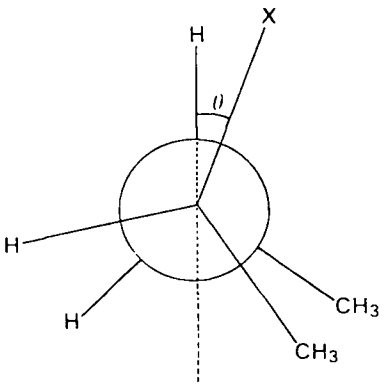


FIGURE 2. Configuration leading to the *cis* olefins in *s*-butyl compounds.

An important feature of the pyrolysis of thio- and isothiocyanates is that the kinetics are not affected by the nature or area of the internal surfaces of the reactor and hence these reactions can be safely regarded as homogeneous gas phase decompositions. The pyrolyses of isopropyl and *t*-butyl isocyanates, on the other hand, are affected by Pyrex glass surfaces so that the reactor has to be previously 'conditioned' in order to eliminate heterogeneous processes[34]. The fact that the equilibrium represented in Scheme 1 is displaced in the direction of the elimination has allowed the determination of the rate constants k_x and k_n without disturbances arising from the reverse reaction, in some instances up to conversions as high as 75%. These results are summarized in the Arrhenius form in Table 4.

B. Thiocyanates

The first detailed mechanistic study in this series, that of *s*-butyl thiocyanate[29], was reported by us in 1971 in an attempt to correlate the so-called quasiheterolytic mechanism of gas-phase pyrolysis with E1 and S_Ni reactions in polar solvents. The reaction exhibits all the characteristics of a unimolecular decomposition and yields 2-butenes (see Table 3) with a high *trans/cis* ratio, suggestive of a concerted *cis* elimination. Later experiments with ethyl-1,1-d_2 thiocyanate and ethyl-d_5 thiocyanate[30] (Table 5) confirmed the 1,2 nature of the elimination and furthermore, that the degree of β-hydrogen bond breaking in the transition state is appreciable. Equally important for the discussion of the reaction mechanism was the finding in the former case that optically active (−)-*s*-butyl thiocyanate does not racemize when subject to pyrolytic conditions.

TABLE 4. Arrhenius parameters for the olefin-forming eliminations in cyanate-type esters

Compound	log A	E(kcal/mol)	Temperature range (°C)	Reference
Ethyl thiocyanate	11·77	40·51	276–343	30
i-Propyl thiocyanate	12·27	39·33	260–320	36
s-Butyl thiocyanate	12·30	38·82	245–305	29
t-Butyl thiocyanate	12·28	37·37	235–285	36
But-3-enyl thiocyanate	12·34	41·88	270–330	36
Ethyl isothiocyanate	12·40	45·35	380–394	31
i-Propyl isothiocyanate	12·99	42·87	276–329	31
s-Butyl isothiocyanate	12·46	41·33	273–325	37
t-Butyl isothiocyanate	13·00	39·46	225–289	31
But-3-enyl isothiocyanate	12·40	45·04	320–386	35
1-Methylprop-2-enyl isothiocyanate	11·84	37·55	245–300	35
i-Propyl isocyanate	12·71	53·29	425–498	34
t-Butyl isocyanate	13·59	52·38	380–440	34

One of the most useful criteria to decide on the incursion of radical chain mechanisms has been the addition of olefinic inhibitors, such as cyclohexene and propylene, to the reaction mixture and, to a lesser extent, radical promoters like oxygen and bromine. None of these substances changes in any way the pyrolysis of thiocyanates, so that one is forced to conclude that these reactions are truly molecular decompositions. On the basis of all this evidence, a cyclic six-centred transition state, formally similar to that for the isomerization of allylic thiocyanates, has been proposed[29] (Figure 3).

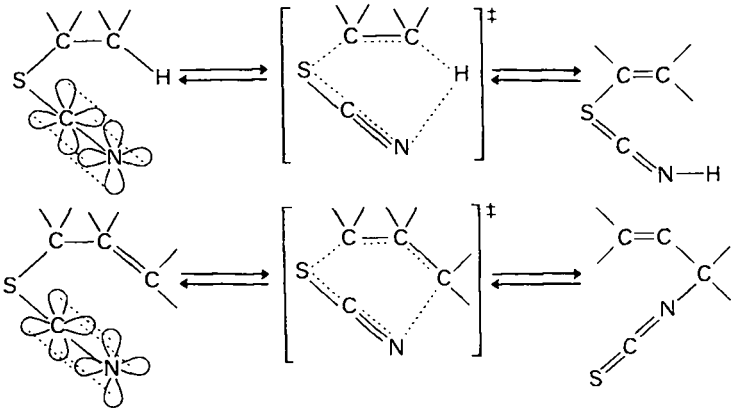


FIGURE 3. The transition states for elimination and isomerization.

A final point which has to be discussed is that of the electronic requirements of such a transition state, and this is suitably done by observing the effects of properly-chosen structural changes on reactivity. Data relevant to this matter are presented in Table 1 above.

Maccoll has proposed[38] that one extreme, that of maximum polarity in the transition state for gas phase olefin-forming eliminations, corresponds to the alkyl halides, while the other extreme, that of the homolytic type reactions, could be represented by the pyrolysis of cyclobutanes. For the latter reaction the effect of methylation on rate is minimum but the effect of

TABLE 5. Relative rates for isotopic substitution

T(K)	$\frac{k_1 \text{ for } C_2H_5SCN}{k_1 \text{ for } C_2H_3D_2SCN}$	T(K)	$\frac{k_1 \text{ for } C_2H_5SCN}{k_1 \text{ for } C_2D_5SCN}$
557·3	1·22	575·5	3·36
566·7	1·20	594·9	3·10
575·8	1·19	605·5	2·97
590·7	1·17	615·1	2·86
602·9	1·15	629·9	2·70
620·8	1·13	642·7	2·58

double bonds in positions where resonance is possible with a developing unsaturation, this being either a formal π-bond or an unpaired electron, results in a large decrease in the activation energy[39]. Now, the magnitude of the rate increments brought about by methyl substitution in the thiocyanate series, and the small but significant effect of the β vinyl and phenyl groups indicates a very low degree of polarity for this reaction. Interestingly enough, this tendency to valence reorganization against charge separation, is maintained even in DMF solution where it has been shown that free ions are not important in solvolysis[5].

Alkyl cyanates have not yet been studied in the gas phase.

C. *Isothiocyanates and Isocyanates*

As was the case with thiocyanates, when vapours of the title compounds are heated at temperatures above 300 °C, the pressure increases smoothly, following a first-order kinetic law, to a final value very nearly twice the initial pressure of the reactant. The general features of the reaction are as explained in Section III.A. and the criteria used when discussing the mechanism of thiocyanate pyrolysis are applied here to show that these reactions are also homogeneous and molecular gas-phase eliminations.

Here again we shall use the effect caused by the substitution of the α hydrogens in the ethyl compound by methyl radicals as a measure of the polarization of the carbon-leaving group bond in the transition state. In this context the pyrolysis of isothiocyanates exhibits a polarity comparable to that of the acetates (Table 1). In fact, the activation energies of these decompositions are correlated with the heterolytic bond dissociation energies $D_{R\cdot X^-}$ by the equation $E_a = 26{\cdot}6 + 0{\cdot}095\ D_{R\cdot X^-}$ (kcal/mol)[37]. The slope of this line is about one third of that found for the alkyl halides[38] but in our case, there is also an independent term which accounts for approximately 65% of the activation energy. All this seems to indicate that the degree of charge separation in the series is roughly one third of that in the latter class of compounds. The effect caused by the introduction of double bonds near the reaction centre is illustrated by the pyrolysis of 1-methylprop-2-enyl, but-3-enyl and but-2-enyl[35] isothiocyanates. It is observed that vinyl substitution not only lowers the activation energy but also the preexponential factor by 5·3(kcal/mol) and 1·2(units of log A) respectively. These values are approximately double those for the organic chlorides.

A comparison of the reactivities of these unsaturated molecules indicates that the main mechanism by which the double bond interacts with the reaction centre is the allylic weakening of the C–N bond.

In regard to the structure of the transition state, a four-centred model

(Figure 4a) was initially proposed, but later this view was modified in favour of the six-centred ring (Figure 4b). This would imply the initial production of *thiocyanic acid* which up to now has escaped detection, followed by a rapid isomerization to *isothiocyanic acid*. Although a unimolecular path for this reaction is difficult to envisage, a head-to-tail bimolecular exchange of hydrogens could account for the non-observance of the former. A way to verify this could be mixed pyrolysis of CD_3CH_2NCS and $CH_3CH_2N^{14}CS$. In the meanwhile the large difference in reactivity between isothiocyanates and isocyanates (Table 1), which closely parallels that found between xanthates and carboxylic and carbonate esters[40] (where doubly bonded oxygen and sulphur atoms abstract a β hydrogen in a six centre transition state), is in favour among other considerations[34] of this last type of structure. Recent calculations[41] of $\log A$ for these reactions, using the methods of Benson and coworkers[42] also support this proposition.

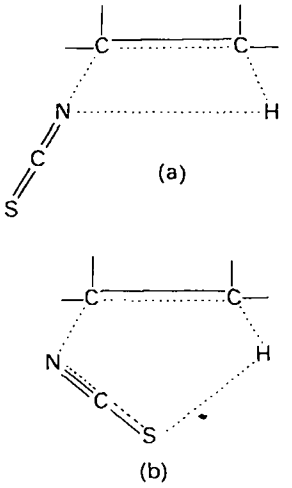


FIGURE 4. Transition state models.

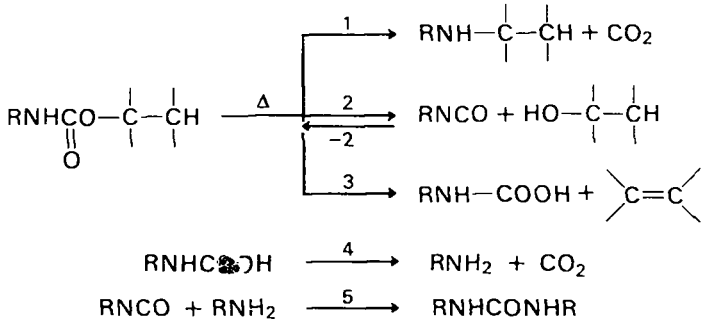
IV. THERMAL SYNTHESIS AND OTHER REACTIONS

Under this heading we discuss a rather heterogeneous group of reactions induced by heat, some of them at low temperatures, in which cyanates and related compounds are formed or react further to give other products. The majority of these reactions are not gas-phase pyrolyses; many are carried out in some solvent or else the pure liquid is heated. Unfortunately most of these studies are concerned with syntheses rather than with mechanisms, and often reaction conditions are poorly defined. A substantial proportion of these results refers to isocyanates due to their industrial importance and

consequently, are covered by patents. Since the solution chemistry of these classes of substances is dealt with in other chapters of this book only those reactions which appear more closely related to, or which suggest areas of research in, the gaseous phase will be considered here.

A. Isocyanates and isothiocyanates

One of the first reactions in this category was the preparation of phenyl isocyanate by thermal decomposition of symmetrical diphenyloxamide by Hofmann[43], as early as 1850. Later, the well known phosgenation processes were employed which in certain cases are performed in the gas phase at temperatures ranging from 150 to 400 °C[44,45]. Other preparative methods included the thermolysis of carbamates and ureas[45]. The first of these, which leads to isocyanates whenever there is an unsubstituted hydrogen on the nitrogen, has been subject to some attention in the last two decades. Thus, Metayer[46] reports that the substituted carbamates of more than nine carbon atoms decompose on distillation to give an alcohol and an isocyanate whereas the unsubstituted ones yield alcohol and an allophanate. The last compound undoubtedly originates from the secondary reaction of *isocyanic acid* and the unreacted carbamate. Similarly McKay and Vavasour[47] found that *N*-benzyl cholesteryl carbamate decomposes at 290 °C, presumably in the fused state, into carbon dioxide, cholesterol, cholest-3,5-diene and *sym*-dibenzyl urea. These authors assume a carboxylic-ester type transition state for the elimination of benzylcarbamic acid which rapidly breaks down into benzyl amine and carbon dioxide. However, they postulated the formation of cholesterol and urea through a single reaction between the carbamate and the amine, while we now know that benzyl isocyanate must have been an intermediate according to the general scheme (Scheme 2)



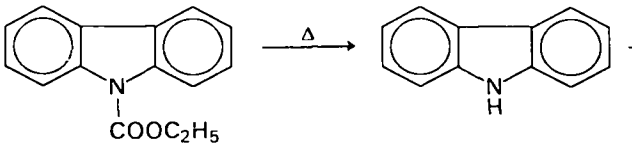
SCHEME 2.

where the relative importance of each process depends upon the structure of the radicals attached to the nitrogen and oxygen atoms in the original carbamate. This has been clearly shown by Dyer and Wright[48] who found, for example, that while ethyl *N*-phenyl carbamate equilibrates with phenyl isocyanate and ethyl alcohol at 230–260 °C, 1-methylbenzyl *N*-phenylcarbamate reacts mainly through path 3 in Scheme 2. In the case of ethyl *N*-carbazolyl carbamate, which apparently reacts only through path 3, they were able to determine an energy of activation of 32 kcal/mol and an entropy of activation of − 16 e.u. at 271 °C for the evolution of carbon dioxide,

$$C_6H_5NHCOOC_2H_5 \rightleftharpoons C_6H_5NCO + C_2H_5OH \quad (2)$$

$$C_6H_5NHCOOCH(CH_3)C_6H_5 \longrightarrow C_6H_5NH_2 + CO_2 + CH_2{=}CHC_6H_5 \quad (3)$$

which followed first-order kinetics. Similar findings are reported by Thorne and collaborators[49,50] for the thermal decomposition of a series of *N*-arylcarbamates of tertiary alcohols in solution.



(4)

The only detailed study of an isocyanate-forming reaction in the gas phase up to now, is that of methyl *N*-methylcarbamate reported by Daly and Ziolkowsky[51]. The compound was pyrolysed between 370 and 422 °C in a static system, using a reactor with a surface-to-volume ratio of 0·8 cm^{-1}. Under these conditions, the reaction is a clean decomposition into methyl isocyanate and methanol. It was also demonstrated that neither the reverse reaction nor transesterification with methyl amines took place. The effect of temperature on rate is given by the equation.

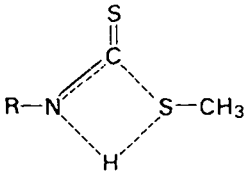
$$k = 10^{12\cdot39} \exp|-48060/RT| \ (s^{-1}) \quad (5)$$

It is interesting to see that this activation energy is at least about 3·5 kcal/mol higher than that of the competing olefin formation whose rate is strongly dependent on the structure of the alcohol from which the carbamate is derived, while substitution on the nitrogen is of much smaller importance in influencing the rate of isocyanate production[52,53]. This explains why in those cases where olefin formation is possible, isocyanates are produced in very low yields. The unsubstituted ethyl carbamate[54] decomposes in carbon coated vessels at 300–400 °C into *isocyanic acid*, carbon dioxide, ethylene and ammonia. The proportion of *isocyanic acid* relative to the total reaction goes from 90% at 300 °C to only 32% at

390 °C. In clean Pyrex glass vessels, small amounts of ethyl amine are also produced.

Following the original work of Kaluza[55] on the preparation of isothiocyanates from amines, extensive use has been made with the purpose of spontaneous or base-catalysed decomposition of compounds RNHC(S)X in solution, where X = SCO_2R[56,57], $SN(Et)_2$[58,59] and $SPOCl_2$[60].

More recently Ottenbrite[61] reported the preparation of a series of aromatic isothiocyanates from amines via thermal decomposition of the methyl dithiocarbamate. This author suggests alternative mechanisms in which the structures $R\overset{+}{N}H{=}C(S^-)SCH_3$ and $R{-}N{=}C(SH)SCH_3$ are intermediates. We feel that in absence of detailed information about this reaction, a four-centred, concerted transition state is a more realistic possibility:



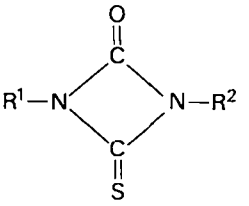
This is formally analogous to that proposed by Daly and colleagues for the methyl *N*-methylcarbamate discussed previously and could conceivably apply to the thermal decomposition of compounds RNHC(S)X. On the other hand the formation of isocyanates from pseudoureas reported by Robinson[62] which occurs at 250–300 °C according to the equation

$$(C_6H_5)_2N{-}\underset{\underset{NH}{\|}}{C}{-}OR \xrightarrow{\Delta} (C_6H_5)_2NH + RNCO \qquad (6)$$

is not easily envisaged as a single step reaction and might be preceded by isomerization to the corresponding urea. As it was shown (in Section III.A) above, the thermal stability of cyanates and related compounds in the gas phase depends upon the availability of β hydrogens as the formation of olefins appears to be the decomposition mode with the lowest activation energy although the inherent stability of the groups —NCX(X=O, S) is high as exemplified by isocyanic acid and phenyl isocyanate[63] which only decompose appreciably above 550 °C. This is in sharp contrast with the situation in dimethylsulphoxide solvent where several aromatic isocyanates are reported to decompose into a mixture of amine and symmetrical urea[64] at 80 °C. In this case, however, a specific interaction with the solvent seems

to be responsible for the enhanced reactivity as the same reactions do not take place in a hydrocarbon medium.

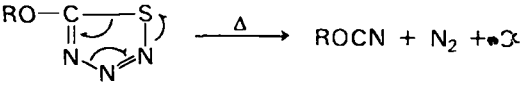
An interesting reaction which so far has not been fully investigated is the equilibration of isocyanates and isothiocyanates[65,66]. The reaction occurred when, for example, pure naphthyl isocyanate and phenyl isothiocyanate were heated together at 220 °C and is believed to proceed through the cyclic intermediate



B. Cyanates and Thiocyanates

The high reactivity of these compounds, which is extreme in the aliphatic series and leads to elimination and isomerization to the corresponding 'iso' form, is responsible to a large extent (especially in the case of the cyanates) for their relatively smaller importance as useful intermediates and for the small number of studies carried out in the gas phase. As pointed out above, the acids themselves only exist in significant concentrations in the 'iso' form, although aryl cyanates trap irreversibly *thiocyanic acid* in the form of aryloxydimercarpo-*S*-triazines[67,68].

One of the first successful methods for the preparation of cyanates included thermolysis of aryl- and alkyloxy 1,2,3,4-thiatriazoles[67,68] probably through the electronic rearrangement indicated below (equation 7).



(7)

By this method aromatic and aliphatic cyanates can be prepared in good yield, but while the former are stable, the latter isomerize to isocyanates exothermally[69,70]. In addition, secondary cyanates eliminate HNCO to form olefins even below boiling point[71]. Thiocyanates, on the other hand, are much more stable to heat and in any case decompose into olefin and acid before any isomerization can take place in the gas phase (see Section III.B). Exceptions to this are the allylic thiocyanates which do isomerize readily when heated in the liquid state[4]. This fact rendered unsuccessful our attempts to study the gaseous isomerization of allyl thiocyanate itself[71]. Spurlock and Newallis[72] have reported the thermal isomerization of

cyclopropylcarbinyl thiocyanate in acetonitrile at 155 °C. Along with the direct isomerization to cyclopropylcarbinyl isothiocyanate which accounts for 75% of the total reaction, cyclobutyl and but-3-enyl thio- and thiocyanates are also formed in significant amounts.

V. THERMODYNAMICS OF THE ELIMINATION

For a generalized stoichiometry of the type $A \rightarrow B + C$, the equilibrium constant is related to the measurable quantities P_f and P_0, the final and initial pressure of the system respectively, by the expression

$$K_p = \frac{(P_f - P_0)^2}{2P_0 - P_f} \tag{8}$$

In turn, for Scheme 1 it can be shown that the following relations hold in the case of ethyl derivatives:

$$K_2 = \frac{P_{HNCS} P_{C_2H_4}}{P_{EtNCS}} \tag{9}$$

$$K_p = \frac{P_{HNCS} P_{C_2H_4}}{P_{EtSCN} + P_{EtNCS}} = \frac{K_1 K_2}{K_1 + K_2} \tag{10}$$

Now it has been observed that starting from either end of Scheme 1, the equilibrium constant or, alternatively, the ratio P_f/P_0 increases with temperature, suggesting a positive enthalpy for these reactions. In fact the value obtained for ethyl thiocyanate[30] from a plot of $\log K_p$ vs. T^{-1} is 16 $\pm$ 2 kcal/mol which refers to the elimination from isothiocyanate because according to equation (10) $K_p = K_2$ if $K_1 \gg K_2$, as is the case.

The only exact experimental heats of formation in these series of compounds are ΔH_f° HNCS(g) = 30·0 $\pm$ 0·8 kcal/mol[73] and ΔH_f° CH_3NCS(g) = 27·10 kcal/mol[74]. Based on these values and known estimation methods[7] the enthalpy of the elimination reactions for the simply alkyl thiocyanates has been estimated[32,33] as 16 $\pm$ 2 kcal/mol and that for isothiocyanates as 20 $\pm$ 2 kcal/mol. This last value agrees reasonably well with that found experimentally for ethyl isothiocyanate (see above). These figures imply an enthalpy of approximately 4 kcal/mol for the thiocyanate–isothiocyanate isomerization.

Other quantities that are important when discussing the mechanism of these reactions are the bond energies and the heat of formation of the thiocyanate radical, which have been estimated[32] as ΔH_f° SCN(g) = 75 $\pm$ 5 kcal/mol. With this last value and literature values of the heat of formation of alkyl radicals[42], lower limits of 73 and 69 kcal/mol for the

bond dissociation energies in isothiocyanates and thiocyanates respectively are set with the help of known methods[75] for the estimation of heats of formation. Similar types of estimates cannot be made for the oxygen analogues as thermodynamic information is even more scarce in this case.

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CHAPTER 16

Syntheses and preparative applications of cyanates (esters of cyanic acid)

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I. INTRODUCTION

The first attempts to prepare alkyl cyanates date as far back as 1857 when Cloez[1] thought that he had obtained these compounds by reacting sodium alkoxides with cyanogen chloride. However, subsequent investigations[2–12] made it clear that the products obtained by Cloez had been mixtures containing mainly trialkyl cyanurates and dialkyl imidocarbonates. The reactions of phenolates with cyanogen halides gave similar results[3,8,9]. Neither could cyanates be isolated from the reaction of alkali cyanides with alkyl hypochlorites[7,8] or by elimination of hydrogen sulphide from *O*-alkyl monothiocarbonates[6,13]. Alkyl formohydroximates could not be dehydrated to cyanic esters (or their polymers) but instead eliminate the corresponding alcohol[11].

Because of these negative results, esters of cyanic acid were for many years considered to be 'non-existent compounds'. In 1960, however, Stroh and Gerber[14] succeeded in preparing cyanates of some sterically-hindered phenols, and similar cyanates were described in 1963 by Hedayatullah and Denivelle[15,16]. In 1964 Kauer and Henderson[17] showed that it was also possible to prepare cyanates of sterically-hindered alcohols. When the latter paper was published steric hindrance had, however, already been shown not to be a necessary requirement since, with due precautions, cyanates could be prepared from normal alcohols and phenols as well. In three papers, submitted for publication almost simultaneously, Jensen and Holm[18] announced the isolation of ethyl cyanate, whereas Martin[19] and Grigat and Pütter[20] described the preparation of phenyl cyanate by two different methods.

In the following years both alkyl and aryl cyanates were studied extensively so that the chemistry of the cyanato group, —OCN, is now as well known as that of most other functional groups.

Previous reviews dealing with organic cyanates have been written by Grigat[21,22], Hedayatullah[23], Martin[24], and Prejzner[25]. The reviews by Grigat contain numerous references to German patents; these have not been included in the present review.

II. SYNTHESES OF CYANATES

Cyanates were first prepared from thiatriazoles (Section II.A) or cyanogen halides (Section II.B) and these methods are still the most important although other modes of formation of cyanates (Section II.C–F) were discovered when their chemical properties had become known.

For comparison Table 1 contains yields of the known alkyl and cycloalkyl cyanates obtained by these methods. For the properties of the numerous aryl cyanates we refer to Tables 1 and 3 in the review by Grigat[21] from 1967. Since then only a few more special cyanates have been described (steroid cyanates[26], azo compounds[27], anthracene derivatives[28], thiophene derivatives[29], and various substituted phenyl cyanates[30–33]).

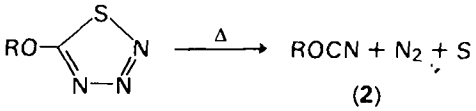
A. Thermolysis of Thiatriazoles

5-Alkoxy- and 5-aryloxy-1,2,3,4-thiatriazoles, **1**, are unstable and may decompose rather violently at room temperature. In ethereal solution at 20 °C a smooth decomposition with the elimination of sulphur and

TABLE 1. Yields (%) of alkyl and cycloalkyl cyanates by methods A–E

	A	B	C	D	E	References
Methyl cyanate	17					34, 39
Ethyl cyanate	91		40–57			34, 38, 39, 50
Propyl cyanate	86					34, 39
Isopropyl cyanate	77					34
Butyl cyanate	78			72	76	34, 39, 51, 52
Isobutyl cyanate	73			75		34, 51
s-Butyl cyanate	77					34
t-Butyl cyanate	48					36
Pentyl cyanate	26				84	35, 52
Isopentyl cyanate					84	52
Neopentyl cyanate	68	4·4				35, 17
4-Pentenyl cyanate	44					37
Hexyl cyanate	50			79		35, 51
Cyclohexyl cyanate			57			36
Nonyl cyanate					67	51
Undecyl cyanate					30	51
2,2,2,-Trifluoroethyl cyanate		80				20
2,2,2-Trichloroethyl cyanate		93				20
2,2,2-Tribromoethyl cyanate		85				20
2,2-Dichloroethyl cyanate		55				20
2-Methyl-2-hexafluoropropyl cyanate		80				48
1,4-Dicyanatobicyclo[2.2.2] octane		41				17
1-Cyanato-3-ethoxy-2,2,4,4-tetramethylcyclobutane		30				17
Ethyl 3-cyanato-2-butenoate		73				20

nitrogen leads to alkyl cyanates[18,34–39] and aryl cyanates[19,40–43] (**2**) in high yields.



(**1**) (**2**) (1)

The thiatriazoles are prepared from alkoxythiocarbonylhydrazines[44] (**3**) and nitrous acid[45,18,34–37] or from *O*-alkyl or *O*-aryl chlorothioformates **4** and sodium azide[19,38–43].

$$RO{-}CS{-}SCH_2CO_2H \xrightarrow{N_2H_4} \underset{(3)}{RO{-}CS{-}NHNH_2} \xrightarrow{HNO_2} \mathbf{1} \qquad (2)$$

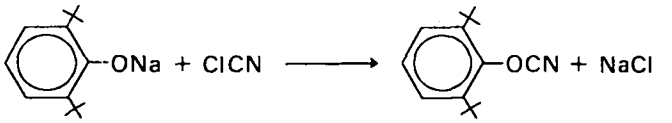
$$\underset{(4)}{RO{-}CS{-}Cl} \xrightarrow{NaN_3} \mathbf{1} \qquad (3)$$

Purification of the alkyl cyanates can be accomplished by distillation under reduced pressure. Due to the facile isomerization of alkyl cyanates to isocyanates the temperature must be kept at 20–40 °C during their preparation. Methyl cyanate is extremely labile and special care has to be taken to avoid isomerization. The higher normal cyanates (from C_4) are more stable and may be distilled at 40 °C without isomerization, but secondary alkyl cyanates undergo facile elimination of cyanic acid with the formation of alkenes. Tertiary cyanates with a neighbouring hydrogen atom are even less stable. *t*-Butyl cyanate could be prepared from the thiatriazole only in petroleum ether: in ethereal solution quantitative formation of cyanic acid and isobutene takes place[36]. Several 5-(2-alkenyloxy)-1,2,3,4-thiatriazoles have been prepared and their decomposition (according to equation (1)) investigated[37]. However, allylic cyanates are evidently extremely unstable and only isocyanates rearranged in the carbon skeleton were obtained. The formation of benzyl cyanate, phenethyl cyanate, and tetramethylene dicyanate from the corresponding thiatriazoles in solution has been demonstrated by infrared spectroscopy. However, they proved too unstable to be isolated, being transformed into isocyanates and isocyanurates even at room temperature, in the latter case with the formation of an insoluble high polymer[36].

Since it is usually more convenient to prepare aryl cyanates by method B, relatively few aryl cyanates have been prepared from aryloxythiatriazoles. These include nitro-, methoxy, and halogen-substituted phenyl cyanates[40,41], 1,4-dicyanatobenzene[40], and 4-biphenylyl cyanate[42,43].

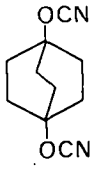
B. Reaction of Phenols or Alcohols with Cyanogen Halides

Addition of cyanogen chloride or bromide to an alkali metal phenolate usually results in the formation of an imidocarbonate or a cyanurate. Only when both *ortho* positions of the phenol carry bulky substituents (such as *t*-butyl, equation 4) can aryl cyanates be prepared in this manner[1–16,46].

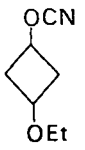


(4)

Cyanates **5**, **6**, **7** derived from sterically hindered alcohols can likewise be prepared from the lithium or sodium salts of the alcohols and cyanogen chloride[17].



(5)



(6)

Me_3CCH_2OCN

(7)

In the absence of sterically hindering groups the cyanate will react with excess phenolate to form an imidocarbonate. The discovery by Grigat and Pütter[20] that this reaction can be prevented by avoiding having the phenolate present in excess has made aryl cyanates generally accessible. The preferred method is to add, gradually, triethylamine to a solution of the phenol and cyanogen chloride or bromide in acetone (equation 5). Only phenols substituted with two or more electron attracting groups (nitro, halogen) yield exclusively or predominantly imidocarbonates also under these conditions[32].

$$ArOH + ClCN + Et_3N \longrightarrow ArOCN + Et_3NHCl \qquad (5)$$

It is also possible to prepare aryl cyanates by addition of a phenolate to excess cyanogen halide[30,47].

These methods can be employed to prepare cyanates derived from aliphatic polyhaloalcohols or enols[20,48] (cf. Table 1) but are not generally applicable to the preparation of alkyl cyanates.

The triethylamine method can in most cases be used as well to prepare cyanates derived from sterically hindered phenols. However, no reaction occurred with 3,3',5,5'-tetra-*t*-butyl-4,4'-biphenyldiol but the dicyanate could be prepared from the lithium salt of this phenol[49].

C. From O-Alkyl Thiocarbamates

Alkyl cyanates are obtained by treatment of *O*-alkyl thiocarbamates (**8**) with heavy metal oxides (HgO, Ag_2O, etc.) in ethereal solution at

0 °C. The water formed by the reaction was removed by means of magnesium sulphate[50].

$$\underset{\textbf{(8)}}{RO{-}CS{-}NH_2} + HgO \longrightarrow ROCN + HgS + H_2O \qquad (6)$$

R = alkyl

O-Ethyl selenocarbamate reacted very fast with HgO but the yield of ethyl cyanate was only 5 %[50].

O-Aryl thiocarbamates are reported not to react with HgO at room temperature but with Ag_2O the formation of the cyanate was shown by infrared spectroscopy[42,43].

D. From O-Alkyl N-Hydroxythiocarbamates

O-Alkyl *N*-hydroxythiocarbamates (**10**) are readily prepared from [(alkoxythiocarbonyl)thio]acetic acids (**9**) and hydroxylamine[51].

$$\underset{\textbf{(9)}}{RO{-}CS{-}SCH_2CO_2H} + NH_2OH \longrightarrow \underset{\textbf{(10)}}{RO{-}CS{-}NHOH} + HSCH_2CO_2H \qquad (7)$$

When treated with an acylating agent such as acetyl chloride or ethyl chloroformate, a rapid Lossen degradation takes place at room temperature with the formation of an alkyl cyanate (equation 8).

$$\underset{\textbf{(10)}}{RO{-}CS{-}NHOH} + ClCO_2Et \longrightarrow (RO{-}CS{-}NHOCO_2Et) \longrightarrow ROCN + S + CO_2 + EtOH \qquad (8)$$

The yields are good and the preparation of alkyl cyanates by this method is considerably faster than from 5-alkoxy-1,2,3,4-thiatriazoles. However, it can be used only to prepare butyl cyanate and its higher homologues. In the latter case it appears preferential to the thiatriazole method.

E. From Thiocyanates

By a procedure similar to that of method C, alkyl cyanates can be obtained from imidothiocarbonates, **12** (prepared from thiocyanates **11**) by treatment with HgO and $MgSO_4$ in ether at 0 °C[52].

$$\underset{\textbf{(11)}}{R'SCN} \overset{+ROH}{\rightleftharpoons} \underset{\textbf{(12)}}{R'S{-}\overset{\overset{NH}{\|}}{C}{-}OR} \overset{-R'SH}{\rightleftharpoons} ROCN \qquad (9)$$

The method is reported to be useful for the preparation of alkyl, cycloalkyl, aralkyl, and aryl cyanates but very few details were given in the publication[52].

F. From Cyanic Acid or Inorganic Cyanates

Although cyanic acid according to spectroscopic evidence (cf. Reference 53) consists exclusively of molecules with the structure HNCO, its reaction with diazoisobutane[53] indicates that HNCO exists in tautomeric equilibrium with HOCN. The reaction afforded a mixture of 14 components among which 4% butyl cyanate and 12% butyl isocyanate were identified by means of gas chromatography, infrared and mass spectrometry.

Similarly a mixture of cyanates and isocyanates may be formed by alkylation of the ambident cyanate ion under S_N1 conditions. The products of the reaction between silver cyanate and various alkyl halides have been investigated by gas chromatography[54]. Propyl and *s*-butyl iodide gave a mixture of cyanates and isocyanates; in all other cases only isocyanates or alkenes were obtained. Hence the reaction has no practical use for the preparation of alkyl cyanates.

III. PHYSICAL PROPERTIES*

A. General Properties and Atomic Distances

Alkyl cyanates of low molecular weight are mobile, colourless, lachrymatory liquids. Higher alkyl cyanates and aryl cyanates are liquids or low-melting solids. They may be purified by distillation but in the case of alkyl cyanates only at reduced pressure to avoid the facile isomerization into isocyanates. The purity may be verified by gas chromatography[18,34] or infrared spectroscopy[39,41].

An X-ray structural analysis has been carried out on 4-chloro-3,5-dimethylphenyl cyanate[55]. The mean bond lengths in the cyanate group are C-N = 1·14 Å and C–O = 1·27 Å. The short C–O bond is a consequence of the sp-hybridization of the carbon atom.

Measurement of the electric dipole moments of substituted aryl cyanates (C_6H_5OCN, 3·93 D) shows that the OCN group is the negative end of the dipole Ph—OCN. The resulting moment of 1,4-dicyanatobenzene (2·73 D) indicates that the vector of the OCN group is not coplanar with the benzene ring[56].

* The mass spectra of cyanates have been discussed in a separate chapter of this volume.

π-Hückel MO calculations have been carried out for phenyl cyanate and some substituted phenyl cyanates. Several reactivity indices have been correlated with experiment[56,24].

Hammett σ-values for the cyanate group have been calculated, by use of ^{19}F nuclear magnetic resonance and infrared measurements, to $\sigma_I = +0{\cdot}75 \pm 0{\cdot}04$ and $\sigma_R^0 = -0{\cdot}27 \pm 0{\cdot}07$ ($\sigma^0 = \sigma_I + \sigma_R^0$)[56].

Refraction indices of alkyl cyanates[34] and of phenyl cyanate[40] have been measured.

B. Infrared and Raman Spectra

Infrared spectra of organic cyanates are characterized by strong bands around 2200–2300 cm^{-1} (νC≡N) and 1160–1235 cm^{-1} (νC—O—C)[41,57,58]. The effect of substituents in aromatic cyanates on the CN frequency is small. That the absorptions in aliphatic cyanates occur at lower frequencies than in aromatic cyanates is ascribed to a greater contribution of the limiting structure $R-\overset{+}{O}=C=\overset{-}{N}$ in the former[59]. A more detailed discussion of the Raman and infrared spectra has been given by Martin[24,41].

Infrared spectra of the complexes between cyanates and $AlCl_3$ and $SnCl_4$ have been reported[60].

C. Nuclear Magnetic Resonance Spectra

The ^1H nuclear magnetic resonance spectra of alkyl cyanates[57] and aryl cyanates[24] exhibit the expected chemical shifts and integrated intensities. Thus comparing ethyl cyanate with ethyl isocyanate, the chemical shift of the α-protons (τ = 5·46, quartet) is quite different from that of the α-protons of the isocyanate which appear at 1·17 p.p.m. higher field. The β-protons (τ = 8·55, triplet) of ethyl cyanate are similarly found at 0·25 p.p.m. lower field than the β-protons of ethyl isocyanate[57].

^{14}N, ^{13}C, and for Y = F, ^{19}F chemical shifts of substituted aryl cyanates 4-Y—C_6H_4—OCN have been measured[61]. The ^{14}N and ^{19}F chemical shifts and the corresponding ^{13}C shift increments have been found to correlate with the appropriate substituent constants σ_R^0, σ_p and σ_I as well as with π-electron densities[61].

D. Ultraviolet Spectra

The ultraviolet spectra above 200 nm of aryl cyanates are characterized by the two bands typical of substituted benzenes: an intense band around

214–224 nm and a sharply structured absorption between 256 and 290 nm[24,40,43]. On substitution both bands are shifted towards red. The fine structure of the low energy band disappears gradually with an increasing number of substituents and structure is absent in the spectrum of 2,4,6-tribromophenyl cyanate. The bands of aryl cyanates appear at lower wavelength than those of the corresponding isocyanates[24,40] which indicates a lower resonance effect of the —OCN group.

E. Salts, Complexes and Associates

Aryl cyanates do not form nitrilium salts with alkyl halides, alkyl sulphonates or dialkyl sulphates[21,60]. On treatment with triethyloxonium tetrafluoroborate aryloxy nitrilium tetrafluoroborates could not be isolated[60]. Other alkylation reactions leading to alkylated urethanes have been investigated, but they probably do not involve a nitrilium ion (see Section V.G).

Proton acids catalyse the trimerization of aryl cyanates, but salts of cyanates have not been obtained. This is in accordance with the low basicity of the cyanate group which is of the same order of magnitude as that of the nitrile group[63]. In inert solvents aryloxycarbonimidoyl halides may be formed (see Section V.G).

Metal halide Lewis acids in the solid state or in concentrated solutions catalyse the trimerization of aryl cyanates and the isomerization of alkyl cyanates[20,34,40]. However, in dilute methylene chloride solutions complexes with $AlCl_3$ and $SnCl_4$ are stable for a longer period of time[60]. The $SbCl_5$ adduct is stable only below $-20\,^{\circ}C$. Infrared measurements indicate complex formation with the cyanate N atom, but complexes formed by coordination to the oxygen atom and the aryl group as well as higher molecular complexes with imidoyl chloride character appear to be present in the solution[60].

Aryl cyanates form 1:1 associates with hydroxylic proton donors[62,63]. The H atom coordinates with the lone pair of the nitrogen atom to form complexes of the structure $YC_6H_4OCN \cdots HOR$. Free energy relationships for the associates have been obtained[63].

Complex formation between cyanates and dimethyl sulphoxide plays a particular role in chemical reactions where the latter is used as solvent (see Section V.E.c).

F. Photochemistry

Irradiation of butyl cyanate (20 mmHg) through quartz (high pressure Hg lamp) for 12 h a 25 °C yields a number of products among which

butyl isocyanate and butyl isocyanurate were isolated in 38 and 39% yield, respectively. When irradiating with light of wavelength above 250 nm only the latter two compounds are reported as being formed[64].

IV. CHEMICAL PROPERTIES: REACTION MECHANISMS

A. Introduction

The cyanates may be regarded as nitriles in which the electron densities on both the carbon and nitrogen atoms have been diminished by the electron-attracting RO group. Consequently, we should expect that the cyanates are more reactive towards nucleophilic addition reactions than ordinary nitriles and that the reactivity will increase with the introduction of electron attracting substituents.

The nucleophilic addition reactions are catalysed by bases. It has been suggested that an activated complex is formed between cyanate and tertiary amines[65,66]. In the absence of other reaction partners, trimerization (aryl cyanates) or isomerization (alkyl cyanates) take place. Addition of weak nucleophiles is also catalysed by acids[67]. With hetero nucleophiles the corresponding addition products (acylation products) can generally be isolated. With carbon nucleophiles these addition compounds often split into ROH and XCN. In some cases the nitrile transfer may be a one-step process, not involving intermediates, with attack on either oxygen or carbon[68–71]. In these cases the cyanates may be regarded as cyanogen phenolates or alkoxides, analogous to cyanogen halides.

The cyanates can, however, also be looked upon as pseudohalides. One type of reaction to be expected from alkyl cyanates is therefore dissociation into carbonium ions, R^+, and cyanate ions, NCO^-, which may lead to nucleophilic substitution reactions or to elimination reactions. Whether an alkyl cyanate will react as an alkoxynitrile or an alkyl pseudohalide depends upon the reagent and the solvent[67,72] used and in some cases both reactions will occur simultaneously. Thus it is generally observed that the strongly nucleophilic carbanions, thiols, alcoholates and alkyl phosphates are acylated. Amino functional compounds are both alkylated and acylated and weak nucleophiles like aryl amines, alcohols and carboxylic acids are predominantly alkylated[67,72].

In agreement with the pronounced nucleophilicity cyanates show low activity towards electrophilic addition.

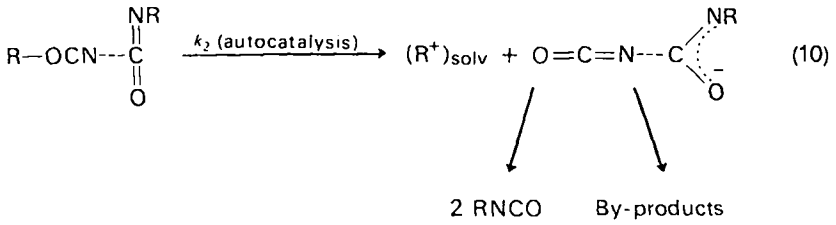
Finally 1,3-dipolar cycloadditions constitute a reaction type expected of electron-deficient triple bonds. Ordinary nitriles are generally less

reactive than alkynes, but due to the electron attracting RO group cyanates undergo facile cycloaddition reactions.

The general picture of the reactions of cyanates conforms well with the expected properties and in the literature 'reaction mechanisms' have frequently been proposed on this basis. However, only in a few cases have serious attempts been made to substantiate the proposed mechanism. The following discussion will deal with these cases only.

B. Isomerization

Alkyl cyanates but not aryl cyanates isomerize to the corresponding isocyanates. A detailed kinetic and mechanistic investigation of the isomerization of ethyl cyanate has been undertaken[73]. With nitrobenzene as solvent an isotope exchange reaction was found to occur between butyl cyanate and ^{15}N-labelled ethyl cyanate with the result that almost equimolecular amounts of the ^{15}N-labelled isocyanates Bu^{15}NCO and Et^{15}NCO were formed. The nearly complete equilibration and solvent and salt effects suggest that the isomerization takes place exclusively via solvent-separated ion pairs. Free ions are not considered to be important in the weakly cation- and anion- solvating medium. In the case of solvents with very low polarity (toluene) and solvents which weakly solvate cations (nitrobenzene, acetonitrile) the isomerization is autocatalysed by the already formed isocyanate assumed to act as shown in equation (10).



(10)

The reaction may proceed further, as it does in toluene, with formation of triethyl isocyanurate.

In nitrobenzene and acetonitrile the rate is approximately 20-times faster than in toluene and isocyanurate is not formed. Addition of $LiClO_4$ to the ethyl cyanate–acetonitrile solution causes a rate increase (positive salt effect) and the isomerization changes from an autocatalytic to an S_Ni reaction. In the cation-solvating solvent DMF, first-order kinetics

are likewise observed and the rate is 6×10^3 times faster than in nitrobenzene or acetonitrile. The isomerization in DMSO is exothermic and too fast to be followed by the technique employed. A complex mixture of products is obtained in this case which has been rationalized in terms of intervention of ethoxydimethylsulphonium cyanate as the primary product from ethyl cyanate and DMSO.

C. Nucleophilic Substitution Reactions

The reaction between alkyl cyanates and hydrogen chloride has been investigated in detail[74]. Reaction of propyl, *s*-butyl and isobutyl cyanate with HCl leads to propyl, *s*-butyl and isobutyl chloride. The isomeric chlorides are not formed. The reaction between optically active *s*-butyl cyanate and HCl in benzene and CCl_4 has been followed polarimetrically. A first-order reaction in cyanate was observed up to 80% conversion of the starting material. Inversion of configuration was found. This has been interpreted as a reaction in which the rate-determining step is C—OCN bond breaking with formation of an ion pair. In the media employed, free ions or solvent-stabilized ions are not important and only little racemization takes place. The ion pair is attacked from the rear by HCl resulting in a stereospecific product formation.

D. Nucleophilic Additions to the Triple Bond

Among nucleophilic additions (Section V.E) to the triple bond some of the more general reactions have been examined.

1. Addition of methanol

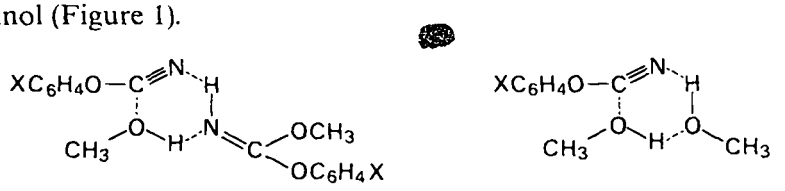
The uncatalysed reaction of aryl cyanates with methanol takes place slowly and yields a complex mixture of products[75]. Kinetic investigations by means of u.v. spectroscopy on the initial step, *viz.* addition of methanol to the aryl cyanate with the formation of an imido ester (equation 11), show that this step is autocatalysed by the already-formed imido ester (pseudo second order)[75].

The low activation energy and high negative activation entropy

$$XC_6H_4OCN + CH_3OH \longrightarrow \begin{matrix} XC_6H_4O \\ \diagdown \\ \quad C{=}NH \\ \diagup \\ CH_3O \end{matrix} \qquad (11)$$

are in accordance with a six-centre transition state involving cyanate,

imido ester and methanol (Figure 1). Addition of methanol in the beginning of the reaction is probably initiated catalytically by a second molecule of methanol (Figure 1).



$\Delta H^{\neq} = 7{\cdot}3$ kcal mol^{-1}

$\Delta S^{\neq} = -38{\cdot}7$ cal K^{-1} mol^{-1}

(for X = H)

FIGURE 1

The Hammett ρ-value for the autocatalytic process is $-0{\cdot}44$ and shows that electron-donating substituents increase the reaction rate. Both the cyanate and the imido ester contain the same substituent and the measured reaction constant is therefore equal to $\rho_1 + \rho_2$ for the aryl cyanate and for the catalyst, respectively. The ρ_1 value is a measure of the substituent effect on the nucleophilic addition to the cyanate group and is expected to have a positive sign as in the phenol- and *N*-methylaniline-addition to aryl cyanates[76,77]. This means that ρ_2 has a larger negative value than ρ and the catalyst thus has the predominant influence on the reaction rate.

The complexity of the reaction mixture obtained is caused by further reactions of the imido ester with methanol. The reaction time of the initial addition of methanol to the cyanate may be reduced considerably by addition of strong bases but the further transformation of the imidoester into side products is also catalysed by base. However, if only weakly basic nucleophiles, such as alkali metal halides, pyridine, etc., are used as catalysts, only the rate of the first step is effectively enhanced and unsymmetrical imido esters may be isolated in high yields[78].

2. Addition of phenols and *N*-methylanilines

The combined action of phenols and *N*-methylanilines on aryl cyanates has been investigated in detail[76].

Infrared measurements have shown that a 1:1 complex is formed between phenols and aryl cyanates in which the proton is associated with the lone-pair of the nitrogen atom[62]. This reaction is accompanied by a shift in the difference between the free and bound OH frequencies ($\Delta\nu$). With substituted phenols and phenyl cyanate it has been shown that the stability of the complex can be correlated with $\Delta\nu$.

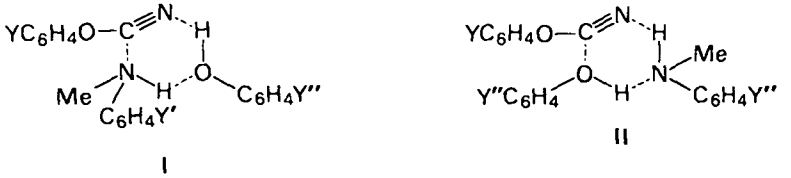
The formation of an imido ester from this complex (equation 12) takes place slowly but is accelerated by proton- or base-catalysis.

$$ArOCN + HOAr' \longrightarrow ArO-\overset{\overset{NH}{\|}}{C}-OAr' \qquad (12)$$

N-Methylaniline does not react with an aryl cyanate in absolute acetone at room temperature or in DMF even at 110 °C. In the presence of proton donors such as water, alcohols or phenols the corresponding isoureas are formed (equation 13).

$$ArOCN + HN(Me)(Ar') \longrightarrow ArO-\overset{\overset{NH}{\|}}{C}-N(Me)(Ar') \qquad (13)$$

For the combined action of equimolar amounts of phenol and *N*-methylaniline on phenyl cyanate it has been found that 1/3 of the cyanate gives the isourea and 2/3 adds phenol to form the imido ester. The activation parameters for both reactions have been calculated from kinetic measurements. The low activation energies and high negative activation entropies are in agreement with highly ordered transition states (Figure 2).



$\Delta H^{\neq} = 9{\cdot}6$ kcal mol^{-1} $\quad$ $\Delta H^{\neq} = 8{\cdot}8$ kcal mol^{-1}

$\Delta S^{\neq} = -42{\cdot}5$ cal K^{-1} mol^{-1} $\quad$ $\Delta S^{\neq} = -43{\cdot}6$ cal K^{-1} mol^{-1}

(for Y = Y' = Y'' = H)

FIGURE 2

The influence of substituents on the individual reactants has been evaluated and leads to a complete mechanistic picture[76,77]:

The formation of the isourea (**I**) is the result of an attack of *N*-methylaniline on the complex between phenol and the aryl cyanate. It is found that a linear correlation exists between the rate constant of attack and σ[79]. Substituents in the cyanate effect the stability of the associate and the electrophilicity of the cyanate group, the latter being more important. The overall rate is largely influenced by the nucleophilicity of the aniline.

The formation of the imido ester (**II**) is the result of an attack of the cyanate on a phenol–amine associate. Substitution within the phenol

effects both the stability of the associate and the nucleophilicity of the complex. The nucleophilicity of the amine determines the stability of the associate and thus the reaction rate.

In both cases the rate is increased when Y and Y′ are electron attracting and Y″ is electron donating. In the transition state **I** cationic character of the amine N atom, and in **II** ionic character of the phenol is expected.

3. Grignard reactions

The nucleophilic attack of Grignard reagents or dibutylmagnesium on alkyl and aryl cyanates has been shown to involve 1 mole of each reactant and to result in the formation of a complex of magnesium alcoholate or phenolate, nitrile and diethyl ether[68] (equation 14).

$$\mathrm{ROCN + RMgX \xrightarrow{Et_2O} RCN, ROMgX, \tfrac{1}{2}(C_2H_5)_2O} \qquad (14)$$

Kinetic measurements on the reaction of aryl cyanates by means of a thermographic method (recording temperature increase in the reaction mixture using a flow technique) show that the reaction is best described by a four-centre mechanism in the rate determining step[69]. For *m*-substituted aryl cyanates k_{obs} values are linearly dependent on the initial concentration of the reagent in excess (pseudo first-order reaction), signifying absence of complex formation prior to the rate-determining step. In the rate-determining step two alternative pathways have been considered (Figure 3): (i) attachment of magnesium directly to the oxygen

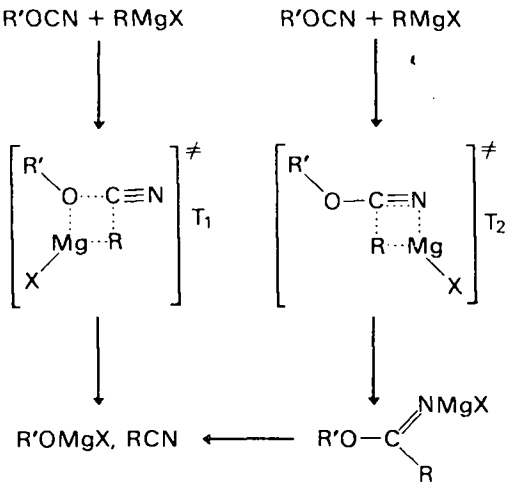


FIGURE 3

atom synchronously with nitrile formation; (ii) attachment of magnesium to nitrogen followed by a further reaction leading to the products observed.

For *m*-substituted aryl cyanates a ρ-value of +0·97 has been determined and for substitution within the aromatic Grignard reagents a ρ-value of −0·80 has been found. Since development of a negative charge is expected if phenolate is formed (via transition state T_1) the polarity of the transition state is rather low (ρ = +0·97). However, concurrently with breaking of the oxygen–carbon bond, a bond is formed to magnesium and this has some covalent character (27%) which may rationalize the findings. The second pathway (via transition state T_2) implies formation of an imido ester salt, but all attempts to obtain evidence for this intermediate have been unsuccessful. This does not rule out the presence of such an intermediate, since the data may be interpreted as meaning that the rate constant for the formation of the final products is much larger than the rate constant for the formation of the imido ester salt. Further support for T_2 is obtained from the fact that in the reaction between imido esters and Grignard reagents, which similarly leads to alcoholates and nitriles, the imido ester cannot be regenerated after mixing of the reactants even when using flow technique. On the other hand, it may well be that proton abstraction from the imido ester by the Grignard reagent proceeds by a cyclic, concerted reaction not leading to salt formation. Thus no conclusive evidence has been obtained for either of the two alternatives.

Quite similar considerations apply to the reactions between alkyl cyanates and Grignard reagents or dibutylmagnesium[70]. On the basis of kinetic data and the ρ-value for substituted phenylmagnesium bromides (*c.* −1·5) the reactions are best described as involving a concerted four-centre mechanism in the rate-determining step but again distinction between T_1 and T_2 cannot be made. In contrast to aryl cyanates the kinetic order in cyanate, with excess organomagnesium reagent (pseudo first-order reaction), is less than one and decreases at high concentrations. In the presence of excess cyanate similar kinetics are observed, the order in organomagnesium reagent being less than one and decreasing at high concentrations. This corresponds to a mechanism involving complex formation between the reactants prior to the rate-determining step.

V. CHEMICAL PROPERTIES: REACTIONS OF CYANATES

A. *Isomerization*

In contrast to aryl cyanates, which cannot be isomerized to isocyanates, most alkyl cyanates easily form isocyanates which in turn may trimerize

to isocyanurates[18,34,38,39]. Cyanates of β-halogen substituted alcohols resemble the aryl cyanates in that they do not isomerize[20]. Cyanates of sterically-hindered alcohols have unusual thermal stability but may be isomerized by means of boron trifluoride[17].

The extent of isomerization may be followed by gas chromatography[18] and infrared spectroscopy[39,54]. The rate of the isomerization increases with the temperature[18,39], the concentration of the cyanate and the polarity of the solvent[54], and is catalysed by proton acids and Lewis acids[17,72] as well as by bases[18].

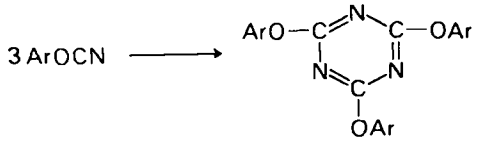
The decomposition of 5-alkoxythiatriazoles to alkyl cyanates sometimes takes an explosive course. The violent reaction is probably caused by the subsequent isomerization of alkyl cyanates and trimerization, the latter reaction being strongly exothermic[80].

The stability of primary alkyl cyanates increases with the chain length[34]. For this reason isobutyl cyanate, rather than methyl or ethyl cyanate, has often been used in investigations of the chemical properties of alkyl cyanates.

Although the formation of benzyl and phenethyl cyanate could be proved by infrared spectroscopy, they are so unstable that only the isocyanates could be isolated[36]. Allylic cyanates isomerize to isocyanates concurrent with rearrangement in the carbon skeleton[37]. For cyanates of secondary alcohols the elimination reaction (cf. Section V.D) is more rapid than the isomerization so that alkenes are formed[34].

B. Trimerization

Aryl cyanates trimerize by heating, forming triaryl cyanurates (2,4,6-triaryloxy-1,3,5-triazines, **13**) in almost quantitative yield[20,27,40]. The reaction is catalysed by proton acids and Lewis acids as well as by bases.

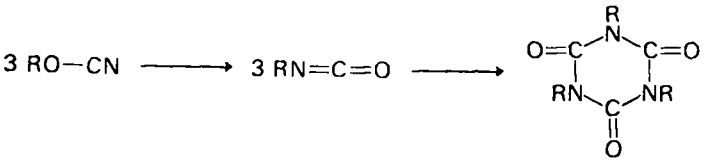


(15)

(13)

By copolymerization with cyanic or thiocyanic acid aryloxydihydroxytriazines and aryloxydimercaptotriazines are formed in good yields[81].

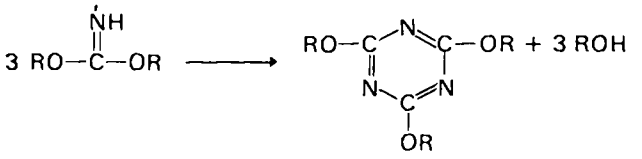
In contrast to the aryl cyanates, the alkyl cyanates first isomerize to isocyanates and then trimerize to trialkyl isocyanurates (1,3,5-trialkyl-2,4,6-trioxohexahydro-1,3,5-triazines[18,34,39,72], **14**).



(16)

(14)

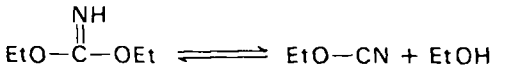
The formation of trialkyl cyanurates in the early attempts to prepare alkyl cyanates gave rise to the opinion that these were unstable because they easily trimerized to cyanurates. When monomeric alkyl cyanates had been prepared it was, however, realized that they do not directly polymerize but first isomerize and then form isocyanurates. The formation of cyanurates (**13**) during attempts to prepare cyanates is explained by a condensation process of dialkyl imidocarbonates.



(17)

(13)

In a few cases, however, isocyanurates had been isolated from imidocarbonates. Houben and Schmidt[10] found that pure diethyl imidocarbonate on standing for several months at room temperature formed triethyl isocyanurate. The explanation of this observation is probably that the imidocarbonate exists in equilibrium with the cyanate (equation 18).



(18)

This may isomerize to the isocyanate which then trimerizes to the isocyanurate. Both processes are catalysed by the imidoester.

At higher temperatures or in the presence of a condensing agent[12] the condensation reaction predominates and the cyanurate is formed.

Hedayatullah has recently found that the reaction between phenols and aryl cyanates to form diaryl imidocarbonates is in fact reversible[82].

C. Nucleophilic Substitution Reactions

Since the alkyl cyanates are pseudohalides they may react in a similar manner as alkyl halides and undergo substitution and elimination reactions.

Nucleophilic substitution[67,72] (alkylation) occurs with weakly basic anions, e.g.:

$$R{-}OCN + I^- \longrightarrow RI + OCN^- \quad (19)$$

With aqueous sodium nitrite a mixture of the corresponding alkyl nitrite and nitroalkane is formed. In the case of ambident anions the most nucleophilic site is the least electronegative atom, so that cyanate ions transform an alkyl cyanate into an isocyanate whereas thiocyanate ions transform it into an alkyl thiocyanate.

Strongly basic anions, such as hydroxide ions and sulphide ions, add to the triple bond.

Weakly basic, neutral nucleophiles are alkylated: ethanol is transformed into diethyl ether by ethyl cyanate and aniline forms *N*-ethyl- and *N*,*N*-diethylaniline. The stronger basic aliphatic amines are generally added to the triple bond.

With hydrogen chloride in inert solvents, alkyl cyanates form the corresponding alkyl chlorides and (polymeric) cyanic acid.

D. Elimination Reactions

Unlike the primary alkyl cyanates, secondary and tertiary alkyl cyanates are not, or only to a slight extent, isomerized to isocyanates. Instead they eliminate cyanic acid (isolated as cyanuric acid) and form alkenes. Propene constitutes 70–93% of the volatile products formed from isopropyl cyanate on heating and only a small amount of isopropyl isocyanate was present. *s*-Butyl cyanate forms three or four hydrocarbons which, presumably, are 1-butene, 2-butene (*cis* and/or *trans*) and isobutene[34]. *t*-Butyl cyanate is a very unstable compound which decomposes even at room temperature with the formation of isobutene and cyanic acid. Cyclohexyl cyanate forms cyclohexene on attempted distillation at atmospheric pressure[36].

In attempts to prepare 2-methyl-2-hexafluoropropyl isocyanate by isomerization of the corresponding cyanate, hexafluoroisobutene was obtained instead[48].

E. Nucleophilic Additions to the Triple Bond

1. Addition of O-, S- and Se-nucleophiles

a. *Water.* In an acid-catalysed reaction both alkyl and aryl cyanates add water with the formation of carbamic esters (**15**).

$$ROCN + H_2O \longrightarrow \underset{\textbf{(15)}}{RO{-}CO{-}NH_2} \qquad (20)$$

Aryl cyanates give an almost quantitative yield of aryl carbamates[14,19,27,40,42,83,84] but the acid-catalysed reaction of alkyl cyanates with water is complicated by their tendency to react as pseudohalides[72]. Thus propyl cyanate and hydrochloric acid give propyl chloride and cyamelide in addition to propyl carbamate.

The addition of water to alkyl cyanates is also catalysed by bases. From the reaction of ethyl cyanate with aqueous sodium hydroxide a 96% yield of ethyl carbamate was isolated[72]. Alkyl cyanates differ in this respect from aryl cyanates which generally are hydrolysed to the corresponding phenols by aqueous alkali metal hydroxides[15,16,83]. 3,3', 5,5'-Tetra-*t*-butyl-4,4'-dicyanatobiphenyl yielded a carbamate with alcoholic KOH[84].

Many different compounds are transformed into their anhydrides by means of cyanates and the elimination of water can, at least formally, be considered as a reaction of the cyanate with water. Thus carboxylic acids[27,67,85–87], sulphonic acids[81,86–87], and monoalkyl phosphates[85,86] are transformed into their anhydrides. In the presence of alcohols carboxylic acids form esters[85,86].

Aldoximes add aryl cyanates with the formation of *O*-(aryloxycarbonimidoyl)aldoximes (**16**) which by heating form the corresponding nitrile (or isocyanide) and a carbamate[86,88,89].

$$ArOCN + HON{=}CHR \longrightarrow \underset{\textbf{(16)}}{ArO{-}\overset{\overset{NH}{\|}}{C}{-}ON{=}CHR} \longrightarrow ArOCONH_2 + RCN \qquad (21)$$

Also carboxyamides can be transformed into nitriles by means of cyanates but the reaction occurs at higher temperatures[86]. *N*-Nitroso-*N*-phenylglycine reacts with a cyanate to form *N*-phenylsydnone[86].

b. *Alcohols and phenols.* Phenols react with aryl cyanates with the formation of imidocarbonates **17**.

$$ArOCN + Ar'OH \longrightarrow \underset{\textbf{(17)}}{ArO{-}\overset{\overset{NH}{\|}}{C}{-}OAr'} \qquad (22)$$

The reaction is catalysed by bases (HO^-, RO^-, triethylamine, etc.). Usually the unsymmetric reaction products are unstable and eliminate

the most acidic phenol on heating to give a cyanate which then trimerizes to a cyanurate[15,27,76,77,83,84].

$$ArO-\overset{\overset{NH}{\|}}{C}-OAr' \longrightarrow ArOH + Ar'OCN \quad \text{(when ArOH is the stronger acid)} \qquad (23)$$

Polyphenols react with aryl cyanates to form poly(imidocarbonates)[23].

The addition of alcohols to aryl cyanates is catalysed both by acids and bases[65,83,85]. In the base-catalysed reaction unsymmetric alkyl aryl imidocarbonates are formed. However, these are difficult to isolate[83] because the base also catalyses a further reaction with excess alcohol, resulting in the formation of the phenol and a symmetric dialkyl imidocarbonate which in part is transformed into a trialkyl cyanurate. In absence of a base the reaction is much slower and the dialkyl imidocarbonate is in part transformed into other products (tetraalkyl orthocarbonate, ammonia, 2-amino-4,6-dialkoxy-1,3,5-triazine and 2-amino-4,6-diaryloxy-1,3,5-triazine)[75,78]. When, however, a very weak nucleophile (e.g., KI or LiBr) is used as the catalyst the unsymmetric alkyl aryl imidocarbonates can be isolated in excellent yields[78].

When the reaction between an aryl cyanate and an alcohol is catalysed by hydrochloric acid, the hydrochloride of the imidocarbonate decomposes spontaneously into the corresponding aryl carbamate and an alkyl chloride (equation 24)[83].

$$ArOCN + ROH + HCl \longrightarrow (ArO)(RO)C{=}NH_2Cl \longrightarrow ArO-CO-NH_2 + RCl \qquad (24)$$

When the alcohol is present in excess the hydrochloride may alternatively react further with the alcohol to form an orthocarbonate (equation 25)[75,85].

$$(ArO)(RO)C{=}NH_2Cl + 3\,ROH \longrightarrow (RO)_4C + ArOH + NH_4Cl \qquad (25)$$

Alkyl cyanates react with alcohols in a base-catalysed reaction with the formation of dialkyl imidocarbonates[72], e.g.

$$EtOCN + EtOH \xrightarrow{EtO^-} (EtO)_2C{=}NH \qquad (26)$$

Unsymmetric dialkyl imidocarbonates disproportionate in a similar manner to alkyl aryl imidocarbonates[17].

Phenol and ethyl cyanate react without a catalyst to give ethyl phenyl imidocarbonate[72]. Ethyl cyanate also reacts with ethanol without a

catalyst but in this case the cyanate reacts as an alkylating agent, transforming ethanol into diethyl ether, while the cyanic acid formed reacts with ethanol to form ethyl carbamate and ethyl allophanate (equation 28)[67,72].

$$EtOCN + EtOH \longrightarrow Et_2O + HNCO$$

$$HNCO + EtOH \longrightarrow EtO{-}CO{-}NH_2 \xrightarrow{HNCO} EtO{-}CO{-}NH{-}CO{-}NH_2 \qquad (28)$$

In the proton-catalysed reaction between alkyl cyanates and alcohols the alkylation and addition reactions probably compete. It has been found[72] that when the reaction is carried out at room temperature the carbamate formed corresponds to the alcohol and not to the alkyl cyanate: thus ethyl cyanate and propyl alcohol form propyl carbamate. This indicates that the cyanate alkylates the acid (HCl) with the formation of cyanic acid which then reacts with the alcohol. At low temperature the addition reaction predominates and an imidoester salt is formed[39].

c. *Dimethyl sulphoxide.* According to Martin[90,90a] aryl cyanates add dimethyl sulphoxide (DMSO) with the formation of a complex **18**.

$$ArO{-}C{\equiv}N + Me_2SO \xrightarrow{H^+} ArO{-}C(=NH){-}O{-}\overset{+}{S}Me_2 \qquad (29)$$

(18)

This complex is very reactive and reacts with nucleophiles with the formation of *O*-aryl carbamates. This reaction can be visualized as the transfer of a methylenesulphonium ion to the nucleophile:

$$ArO{-}C(=NH){-}O{-}\overset{+}{S}Me_2 \longrightarrow ArO{-}CO{-}NH_2 + (H_2C{=}\overset{+}{S}{-}CH_3) \qquad (30)$$

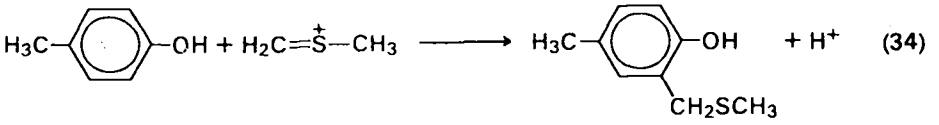
With *N*-nucleophiles or non-aromatic *C*-nucleophiles sulphuranylidene derivatives are formed, e.g.:

$$(NC)_2CH_2 + H_2C{=}\overset{+}{S}{-}CH_3 \longrightarrow (NC)_2C{=}SMe_2 + H^+ \qquad (31)$$

$$ArSO_2NH_2 + H_2C{=}\overset{+}{S}{-}CH_3 \longrightarrow ArSO_2N{=}SMe_2 + H^+ \qquad (32)$$

With *O*-nucleophiles and aromatic *C*-nucleophiles the predominant reaction is the formation of (methylthio)methyl derivatives, e.g.:

$$RCH_2OH + H_2C{=}\overset{+}{S}{-}CH_3 \longrightarrow RCH_2{-}O{-}CH_2{-}SCH_3 + H^+ \quad (33)$$



(34)

d. *Hydrogen sulphide and selenide.* The addition of hydrogen sulphide[18,27,28,30,31,34,39,43,91,94] and hydrogen selenide[72] to alkyl or aryl cyanates takes place in a smooth reaction and usually with excellent yields of thio- or seleno-carbamates, **19**.

$$ROCN + H_2Y \longrightarrow RO{-}CY{-}NH_2 \quad (35)$$

(19)

(Y = S,Se)

The reaction is strongly catalysed by bases (triethylamine, pyridine). For the preparation of thiocarbamates it may be convenient to use a thiosulphate instead of hydrogen sulphide[92].

The reaction of hydrogen selenide with alkyl cyanates also gives rise to unstable compounds which seem to be bis(alkoxycarbonimidoyl) selenides[72], **20**.

$$2\,ROCN + H_2Se \longrightarrow RO{-}\overset{\overset{NH}{\|}}{C}{-}Se{-}\overset{\overset{NH}{\|}}{C}{-}OR \quad (36)$$

(20)

Because of their ability to react with hydrogen sulphide cyanates may induce reactions in which hydrogen sulphide is eliminated. Thiocarboxylic acids form diacyl sulphides (**21**) or, in the presence of an alcohol or an amine, form esters or amides[85–87] (equation 38):

$$2\,RCOSH + R'OCN \longrightarrow (RCO)_2S + R'O{-}CS{-}NH_2 \quad (37)$$

(21)

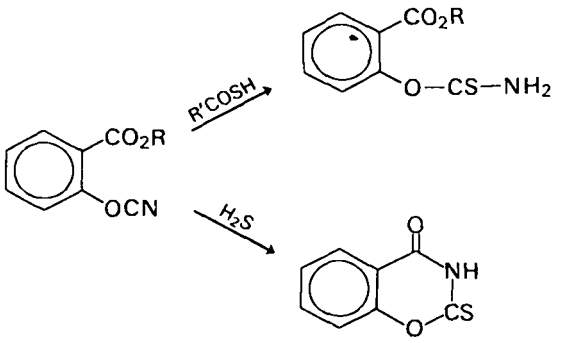
$$RCOSH + R'NH_2 + R'OCN \longrightarrow RCONHR' + R'O{-}CS{-}NH_2 \quad (38)$$

Analogously dithiocarbamates may form thioureas. However, a trialkylammonium salt of an *N*-monoalkyldithiocarbamate forms an isothiocyanate[85] (equation 39):

$$RNHCS_2^-{\cdot}R_3\overset{+}{N}H + R'OCN \longrightarrow RNCS + R_3N + R'O{-}CS{-}NH_2 \quad (39)$$

Thioamides and aryl cyanates give nitriles in almost quantitative yields, and thioureas may form either cyanamides or carbodiimides[93]. With xanthates the corresponding thioanhydrides are formed[87].

o-Cyanatobenzoates react at low temperature with thiocarboxylic acids to form thiocarbamates whereas the reaction with H_2S or thioureas is accompanied by ring-closure[87] (equation 40):



(40)

e. *Thiols.* Both alkyl and aryl cyanates add thiols without a catalyst to form imidothiocarbonates[43,72,83] (**22**)

$$ROCN + R'SH \longrightarrow RO-\overset{\overset{NH}{\|}}{C}-SR' \quad (41)$$

(**22**)

However, the aryl derivatives decompose at room temperature into a phenol and a thiocyanate (equation 42) and often the intermediate imidothiocarbamate could not be isolated[83].

$$ArO-\overset{\overset{NH}{\|}}{C}-SR \longrightarrow ArOH + RSCN \quad (42)$$

The aliphatic imidothiocarbonates seem to be somewhat more stable[72]. By means of a thiol scavenger they may eliminate the thiol and form a cyanate. This reaction has been used to prepare alkyl cyanates, the imidothiocarbonates being prepared from a thiocyanate and an alcohol[52] (cf. Section II.E).

When the sodium salt of a thiol is applied, the reaction with alkyl cyanates takes a different course, depending upon the solvent. In DMSO an *S*-alkylation is the predominant reaction. In ethanol solution alkylation only occurs to a minor extent, but the imidothiocarbonate is split into an

alcohol and a thiocyanate which reacts with thiolate ion to form a disulphide and cyanide[67] (equation 43).

$$ROCN + R'S^- \longrightarrow (RO-\overset{\overset{N^-}{\|}}{C}-SR') \longrightarrow$$

$$RO^- + R'SCN \xrightarrow{R'S^-} R'S-SR' + CN^- \qquad (43)$$

f. *Carboxylic acids.* Addition of a carboxylic acid to the triple bond of a cyanate has been observed in one case. Ethyl cyanate reacted with benzoic acid to form *N*-benzoyl *O*-ethyl carbamate[72], **23**.

$$EtOCN + PhCO_2H \longrightarrow EtO-CO-NHCOPh \qquad (44)$$

(23)

However, generally alkyl cyanates either alkylate free carboxylic acids to esters (particularly in DMSO or DMF) or form acid anhydrides[27,67]. The latter reaction seems to be general for aryl cyanates[85–87]. Alkali salts of carboxylic acids are exclusively alkylated by alkyl cyanates[67].

Thiocarboxylic acids form diacyl sulphides both with alkyl and aryl cyanates[72,85,87] (equation 37) but their salts are *S*-alkylated by alkyl cyanates[67].

2. Addition of *N*-Nucleophiles

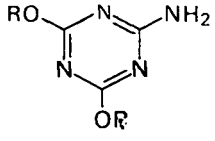
a. *Ammonia and primary amines.* In ethereal solution ammonia reacts with cyanates to form esters of imidobis(carbonimidic) (or iminobis(formimidic)) acids (isobiurets, **24**) even when ammonia is present in large excess[72,95].

$$2\,ROCN + NH_3 \longrightarrow RO-\overset{\overset{NH}{\|}}{C}-NH-\overset{\overset{NH}{\|}}{C}-OR \qquad (45)$$

(24)

In alcohol or water this ester reacts with a third molecule of the cyanate and forms a 2-amino-4,6-diaryloxy(dialkyloxy)-1,3,5-triazine[95], **25**.

$$RO-\overset{\overset{NH}{\|}}{C}-NH-\overset{\overset{NH}{\|}}{C}-OR + ROCN \longrightarrow \qquad (46)$$



(25)

Primary amines react in an analogous way[18,27,30,38,67,72,85,86,95,96], but it is now possible to isolate the initial product of the addition reaction, an isourea (**26**):

$$ROCN + R'NH_2 \longrightarrow RO-C(=NR')-NH_2 \rightleftharpoons RO-C(NHR')=NH \qquad (47)$$

(**26**)

Equivalent amounts of an alkyl cyanate and an aliphatic primary amine usually give an isourea in almost quantitative yield[72]. Only in the case of *t*-butylamine did the reaction not stop at the isourea. In a side reaction this amine was also alkylated[72], like primary aromatic amines which are alkylated by alkyl cyanates (Section V.C).

Aryl cyanates form isoureas both with aliphatic and aromatic primary amines. However, the reaction only stops at the isourea stage when the reaction is carried out with a salt of the amine.

The reaction of an isourea with a second molecule of the cyanate might in principle give either a symmetric (**27**) or an unsymmetric (**28**) isobiuret.

$$RO-C(=NH)-N(R')-C(=NH)-OR \quad \text{or} \quad RO-C(=NR')-N=C(NH_2)-OR$$

(**27**) (**28**) (and possible tautomers)

Grigat[95] assumed that these compounds corresponded to the symmetric formula **27**. Infrared evidence[67,72] however, indicates that the unsymmetric compounds are formed. Further, the predominant tautomer seems to be that with an NH_2 group **28**. In the case of isobiurets, **28** has been suggested as being stabilized by the presence of conjugated double bonds.

The reaction between cyanates and α-aminocarboxylic acids normally stops at the isourea stage[95] (equation 48).

$$ROCN + H_2N-CH_2CO_2H \longrightarrow RO-C(=NH)-NH-CH_2CO_2H \qquad (48)$$

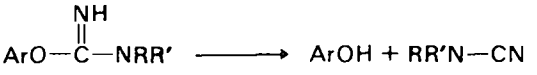
However, esters of amino acids react as primary amines adding 2 moles of the cyanate[22].

b. *Secondary amines.* Aryl cyanates react with secondary amines to form *N,N*-disubstituted isoureas[67,85,95], **29**.

$$ArOCN + RR'NH \longrightarrow ArO-C(=NH)-NRR' \qquad (49)$$

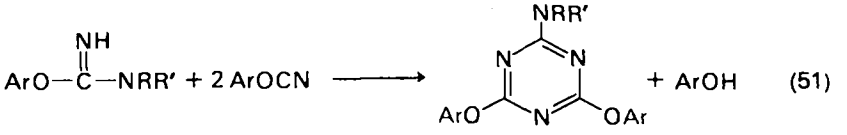
(**29**)

These isoureas are stable as salts but are cleaved by strong bases into phenols and cyanamides (equation 50).



(50)

The NH group of the isoureas reacts with isocyanates and can be alkylated or acylated. With excess aryl cyanate the isoureas may form triazines[95] (equation 51).

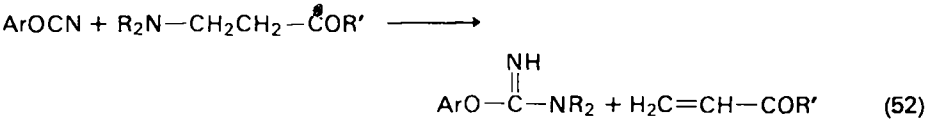


(51)

Heteroaromatic compounds with an NH group, e.g. diazoles and triazoles, react in the same way as secondary amines with aryl cyanates[95].

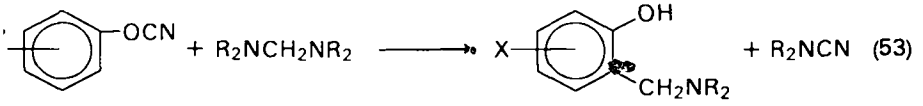
c. *Tertiary amines.* Cyanates do not usually react with tertiary amines which mainly catalyse their trimerization to cyanurates[65]. The following special types of tertiary amines do, however, react with aryl cyanates in rather complicated reactions. The primary reaction may be visualized as an attack of the nucleophilic amine nitrogen on the nitrile group, resulting in a scission of the amine.

Martin and Weise[66] have carried out an extensive investigation of the reactions of aryl cyanates with Mannich bases, tetraalkylmethylenediamines and dialkylaminoformaldehyde acetals and compared it with the von Braun reaction with cyanogen bromide. Mannich bases give a vinyl ketone and an isourea (equation 52) which reacts further with the aryl cyanate to give a triazine, as mentioned above.



(52)

Tetraalkylmethylenediamines react to give dialkylcyanamides (equation 53).



(53)

The dialkylaminomethylphenol may react further both with the cyanate and with the methylenediamine.

d. *Silylamines.* The reaction of aryl cyanates with trimethylsilylamines[97] occurs primarily as an addition of the nucleophilic nitrogen atom of the silylamine to the carbon atom of the nitrile group and of the silyl group to the nitrogen atom, i.e. with the formation of *N*-silylated isoureas **30**, **31**, **32**, or isobiurets **33**. The primary products are desilylated by further reactions with the aryl cyanate with the formation of aryl trimethylsilyl ethers together with triazines or *N*-cyanoisoureas (sometimes followed by polymerization).

$$ArOCN + Me_3Si{-}NR_2 \longrightarrow ArO{-}\underset{\displaystyle NR_2}{\overset{\displaystyle |}{C}}{=}N{-}SiMe_3 \qquad (54)$$

(30)

Compound **30** may react further with the aryl cyanate to form a 2-dialkylamino-4,6-diaryloxy-1,3,5-triazine.

$$ArOCN + Me_3Si{-}NHR \longrightarrow$$

$$ArO\underset{\displaystyle NHR}{\overset{\displaystyle |}{C}}{=}N{-}SiMe_3 \xrightarrow{ArOCN} ArO\underset{\displaystyle NHR}{\overset{\displaystyle |}{C}}{=}N{-}CN + ArOSiMe_3 \qquad (55)$$

(31)

$$ArOCN + (Me_3Si)_2NH \longrightarrow$$

$$ArO\underset{\displaystyle HN{-}SiMe_3}{\overset{\displaystyle |}{C}}{=}N{-}SiMe_3 \xrightarrow{ArOCN} ArO\underset{\displaystyle HN{-}SiMe_3}{\overset{\displaystyle |}{C}}{=}N{-}CN + ArOSiMe_3 \qquad (56)$$

(32)

$$2\ ArOCN + (Me_3Si)_2NR \longrightarrow$$

$$\begin{array}{l} ArO{-}C{=}N{-}SiMe_3 \\ \quad\ \ | \\ \quad RN \\ \quad\ \ | \\ ArO{-}C{=}N{-}SiMe_3 \end{array} \xrightarrow{2\ ArOCN} \begin{array}{l} ArO{-}C{=}N{-}CN \\ \quad\ \ | \\ \quad RN \\ \quad\ \ | \\ ArO{-}C{=}C{-}CN \end{array} + 2\ ArOSiMe_3 \qquad (57)$$

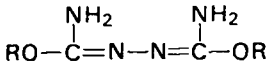
(33)

e. *Hydrazines.* Hydrazine reacts with aryl cyanates[27,30,46,67,98] or alkyl cyanates[67] to give a diacylhydrazine, **34**,

$$2\ ROCN + H_2N{-}NH_2 \longrightarrow RO{-}\overset{\displaystyle NH}{\overset{\displaystyle \|}{C}}{-}NH{-}NH{-}\overset{\displaystyle NH}{\overset{\displaystyle \|}{C}}{-}OR \qquad (58)$$

(34)

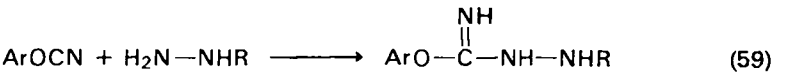
or the tautomeric azine, **35**.



(35)

Infrared spectroscopic evidence indicates that the products in fact have the latter structure[67].

Monosubstituted or 1,1-disubstituted hydrazines and hydrazones react with only 1 mole of an aryl cyanate with the formation of isosemicarbazides (equation 59) or isosemicarbazones[98].



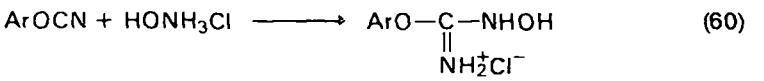
(59)

Phenylhydrazine is ethylated by ethyl cyanate and the cyanic acid generated reacts with excess phenylhydrazine to form 1-phenylsemicarbazide[67].

Similarly 1,2-disubstituted hydrazines react with only 1 mole of phenyl, trichloroethyl, or trifluoroethyl cyanate (the less reactive 1,2-diisopropyl- and 1-isopropyl-2-phenylhydrazine reacted only with the trihaloethyl cyanates)[99]. The isosemicarbazides formed were able to undergo a subsequent reaction with phenyl isocyanate, in agreement with the general experience that cyanates are less reactive than isocyanates towards nucleophilic reagents.

As would be expected arylene dicyanates react with hydrazine to form chain polymers[23].

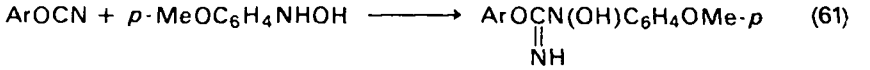
f. *Hydroxylamines.* Hydroxylammonium chloride and aryl cyanates react to give hydrochlorides of *O*-aryl-*N*-hydroxyisoureas[27,30,46,100] **36**.



(60)

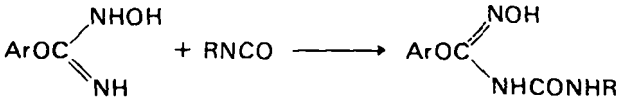
(36)

The free bases separate on addition of sodium carbonate but are unstable and decompose with elimination of the phenol. *N*-Arylhydroxylamines give more stable products when their aryl group is substituted with electron-donating groups, e.g.:



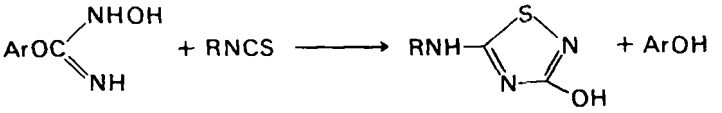
(61)

The hydroxyl group of *O*-aryl-*N*-hydroxyisoureas may be acylated or sulphonylated[100]. Isocyanates also add but probably react with the NH-group (equation 62).



(62)

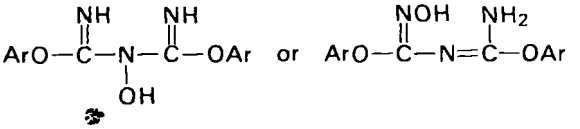
Isothiocyanates react with elimination of the phenol and the formation of 1,2,4-thiadiazoles (**37**)[100].



(63)

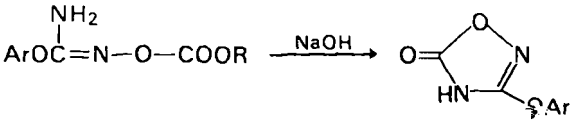
(**37**)

The *O*-aryl-*N*-hydroxyisoureas may react with a second molecule of the aryl cyanate. Grigat[21] has assigned a symmetric formula **37** to the products formed but, as in the case of the products of the reaction with primary amines, they probably correspond to the asymmetric formula **38**.



(**37**) (**38**)

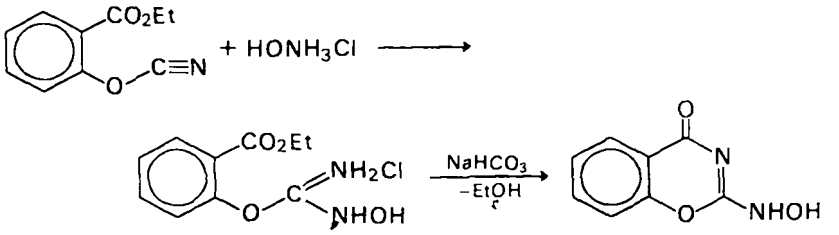
The acyl derivatives obtained by acylation with alkyl chloroformates or *S*-alkyl chlorothioformates undergo base-catalysed ring-closure to 1,2,4-oxadiazolin-5-ones[100], **39**.



(64)

(**39**)

Aryl cyanates with a $-CO_2Et$ group in the *ortho* position react with hydroxylamine to give 2-hydroxylamino-4*H*-1,3-benzoxazin-4-ones, **40**.



(65)

(**40**)

The reactions of aryl cyanates with hydroxylamine has chiefly been studied by Grigat and Pütter[100]. Hedayatullah and coworkers[27,30,43,46] have prepared hydroxylamine derivatives of aryl cyanates of special types. Martin and coworkers[67] have prepared *O*-ethyl-*N*-hydroxyisoureas from ethyl cyanate and hydroxylamine or *N*-4-tolylhydroxylamine. In contrast to their aromatic analogues the derivatives of alkyl cyanates are stable as the free bases.

g. *Oximes.* Ketoximes, including nitrosophenols (=quinone monoximes), react with aryl cyanates to form aryloxycarbonimidoyl ketoximes[88], **41**.

$$\mathrm{ArOCN + HON{=}CRR' \longrightarrow ArO{-}\overset{\overset{\mathrm{NH}}{\|}}{\mathrm{C}}{-}O{-}N{=}CRR'} \qquad (66)$$

(41)

On addition of hydrochloric acid these products undergo a Beckmann rearrangement and hydrolysis (equation 67).

$$\mathrm{ArO\overset{\overset{\mathrm{NH}}{\|}}{C}{-}O{-}N{=}CR_2 \xrightarrow{HCl + H_2O} ArOCONH_2 + RCONHR} \qquad (67)$$

Aldoximes also give aryloxycarbimidoyl derivatives on the reaction with aryl cyanates, but they are unstable and decompose at room temperature or on heating into nitriles[88].

In the reaction of aryl cyanates with hydroxamic acids the intermediate aryloxycarbimidoyl derivative is cleaved into an aryl carbamate and an isocyanate (Lossen rearrangement) which reacts with additional hydroxamic acid so that the resulting product is an *O*-carbamoylhydroxamic acid[87].

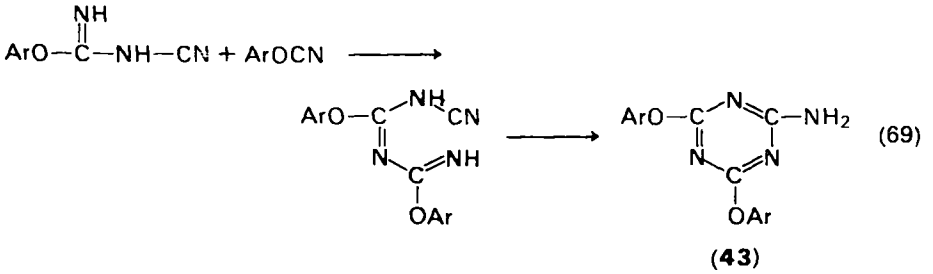
h. *Amides and ureas.* Carboxamides react with cyanates only at higher temperatures and then form nitriles[86]. Ureas do not react with cyanates[22].

However, cyanamides react with aryl cyanates to form *N*-cyanoisoureas[101], **42**.

$$\mathrm{ArOCN + RNH{-}CN \longrightarrow ArO{-}\overset{\overset{\mathrm{NH}}{\|}}{\mathrm{C}}{-}NR{-}CN} \qquad (68)$$

(42)

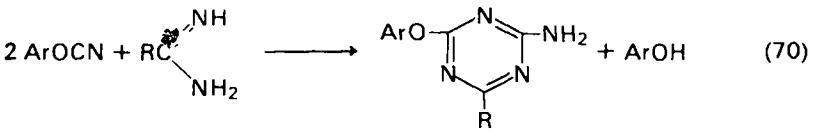
The reaction product of unsubstituted cyanamide (R = H) reacts in alkaline solution with a second molecule of the cyanate to form a 2-amino-4,6-diaryloxy-1,3,5-triazine **43**.



(69)

(43)

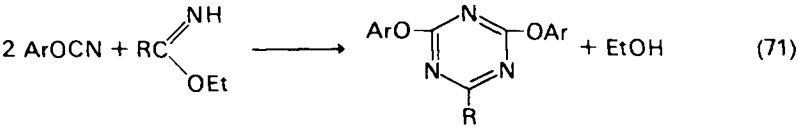
Guanidine[93], and amidines in general[22], react with aryl cyanates to form triazines, **44**.



(70)

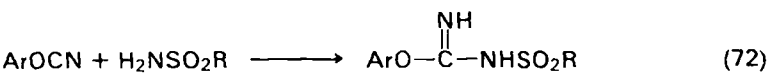
(44)

Imidoesters also form triazines[22] but incorporate 2 moles of the aryl cyanate and eliminate the alkoxy group (equation 71).



(71)

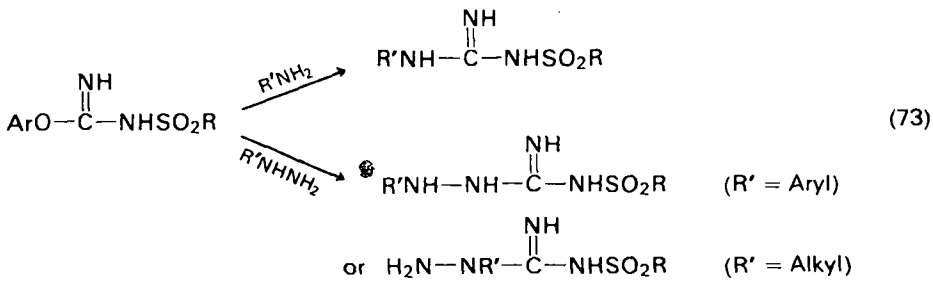
Sulphonamides react with aryl cyanates in a base-catalysed reaction to form *N*-sulphonylisoureas[81], **45**.



(72)

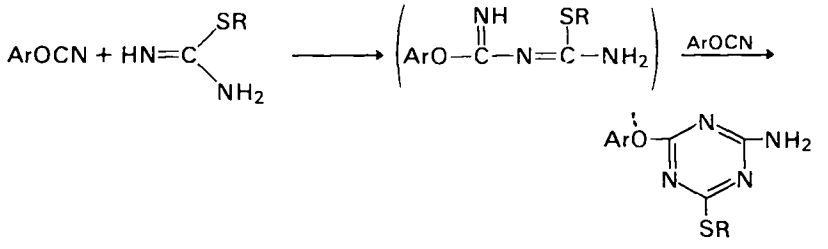
(45)

These products react with amines or hydrazines with the elimination of the aryloxy group (equation 73).



(73)

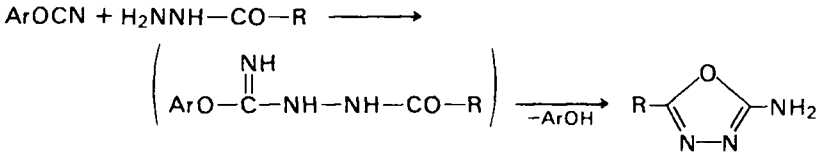
Thioamides and thioureas react with cyanates with elimination of hydrogen sulphide and the formation of nitriles, cyanamides or carbodiimides[93]. However, addition of an *S*-alkylisothiourea occurs in a similar way to the addition of isoureas (**28**) except that the primary reaction product cannot be isolated. It reacts immediately with a second molecule of the cyanate and forms a 2-amino-4-alkylthio-6-aryloxy-1,3,5-triazine[93], **46**.



(74)

(46)

i. *Hydrazides.* Aryl cyanates react at room temperature with hydrazides of carboxylic acids with elimination of the phenol and formation of a 2-amino-1,3,4-oxadiazole[98], **47**.



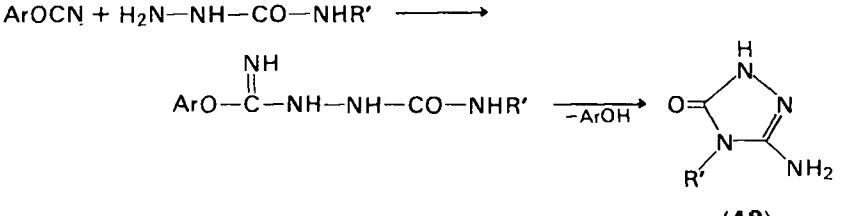
(75)

(47)

In an analogous reaction thiohydrazides form 2-amino-1,3,4-thiadiazoles[87].

An arylene dicyanate and a dihydrazide form a compound with two aminooxadiazole groups rather than a polymer[23].

In the reaction between cyanates and semicarbazides (hydrazides with R = NH_2 or NHR') the ring closure may be effected by means of the NH_2 (or NHR') group so that a triazolinone (**48**) is formed[101].

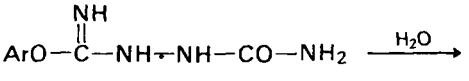


(76)

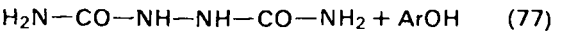
(48)

However, ring closure only takes place on heating and the open-chain monosubstituted, as well as a 1,1-disubstituted, semicarbazide can usually be isolated[85,101].

Unsubstituted semicarbazide does not give a triazolinone but in the presence of water the 1-(aryloxycarbonimidoyl)semicarbazide (**49**) gives hydrazine-1,2-dicarboxamide[101], **50**.

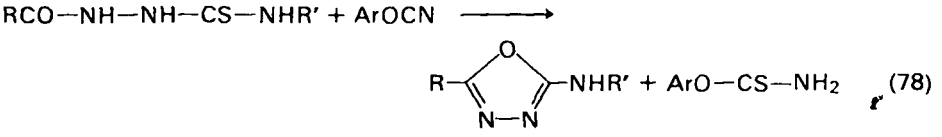


(**49**)



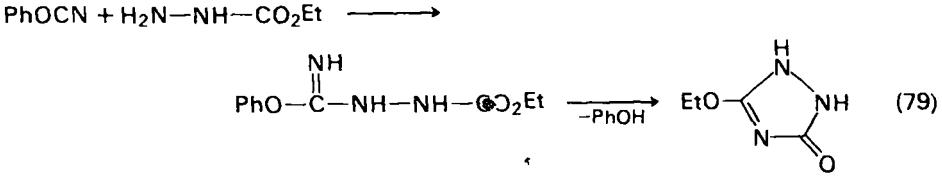
(**50**)

1-Acylthiosemicarbazides eliminate hydrogen sulphide under the influence of aryl cyanates and form 2-amino-1,3,4-oxadiazoles[22] (**51**) and the corresponding aryl thiocarbamates.

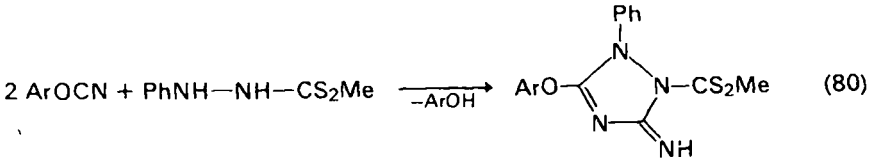


(**51**)

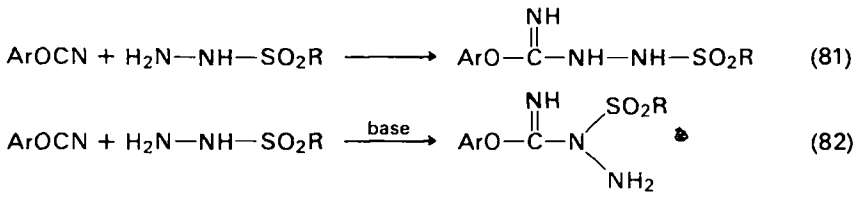
Esters of hydrazinecarboxylic acid (carbazates) form 3-(aryloxycarbonimidoyl)carbazates and only in one case has spontaneous ring-closure to a triazolinone been observed[102] (equation 79).



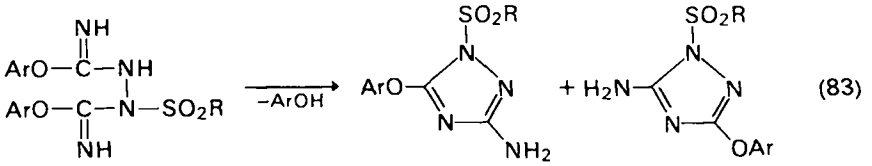
A dithiocarbazate on the other hand was found to react in a different manner[92] (equation 80) but this may be because it was a 3-phenyl derivative (apparently no dithiocarbazate with a free NH_2 group has been investigated).



Sulphonohydrazides react differently in neutral (equation 81) and basic (equation 82) solution[25,81]: in basic solution it is the more acidic NH group which reacts with the cyanate.

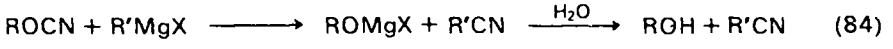


Both these substituted hydrazides may, however, add a second molecule of the cyanate to give the same disubstituted product which may cyclize to a mixture of two isomeric 1,2,4-triazoles (equation 83).



3. Addition of *C*-Nucleophiles

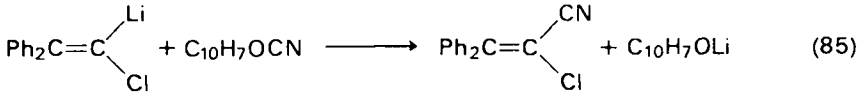
a. *Organometallic compounds.* Grignard reagents react with cyanates with the formation of nitriles[67–70,92,103] (equation 84).



The reaction proceeds well with both alkyl and aryl cyanates[68]. Contrary to the statement of Martin and Rackow[103] it is not necessary to use excess Grignard reagent to bring the reaction to completion[68]. With excess Grignard reagent the nitriles react to form ketones (the intermediate imine was isolated from the reaction of phenylmagnesium bromide with isobutyl cyanate[68]).

The magnesium salt of an imidoester has been postulated as an intermediate in reaction (84)[92,103]. However, no evidence for this has been found despite careful scrutiny[68–70].

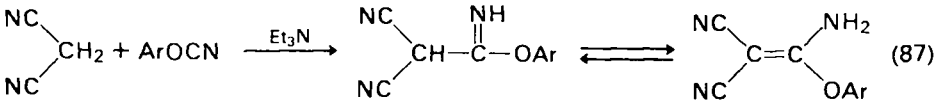
The reaction of 1-chloro-1-lithio-2,2-diphenylethylene with 1-naphthyl cyanate similarly results in the replacement of the metal atom by the nitrile group[104] (equation 85).



b. *Active methylene compounds.* Reactions of aryl cyanates with sodium or magnesium salts of active methylene compounds, such as diethyl malonate, ethyl cyanoacetate, malononitrile, ethyl acetoacetate or acetylacetone, also result in the transfer of a cyano group from the cyanate with the formation of diethyl cyanomalonate, ethyl dicyanoacetate, tricyanomethane, etc.[65,92,103] (equation 86).

(86)

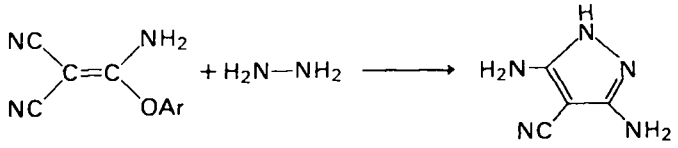
An imidoester was not observed when the metal salts were used as starting materials[92,103]. The carbon acids themselves could, however, be induced to react when triethylamine was used as a catalyst[65] and under these conditions the intermediate could be isolated, e.g.



(87)

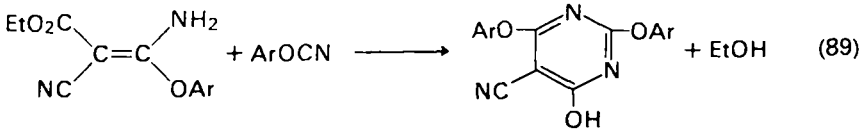
(52)

The reaction goes most easily when the methylene compound contains a cyano group[65] but this is not a necessary condition[105]. According to infrared and n.m.r. spectroscopic evidence these compounds have the enamine structure[65] (**52**). They are quite stable but eliminate the OAr group on hydrolysis, aminolysis or hydrazinolysis. In the latter reaction a pyrazole is formed[65] (equation 88).



(88)

If the enamines contain a cyano group they may react with a second molecule of the cyanate to form pyrimidines[106] (equation 89).

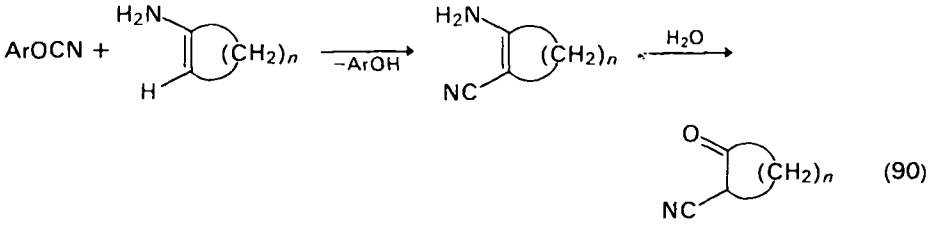


(89)

The derivatives of ketocarboxylates also form pyrimidines but with elimination of water instead of alcohol and only with certain aryl cyanates ($4\text{-}O_2NC_6H_4OCN$)[105].

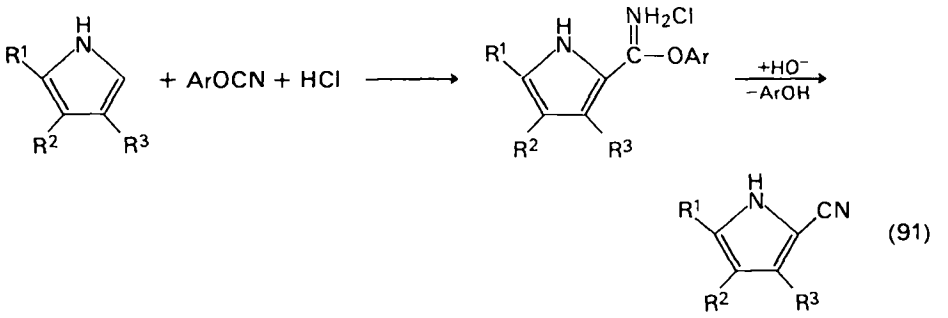
Aryl cyanates can also be used to introduce a cyano group into the methylene group of certain phosphonic esters, $(RO)_2OP{-}CH_2{-}COPh$[107].

c. *Enamines.* Aryl cyanates react with enamines with the formation of cyanoenamines[65,92,103] which can be hydrolysed to cyanoketones[103] (equation 90).



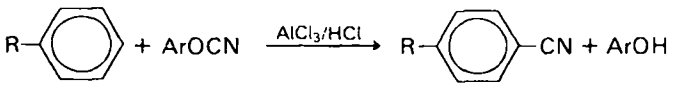
(90)

d. *Pyrroles.* Pyrroles unsubstituted in the 2- or 5-position react with aryl cyanates in the presence of hydrogen chloride to form hydrochlorides of 2-(aryloxycarbonimidoyl)pyrroles which can be transformed into 2-cyanopyrroles[103] (equation 91).



(91)

e. *Aromatic compounds.* The nitrile group can be introduced into aromatic compounds by means of aryl cyanates with $AlCl_3$ + HCl as catalyst[103], e.g.:



(92)

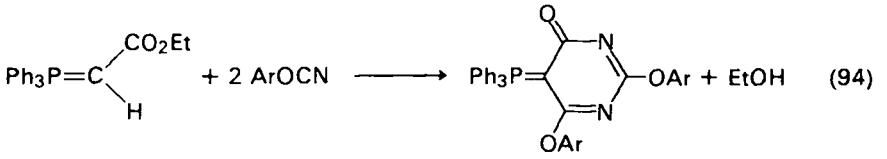
R = CH_3, CH_3O

f. *Ylids.* Unsubstituted or monosubstituted methylenephosphoranes react readily with aryl cyanates in DMSO or THF to form cyanomethylenephosphoranes[107] (equation 93).

$$Ph_3P{=}CHR + ArOCN \longrightarrow (Ph_3\overset{+}{P}{-}CHRCNArO^-) \xrightarrow[-ArOH]{} Ph_3P{=}C(R)(CN) \quad (93)$$

With the unsubstituted methylenephosphorane (R = H) the dicyanomethylenephosphorane is obtained. This reaction is, however, rather complex and methyldiphenylphosphine oxide, diphenyl carbonate and triphenylphenoxyphosphonium phenolate were obtained as by-products[107].

When R = CO_2Me or CO_2Et the phosphoranes react with 2 moles of the cyanate to give pyrimidine derivatives (equation 94).



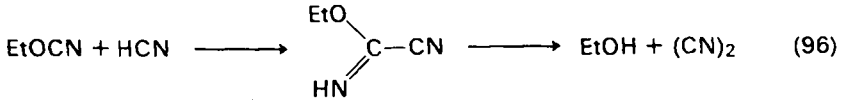
(94)

On hydrolysis of this compound barbituric acid is formed.

g. *Cyanide ion.* Ionic cyanides react with aryl cyanates to form dicyanogen[92,103,108] (equation 95).

$$ArOCN + CN^- \longrightarrow ArO^- + (CN)_2 \quad (95)$$

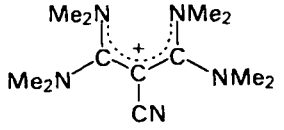
An intermediate was not observed in this reaction. When using ethyl cyanate and hydrogen cyanide, Wentrup[108] was able to isolate ethyl cyanoformimidate. This compound decomposes at room temperature into ethanol and dicyanogen (equation 96).



(96)

h. *Allenetetramines.* Phenyl cyanate reacts in perchloric acid in an exothermic reaction with allenetetrakis(dimethylamine)[109]. The resulting salt (**53**) is formed by transfer of a cyano group; an intermediate was not observed.

$$(MeN_2)_2C{=}C{=}C(NMe_2)_2 + PhOCN + HClO_4 \xrightarrow[-PhOH]{}$$



ClO_4^- (97)

(**53**)

F. Nucleophilic Addition to the Oxygen Atom

Only a few examples are known where nucleophilic addition apparently occurs to the oxygen atom of the —OCN group. Sodium salts of *O,O*-dialkylphosphonoates (dialkyl phosphites) react with both aliphatic and aromatic cyanates with the formation of esters of phosphoric acid[71] (equation 98).

$$(RO)_2PO^- + ROCN \longrightarrow (RO)_3PO + CN^- \qquad (98)$$

The reaction of cyanates with trialkyl phosphites is more complex and indicates that the phosphorus atom can be added as a nucleophile either to the oxygen atom or the carbon atom of the —OCN group with the formation of intermediate phosphonium compounds (**54** and **55**)[71,110].

$$(RO)_3P + ArOCN \longrightarrow \underset{(\mathbf{54})}{[(RO)_3(ArO)P^+CN^-]} \text{ or } \underset{(\mathbf{55})}{[(RO)_3(CN)P^+ArO^-]} \qquad (99)$$

The first complex (**54**) decomposes with the formation of a phosphate, $(RO)_2(ArO)PO$, together with a nitrile, RCN, and an isocyanide, RNC. The simultaneous formation of the latter two compounds indicates that they are formed by alkylation of the ambident cyanide ion.

The second complex (**55**) decomposes with the formation of a dialkyl cyanophosphate, $(RO)_2(CN)PO$, and an ether, ROAr.

G. Electrophilic Additions

1. Addition of proton acids and Lewis acids

The first attempts to induce cyanates to undergo electrophilic additions at the —OCN group suggested that they would be rather inactive in such reactions. They form unstable complexes with Lewis acids[60,111] such as $SbCl_5$ and $SnCl_4$, but unlike the analogous complexes with nitriles these cannot be alkylated to *N*-alkylnitrilium salts. The formation of phenetol from triethyloxonium tetrafluoroborate and phenyl cyanate indicates that if alkylation takes place it occurs at the oxygen atom. *N*-Alkylation occurs in DMSO but only after an initial attack on the carbon atom (see Section V.G.4).

However, hydrogen halides are added without difficulty with the formation of aryloxycarbonimidoyl halides which may be isolated as hexachloroantimonates[111] (equation 100).

$$ArOCN + 2\,HCl + SbCl_5 \longrightarrow ArO{-}\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}{=}NH_2^+\,SbCl_6^- \qquad (100)$$

It has also been found that phosphorus pentachloride, in addition to catalysing trimerization of aryl cyanates to cyanurates, forms hexachlorophosphates of ions derived by addition of PCl_4^+ to the nitrile group[112,113] (equation 101).

$$ArOCN + 2\,PCl_5 \longrightarrow \left[ArO{-}\underset{\displaystyle Cl}{\overset{|}{C}}{=}N{-}PCl_3\right]^+[PCl_6]^- \xrightarrow{ArOCN} [(ArOCCl{=}N)_2PCl_2]^+[PCl_6]^- \xrightarrow{ArOCN} [(ArOCCl{=}N)_3PCl]^+[PCl_6]^- \quad (101)$$

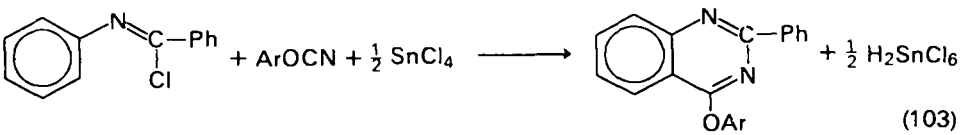
2. Addition of acyl halides

Aryl cyanates react with acyl chlorides in the presence of $SbCl_5$ or $SnCl_4$, but these reactions occur much less readily than the analogous reactions with nitriles. Martin and coworkers[111] succeeded in obtaining a diazapyrylium salt, **56**, from phenyl cyanate and benzoyl chloride.

$$2\,ArOCN + C_6H_5COCl + SbCl_5 \longrightarrow \text{(56)}\ SbCl_6^- \quad (102)$$

(56)

Further, the same authors found that aryl cyanates reacted with *N*-phenylbenzimidoyl chloride and $SnCl_4$ with the formation of 2-phenyl-4-aryloxyquinazolines (**57**).

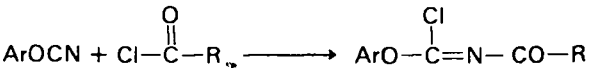


$$+ ArOCN + \tfrac{1}{2}\,SnCl_4 \longrightarrow \text{(57)} + \tfrac{1}{2}\,H_2SnCl_6 \quad (103)$$

(57)

Against the background of these results the recent discovery by Grigat[87,114] that aryl cyanates may react with acyl halides under mild conditions was rather surprising. The resulting compounds are very reactive and can enter into numerous reactions leading to new compounds. Grigat[22] has recently given an extensive review of this new development of cyanate chemistry which has hitherto only been published in the patent literature. In the following only the main features of these reactions will be discussed.

Aryl cyanates and carboxylic acid chlorides react with the formation of the hitherto unknown *N*-acyl chloroimidocarbonates, **58**,



(104)

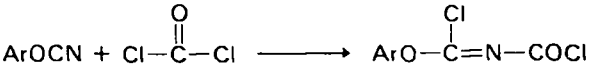
(58)

and analogously with chloroformates:

(105)

Surprisingly these compounds are so stable that they can be distilled in a vacuum.

The reaction with carbonyl chloride takes place even at 0 °C (equation 106).



(106)

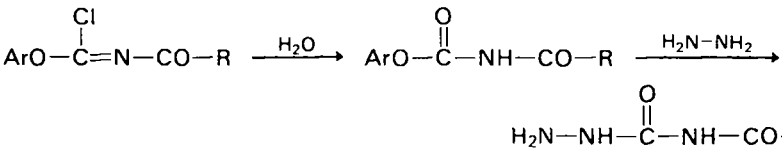
On further reaction with the aryl cyanate, $(ArOCCl{=}N)_2CO$ may be formed.

Oxalyl chloride reacts analogously with either 1 or 2 moles of ArOCN.

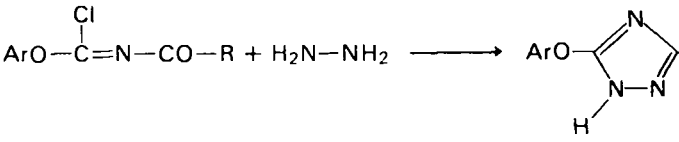
Sulphenyl chlorides may similarly be added to aryl cyanates:

(107)

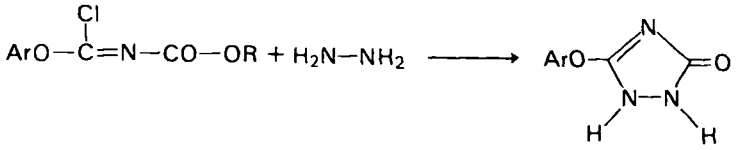
The halogen atoms of these products have been substituted with numerous nucleophiles to give compounds that still contain the ArO— group. This may, however, be replaced in subsequent reactions with nucleophiles. Because of the presence of various reactive groups in these compounds they may undergo cyclization reactions of many kinds. Since these reactions do not strictly belong to the chemistry of the cyanate group, only a few examples will be mentioned:



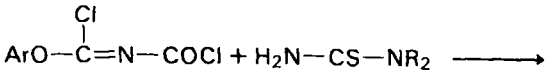
(108)

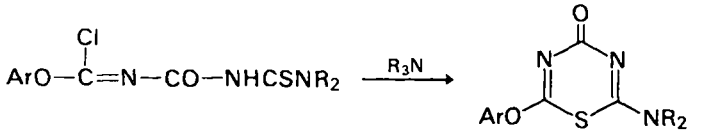


(109)

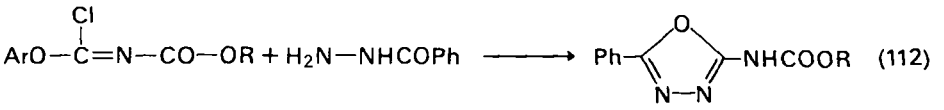


(110)

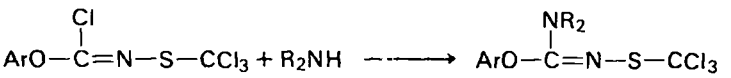




(111)



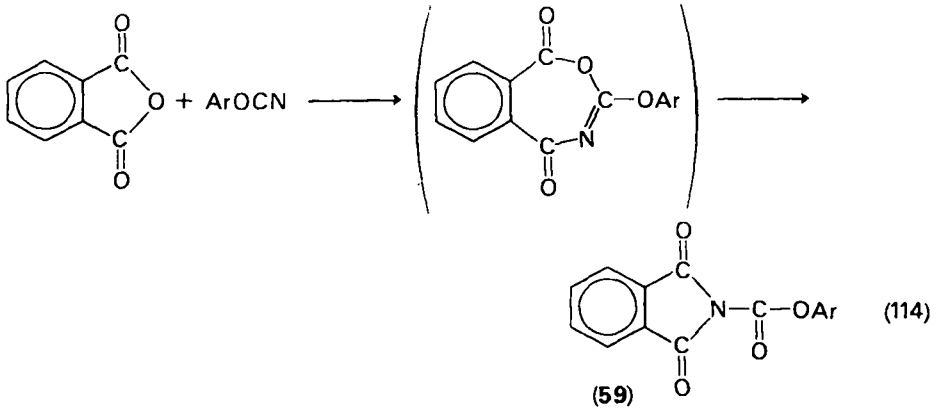
(112)



(113)

3. Addition of acid anhydrides

Only some special types of acid anhydrides react with cyanates[22,87]. Anhydrides of very strong carboxylic acids (trichloroacetic acid, etc.) react in principle as acid halides. Cyclic anhydrides form derivatives of cyclic imides (**59**) probably with a seven-membered ring intermediate[115] (equation 114).

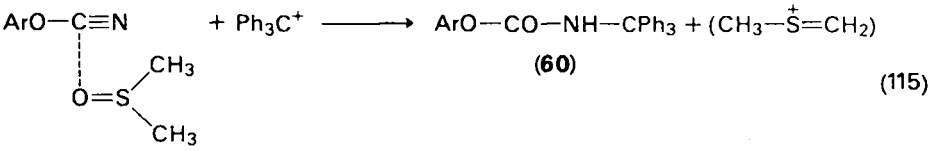


(114)

(**59**)

4. *N*-Alkylation

Martin and Weise[116] have found that trityl perchlorate in dimethyl sulphoxide (DMSO) transforms aryl cyanates into *N*-tritylated *O*-aryl carbamates (**60**) and has shown that this process proceeds via a complex between the cyanate and DMSO (cf. Section V.E.1.c).



(115)

The methylenesulphonium ion reacts further with DMSO in a complex reaction and the nature of the reaction products (dimethyl sulphide etc.) provides evidence that the oxygen atom of the carbamate originates in DMSO and not from hydrolysis of a primary product $ArO-\overset{+}{C}=\overset{\oplus}{N}-CPh_3$.

Grochowski and Tomasik[117–119] have shown that tertiary alcohols, alkenes and aldehydes react similarly with aryl cyanates in concentrated sulphuric acid to give *N*-alkylated *O*-aryl carbamates (equations 116–119).

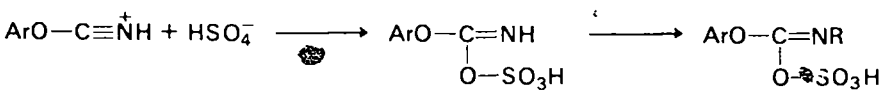
$$ArOCN + Me_3COH \xrightarrow{H_2SO_4} ArO-CO-NH-CMe_3 \quad (116)$$

$$ArOCN + H_3C-CH=C(CH_3)_2 \xrightarrow{H_2SO_4} ArO-CO-NH-C(CH_3)_2C_2H_5 \quad (117)$$

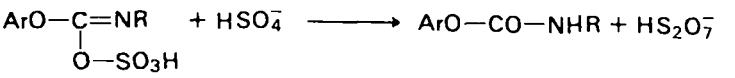
$$ArOCN + CCl_3CHO \xrightarrow{H_2SO_4} ArO-CO-NH-CHOHCCl_3 \xrightarrow{ArOCN,\ H_2SO_4} (ArO-CO-NH)_2CHCCl_3 \quad (118)$$

$$2\ ArOCN + C_6H_5CHO \xrightarrow{H_2SO_4} (ArO-CO-NH)_2CHC_6H_5 \quad (119)$$

In contrast to their lower reactivity towards electrophilic addition the aryl cyanates compete favourably with nitriles for these alkylating agents. However, mechanistic details of the reaction are unknown and the reactions may be initiated not by electrophilic alkylation but by acid-catalysed nucleophilic attack of sulphuric acid on the carbon atom of the —OCN group followed by alkylation:



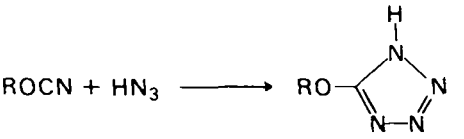
The formation of the urethane formally requires one molecule of water. It is unknown whether this is provided by subsequent hydrolysis or whether the urethane is formed already in the reaction mixture:



H. Cycloadditions

Cyanates are more reactive than most nitriles in additions to 1,3-dipolar compounds.

With sodium azide, aryl cyanates react smoothly to form the sodium salts of 5-aryloxytetrazoles[85,92,120,121]. Alkyl cyanates also act as alkylating agents on sodium azide and form alkyl azides[35,67]. However, in ethereal solution hydrogen azide adds to alkyl cyanates to give 5-alkoxytetrazoles[35,67] **61** (equation 120).

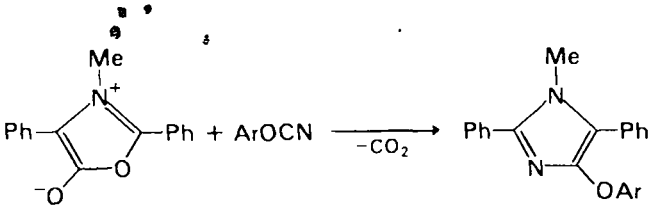


(120)

(61)

Aryl cyanates also react with diazo compounds[120,121], nitrones[92,121], and nitrile oxides[85,120] to give the expected 1,3-dipolar cycloaddition products.

The mesoionic oxazolone (**62**) reacts with 2,6-dimethylphenyl cyanate with the formation of an imidazole[122] (**63**).

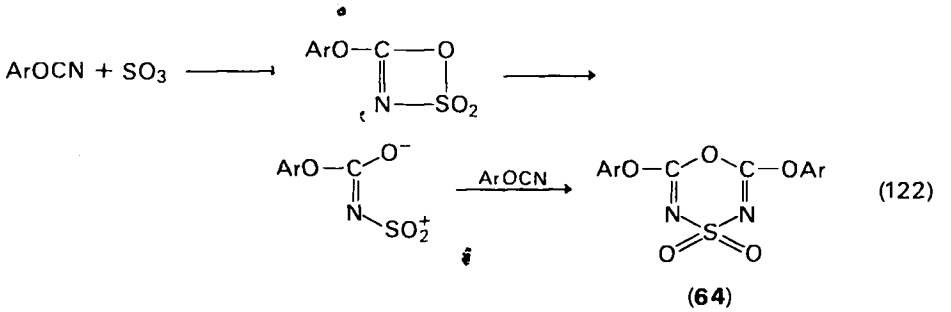


(121)

(62) **(63)**

The reaction of aryl cyanates with sulphur trioxide can be regarded as a 1,2- followed by a 1,4-dipolar cycloaddition reaction. The cyanate first reacts with one molecule of SO_3 to form a 1,4-dipolar molecule which reacts with a second molecule of the cyanate as the dipolarophile

to form a 1,4,3,5-oxathiadiazine-4,4-dioxide, **64**. Martin and Weise[111] assigned an unsymmetrical structure to the reaction products but Grigat[22] has shown that only the isomers with the symmetrical structure are formed. For reactions of **64** see the review by Grigat[22].



(122)

(64)

VI. CONCLUSION

Most papers on the chemistry of cyanic esters have been published by the groups who discovered these compounds and thus it seems that the synthetic potentialities of cyanates have not been generally appreciated.

In organic synthesis cyanates may be employed to eliminate water or hydrogen sulphide (cf. Sections V.E.1.a and V.E.1.d). Probably cyanates would often compare favourably with other reagents used for this purpose (carbodiimides, etc.). Further, their ability to function as nitrile-transferring agents (cf. Section V.3) has wide applicability. Probably the reaction with an aryl cyanate would in certain cases turn out to be the most convenient method to transform an aromatic compound into a nitrile.

Carbamates, thiocarbamates, and selenocarbamates may be prepared in excellent yields from cyanates. Certain types of compound, such as isobiurets (Section V.2.a), unsymmetric imidoesters (Sections IV.D.1 and V.E.1.b), and *N*-hydroxyisoureas (Section V.2.f), have first been made accessible through the reactions of cyanates.

The formation of triazines and several other heterocyclic compounds have been mentioned in Section V. A very general reaction is the formation of benzoxazinones[27,31,123] and other *ortho*-fused 1,3-oxazin-4-ones[28,29] from derivatives of aromatic and heteroaromatic carboxylic acids substituted with the cyanato group in the *ortho* position. Another general type of reaction is the formation of various heterocyclic compounds by reaction of aryl cyanates with *ortho*-substituted aromatic compounds, such as esters and amides of salicyclic and anthranilic acids[22,123], *o*-aminophenol[22], *o*-phenylenediamine[22], catechol[124], etc., or α-substituted

derivatives of phenylacetic acid, such as mandelamide, mandelonitrile, and α-hydroximinophenylacetonitrile[22].

By and large the cyanates exhibit a remarkable versatility in their reactions and it seems that these compounds might be utilized to a greater extent than hitherto for synthetic purposes.

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