ANIONIC SIGMA COMPLEXES

MICHAEL J. STRAUSS

Chemistry Department, University of Vermont, Burlington, Vermont 05401

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Contents

I. Introduction

The interaction of electron-deficient aromatics with nucleophiles has fascinated chemists since the late 19th century. This interest was generated, in part, by intensely colored solutions sometimes observed which provided a means for determining the extent and type of interaction. It has become clear that several kinds of interaction can occur, depending upon reactant structure and solvent environment. Generally there is a transfer of charge from nucleophile to aromatic. The type of interaction is characterized by the extent of such transfer and the way in which it occurs. Donor–acceptor (π) complexes may form in which bonding is quite weak and delocalized. Stronger interaction may result in covalently bonded σ complexes. Complete electron transfer results in radical ions. All these interactions may be complicated by concurrent or subsequent substitution of an aromatic substituent. This review is concerned with those interactions leading to stable[1] anionic σ complexes and the structural and chemical characteristics of these species.

A. PURPOSE AND SCOPE

There have been several short reviews of anionic σ-complex structure and reactivity.[2-5] Nevertheless, progress in this field has been so rapid that much additional information has become available since these reviews were published. An attempt is made here to summarize all the important work which has been done through January 31, 1970.[6] Partial duplication of earlier reviews is unavoidable, but the emphasis is on important aspects (*i.e.*, thermodynamic stability, molecular orbital calculations, detailed structural analysis, etc.) which have not been discussed in depth. No attempt is made to cover the early history of the subject, although certain historical points of interest are noted. Discussion of charge-transfer complexes is included only when relevant to the subject at hand as several books and reviews cover this topic extensively.[7-12] One recent review has dealt with relationships between σ-complex formation, charge-transfer complexation, electron transfer, and proton-abstraction processes.[3] It should also be noted that anionic σ complexes are formally analogous to the intermediates in aromatic nucleophilic substitution, a topic which also has been the subject of several reviews[13-17] and a book.[18] Details of the chemistry and structural characteristics of stable σ complexes are notably absent in these discussions however.

Previous discussions of σ-complex chemistry[2,5] have been divided into sections according to complex structure. Although this is logically consistent and produces few subsections, the main dvisions presented here are based on methods of investigation (*i.e.*, pmr, ir, uv–visible, etc.). This allows a more ready comparison of spectral and chemical characteristics at the cost of some subsection duplication.

B. NOMENCLATURE

In 1900, a quinoid structure (**1**) was proposed by Jackson and Gazzolo for the colored adducts formed from picryl ethers and potassium alkoxides.[19] Meisenheimer obtained sub-

(1) The term stable is meant to include those complexes which, although not isolable, can be observed for short periods of time in solution at low temperatures.

(2) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

(3) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, **22**, 123 (1968).

(4) P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969).

(5) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).

(6) Certain authors have kindly supplied preprints of papers in press which has allowed inclusion of some work published later than this date (see Acknowledgments).

(7) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(8) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.

(9) J. N. Murrell, *Quart. Rev., Chem. Soc.*, **15**, 191 (1961).

(10) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).

(11) R. Foster, "Molecular Complexes," Academic Press, London, 1969.

(12) J. Rose, "Molecular Complexes," Pergamon Press, New York, N. Y., 1967.

(13) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

(14) F. Pietra, *Quart. Rev., Chem. Soc.*, **4**, 505 (1969).

(15) J. Miller, *Rev. Pure Appl. Chem.*, **1**, 171 (1951).

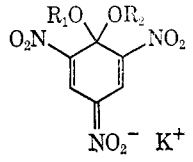
(16) J. F. Bunnett, *Quart. Rev., Chem. Soc.*, **12**, 1 (1958).

(17) S. D. Ross, *Progr. Phys. Org. Chem.*, **1**, 31 (1963).

(18) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Barking, Essex, England, 1968.

(19) C. J. Jackson and F. H. Gazzolo, *Amer. Chem. J.*, **23**, 376 (1900).

stantial evidence for **1** ($R_1 = CH_3$, $R_2 = C_2H_5$) by isolating the same product from 2,4,6-trinitroanisole and potassium eth-



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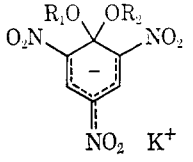


2

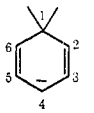
oxide, and from 2,4,6-trinitrophenetole and potassium methoxide.[20] Such addition complexes have been found to adequately describe adducts which form from a wide variety of nucleophiles and electron-deficient aromatics. They are commonly termed Meisenheimer or Jackson–Meisenheimer complexes. Crystal-structure determinations[21,22] have conclusively established the structure of complexes like **1** ($R_1 = R_2 = CH_2CH_3$, $R_1 = R_2 = CH_3$). In recent years, the quinoid structure **1** has been abandoned for a more "modern" delocalized structure (**2**). Molecular orbital calculations[23–25] and crystal-structure determinations[21] indicate that most of the negative charge is located on the NO_2 group *para* to the sp^3 ring carbon. Therefore, Jackson's originally proposed structure (**1**) is a more suitable representation than **2**, and the quinoid form is used here. Complexes with substituents other than a NO_2 group *para* to the sp^3 ring carbon will be represented as delocalized structures, analogous to **2**. Since several polynitro aromatics are referred to repeatedly throughout the text, the following abbreviations are used:[26]

TNB = trinitrobenzene
DNB = dinitrobenzene
TNA = trinitroanisole
DNA = dinitroanisole

The common abbreviation DMSO is used for dimethyl sulfoxide, and NO_2 for nitro. All other functional groups are written out (*i.e.*, methoxyl).

The anionic ring of six-membered carbocyclic σ complexes has been termed cyclohexadienylide,[27] benzenide,[18] cyclohexadienate,[28] and cyclopentadienide.[29] The term cyclohexadienate is used here. In most cases the complexes will be referred to by number; this avoids repetition of cumbersome names and also the problem of a consistent nomenclature for fused-ring and heterocyclic complexes (*i.e.*, from electron-deficient naphthalenes, anthracenes, pyridines, and pyrimidines). Numbering of the complex ring starts at the sp^3 ring carbon (C-1) and proceeds to the right as in the canonical forms **3** and **4**. The term "substituted cyclohexadienate" refers to substitution on the anionic ring of the complex at a position other than C-1.

(20) J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **323**, 205 (1902).
(21) R. Destro, C. Gramaccioli, and M. Simonetta, *Acta Crystallogr.*, **24**, 1369 (1968).
(22) H. Ueda, N. Sakabe, J. Tanaka, and A. Furusaki, *Bull. Chem. Soc. Jap.*, **41**, 2866 (1968).
(23) P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, **50**, 848 (1967).
(24) R. Destro, *Rend. Ist. Lombardo Sci. Lett.*, **101**, 725 (1967); *Chem. Abstr.*, **69**, 46186t (1968).
(25) H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, **12**, 117 (1968).
(26) The substituent positions will be specified in each case, *i.e.*, 1,2,4-TNB.
(27) J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34**, 689 (1969).
(28) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **90**, 4982 (1968).
(29) M. J. Strauss and R. G. Johanson, *Chem. Ind. (London)*, **8**, 242 (1969).



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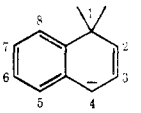

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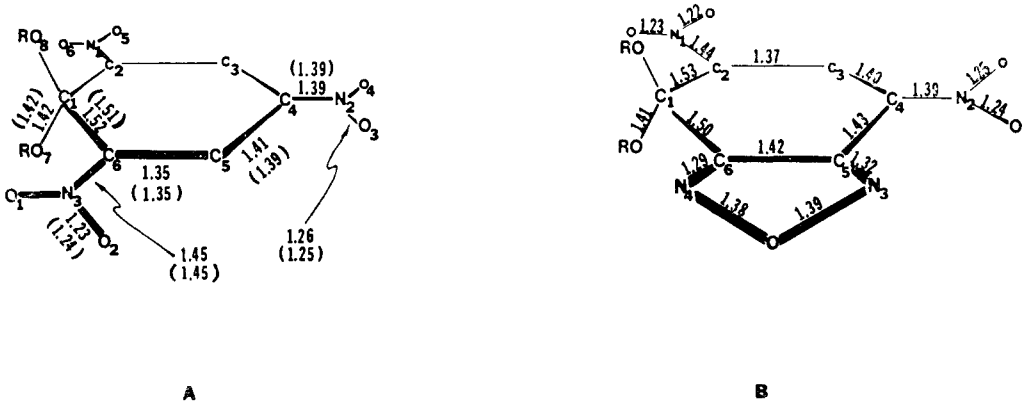
II. Structural Characterization of the Complex

A major development in the structural characterization of anionic σ complexes occurred in 1964 with a report of the pmr spectrum of **1** ($R_1 = R_2 = CH_3$).[30] Two years later enough pmr spectral data were available for a short review.[2] Coupled with evidence from visible and infrared spectroscopy, structures were assigned to a wide variety of such complexes. Recent crystallographic studies have supported the structures deduced by spectroscopic methods.

A. CRYSTAL STRUCTURES

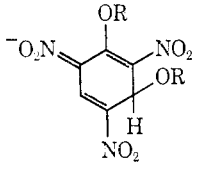
The crystal structures of three σ complexes have been determined.[21,22,31] Two of these are picryl ether adducts with methoxide[21,22] and the third is a methoxide adduct of 4-methoxy-5,7-dinitrobenzofurazan.[31] The structural parameters have several interesting features in common (Figure 1). In each complex, the C-4–N-2 bond is significantly shorter than the C-2–N-1 or C-6–N-3 bonds. This is in accord with a structure in which resonance contributors like **1** are more important than those which have a single C-4–N-2 bond. It is therefore likely that a large proportion of negative charge is localized on oxygen atoms of the NO_2 group *para* to C-1. This conclusion is supported by molecular orbital calculations (*vide infra*) and by the C-2–C-3 and C-5–C-6 bond lengths (Figure 1) which are shorter than the other C–C ring bonds. The rings are essentially planar in all the structures, and a C-2–C-1–C-6 bond angle of 109° in the 2,4,6-trinitrocyclohexadienate complexes results in considerable strain. This is partially reflected in the O-7–C-1–O-8 angle of 100°.[22] Ring planarity and concomitant ring strain may result from steric compression between geminal-alkoxyl and *ortho* ring carbons, C-2 and C-6. The distance between one of these ring carbons and a methoxyl group[22] is 2.95 Å, less than the sum of the van der Waals radii of two carbon atoms. The plane containing the two alkoxy oxygens and C-1 is perpendicular to the ring plane and bisects the latter in the 2,4,6-trinitrocyclohexadienate complexes. The C–O bond length, close to that observed in aliphatic ethers,[21] is much greater than that in 2,4,6-trinitrophenetole.[32] The latter has double-bond character from delocalization of an oxygen lone pair into the aromatic ring. These observations are in accord with complexes in which C-1 has considerable sp^3 character. The NO_2 groups *ortho* to C-1 are nearly coplanar with the ring,[21,22,31] whereas dihedral angles up to 62° have been observed between the ring and NO_2 groups *ortho* to ethoxyl in trinitrophenetole,[32] presumably owing to steric compression between these functions. Release of this compression in the complex may be one of the primary reasons for greater thermodynamic stability of geminal alkoxy σ complexes like **1**, relative to 1,2 complexes like **5** (*vide infra*).

(30) M. R. Crampton and V. Gold, *J. Chem. Soc.*, 3293 (1964).
(31) G. G. Messmer and G. J. Palenik, *Chem. Commun.*, 470 (1969).
(32) C. M. Gramaccioli, R. Destro, and M. Simonetta, *Acta Crystallogr.*, **24**, 129 (1968).



A B

Figure 1. Pertinent structural parameters for (A) 1,1-dialkoxy-2,4,6-trinitrocyclohexadienate complexes[21,22] (values in parentheses, R = CH_3CH_2; unparenthesized, R = CH_3) and (B) the methoxide complex of 4-methoxy-5,7-dinitrobenzofurazan.[31] All bond lengths are in angstroms, to three significant figures.



5

In **5** there is no release of steric compression between the alkoxyl of the parent ether and adjacent NO_2 groups. Such compression may even be increased, as enhanced conjugative interactions in **5** might hinder rotation of NO_2 groups out of the ring plane.

The methoxide complex of 4-methoxy-5,7-dinitrobenzofurazan (Figure 1B) has a distorted dinitrocyclohexadienate ring, whereas the trinitrocyclohexadienate complexes are symmetrical with respect to C-1.[31] This is used as evidence for enhanced electron-withdrawing power of the furazan ring relative to a NO_2 group, but without comparisons of bond lengths in the parent furazan and strain effects in this fused-ring system, arguments based on relative bond lengths in the complex are not compelling.

Certain structural features shown in Figure 1 are likely to be characteristic of σ complexes in general. The plane of the anionic ring will tend toward a perpendicular arrangement with respect to that of C-1 and its substituents, and a NO_2 group *para* to C-1 will carry a large portion of the charge originally associated with the attacking nucleophile. These characteristics are consistent with interpretations of pmr spectra. Prediction of conformational preference in solution based on the results of crystal-structure determinations should be made cautiously. Intermolecular forces in the crystal have a profound and many times dominant effect on conformation.

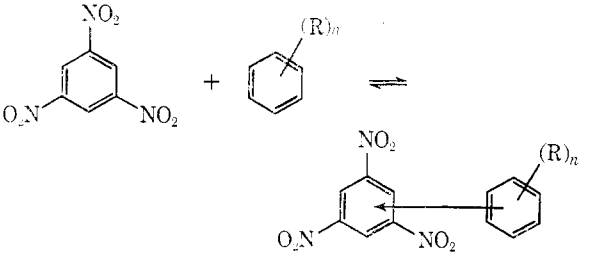
B. PMR SPECTRA

Much anionic σ-complex chemistry has been studied by pmr spectroscopy, and a pertinent review of the area must include a discussion of those chemical transformations and properties which are most easily studied by this technique. Since 1964, the pmr spectra of nearly 200 different anionic σ complexes have been reported. Some relevant proton chemical shifts are summarized in Tables I, III, IV, VI, VII, and VIII. Cations are not listed, as shift differences caused by cation variation are very small. An attempt is made here to correlate and explain these shifts in terms of structural characteristics and charge distribution in the complex. Splitting patterns are discussed for complexes of particular interest. For comparative purposes the complexes have been categorized into 11 groups and are listed within each group in order of decreasing electronegativity of the atom(s) attached to C-1.

1. 2,4,6-Trinitrocyclohexadienates (6, 19, 20, *and* 31)

a. From 1,3,5-TNB

The pmr spectrum of 1,3,5-TNB in a variety of nonbasic solvents shows a singlet at $\tau \sim 0.8$.[33-36] Addition of a basic or electron-rich species to the solution causes characteristic changes in the spectrum. With aromatic amines or other aromatic donor hydrocarbons, weakly bonded charge-transfer complexes are formed, and the singlet from 1,3,5-TNB remains unchanged except for an upfield shift which is proportional to donor concentration.[37-39] These observations are consistent with a donor–acceptor equilibrium (eq 1), which is rapid compared to the pmr time scale. The TNB

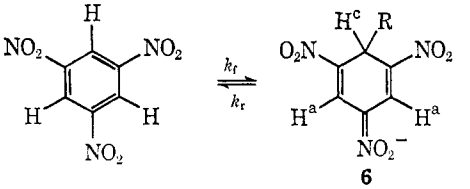


(1)

protons resonate at a frequency which is a weighted average of the frequencies of complexed and uncomplexed aromatic. The extent of upfield shift from pure 1,3,5-TNB has been used to compute equilibrium constants for the interaction with

(33) E. Buncel, A. R. Norris, and W. Proudlock, *Can. J. Chem.*, **46**, 2759 (1968).
(34) R. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965).
(35) M. R. Crampton and V. Gold, *Chem. Commun.*, 256 (1965).
(36) C. A. Fyfe, *Can. J. Chem.*, **46**, 3047 (1968).
(37) M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964).
(38) R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, **61**, 1626 (1965).
(39) R. Foster and C. A. Fyfe in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 4, Pergamon Press, New York N. Y., 1969, Chapter 1.

various donors.[38-43] Quite different spectral changes are observed on addition of primary or secondary aliphatic amines, alkoxides, hydroxides, sulfides, etc., to a solution of 1,3,5-TNB in polar solvents. New resonances appear at high field which increase *as the low-field, 1,3,5-TNB resonance decreases.* Observation of discrete resonances for both 1,3,5-TNB and the resultant complex in the same solution is in accord with formation of a species which undergoes nucleophilic exchange slowly.[30,44,45] Since there are two new resonances for the complex, it must be sufficiently long-lived for both to appear separately.[30] These observations are explained by equilibrium 2, where k_r is small.[46] The high-field ring proton resonance of



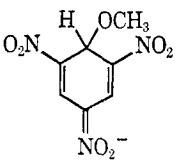
(2)

6

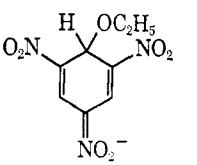
6 results from H^c, which is bonded to sp^3 carbon. The sp^2 ring protons, H^a, are shifted upfield from the 1,3,5-TNB resonance to a lesser extent. This latter upfield shift has been attributed to increased negative charge in the ring of the complex,[30] although diminished diamagnetic anisotropy resulting from decreased ring current may also be important.[23] The H^a resonance of **6** ranges from τ 1.3 to 1.8, and that for H^c from τ 3.6 to 5.0 (Table I). The exact shift for the latter absorption depends on the electronegativity of the atom attached to C-1. For R = OR, NR_2, and CR_3, the H^c resonance occurs at τ 3.6–4.0, 4.3–4.5, and 4.5–5.0, respectively. There are exceptions to this trend which can be understood in terms of unique structural features of particular complexes. Specific systems are now considered.

i. With Oxygen Bases. The pmr spectrum of **6a**, prepared by reaction of 1,3,5-TNB with sodium methoxide, shows a coupled doublet and triplet ($J \sim 1$ cps) for the sp^2 and sp^3 ring protons, centered at τ 1.3 (2 H) and 3.7 (1 H). The methoxyl resonance is a singlet at τ 6.7, about 1 ppm upfield from that of 2,4,6-TNA. This shift difference is expected for methoxyl groups bonded to aliphatic and electron-deficient aromatic carbon. A similar spectrum is observed for **6b**.[34] With both **6a** and **6b**, a slow solvolysis occurs in acetone[34] yielding **6c**. The alkoxy complexes are stable in DMSO and will add a second equivalent of alkoxide in this solvent (see section II.B.3).

Hydroxide adds to 1,3,5-TNB yielding **6d**, which has a pmr spectrum similar to the alkoxide complexes.[47] **6d** forms readily in anhydrous DMSO solutions of sodium hydroxide and 1,3,5-TNB and has been obtained as a crystalline solid by precipitation with ether. **6d** also forms in wet DMSO solutions of 1,3,5-TNB and amines and has mistakenly been identified as



6a



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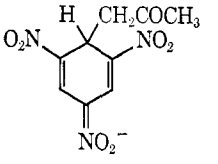
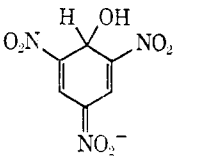


6c



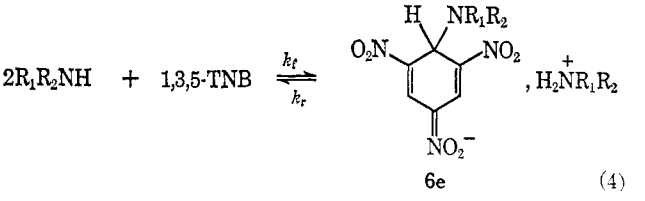
6d

6 (R = $(CH_3)_2SO$–) in this solvent.[48] In aqueous dioxane solutions of 1,3,5-TNB and amines, it has been identified by a relaxation time for the equilibrium

$$\text{1,3,5-TNB} + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \textbf{6d} \qquad (3)$$

which is independent of amine concentration[49] (see section V).

ii. With Nitrogen Bases. Addition of ammonia,[50] methylamine,[2,50] dimethylamine,[2] diethylamine,[2,50,51] piperidine,[50] or 2-aminoethanol[2] to DMSO solutions of 1,3,5-TNB yields the ammonium or alkylammonium salt of **6e**; 2 equiv of amine is required per equivalent of aromatic (eq 4). Although

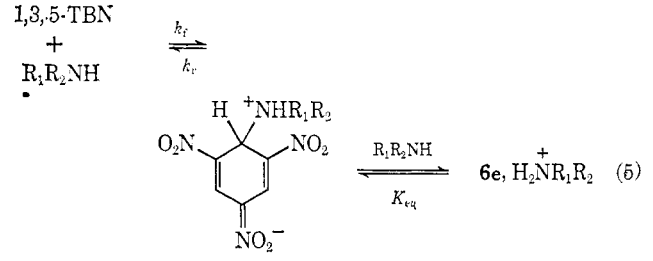


6e (4)

the chemical shift of the sp^2 ring protons is the same as that in oxygen base complexes, the sp^3 ring proton resonance appears about 0.7 ppm upfield from that in structures like **6a**. The ^+NH proton resonance appears as a singlet at low field. The sp^2 and sp^3 protons are not coupled in **6e**, in contrast to a coupling constant of ~1 cps for the oxygen-base analogs. This difference is attributed to a shorter lifetime for the amine complexes,[50] a conclusion supported by observed broadening of the ring proton resonances in excess aromatic. Line-width measurements on the piperidine complex spectrum provide an estimated lifetime of about 0.1 sec.[50] This result is supported by determinations of k_f and k_r for similar amine complexes in aqueous dioxane (section V). The pmr results are supported by conductivity measurements which show a linear increase in the conductance of solutions of 1,3,5-TNB in DMSO as primary or secondary amines are added. The increase drops markedly at a 2:1 ratio of amine to aromatic.[50] With tertiary amines the conductance remains close to zero and no profound changes are observed in the pmr spectrum of the starting aromatic. **6e** could form by attack of amine on the aromatic to produce a zwitterion **7**, followed by proton loss to a second molecule of amine (eq 5), or by direct attack of amide ion, formed by autoprotolysis, on the aromatic (eq 6). The latter process is considered less likely as the rapidity of intercon-

(40) R. Foster, C. A. Fyfe, and M. I. Foreman, *Chem. Commun.*, 914 (1964).
(41) R. Foster and C. A. Fyfe, *ibid.*, 642 (1965).
(42) R. Foster and C. A. Fyfe, *J. Chem. Soc. B*, 926 (1966).
(43) N. M. D. Brown, R. Foster, and C. A. Fyfe, *ibid.*, 406 (1967).
(44) In certain instances, rapid nucleophilic exchange between a TNB σ complex and free TNB has been observed; see ref 67.
(45) K. L. Servis, *J. Amer. Chem. Soc.*, **87**, 5495 (1965).
(46) The situation is much more complex with neutral nucleophiles or when lyate ion is involved (*vide infra*).
(47) C. A. Fyfe, M. I. Foreman, and R. Foster, *Tetrahedron Lett.*, **20**, 1521 (1969).
(48) R. Foster and C. A. Fyfe, *Tetrahedron*, **22**, 1831 (1966).
(49) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **92**, 129 (1970).
(50) M. R. Crampton and V. Gold, *J. Chem. Soc. B*, 23, (1967).
(51) K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967).

version of free aromatic and complex evidenced by pmr would require tremendously large rate constants for amide ion attack since the concentration of this species should be quite small.[50]



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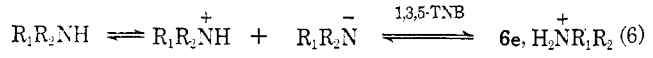
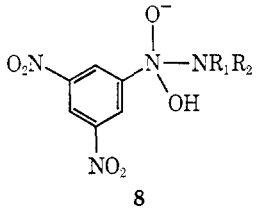
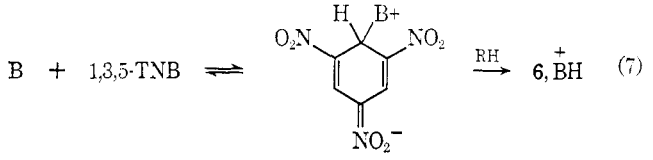


In aqueous dioxane, the anionic complex **6e** has been shown to form *via* the zwitterion **7**, and the rate constants k_f and k_r (eq 5), as well as pK of **7** (R_1 = *n*-Bu, R_2 = H; R_1 = R_2 = $-(CH_2)_5-$), have been determined by a temperature jump method (section V).[49] In this same solvent mixture, evidence was obtained for attack on a NO_2 group to yield the oxyhydroxylamine **8** (R_1 = *n*-Bu, R_2 = H; R_1, R_2 = $-(CH_2)_5-$).[49]

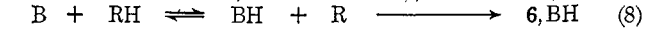


8

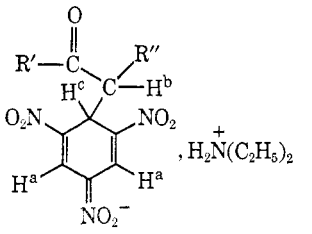
iii. With Carbon Bases. Although 1,3,5-TNB is unreactive with and quite soluble in simple ketones, aldehydes, nitriles, DMSO, chloroform, and nitroalkanes, addition of base to solutions of this aromatic in these solvents can result in lyate σ complexes. These could result from base attack to yield **9**, followed by reaction of **9** with solvent (eq 7), or by direct attack of lyate ion on the aromatic (eq 8). Such processes may compete with conversion of **9** to a stable complex by proton loss from the positive moiety, as in eq 5. The type of interaction in any particular case depends on solvent acidity, the basicity of B, and the stability of the complex formed. The



9



situation is simplified considerably if B is the conjugate base of the solvent. The most extensively studied oxygen-base complexes are of this type (RO^-–ROH). In certain solvents, one reaction may predominate to such an extent that only a single type of complex is formed. In DMSO–methanol–methoxide solutions of 1,3,5-TNB only **6a** is observed,[30] whereas in acetone–triethylamine solutions of 1,3,5-TNB only **6c** is observed.[52] In acetone–diethylamine solutions both the amide and acetonate σ complexes **6e** (R_1 = R_2 = C_2H_5) and **6c** are formed.[48] Generally, solutions of 1,3,5-TNB and triethylamine in ketonic solvents yield complexes like **10**, which have been characterized by pmr.[52,53] The spectra have



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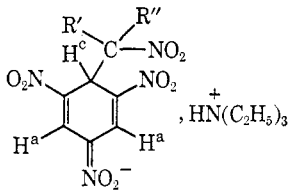


11

several interesting features. There is no evidence for enolic structures having an exocyclic C-1–O bond. A large coupling (J = 3–6 cps) is observed between H^c and H^b, and the former proton appears at significantly higher field than in complexes formed from oxygen and nitrogen bases (Table I). With ketones having two different kinds of α protons, a mixture of isomeric complexes may form. This has been observed with methyl ethyl ketone and acetonylacetone but not with methyl isopropyl ketone. Pmr spectra of the ketonic complexes **10** dissolved in acetone-d_6 or in different ketones show no evidence for exchange with solvent. Interestingly, the H^c resonance moves downfield and $J_{H^c-H^b}$ decreases when the exocyclic carbon changes from secondary to tertiary.[52] A similar but less dramatic change is observed for the H^a chemical shift. The same spectral changes are observed with complexes of simple nitroalkanes,[36] **11** (R′ and/or R″ = H^b). In these cases a slight increase in the long-range coupling $J_{H^c-H^a}$ is observed as the exocyclic carbon bonded to C-1 changes from secondary (0.5 cps) to tertiary (1.0 cps) to quaternary (1.4 cps). This has been attributed to changes in the relative orientations of H^a and H^c, a more perpendicular arrangement being favored when larger groups are bonded to the exocyclic carbon.[36]

In certain complexes containing an asymmetric carbon α to C-1, the sp^2 ring protons become magnetically nonequivalent and show a chemical shift difference of about 0.1 ppm.[54] It has been argued that this difference is a result of large barriers to rotation about the sp^3 bond between C-1 and the exocyclic substituent.[54] Gutowsky has derived a relationship between such a chemical shift difference and the intrinsic asymmetry and rotamer populations in a molecule[55]

$$\Delta\tau = \sum_n \left(X_n - \frac{1}{3}\right)\Delta\tau_n^0 + \sum_n \left(X_n - \frac{1}{3}\right)\Delta\tau_n + \sum_n \frac{1}{3}\Delta\tau_n \quad (9)$$

where X_n is the mole fraction of rotamer n, $\Delta\tau_n^0$ is the shift difference between H^α and H^β (Figure 2A, when X = H), and $\Delta\tau_n$ is the change in this *difference* in the rotamer n when X is some group other than H. The first term of eq 9 is related to the intrinsic asymmetry and rotamer populations whereas the second two are related to the *effectiveness* of X in causing a shift difference relative to hydrogen. A similar asymmetry effect is created if, instead of changing X from hydrogen to

(52) R. Foster and C. A. Fyfe, *J. Chem. Soc. B*, 53 (1966).

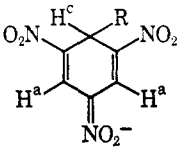
(53) D. Deatt and M. J. Strauss, unpublished work.

(54) M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. B*, 147 (1970).

(55) H. S. Gutowsky, *J. Chem. Phys.*, **30**, 11 (1959).

Table I

Proton Chemical Shifts of 2,4,6-Trinitrocyclohexadienates



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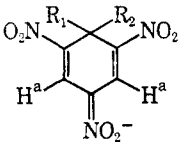

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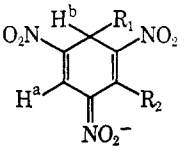

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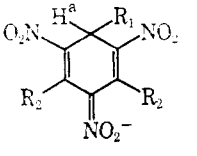


31

R	τ, ppm H^a	H^b	H^c	Solvent[a]	Ref
		Compound **6**			
$CH_3CH^b_2O$	1.5	6.3	3.6–3.7	CH_3COCH_3	34
C_2H_5O	1.6		3.7	CH_3SOCH_3	34
CH^b_3O	1.3–1.6	6.7	3.7–3.9	CH_3COCH_3	34
CH_3O	1.5		3.8	CH_3SOCH_3	34
CH_3O	1.4		3.7	CH_3CN	34, 30
H^bO	1.8	5.5	3.7	CH_3SOCH_3	5, 47
H_2N	1.7		4.5	CH_3SOCH_3	50
CH_3NH	1.5		4.3	CH_3SOCH_3	2, 50
$(CH_3)_2N$	1.5		4.4	CH_3SOCH_3	2, 50
$(C_2H_5)_2N$	1.5		4.3	CH_3SOCH_3	2, 50, 51
Piperidinyl, $C_5H_{10}N$–	1.5		4.4	CH_3SOCH_3	50
$HO(CH_2)_2NH$	1.6		4.3	CH_3SOCH_3	2
$C_2H_5CO(CH)CH_3$	1.5		4.6	CH_3SOCH_3	52
$CH_3COCH_2(CH)COCH_3$	1.5		4.6	$CH_3CO(CH_2)COCH_3$	52
$CH_3CO(CH)CH_3$	1.5		4.6	CH_3SOCH_3	52
$CH_3CH_2COCH_2$	1.7		5.0	CH_3SOCH_3	52
$(CH_3)_2CHCOCH_2$	1.7		5.0	CH_3SOCH_3	52
$CH_3CO(CH_2)_2COCH_2$	1.7		4.9	$CH_3CO(CH_2)COCH_2$	52
$CH_3COCH^b_2$	1.6	7.4	4.8	CH_3COCH_3	34, 52
CH_3COCH_2	1.6		4.9	CH_3CN	34
CH_3COCH_2	1.7		5.0	CH_3SOCH_3	34
NC	1.6		4.5	$CHCl_3$	64
$CH^b_3C[^+N(CH_2CH_3)_3]CN$	1.5–1.6	6.2	5.0	CH_3SOCH_3	29
$CH_3(CH)CH^bO$	1.6	0.3	4.8	CH_3SOCH_3	63
$C_6H_5CH_2CO(CH)C_6H_5$			4.3	CH_3SOCH_3	54
	1.6–1.7		5.0	CH_3SOCH_3	54
	1.7		5.0	CH_3SOCH_3	54
$c\text{-}C_3H_5COCH^b_2$	1.7	7.2	4.9	CH_3SOCH_3	53
CH_3SOCH_2	1.6		3.1	CH_3SOCH_3	47
$C_6H_5(CH)CN$	1.7–1.8		4.5	CH_3SOCH_3	54
O_2NCH_2	1.6		4.7	CH_3SOCH_3–CH_3NO_2	36
$CH_3(CH)NO_2$	1.5		4.3	CH_3SOCH_3–$C_2H_5NO_2$	36
$C_2H_5(CH)NO_2$	1.5		4.4	CH_3SOCH_3–$C_3H_7NO_2$	36
$(CH_3)_2(C)NO_2$	1.5		4.1	$(CH_3)_2CHNO_2$	36
Cl_3C	1.4		3.6	CH_3SOCH_3	65
C_2H_5S	1.7		4.2	CH_3SOCH_3–CH_3OH	67
C_6H_5S	2.5		2.5	CH_3SOCH_3	67
^-O_3S	1.7		4.0	CH_3SOCH_3–H_2O	66

Compound **19**

R_1	R_2	τ, ppm H^a	H^b	H^c	Solvent[a]	Ref
CH^b_3O	CH^b_3O	1.1	6.9		CH_3COCH_3	34
CH^b_3O	CH^b_3O	1.1–1.2	6.9		CH_3CN	30, 34
CH^b_3O	CH^b_3O	1.3–1.6	6.9		CH_3SOCH_3	30, 34, 51
$CH^c_3CH^b_2O$	$CH^c_3CH^b_2O$	1.2	6.7	8.8	CH_3COCH_3	34
C_2H_5O	C_2H_5O	1.2			CH_3CN	34
C_2H_5O	C_2H_5O	1.3			CH_3SOCH_3	34
CH^b_3O	$CH_3CH^c_2O$	1.1	6.9	6.7	CH_3COCH_3	34
CH_3O	C_2H_5O	1.2			CH_3CN	34
CH_3O	C_2H_5O	1.3			CH_3SOCH_3	34

Table I (Continued)

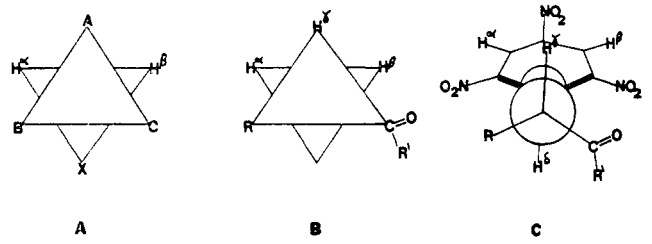
R_1	R_2	τ, ppm H^a	H^b	H^c	Solvent[a]	Ref
$CH_3(CH_2)_3O$	$CH_3(CH_2)_3O$	1.1			CH_3COCH_3	34
$CH_3(CH_2)_3O$	$CH_3(CH_2)_3O$	1.2			CH_3CN	34
$CH_3(CH_2)_3O$	$CH_3(CH_2)_3O$	1.3			CH_3SOCH_3	34
CH^b_3O	$(CH_3)_2CH^cO$	1.1	6.1	6.1	CH_3COCH_3	34
CH_3O	$(CH_3)_2CHO$	1.2			CH_3CN	34
CH_3O	$(CH_3)_2CHO$	1.3			CH_3SOCH_3	34
$-OCH^b_2CH^b_2O-$		1.3	5.7		CH_3COCH_3	2
NC	CH^b_3O	1.1	6.9		$CHCl_3$	77
NC	CH^b_3O	1.3	7.0		CH_3SOCH_3	77
NC	CH^bO	1.5	−0.14		$CHCl_3$	33, 77
$C_2H_5O_2C(CH)COCH_3$	CH^b_3O	1.3	6.6		CH_3SOCH_3	74
N_3	CH^b_3O	1.4	6.9		....	76
		Compound **20**				
CH_3O	C_2H_5O	1.5	3.8		CH_3SOCH_3	2
CH_3O	CH_3O	1.1	*b*		CH_3SOCH_3	75
CH_3O	CH^c_3O	1.6	3.8	6.5	CH_3SOCH_3	27, 51
CH_3O	$(CH_3)_2N$	1.5	3.8		CH_3SOCH_3–H_2O	66
CH_3O	$(C_2H_5)_2N$	1.5	3.7		CH_3SOCH_3	51
C_2H_5O	$(C_2H_5)_2N$	1.3	4.1		CH_3SOCH_3	2
C_2H_5O	H_2N	1.4	3.8		CH_3SOCH_3–C_2H_5OH	5
CH_3O	H_2N	1.4–1.5	3.9		CH_3SOCH_3	51, 69
CH_3O	NH^-	1.3	3.9		CH_3SOCH_3	51
CH_3O	CH_3NH	1.5	3.8		CH_3SOCH_3–CH_3OH	51, 69
CH_3O	CH_3N^-	1.3–1.4	3.8–3.9		CH_3SOCH_3–H_2O	51, 69
CH_3O	$C_6H_5N^-$	1.3	3.8		CH_3SOCH_3–H_2O	51, 69
HO	CH_3N^-	1.4	3.8		CH_3SOCH_3–H_2O	69
HO	CH_3NH	1.5	3.8		CH_3SOCH_3–H_2O	69
HO	H_2N	1.6	3.9		CH_3SOCH_3–CH_3OH	69
HO	$(CH_3)_2N$	1.6	3.9		CH_3SOCH_3–H_2O	69
NC	CH^c_3O	1.4	4.3	6.0	$CHCl_3$	77
NC	CH^c_3O	1.5	4.3	6.2	CH_3SOCH_3	77
NC	CH^c_3	1.4–1.5	4.2–4.3	7.3	$CHCl_3$	77
Cl_2C	CH_3O	1.4	3.4		CH_3SOCH_3	65
O_2NCH_2	$(CH_3)_2N$	1.6	4.3		CH_3SOCH_3–CH_3NO_2	36
CH_3COCH_2	$(CH_3)_2N$	1.6	4.6		CH_3SOCH_3	75
CH_3COCH_2	C_2H_5O	1.6	4.7		CH_3SOCH_3	75
CH_3COCH_2	CH^c_3O	1.6	4.8	6.1	CH_3COCH_3	78
CH_3COCH_2	C_6H_5O	1.6	4.7		CH_3SOCH_3	75
CH_3COCH_2	Cl	1.6	4.8		CH_3SOCH_3	75
^-O_3S	C_6H_5NH	1.6	3.8		CH_3SOCH_3–H_2O	66
^-O_3S	CH^c_3NH	1.7	3.9	6.9	CH_3SOCH_3–H_2O	66
^-O_3S	$(CH^c_3)_2N$	1.6	3.9	7.0	CH_3SOCH_3–H_2O	66
^-O_3S	H_2N	1.6	3.9		CH_3SOCH_3–H_2O	66
^-O_3S	CH^c_3O	1.6	3.9	6.1	CH_3SOCH_3–H_2O	66
C_2H_5S	CH_3NH	1.6	4.0		CH_3SOCH_3–H_2O	67
C_2H_5S	H_2N	1.5	4.3		CH_3SOCH_3–H_2O	67
		Compound **31**				
CH_3O	OCH_3	3.9			CH_3SOCH_3	75
CH_3COCH_3	F	4.9			CH_3SOCH_3	75

[a] The solvents are deuterated in some cases. [b] This position is substituted with a methoxyl group.

some other group, it is removed entirely. The effect may persist even when H^α and H^β are not bonded to the same carbon. This situation is realized in the ketonic σ complex shown in Figures 2B and 2C, where $\Delta\tau_n$ is now the chemical shift difference between H^α and H^β in going from a reference state where these protons are indistinguishable on rapid rotation (not physically realizable) to a state where the environments are distinguishable on rotation. The measured chemical shift differences of the sp^2 ring protons H^α and H^β as well as $J_{\gamma\delta}$ coupling constants for several complexes are summarized in Table II.

Since $\Delta\tau_{\alpha\beta}$ for the diethyl ketone complex is zero, $\Sigma_n\Delta\tau_n$ must be zero in this instance, and, in addition, either $\Sigma_n\Delta\tau_n{}^0$ is zero or the rotamer populations are all equal. It has been assumed that since the distance between C-1 and the sp^2 protons is large, $\Sigma_n\Delta\tau_n{}^0$ is zero, and no conclusion can be made about rotamer populations for this complex. If $\Sigma_n\Delta\tau_n$ and $\Sigma_n\Delta\tau_n{}^0$ are very small for the diethyl ketone complex, these terms are probably small for the other complexes and measured values of $\Delta\tau_{\alpha\beta}$ are likely a result of large differences in rotamer populations.

The pmr spectrum of **6a** in acetone slowly changes to that

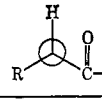


A B C

Figure 2. Representation of an asymmetric environment in an anionic σ complex.

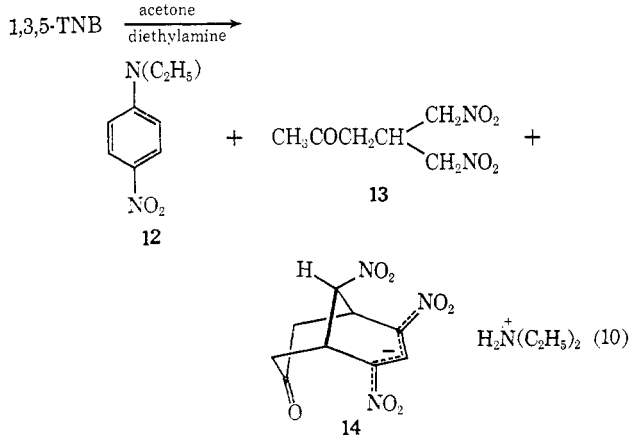
Table II[a]

Chemical Shift Differences and Coupling Constants of Asymmetric 1,3,5-Trinitrocyclohexadienates[54]

	$\Delta\tau_{\alpha\beta}$, cps	$J_{\gamma\delta}$
$C_2H_5CO(CH)CH_3$	0	3
	4.1	5.0
	5.4	1
$C_6H_5CH_2CO(CH)C_6H_5$	6.5	3.0
$C_6H_5(CH)CN$	6.3	3.5

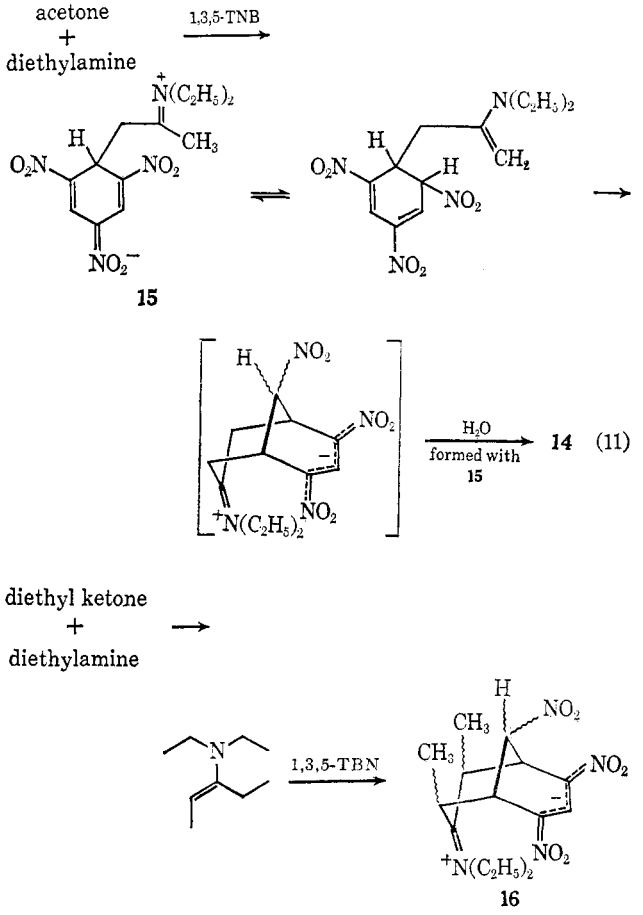
[a] See Figure 2C.

of **6c**, which shows a triplet for the sp^3 ring proton centered at τ 4.8 (J = 9 cps).[34] During this transformation the sum of sp^2 ring-proton peak areas in **6a** and **6c** remains constant as do the sp^3 proton peak areas. When methoxide is added to a solution of 1,3,5-TNB in acetone, the pmr spectrum of the solution shows resonances for both acetonate and methoxy complexes **6c** and **6a**. The former increase with time at the expense of the latter.[34] Transient resonances for both acetonate and diethylamide complexes, **6c** and **6e** ($R_1 = R_2 = C_2H_5$), are observed in acetone solutions of 1,3,5-TNB and diethylamine. In this instance, the final spectrum is characteristic of a mixture of **12**, **13**, and **14** (eq 10).[48,56-59] The mechanism



(10)

of formation of **12** and **13** is not known, but an immonium σ complex (**15**) has been proposed as a precursor to the bicyclic product (**14**) (eq 11).[59] This mechanistic route is supported by the isolation of **16** from the reaction of 1,3,5-TNB and the enamine prepared from diethyl ketone and diethylamine.[60] Interestingly, solutions of 1,3,5-TNB and primary, secondary, or tertiary amines in ketonic solvents, such as ethyl acetoacetate, acetylacetone, dicarbomethoxyacetone, and dibenzyl ketone, form *only* bicyclic structures like **18**. The intermediate σ complexes **10a**, although observable by pmr and visible spectroscopy, cannot be isolated.[61,62] Formation of **18** (R and R′ are electron-withdrawing functions) does not necessarily proceed through an immonium complex like **15**, as the reactions are effected by tertiary amines which preclude formation of such intermediates. In addition, acetone and diethyl ketone form only stable complexes like **10a** (R′ =



(11)

R = CH_3 or H) with triethylamine and 1,3,5-TNB.[59,60] Immonium intermediates like **15**, prepared from ketones containing electron-withdrawing substituents, should also be quite unreactive toward further cyclization (eq 11). A two-step cyclization has been proposed to account for the formation of **18** (R and R′ are electron-withdrawing functions).[61] 1,3,5-TNB is not the only electron-deficient aromatic which can yield bicyclic complexes like **18** and **14**; 1-X substituted, 3,5-dinitro aromatic substrates form analogous structures in which X is part of the delocalized propenide function.[61]

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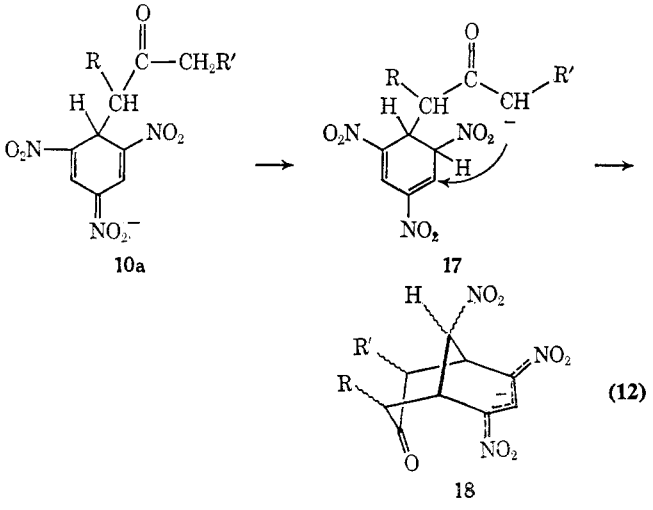
(60) H. Schran and M. J. Strauss, unpublished results.
(61) M. J. Strauss, H. Schran, T. Jensen, and K. O'Connor, *J. Org. Chem.*, 35, 383 (1970).
(62) M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. C*, 2112 (1969).

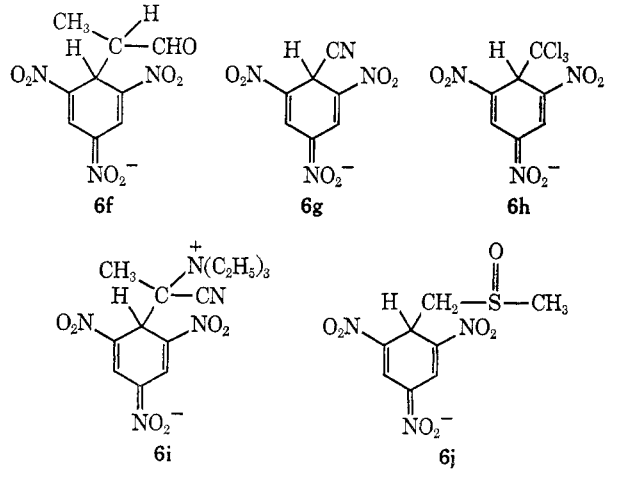


10a 17 18 (12)

Addition of triethylamine to a propionaldehyde solution of 1,3,5-TNB yields **6f** which has been characterized by pmr.[63] The sp^2 ring proton resonance is a singlet even though the exocyclic carbon is asymmetric.

Solutions of tetraphenylarsonium cyanide in chloroform have pmr spectra characteristic of **6g**.[64] The sp^2 and sp^3 proton resonances appear as singlets at τ 1.6 and 4.5. Resonances for both the complex and free aromatic are observed in the same solution, indicating slow cyanide exchange.

In DMSO solution, chloroform, 1,3,5-TNB, and sodium methoxide yield **6h**, which has sp^2 and sp^3 proton resonances at τ 1.4 (d, 2 H), and 3.6 (t, 1 H).[65] The latter resonance is at very low field relative to sp^3 ring proton resonances of complexes with other carbon bases (Table I), presumably because of electronegative chlorine. The complex **6h** is also formed on addition of chloroform to a DMSO solution of **6a**.[65]

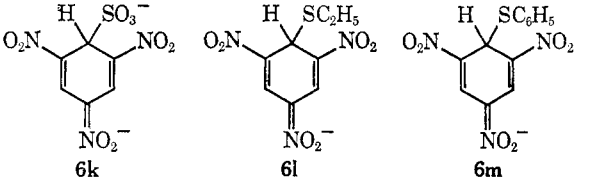


6f 6g 6h

6i 6j

Addition of triethylamine to a solution of 1,3,5-TNB in acrylonitrile yields the zwitterion **6i**, which has been characterized by pmr.[29] The complex decomposes in DMSO, the only solvent which dissolves a sufficient amount for pmr analysis, but does not decompose in acid. A σ complex between the conjugate base of DMSO and 1,3,5-TNB has been proposed in which bonding occurs between oxygen or sulfur and C-1.[34,48] This kind of exocyclic bond was proposed because the sp^3 ring proton resonance is a singlet. The spectrum was later shown to result from the hydroxide complex **6d**.[47] The DMSO complex **6j** was subsequently prepared under anhydrous conditions[47] and shows a triplet sp^3 ring proton resonance ($J \simeq 1$ cps) at τ 3.1. The low-field position and very small coupling of this resonance with adjacent methylene protons are puzzling.

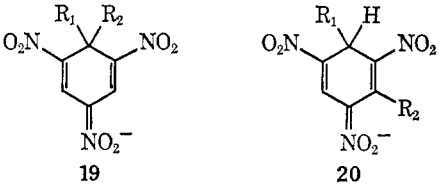
iv. With Sulfur Bases. Sulfite,[66] thioethoxide,[67] and thiophenoxide[67] ions add to 1,3,5-TNB, yielding the corresponding complexes **6k**, **6l**, and **6m**, respectively. The sp^3 ring proton resonances are at significantly lower field than those of complexes with carbon bases. **6m** shows only one ring proton resonance at τ 2.5, a result of rapid exchange with free 1,3,5-TNB. The sulfite complex **6k** has a formal positive charge on sulfur which deshields the sp^3 ring proton resonance to τ 4.0. The thioethoxide complex **6l** has the highest sp^3 ring proton resonance at τ 4.2. This may, in part, be a solvent effect, as spectra of the various complexes were determined in different mixtures of DMSO, methanol, and water (Table I).



6k 6l 6m

b. From 1-Substituted-2,4,6-TNB

Nucleophilic addition of R_1 to 1-R_2-2,4,6-TNB can occur at the substituted or unsubstituted positions to give the isomeric complexes **19** and **20**. In a number of systems, **20** is formed

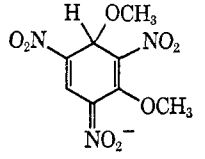


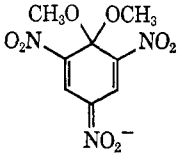
19 20

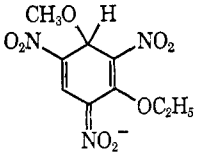
initially in a kinetically favored addition and is then transformed to the more thermodynamically stable **19**. If an aza function is substituted for a NO_2 group, a complex analogous to **20** may be thermodynamically favored. The energetics of such transformations are discussed in more detail in section V.

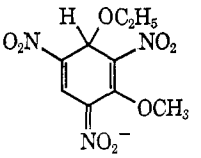
i. Picryl Ethers. The pmr spectrum of a methanol–DMSO solution of 2,4,6-TNA changes dramatically on addition of 1 equiv of sodium methoxide. The low-field aromatic proton resonance diminishes in intensity as coupled resonances (J = 1.5–2 cps) at τ 1.6 (d) and 3.8 (d) characteristic of **20a** increase.[27,51] During the next 15 min these latter bands slowly diminish in intensity, and a singlet at τ 1.3, characteristic of the sp^2 protons in **19a**, increases. The complex **20a** cannot be isolated, but crystals of **19a** are easily obtained as the sodium salt. The pmr spectrum of the mixed complex **20b** was reported in a recent review,[2] but the references cited refer to the dimethoxy complex **20a**. The complex **20b** would presumably form initially on addition of sodium methoxide to 2,4,6-trinitrophenetole. The transient species observed by visible

(63) M. J. Strauss, *Tetrahedron Lett.*, 2021 (1969).
(64) A. R. Norris, *J. Org. Chem.*, **34**, 1486 (1969).
(65) S. M. Shein, A. D. Khmelinskaya, and V. V. Brovko, *Chem. Commun.*, 1043 (1969).
(66) M. R. Crampton, *J. Chem. Soc. B*, 1341 (1967); see also ref 115.
(67) M. R. Crampton, *ibid.*, 1208 (1968).


20a


19a

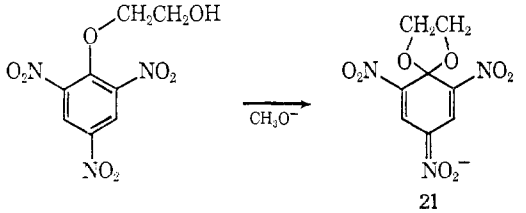

20b


20c

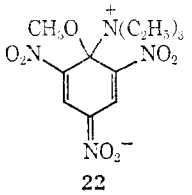
spectroscopic examination of a solution of 2,4,6-TNA and sodium ethoxide,[68] originally thought to be a charge-transfer complex, is more likely **20c**. The isomerization from **20a** to **19a** is catalyzed by methanol and by methoxide.[69] When sodium methoxide is added to a methanolic solution of 2,4,6-TNA, the pmr spectrum of the mixture immediately after addition shows resonances only for **19a**. In 30/70 mol % methanol/DMSO resonances for **20a** form rapidly and then disappear with a half-life of ~3 min in 0.2 *M* methoxide and ~30 sec in 0.51 *M* methoxide. An intermolecular rather than intramolecular rearrangement has been suggested on the basis of these observations. Specific mechanistic routes are considered in section V.

A series of symmetrical and mixed complexes **19** (R_1, R_2 = CH_3O, C_2H_5O, *n*-C_4H_9O, and *sec*-C_3H_7O) have been prepared and their pmr spectra recorded in acetonitrile, DMSO, and acetone.[34] The sp^2 proton chemical shifts are about the same in all three solvents.

Intramolecular attack occurs to yield the spiro σ complex **21** when methoxide is added to 1-(2′-hydroxyethoxy)-2,4,6-TNB.[70,71] The sp^2 and methylene proton resonances are singlets at τ 1.3 and 5.7, respectively.


21

There are few examples of picryl ether–amine σ complexes. An early report of the pmr spectrum of **22** generated in DMSO solution from 2,4,6-TNA and triethylamine[51] was later corrected; the spectrum was shown to result from methyltriethylammonium picrate,[72] **23a**. The pmr spectrum of a DMSO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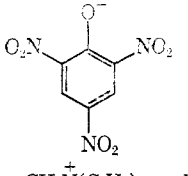
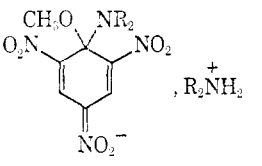

23a, $CH_3\overset{+}{N}(C_2H_5)_3$, salt

23b, $CH_3\overset{+}{N}H(C_2H_5)_2$, salt

solution of 2,4,6-TNA and diethylamine was attributed to **24** (R = C_2H_5),[51] but the ring proton resonances at τ 1.4 could be those of the methyldiethylammonium picrate (**23b**). Formation of the latter would explain the reported difficulty in equilibrating the product with its isomer **25** (R = C_2H_5), which can be prepared from sodium methoxide and N,N-diethylpicramide (*vide infra*).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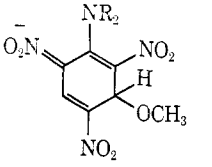
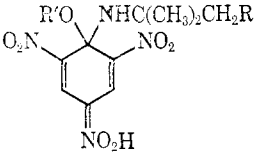

25

A series of neutral σ complexes (**26**) have been prepared from hindered picryl ethers and hindered amines[73] at −57°. In **26** (R = H, R′ = C_6H_5), the ring proton resonance appears at τ 1.6 (Table I). In addition, resonances at τ −1.9 (NO_2H) and 3.9 (NH) are observed. This is the first report of a complex in which the NO_2 group *para* to the sp^3 ring carbon is protonated. With excess amine, the neutral complexes **26** yield the anionic σ-complex salts **27**. If cold solutions of **26**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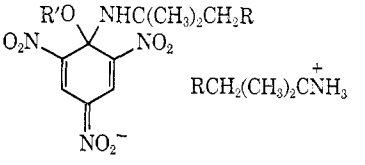
27

in tetrahydrofuran are warmed to room temperature, alkoxide is lost, and a substituted picramide is formed. Interestingly, 2,4,6-TNA gives red complexes with hindered amines in methanol, but picramides form rapidly even at low temperatures. In toluene solutions of 2,4,6-TNA, only alkylation of hindered amines occurs, yielding salts analogous to **23a** and **23b**. With *t*-butylamine, alkylation and substitution are competitive. Unhindered amines (*i.e.*, $C_6H_5NH_2$) displace methoxide to give picramides as the only product, even in toluene. When triethylamine is added to a solution of 2,4,6-TNA in acetone, **23a** is obtained.[74] Under similar conditions, 2,4,6-trinitrophenetole and 2,4,6-trinitrodiphenyl ether suffer acetonate attack at C-3 to give complexes like **20** (*vide infra*).[75] The pmr spectrum of a solution of 2,4,6-TNA and tetraethylammonium azide in acetonitrile at −10° shows resonances at τ 1.4 and 6.9 for the ring and methoxyl protons of **19b**.[76] In contrast, the pmr spectrum of a chloroform solution of tetraphenylarsonium cyanide and 2,4,6-TNA at −30° shows resonances for both **19c** and **20d** in a 20:80 ratio.[77] These remain unchanged for several hours. The ring proton resonances of the latter complex are coupled doublets (J = 0.8 cps) at τ 1.4 and 4.3. On warming, these increase in intensity while resonances attributed to **19c** decrease. This behavior is suggestive of a more negative heat of formation for **19c**.[77]

(68) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, 2528 (1956).
(69) M. R. Crampton and V. Gold, *ibid.*, *B*, 893 (1966).
(70) R. Foster, C. A. Fyfe, and J. W. Morris, *Recl. Trav. Chim. Pays-Bas*, **84**, 516 (1965).
(71) J. Murto, *Suom. Kemistilehti, B*, **38**, 255 (1965).
(72) K. L. Servis, personal communication.
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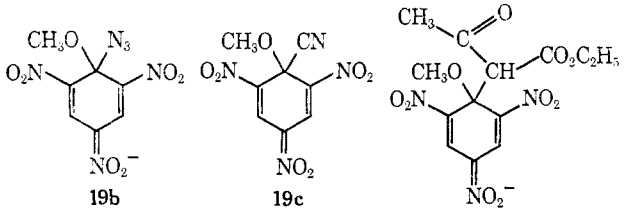
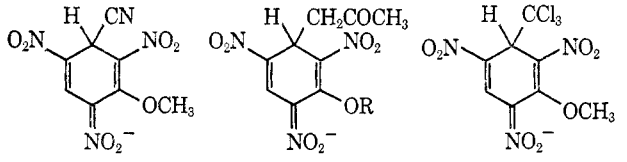
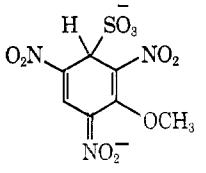
(74) M. J. Strauss, *Chem. Commun.*, 76 (1970).
(75) R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *Tetrahedron*, **23**, 227 (1967).
(76) P. Caveng and H. Zollinger, *Helv. Chem. Acta*, **50**, 861 (1967).
(77) A. R. Norris, *Can. J. Chem.*, **47**, 2895 (1969).



19b **19c** **19d**



20d **20e** **20f**



20g

Pmr spectra of solutions of 2,4,6-trinitroalkyl and 2,4,6-trinitrophenyl ethers in alkaline acetone show resonances characteristic of **20e**.[75,78] The sp^2 and sp^3 ring proton resonances appear at τ 1.6 and 4.7 and are coupled by 1–2 cps. Attack of acetonate at C-1 was not observed. Triethylamine was used to initiate acetonate attack on the ethyl and phenyl ethers but methoxide was used with 2,4,6-TNA,[78] as amines are alkylated by this aromatic (*vide supra*). It has been reported that methoxide is methylated by 2,4,6-TNA,[79] but most workers have detected only σ-complex formation.

The pmr spectrum of a complex prepared by addition of potassium *t*-butoxide to a tetrahydrofuran solution of 2,4,6-TNA shows resonances for **19d** indicating addition has occurred at C-1.[74] Acidification of an aqueous solution of this complex results in picryl ethylacetoacetate. Preliminary formation of a C-3 complex in solution is not precluded however.

A pmr spectrum characterizing **20f** is obtained from a solution of sodium methoxide, 2,4,6-TNA, and chloroform in DMSO.[65] The same spectrum results when **19a** is added to a chloroform–DMSO mixture, indicating a solvolysis occurs similar to that observed in acetone.[34]

Sulfite attacks C-3 in 2,4,6-TNA[66] to give **20g** which has coupled resonances at τ 1.6 and 3.9. At higher sulfite concentration, 2 equiv adds to give a propenide complex (see section II.B.3).

ii. Picramides. Addition at C-1 is not observed with picramides. Addition at C-3 usually occurs, in addition to loss of the weakly acidic proton(s) bonded to nitrogen. Proton loss can become competitive with base addition, which can occur on picramide or its conjugate base. Hydroxide and alkoxide both react with picramide and substituted picramides by addition and proton abstraction processes.[2,5,51,60,69] In DMSO, picramide suffers ~80% addition at C-3 and ~20% NH proton abstraction when methanolic methoxide is added.[51,66] The pmr spectrum of a 1:1 equivalent mixture of methoxide and this aromatic shows two coupled doublets ($J \sim 1.5$ cps) at τ 1.4 and 3.9, for the sp^2 and sp^3 ring protons in **20h**, and a singlet at τ 1.5 from the sp^2 ring protons in the conjugate base of picramide.[51,69] If less than an equivalent amount of methoxide is added, this latter singlet appears at a τ value between that of the sp^2 protons of picramide and its conjugate base, indicating rapid interconversion of these two species. As the methoxide concentration increases, the singlet shifts toward τ 1.5 and decreases as the resonances for **20h** increase. These latter resonances *do not* shift, indicating

19e **19f** **20h**

20i **20j** **20k**

the complex is long-lived.[69] Early reports of the C-1 complex **19e** were based on the observation of identical products from the reaction of picramide with methoxide and from 2,4,6-TNA with ammonia.[80] It was subsequently shown that ammonia converts 2,4,6-TNA to picramide which then adds methoxide at C-3.[69] In DMSO–ethanol solutions of ethoxide and picramide, more of the conjugate base of picramide forms than in methoxide solutions. With *t*-butoxide–butanol–DMSO, only the conjugate base is formed. The extent of complex formation with picramide thus appears to diminish as the bulk of the attacking base increases in the order $CH_3O < C_2H_5O < t\text{-BuO}$. Pmr spectra of aqueous DMSO solutions of picramide and sodium hydroxide show that ~70% of the product is **20i**.[69] Decreasing the water content increases the amount of conjugate base. The NH and OH resonances appear as a broad singlet in all these picramide base mixtures.

The pmr spectrum of an equivalent mixture of N-methylpicramide and methoxide in DMSO–methanol shows resonances for both the conjugate base and complex **20j**. The former accounts for ~80% of the total. The greater preference for conjugate base formation with N-methylpicramide relative to picramide has been rationalized on the basis of increased stability of the exocyclic bond from C-1 to nitrogen, which has considerable double-bond character in the conjugate base.[51] Restricted rotation about this bond is evidenced by the pmr spectrum of the anion, which has a complex resonance pattern for the nonequivalent sp^2 ring protons.[51] As excess methoxide is added to the mixture of **20j** and the conjugate base of N-methylpicramide, **20j** loses an NH proton and the pmr spectrum of the mixture shows resonances for the corresponding dianion.[51,69] Similar transformations have been observed by pmr in aqueous DMSO solutions of N-methylpicramide and sodium hydroxide.[69] As expected, the acid-strengthening effect of phenyl in N-phenylpicramide results in complete conversion of this aromatic to its conjugate base when 1 equiv of methoxide is added. The anionic ring protons show only a single resonance because of rapid rotation about the C-1–N bond.[51]

(78) M. Kimura, O. Nobaru, and M. Kawazoi, *Chem. Pharm. Bull. Jap.*, **17**, 531 (1969).

(79) V. A. Sokolenko, *Org. Reactivi (USSR)*, **2** 208 (1965).

(80) R. C. Farmer, *J. Chem. Soc.*, 343 (1959).

Both methoxide and hydroxide add to C-3 of N,N-dimethylpicramide to yield the complex **20k** (R_1 = CH_3O or HO, R_2 = CH_3).[59,60] The pmr spectra of these complexes in DMSO are characterized by two low-field doublets ($J \sim 2$ cps) for the sp^2 and sp^3 ring protons at τ 1.5–1.6 and 3.8–3.9. Since there are no ionizable protons in this aromatic, at higher base concentrations addition of a second molecule of base occurs to give a propenide complex (section II.B.3). The complex **20k** (R_1 = CH_3O, R_2 = CH_3), on standing for long periods of time in DMSO–methanol solution, is converted to **19a** (R_1 = R_2 = CH_3O). There is no evidence for **19f**.

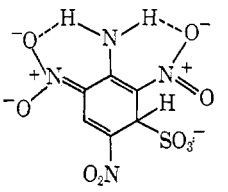
Interestingly, the pmr spectrum of **20k** (R_1 = CH_3O, R_2 = $(C_2H_5)_2N$), prepared from methoxide and N,N-diethylpicramide, shows N-ethyl resonances characteristic of an ABX_3 spin system.[51] The AB methylene results from the asymmetric center at C-3. This asymmetry effect is analogous to that observed when the asymmetric center is in the side chain and the nonequivalent protons are at C-3 and C-6 (section II.B.1).

Picramides do not react with amines in DMSO solution.[51,75] There has been no report of the reaction of sodium amide with picramide, but proton abstraction and concurrent or subsequent addition would undoubtedly occur, as both have been observed with 2,4-dinitroaniline in liquid ammonia[81] (section II.B.2).

Although N,N-dimethylpicramide does not react with amines in DMSO,[34] addition of triethylamine to nitromethane[36] or acetone[75] solutions of this aromatic results in lyate attack to give **20k** (R_1 = CH_3COCH_2 or O_2NCH_2 and R_2 = CH_3). Pmr spectra of these solutions show resonances at τ 1.6 and 4.3–4.6 for the sp^2 and sp^3 ring protons. The latter is at ~0.5 ppm higher field than in the analogous complexes formed with alkoxide or hydroxide. Interestingly, protons in the methylene group of **20k** (R_1 = O_2NCH_2, R_2 = CH_3) are nonequivalent because of asymmetry in the ring. The sp^3 proton bonded to C-1 thus appears as eight lines due to coupling with three nonequivalent protons.[36] A similar effect would be expected for the acetone complex **20k** (R_1 = CH_3COCH_2, R_2 = CH_3), but it was not detected.[75]

Sulfur bases add to unsubstituted positions in picramides without preliminary or subsequent proton abstraction.[66,67] One equivalent of sulfite adds to C-3 of N-methylpicramide, N-phenylpicramide, and N,N-dimethylpicramide in aqueous DMSO solutions.[66] The sp^2 and sp^3 ring proton resonances of these complexes, **20k** (R_1 = ^-O_3S), are coupled doublets (J = 1.5 cps) centered at τ 1.6 and 3.9, respectively. In addition, a low-field shift of the NH resonance relative to the parent aromatic is observed for the picramide and N-substituted picramide complexes. This shift has been attributed to hydrogen-bonded structures like **28**, **29**, and **30**, a conclusion supported by two singlet resonances observed at τ −0.1 and −0.6 for the NH_2 in **28**. Only one resonance is observed for the N-substituted complexes, indicative of rapid rotation in one of the isomers, **29** or **30**.[66] Since the NO_2 group *para* to the sp^3 carbon carries most of the negative charge, **30** seems more likely if a single isomer is present.

Complexes with pmr spectra similar to those of **28**, **29**, and **30** are obtained when thioethoxide or thiophenoxide is added to solutions of picramides.[67] Nonequivalence of the amino protons is again observed, indicative of hydrogen bonding.[5,67]



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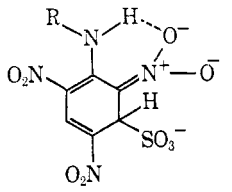

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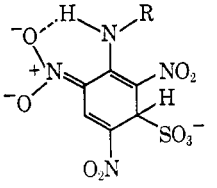
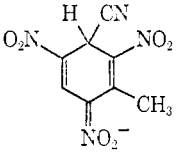
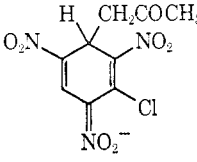


30

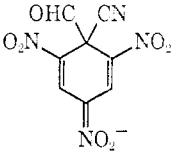
iii. Other Picrylic and Related Systems. 2,4,6-Trinitrotoluene adds cyanide at C-3 to give **20l**[77] whereas 2,4,6-trinitrobenzaldehyde adds cyanide at C-1 to give **19g**.[33,77] The other possible isomer in each case cannot be observed by pmr even



20l



20m



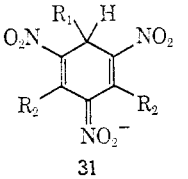
19g

at −30°. The pmr spectrum of **20l** in deuteriochloroform has singlet absorptions at τ 1.4, 4.2, and 7.3 for the sp^2 and sp^3 ring protons and methyl group, respectively. These singlets could mean that the complex is very short-lived. At room temperature decomposition occurs after several hours. The pmr spectrum of **19g** has singlet resonances at τ −0.14 and 1.5 for the aldehydic and ring protons.

The pmr spectrum of an acetone solution of picryl chloride and triethylamine has a triplet centered at τ 4.8 (J = 6 cps), consistent with **20m**.[75]

c. From 1,3-Disubstituted-2,4,6-TNB

The pmr spectrum of a DMSO solution of sodium methoxide and 1,3-dimethoxy-2,4,6-TNB has a singlet ring proton resonance at τ 3.9, 2.9 ppm upfield from the singlet observed in the absence of base.[75] The τ 3.9 resonance slowly diminishes in intensity at the expense of a new peak which forms at τ 1.1, consistent with conversion of the initially formed complex



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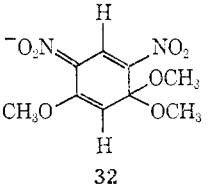


32

31 (R_1 = R_2 = CH_3O) to **32** (R_1 = R_2 = CH_3O). This rearrangement is analogous to that observed with methoxide complexes of 2,4,6-TNA.

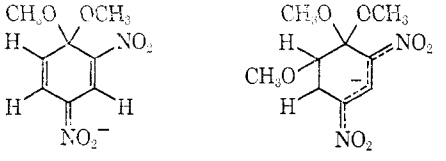
When triethylamine is added to an acetone solution of 1,3-difluoro-2,4,6-TNB, the singlet proton resonance of the starting aromatic at τ 0.7 is shifted to τ 4.9 and appears as a multiplet (J_{H-H} = 6 cps, J_{H-F} = 9.5 cps), indicating attack of acetonate at the unsubstituted ring position to give **31** (R_1 = CH_3COCH_2, R_2 = F).[75]

(81) T. Birchall and W. L. Jolly, *J. Amer. Chem. Soc.*, **88**, 5439 (1966).

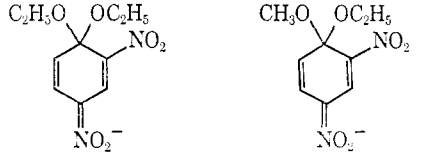
2. *Mononitro- and Dinitrocyclohexadienates* (33, 39, 40, *and* 43)

a. From Alkoxydinitrobenzenes, Alkoxydinitrocyanobenzenes, Alkoxydicyanonitrobenzenes, and Oxygen Bases

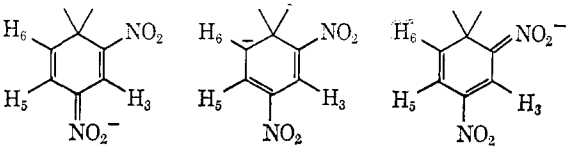
1,3-DNB reacts with alkoxide in DMSO to give small concentrations of a radical species[82] which precludes pmr analysis of the solution. On the other hand, 2,4-DNA adds methoxide at C-1 to give **33a**. This different behavior may result, in part, from an increased propensity for attack at C-1 owing to positive polarization at this site, induced by the adjacent oxygen. The pmr spectrum of **33a** has recently been analyzed in some detail.[83] In DMSO, the methoxyl proton resonance appears as a singlet (6H) at τ 7.1, 1.2 ppm upfield from the methoxyl resonance of 2,4-DNA. This shift results from the hybridizational change at C-1 and is also observed on formation of the C-1 methoxide complex of 2,4,6-TNA. The sp^2 ring proton resonances of the methoxide complex of 2,4-DNA are characteristic of an AMX spin system and confirm that attack has occurred at C-1.[69,83] At high concentrations of methoxide, changes in the pmr spectrum result from formation of 2,4-dinitrophenolate anion,[69] and not the complex **34** as originally supposed.[34] A pmr spectrum similar to that of **33a** is observed when ethoxide is added to a DMSO solution of 2,4-dinitrophenetole, indicating formation of **33b**.[83] The ethoxyl groups are equivalent in this complex. The alkoxyl resonances in the unsymmetrical complex **33c**, prepared from 2,4,6-TNA and ethoxide or 2,4,6-trinitrophenetole and methoxide, appear at the same frequencies as the methoxyl and ethoxyl resonances in **33a** and **33b**, except for a slight downfield shift of the methylene resonance in **33c** relative to **33b**.[83] The sp^2 ring proton resonances in **33a**, **33b**, and **33c** are upfield from the aromatic protons of the parent ethers. The simplest explanation for this upfield shift is an increase in ring charge density as suggested by the canonical forms which can be written[83] (**35–37**). The greatest shift is observed for H-6, as C-6 is the only carbon bonded to hydrogen which can formally carry the negative charge. Since H-3 is flanked by two NO_2 groups and H-5 by only one, the difference in shift difference from the parent ethers for these protons is not surprising. Such arguments are somewhat oversimplified. There is some theoretical evidence that charge density decreases in the ring upon complex formation,[23] although this latter point has been questioned recently.[25] Changes in ring current and NO_2-group anisotropy on going from the parent ether to the complex may be of importance.[23]



33a 34



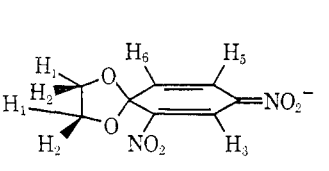
33b 33c



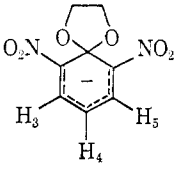
35 36 37

H	Δτ, ppm (from parent ether)[83]
3	0.04–0.07
5	1.3–1.4
6	2.5–2.6

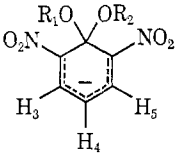
There have been two reports of the pmr spectrum of **33d**, prepared from 1-(β-hydroxyethoxy)-2,4-dinitrobenzene and methoxide.[75,84] The earlier work[75] reported the methylene protons as a singlet. The resonances of H-3, H-5, and H-6 appear centered at τ 1.4, 3.2, and 5.7 as an AMX spin system,



33d



33e



33f

similar to that of **33a**. A recent detailed study of the methylene resonance of **33d** reveals an A_2B_2 spin system with 18 of the 24 transitions observable in the spectrum.[84] The multiplet is centered at τ 5.9 and has a total width of 30 cps. Analysis provides values of τ 5.87 and 5.97 for H-2 and H-1, respectively, with J_{cis} = 7.2, J_{trans} = 6.1, and J_{gem} = 7.6 cps. As expected, the methylene proton resonances of **33e**, prepared from methoxide and 1-(β-hydroxyethoxy)-2,6-dinitrobenzene, are equivalent.[52,75,84] The sp^2 ring proton resonances appear as an A_2B spin system with H-3 and H-5 at τ 2.7 (doublets) and H-4 at τ 5.2 (triplet); $J_{34} = J_{35}$ = 8.2 cps. Similar ring proton resonances are observed for **33f** ($R_1 = R_2 = CH_3$ or $R_1 = CH_3$, $R_2 = C_2H_5$), consistent with attack of methoxide at C-1 in all the 2,6-dinitroanisoles studied. Methoxide also adds to C-1 of 1,5-dimethoxy-2,4-dinitrobenzene giving **38**, with H-3 and H-5 chemical shifts[75] similar to those of **33a**, **33b**, and **33c**. Addition of alkoxide to C-5 of 2,4-DNA has not been detected, even as a fast reaction preceding attack at C-1. The situation is quite different with dinitrocyanoanisoles and dicyanonitroanisoles. Pmr spectra of DMSO–methoxide solutions of these aromatics show resonances characteristic,[27,85,86] of **39a–d** and **40a–c**, indicative of isomeric addition to substituted and unsubstituted positions, as observed with

(82) G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **84**, 4153 (1962).

(83) W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **32**, 2506 (1967).

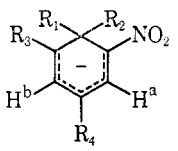
(84) E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffin, *ibid.*, **33**, 4141 (1968).

(85) J. E. Dickeson, L. K. Dyall, and V. A. Pickles, *Aust. J. Chem.*, **21**, 1267 (1968).

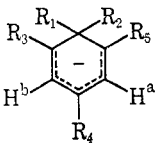
(86) E. J. Fendler, J. H. Fendler, C. E. Griffin, and J. W. Larson, *J. Org. Chem.*, **35**, 287 (1970).

Table III

Proton Chemical Shifts of Dinitro-, Monosubstituted Dinitro-, and Disubstituted Mononitrocyclohexadienates



33



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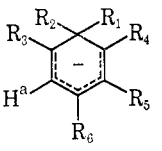

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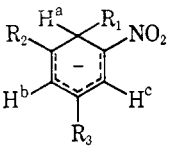


43

Compound **33**

R_1	R_2	R_3	R_4	τ, ppm[a] H^a	H^b	H^c	H^d	Ref
$-OCH_2CH_2O-$		H^c	NO_2	1.5	3.1–3.2	4.6–4.7		2, 75, 84
CH^d_3O	CH^d_3O	H^c	NO_2	1.3	2.7	4.8–4.9	7.1	2, 69, 75, 76, 83
CH^d_3O	C_2H_5O	H^c	NO_2	1.3	2.8	4.9	7.1	2, 75, 83
C_2H_5O	C_2H_5O	H^c	NO_2	1.3	2.8	4.9		2, 75, 83
$-OCH_2CH_2O-$		NO_2	H^c	2.2	2.2	4.9		2, 75, 84
CH_3O	CH_3O	NO_2	H^c	2.1	2.1	5.0		2, 75
CH_3O	C_2H_5O	NO_2	H^c	2.2	2.2	5.0		2, 75

Compound **39**

R_1	R_2	R_3	R_4	R_5	τ, ppm[a] H^a	H^b	H^c	Ref
CH^c_3O	CH^c_3O	CN	NO_2	NO_2	1.3	1.7–2.1	7.0	27, 76
CH^c_3O	CH^c_3O	NO_2	CN	NO_2	2.0	2.0	7.0	27, 85
CH^c_3O	CH^c_3O	CN	NO_2	CN	2.1	2.1	7.0	86
CH^c_3O	CH^c_3O	NO_2	CN	CN	2.7	2.0	7.1	86
CH_3O	H^c	CN	NO_2	NO_2	1.9	2.6	4.6	87
HO	H^c	CN	NO_2	NO_2	1.8	2.5	4.5	87
CH_3O	H^c	CF_3	NO_2	NO_2	2.0	2.9	4.6	87
HO	H	CF_3	NO_2	NO_2	1.8	2.7		87

Compound **40**

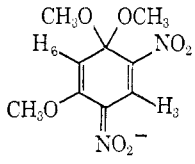
R_1	R_2	R_3	R_4	R_5	R_6	τ, ppm H^a	H^b	H^c	Solvent	Ref
CH_3O	H^b	NO_2	NO_2	^-NH	H^c	3.0	4.8	4.4	NH_3	81
HO	H^b	NO_2	NO_2	^-NH	H^c	3.0	4.8	4.4	NH_3	81
H_2N	H^b	NO_2	NO_2	^-NH	H^c	3.1	4.8	4.5	NH_3	81
CH_3O^b	H^b	NO_2	CN	CH^c_3O	NO_2	1.5	4.5	6.2	CH_3SOCH_3–CH_3OH	27
CH_3O^b	H^b	CN	NO_2	CH^c_3O	NO_2	2.2	4.8	6.2	CH_3SOCH_3–CH_3OH	27
CH_3O^b	H^b	CN	CN	CH^c_3O	NO_2	2.1	4.9	5.8	CH_3SOCH_3–CH_3OH	86
CH_3O	CH_3O	H^b	NO_2	CH_3O	NO_2	1.3	4.0		CH_3SOCH_3	75

Compound **43**

R_1	R_2	R_3	τ, ppm[a] H^a	H^b	H^c	H^d	Ref
CH_3COCH_2	CN	NO_2	5.8	2.8	1.9		87
CH_3COCH_2	CF_3	NO_2	5.7	3.0	2.1		87
CH_3COCH_2	NO_2	CN	5.1	2.6	2.6		87
CH_3COCH_2	NO_2	CF_3		2.7	2.7		87
CH_3COCH_2	H^d	NO_2	5.8	3.4	1.7	4.6	36, 88
O_2NCH_2[c]	H^d	NO_2	5.7	3.3	1.7	4.7	36
$C_2H_5CO(CH)CH_3$	CN	NO_2	5.7	2.6	1.8		87
$C_2H_5CO(CH)CH_3$	NO_2	CN	5.5	2.4	2.4		87

[a] The solvent is CH_3SOCH_3 or CD_3SOCD_3. [b] This methoxyl absorbs at τ 6.9–7.0. [c] Determined in a mixture of CH_3NO_2 and CH_3SOCH_3.

2,4,6-TNA. The complexes **40a**, **40b**, and **40c** cannot be isolated as crystalline salts, as they convert to the more stable **39a**, **39b**, and **39c** in solution. Such conversion can be observed by pmr when, for example, methoxide is added to a DMSO solution of 2,4-dinitro-6-cyanoanisole. Initially, transient coupled doublets (J = 2 cps) at τ 1.5 and 4.5, and two singlets at τ 6.2 and 6.9, are observed.[27] The singlets result from the methoxyl protons of **40a**, analogous to the methoxyl proton chemical shifts of **20a**.[51] It has been noted that such analogies do not unequivocally establish a 1,3-relationship for the methoxyl groups, even though a 1,1-dimethoxy complex is ruled out for this transient species.[27]



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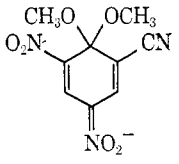
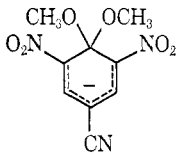
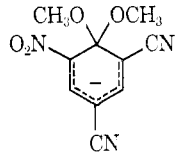


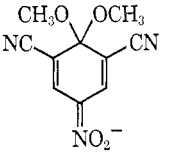
39a



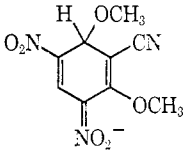
39b



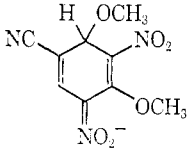
39c



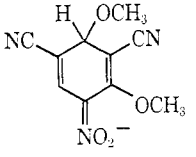
39d



40a

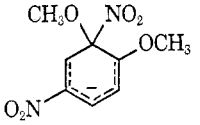


40b

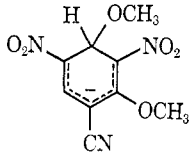


40c

The methoxyl proton resonances of **41** have similar chemical shifts.[27] The possibility of an analogous structure, instead of **40a**, is ruled out by the ring proton resonances. Complex **42**



41

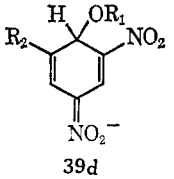


42

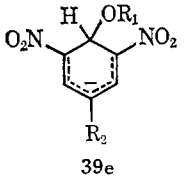
has been considered and ruled out, as the sp^3 ring proton resonance of **42** should have a chemical shift quite similar to that of the sp^3 ring proton resonance of **20a**, which it does not (Table III). The observed chemical shift is identical with that of the sp^3 ring proton resonance of **40b**, which is flanked by NO_2 and cyano groups. Similar arguments based on sp^2 ring proton chemical shifts lead to the same conclusion.[27] The proton chemical shifts and splitting patterns of **40b** and **40c**, as well as **39a–d**, are all consistent with the indicated structures. Formation of the unstable transients **40**, by attack at an unsubstituted ring position, always occurs *para* to a NO_2 group. The more thermodynamically favored complexes **39** all contain a geminal dimethoxy function, regardless of the substituent *para* to the sp^3 ring carbon.

b. From Cyano- and Trifluoromethyldinitrobenzenes and Oxygen Bases

Reaction of 1-substituted 3,5-dinitrobenzenes with hydroxide or alkoxide gives **39d** (R_1 = H or alkyl).[87] There is no evidence for **39e**. The pmr spectrum of a wet DMSO solution of



39d

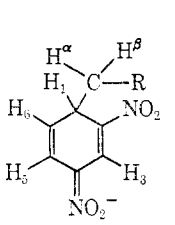


39e

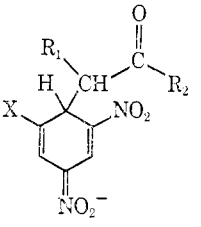
sodium methoxide and 1-cyano-3,5-dinitrobenzene has resonances consistent with **39d** (R_1 = H and CH_3, R_2 = CN). Protons of the major product (R = CH_3) appear as a pair of doublets at τ.9 and 2.7, ruling out the symmetrical **39e**. The minor product (R = H) has a similar spectrum. Almost identical spectra result from treatment of a wet DMSO solution of 1-trifluoromethyl-3,5-dinitrobenzene with sodium methoxide. Thus, base atack in these systems always occurs *para* to a NO_2 group.

c. From Dinitro-, Dinitrocyano-, and Dinitrotrifluoromethylbenzenes and Carbon Bases

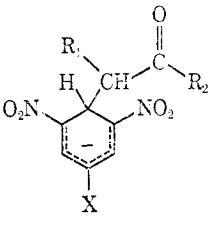
Addition of triethylamine to a solution of 1,3-DNB in nitromethane[36,88] or acetone[88] results in lyate attack to give **43a** (R = NO_2 or $COCH_3$). The ring-proton chemical shifts (Table III) and coupling constants for these complexes, J_{35} =



43a



43b



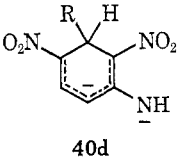
43c

1.9–2, J_{56} = 10.2, and J_{16} = 4.4–5.0 cps, are quite similar. The methylene protons of the acetonyl side chain in **43a** (R = $COCH_3$) are nonequivalent as C-1 is asymmetric. This results in a quintuplet for H-1 due to coupling with H^α, J = 5.0 cps, H^β, J = 10.0 cps, and H-6, J = 5.0 cps.

The pmr spectra of solutions of 1-cyano-3,5-dinitrobenzene or 1-trifluoromethyl-3,5-dinitrobenzene in ketonic solvents containing triethylamine show resonances for a mixture of the isomeric complexes **43b** and **43c**.[87] The spectra are complicated to some extent by line broadening due to free radicals. Both the acetone and diethyl ketone complexes were prepared *in situ*. The pertinent proton chemical shifts are summarized in Table III.

d. From Dinitroanilines

The pmr spectra of solutions of 2,4- and 2,6-dinitroaniline in methanolic sodium methoxide show resonances for the conjugate base of the aromatic.[69] There is no evidence for methoxide addition. In liquid ammonia, methoxide, hydroxide, and amide ion all add to C-3 of the conjugate base to give **40d** (R = CH_3O, HO, H_2N).[81] The proton chemical shifts for these complexes are summarized in Table III.



40d

3. Propenide Complexes (44)

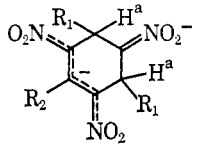
In the presence of excess base, trinitrocyclohexadienate and related σ complexes can equilibrate with complexes formed by two- and threefold addition (eq 13). Complexes like **6** and

(87) M. I. Foreman and R. Foster, *Can. J. Chem.*, 47, 729 (1969).

(88) C. A. Fyfe and R. Foster, *Chem. Commun.*, 1219 (1967).

Table IV

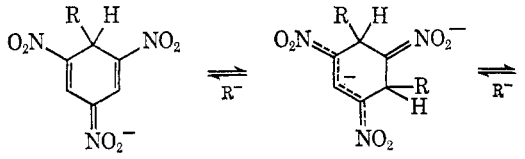
Proton Chemical Shifts of Nitrodinitropropenide Complexes



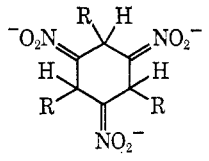
44

R_1	R_2	τ, ppm H^a	τ, ppm H^b	Solvent	Ref
HO	O^-	4.0		H_2O	89
HO	$(CH_3)_2N$	4.0		CH_3SOCH_3–H_2O	69
CH_3O	$(CH_3)_2N$	4.0		CH_3SOCH_3–H_2O	51, 69
CH_3O	H^b	4.9	1.4	CH_3SOCH_3	34, 51
CH_3COCH_2	$(CH_3)_2N$	5.3		CH_3SOCH_3	75
CH_3CH_2S	CH_3NH	4.0		CH_3SOCH_3–H_2O	67
^-O_3S	CH_3O	3.9	1.4	H_2O	66
^-O_3S	H_2N	3.8		H_2O	66
^-O_3S	CH_3NH^b	3.8,[a] 3.9[a]	6.9	H_2O	66
^-O_3S	$(CH^b_3)_2N$	3.7	6.9	H_2O	66
^-O_3S	C_6H_5NH	3.7		H_2O	66
^-O_3S	$C_6H_5(CH^b_3)N$	3.8,[a] 3.9[a]	6.5	H_2O	66
^-O_3S	H^b	3.9	1.4	H_2O	66
^-O_3S	O^-	3.8		H_2O	89

[a] Because of asymmetry, two different H^a resonances appear. See ref 66.



6 44a



45 (13)

44a have been well characterized by pmr and visible spectroscopy. Complexes like **45** are colorless and form only in a large excess of base.

Two equivalents of sulfite add to several electron-deficient aromatics[66,89] to give propenide complexes like **44a** (R = ^-O_3S) when the concentration of aromatic is 10^{-4} *M* and the sulfite concentration is ~1 *M*. At low concentrations of sulfite, **6** (R = ^-O_3S) predominates (*vide supra*). The pmr spectrum of a dilute solution of 1,3,5-TNB in 0.8 *M* aqueous sodium sulfite shows two resonances, at τ 3.9 (2 H) and 1.4 (1 H), for **44b**. These are not coupled—an unexpected result, since the sp^3 proton in **6** (R = ^-O_3S) does exhibit a small coupling (*J* = 1–2 cps). Similar complexes, **44c** and **44d**, are formed from 2,4,6-TNA and picramides.[89] The chemical shifts of methoxyl and amide protons in **44c** and **44d** are similar to those of the parent aromatic, indicating no hybridizational change at the central carbon of the propenide function. The proton chemical shifts for a series of such complexes, **44d** (R_2N = H_2N, $HNCH_3$, $N(CH_3)_2$, NHC_6H_5, and $NCH_3C_6H_5$), are summarized in Table IV. When the R_2N function of **44d** is symmetrical (*i.e.*, H_2N or $(CH_3)_2N$), only a single resonance is observed for the sp^3 ring protons; when it is unsymmetrical (*i.e.*, CH_3NH), two are observed.[89] This could result from restricted rotation about the nitrogen to ring carbon bond, which may have appreciable double-bond character, or from hydrogen-bonded structures like **46**, similar to **29** and **30** (*vide supra*). The possibility exists that the spectrum is actually that of an equimolar mixture of *cis* and *trans* isomers, **47** and **48**, which have identical N-methyl chemical shifts. The question of *cis–trans* isomerism in **44** is puzzling. There is no definite evidence for such isomerism even though **44b** is stable enough to be isolated as the sodium salt.[90] All the sulfite complexes, **44**, are insoluble in DMSO but quite soluble in water. This is expected as they carry four formal negative charges and should be well solvated in aqueous solution. All the pmr spectral studies of sulfite complexes like **44** have been done in aqueous solution.[66,89]

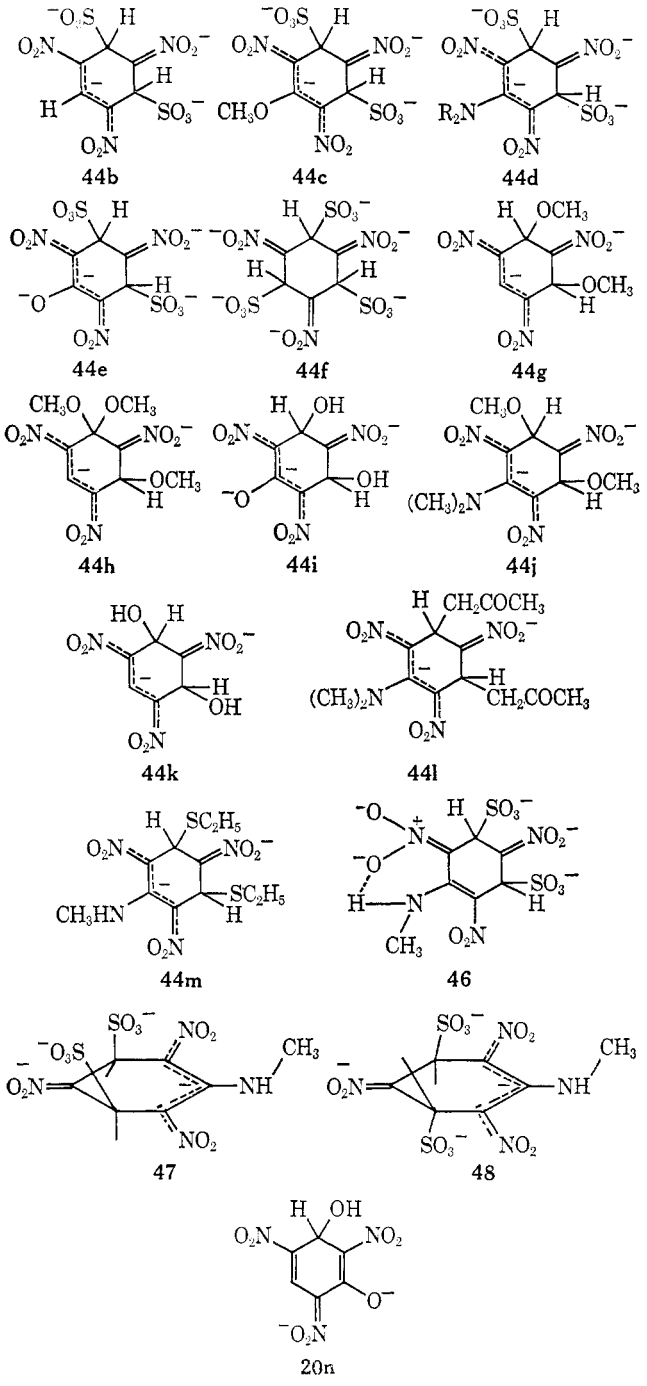
Picric acid reacts with 2 *M* sodium sulfite to yield **44e**, which has five formal negative charges. The pmr spectrum of the solution shows a sharp singlet at τ 3.8 consistent with **44e** or **44f**. Equilibrium constant measurements have established structure as **44e**.[89]

Oxygen bases are also effective in producing complexes like **44**.[34,51,66,69,89] Addition of methoxide to DMSO solutions of 1,3,5-TNB yields **6a**, which is converted to **44g** as the concentration of methoxide increases.[2,5,34,51,69] The pmr spectrum of **44g** is similar to that of the sulfite complex **44b** (Table IV). A DMSO solution of 2,4,6-TNA and concentrated sodium methoxide has a pmr spectrum consistent with the analogous complex **44h**[51] (Table III), whereas a concentrated sodium hydroxide solution of picric acid[89] shows a single sp^3 proton resonance at τ 4.0 for **44i**. There is no pmr evidence for **20n**.

Both methoxide and hydroxide react with N,N-dimethylpicramide[51,69] by a process analogous to eq 13. Pmr spectra of

(89) M. R. Crampton and M. El Ghariani, *J. Chem. Soc. B*, 330 (1969).

(90) R. A. Henry, *J. Org. Chem.*, 27, 2637 (1962).



44b 44c 44d

44e 44f 44g

44h 44i 44j

44k 44l

44m 46

47 48

20n

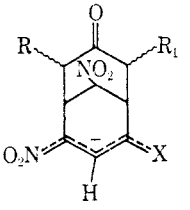
the complexes **44j** and **44k**, in DMSO and aqueous DMSO, show singlets for the sp^3 ring protons at τ 4.0. A solution of **44j** in acetone solvolyzes to **44l**, which is also formed in acetone solutions of N,N-dimethylpicramide containing a large excess of triethylamine.[76] The sp^3 ring protons of **44l** appear as a triplet at τ 5.3.

Thioethoxide reacts with N-methylpicramide to give **44m** which has a singlet resonance at τ 4.0 for the sp^3 ring protons.[67]

Bicyclic dinitro-, cyanonitro-, and carbomethoxynitropropenide complexes have been prepared by reaction of various electron-deficient aromatics with triethylamine in ketonic solvents[61] (eq 12). Chemical shifts of the propenide protons in these complexes, **49**, are summarized in Table V. Shift values for the sp^2 ring protons of dinitropropenide complexes **49** (X = NO_2) are similar to those of the monocyclic σ complexes listed in Table IV.

Table V

Propenide Proton Chemical Shifts in 49



49

X	τ, ppm[a] H chemical shift
NO_2	1.4–1.7
CO_2CH_3	2.0–2.1
CN	2.3–2.6

[a] The range of values reflects variation in R and R′.

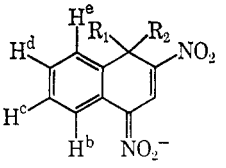
4. *Naphthalene σ Complexes* (50)

The pmr spectra of several naphthalene σ complexes (**50**), prepared by addition of base to 2,4-dinitronaphthalene and 2,4-dinitronaphthyl alkyl ethers, have been reported (Table VI). These have several interesting features.[91] The spectrum of **50a** shows a complex pattern for the methylene resonance of the ethoxyl groups, which contains 13 resolved transitions. This has been attributed to restricted rotation about the C-1–O bonds resulting in an ABX_3 spectrum for the ethyl group. A total of 16 transitions is predicted for the AB part.[91] Irradiation of the methyl collapses the methylene resonance to an AB quartet, confirming this interpretation. Similar nonequivalence is observed in **50b**. The ring proton chemical shifts for **50a** and **50b** are significantly different from those of the parent ethers. The magnitude of the difference for each proton depends in part upon the charge density difference between the parent ether and complex at the various ring positions. In cyclohexadienate complexes, the canonical forms **36**, **37**, and **38** allow a reasonably straightforward interpretation. The ABCD spin pattern for the unsubstituted naphthalene ring in **50** makes chemical shift assignments more difficult. The sp^2 ring proton H-3 and the *peri* proton H-8 of **50a** are both at *lower* field than in the parent ethyl 2,4-dinitronaphthyl ether.[91] All the other ring protons in **50a** are at higher field than those in the parent ether. These shift differences are less than those observed in monocyclic systems. The low-field shift of H-8 has been rationalized on the basis of a decreased anisotropic *peri* shielding by alkoxyl, resulting from the hybridizational change at C-1.[91] This effect is thought to more than compensate for increasing charge density at C-8. A decrease in charge density in the substituted ring upon complex formation would rationalize the downfield shift of H-3. This is in accord with HMO calculations which predict such a charge decrease,[23] but these calculations also predict a similar decrease in ring charge density for dinitrocyclohexadienate complexes where only shielding is observed. In addition, more sophisticated calculations predict a charge *increase* in the ring.[25] It would appear that changes in NO_2-group anisotropy, ring current, charge density, etc., are difficult to predict, and by proper choice of these effects either upfield or downfield shifts can be rational-

(91) J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 977 (1968).

Table VI

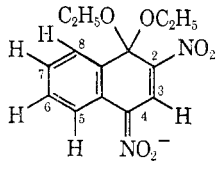
Proton Chemical Shifts of Naphthalene Complexes[a]



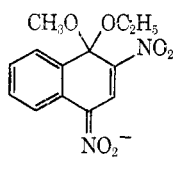
50

R_1	R_2	H^a	H^b	H^c	H^d	H^e	H^f	Re
				τ, ppm				
$-OCH_2CH_2O-$		0.9		2.6[b]		5.6[b]		84
CH^f_3O	CH^f_3O	0.7	2.3	2.7[b]		1.2	7.2	91
CH^f_3O	C_2H_5O	0.8	2.2	2.7[b]		1.2	7.3	91
C_2H_5O	C_2H_5O	0.8	2.2	2.7[b]		1.3		91
H^f	CH_3O	1.1	1.3	2.7[b]			5.2	75
H^f	CH_3COCH_2	1.2	1.4	2.7[b]			4.9	75
H^f	CH_2NO_2	3.2	1.3	2.7[b]			4.9	36

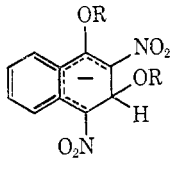
[a] In CD_3SOCD_3. [b] Multiplet.



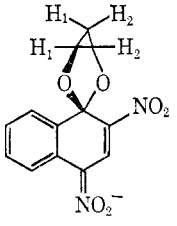
50a



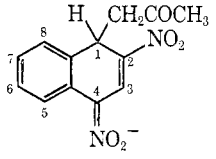
50b



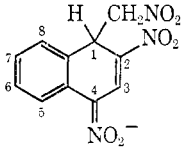
50c



50d



50e



50f

ized. Pmr spectra similar to those of **50a** and **50b** are observed for all the other 1,1-dialkoxy σ complexes listed in Table VI, and these have been analyzed in some detail. There is no pmr evidence for **50c** as a transient species. Evidence for **50c** has been obtained by visible spectroscopy (*vide infra*).[92]

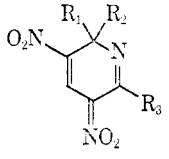
The pmr spectrum of **50d**, prepared from 1-(β-hydroxyethoxy)-2,6-dinitronaphthalene, has several interesting features.[84] The sp^2 ring proton chemical shifts are similar to those of **50a**, but the methylene protons H-1 and H-2 are only slightly nonequivalent, in contrast with those of the spiro dinitrocyclohexadienate complex **33d**. This has been attributed to similar anisotropic effects for the 2-NO_2 and benzo groups in **50d**.[84]

Pmr spectra of the naphthalene σ complexes **50e** and **50f**, formed from acetone and nitromethane solutions of 2,4-dinitronaphthalene and triethylamine, have been reported.[36,75] The sp^2 proton on the substituted ring appears at surprisingly high field (τ 1.1–3.2) relative to shifts observed for the dialkoxy complexes **50a** and **50b** (τ 0.7–0.9). The sp^3 ring proton, H-1, appears at high field (τ 4.9–5.2) as expected, but H-5 is at lower field than in **50a** and **50b**. The other ring proton resonances H-6, H-7, and H-8 are not resolved.

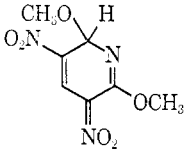
(92) F. Millot and F. Terrier, *Bull. Soc. Chim. Fr.*, 2692 (1969).

5. *Pyridine and Pyrimidine σ Complexes* (51–54)

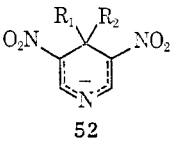
Since the aza group is a well-known activating function in nucleophilic aromatic substitution,[93] it is not surprising that reasonably stable anionic σ complexes like **51–54** can be obtained from electron-deficient pyridines or pyrimidines and base[36,85,94–97] (Table VII). Addition of methoxide to 4-chloro- or 4-methoxy-3,5-dinitropyridine gives **52a**.[85,96,97] Methoxide attack on 4-chloro-3,5-dinitropyridine results in displacement



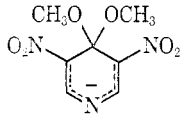
51



51a



52



52a

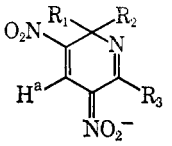
55

of chloride and the product ether adds another methoxide to give the final product.[85] The pmr spectrum[85,97] of **52a** shows singlets at τ 7.0–7.1 and 1.2–1.5 for the methoxyl and ring protons, respectively. The latter resonance is at slightly higher field ($\Delta\tau$ ~0.2 ppm) than that for the ring protons of **19a**. The pmr spectrum of a DMSO solution of 3,5-dinitro-2-methoxypyridine and 1 equiv of sodium methoxide[95] shows two doublets, at τ 1.4 and 4.0 ($J \cong 1$ cps), and two singlets, at τ 6.2 and 6.7, with relative intensities of 1:1:3:3. Comparison of this spectrum with that of the parent aromatic indicates that either **51a** or **55** has formed. Complex **55** has been ruled out, as the pmr spectrum of

(93) G. Illuminati, *Advan. Heterocycl. Chem.*, 3, 285 (1964).
(94) C. A. Fyfe, *Tetrahedron Lett.*, 6, 659 (1968).
(95) C. Abbolito, C. Iavarone, G. Illuminatti, F. Stegel, and A. Vazzoler, *J. Amer. Chem. Soc.*, 91, 6746 (1969).
(96) G. Illuminati and F. Stegel, *Tetrahedron Lett.*, 4169 (1968).
(97) P. Bemporad, G. Illuminati, and F. Stegel, *J. Amer. Chem. Soc.*, 91, 6742 (1969).

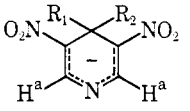
Table VII

Proton Chemical Shifts of Pyridine and Pyrimidine Complexes[a]



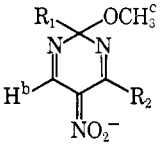
51

R_1	R_2	R_3	τ, ppm H^a	H^b	H^c	Solvent	Ref
H^c	CH_3O	H^b	1.7	1.4	3.9	CH_3SOCH_3	94
H^c	CH_3O	CH_3O	1.4		4.0	CH_3SOCH_3	95
$-OCH^cCH^c_2O-$		H^b	1.6		5.9	CH_3SOCH_3	94
H^c	$(C_2H_5)_2N$	H^b	1.7	1.4	4.1	CH_3SOCH_3	94
H^c	O_2NCH_2	H^b	1.5	1.7	4.2	CH_3NO_2	36
H^c	CH_3COCH_2	$N(CH_3)_2$	1.9		4.9	CH_3SOCH_3	94
H^c	CH_3COCH_2	H^b	1	1.6	4.5	CH_3SOCH_3	94



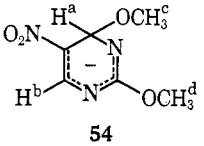
52

R_1	R_2	τ, ppm H^a	H^b	Solvent	Ref
CH^b_3O	CH^b_3O	1.2–1.5	7.0–7.1	CH_3SOCH_3	85, 97
CH^b_3O	CH^b_3O	1.4	6.9	CH_3OH	85
H^b	O_2NCH_2	1.8	4.7	CH_3NO_2	36
H^b	CH_3COCH_2	1.8	5.1	CH_3SOCH_3	94



53

R_1	R_2	τ, ppm[b] H^a	H^b	H^c	H^d	Ref
H^a	H^b	4.5	1.8	6.8		98
H^a	CH_3O	4.3	1.6	6.8	6.4	98
CH_3O	H^b		1.7			98



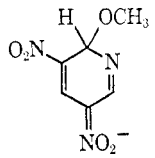
54

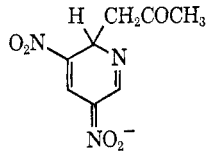
τ, ppm[b] H^a	H^b	H^c	H^d	Ref
4.2	1.7	6.9	6.4	98

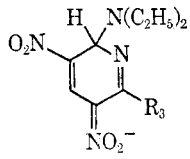
[a] The solvents are deuterated in some cases. [b] In CD_3SOCD_3.

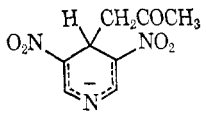
the complex formed from 6-deuterio-3,5-dinitro-2-methoxypyridine is consistent only with **51a**. Demethylation of **51a** occurs in methanol solution.[95] There is no evidence for rearrangement of **51a** to a geminal dimethoxy complex, in contrast to the behavior of **20a** which rapidly rearranges to **19a**. (This point is discussed further in section V.)

Reaction of methoxide and 3,5-dinitropyridine gives **51b**, which has resonances at τ 1.7, 1.4, and 3.9 for the two sp^2 and one sp^3 ring protons, respectively.[94] This complex solvolyzes in acetone to yield a mixture of **51c** and **52b**, the latter predominating.[94] An analogous mixture is obtained on adding triethylamine to a nitromethane solution of 3,5-


51b

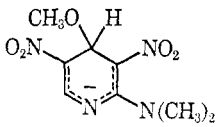

51c

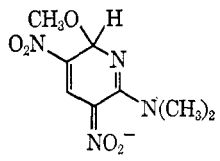

51d


52b

dinitropyridine, which causes isomeric lyate addition to the aromatic.[94] Addition of diethylamine to 3,5-dinitropyridine gives **51d** as the diethylammonium salt.[94]

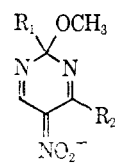
The pmr spectrum of a DMSO solution of methoxide and 2-dimethylamino-3,5-dinitropyridine shows resonances at τ 1.8 and 3.9 which could be attributed to **56** or **57**. If the relative stability of these structures is analogous to that

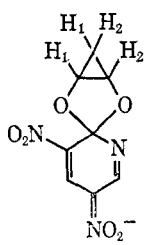

56


57

of **54** and **55**, **57** is more probable than **56**, as the former has a NO_2 group *para* to the sp^3 ring carbon. The complex **56** or **57** solvolyzes in acetone[96] to give a single acetonate complex with resonances at τ 1.7 and 4.9. A structure analogous to **57** in which methoxyl is replaced by acetonate is probably responsible for these absorptions.

The spiro complex **58** has been prepared from 2-(β-hydroxyethoxy)-3,5-dinitropyridine and sodium methoxide in DMSO.[94] The pmr spectrum of this complex exhibits a quartet at τ 1.6 for the ring protons and a singlet at τ 5.9 for the methylenes. The latter singlet is rather unexpected, since the methylene protons are nonequivalent. The NO_2 and aza groups must have similar anisotropic effects in **58**,


53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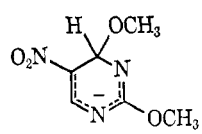
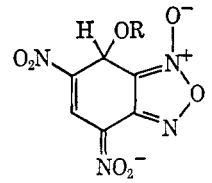

54

as do the benzo and NO_2 groups in **50d**.

Initial evidence that methoxynitropyrimidines add base[96] has been substantiated by pmr spectra of the resulting complexes **53** and **54**.[98]

6. *Miscellaneous Complexes (Table VIII)*

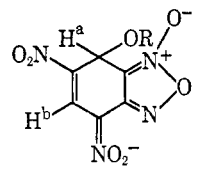
Several σ complexes (**59**) prepared from 4,6-dinitrobenzofuroxan and hydroxide[99–101] or methoxide[100] have been characterized by pmr. This aromatic is so reactive that **59** (R = H) forms in water, yielding acidic solutions. On addition of


59

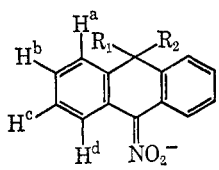
base, salts of **59** can be isolated. The pmr spectrum of **59**, prepared from 5-deuterio-4,6-dinitrobenzofuroxan[100] and base, definitely establishes the structure as **59** and not one in which attack has occurred between the two NO_2 groups.

Table VIII

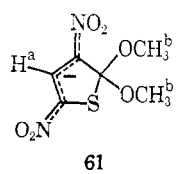
Proton Chemical Shifts of Miscellaneous σ Complexes[a]


59

R	τ, ppm H^a	H^b	H^c	Solvent	Ref
CH^c_3	1.0	4.0	6.6	CH_3SOCH_3	99
H^c	1.3	4.1	3.7	CH_3SOCH_3	99
H	1.4	4.0		H_2O	100
H	1.1	3.8		CH_3SOCH_3	101


60

R_1	R_2	τ, ppm H^a	H^b	H^c	H^d	Ref
CH_3O	CH_3O		—2.9[b]—		1.1	75
CH_3O	H	5.0	—2.8[b]—		1.2	75
CH_3COCH_2	H	5.7	—2.9[b]—		1.3	75


61

τ, ppm H^a	H^b	Solvent	Ref
2.1	6.7	CH_3SOCH_3	102

[a] Determined in CH_3SOCH_3 or CD_3SOCD_3 except where indicated. [b] Multiplet.

The pmr spectra of several σ complexes prepared from nitroanthracenes and base have been reported.[75] Two benzo groups stabilize the negative charge sufficiently so that an

(98) M. E. C. Biffin, J. Miller, A. G. Moritz, and D. B. Paul, *Aust. J. Chem.*, **22**, 2561 (1969).
(99) A. J. Boulton and D. P. Clifford, *J. Chem. Soc.*, 5414 (1965).
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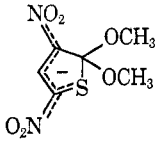
(101) N. P. Norris and J. Osmundson, *ibid.*, **30**, 2407 (1965).

appreciable concentration of **60** can exist in DMSO. Early workers reported isolation of anthracene σ complexes,[20] but

60

more recent attempts[65] have been unsuccessful. Solvolysis of **60** (R_1 = H, R_2 = CH_3O) occurs in acetone to give **60** (R_1 = H, R_2 = CH_3COCH_2).

The pmr spectrum of a thiophene σ complex with alkoxide, **61**, has been described.[102]



61

C. ELECTRONIC SPECTRA

Since visible spectra of anionic σ complexes are usually obtained at concentrations and in solvents which differ from those used in pmr characterizations, some degree of uncertainty may exist in some cases as to whether a single species is responsible for both types of spectra. Electronic spectra are qualitatively explained by transitions between the highest occupied molecular orbital and lowest unoccupied molecular orbitals in the delocalized anion, calculated from a simple HMO model.[103,104] Transitions in the visible can be formulated as charge transfer between the ring and NO_2 groups.[25] The energetics of these transitions are discussed in section III. The spectral characteristics of individual systems and the effects of solvent and substrate structure are discussed below. Most complexes have been characterized by pmr, as electronic spectra are of limited value in providing detailed structural information.

1. Cyclohexadienate and Propenide Complexes

a. From 1,3,5-TNB and Picryl Ethers

Addition of base to a variety of electron-deficient aromatics in polar solvents gives solutions with visible spectra like that shown in Figure 3A. The extinction coefficient of the shorter wavelength absorption is usually about twice that of the absorption at longer wavelength, and both are much higher than extinction coefficients associated with charge-transfer bands of aromatic π complexes. The exact λ_{max} and ϵ_{max} depend on the nature of R_3, R_4, and R_5, and to a lesser extent on R_1 and R_2 (Figure 3). Most 2,4,6-trinitrocyclohexadienate complexes have two maxima in the visible, whereas many substituted and unsubstituted dinitrocyclohexadienates have only one, the other being shifted to the ultraviolet. In excess base, twofold addition can occur to give propenide complexes which have only a single maximum (Figure 3B). The absorption maxima for representative cyclohexadienate complexes

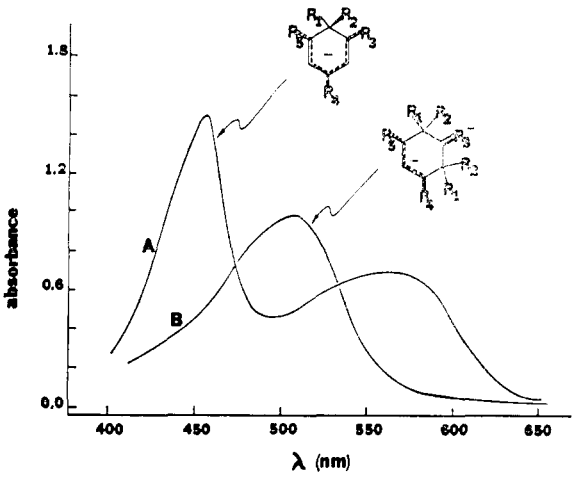


Figure 3. Visible absorption spectra of (A) cyclohexadienate and (B) propenide complexes.

in various solvents are summarized in Tables IX, X, and XI. In most cases the complexes listed have been structurally characterized by pmr.

There has been some controversy about the species responsible for colors produced by aliphatic amines and 1,3,5-TNB. In addition to anionic σ complexes, π complexes,[105] zwitterionic σ complexes,[29,106,107] anion radicals,[108,109] and aromatic anions[110] have all been proposed. It has become clear that the type of interaction depends on the solvent, and whether or not the amine is tertiary. With aromatic amines, the interactions are undoubtedly of the charge-transfer (π) type.[7,8] In nonpolar solvents such as cyclohexane and in polar aprotic solvents such as DMSO, tertiary aliphatic amines also form only π complexes with 1,3,5-TNB, and the solutions show little absorption in the visible.[50,121-123] With primary and secondary amines, red solutions are produced in both polar and nonpolar solvents, which exhibit the typical double maxima of **19** (Figure 3A).[50,107,108,123-126] The species re-

(102) G. Illuminati, G. Doddi, and F. Stegel, *Chem. Commun.*, 953, (1969).
(103) T. Abe, *Bull. Chem. Soc. Jap.*, 37, 508 (1964).
(104) T. Abe, *ibid.*, 39, 627 (1966).
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(109) R. E. Miller and W. F. K. Wynne-Jones, *Nature*, 186, 149 (1960).
(110) V. Balish, and V. Rama Krishnan, *Recl. Trav. Chim. Pays-Bas*, 78, 783 (1959).
(111) V. Gold and C. Rochester, *J. Chem. Soc.*, 1687 (1964).
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(119) M. Kimura, M. Kawata, M. Nakadate, N. Obi, and M. Kawazoe, *Chem. Pharm. Bull. Jap.*, 16, 634 (1968).
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(125) P. Walden, *Z. Phys. Chem.*, 168, 419 (1934).
(126) D. J. Glover and E. G. Kayser, *Anal. Chem.*, 40, 2055 (1968).

Table IX

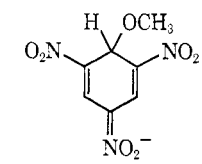
Visible Absorption Maxima of Trinitrocyclohexadienates

19

R_1	R_2	λ_{max_1}, nm	λ_{max_2}, nm	Solvent	Ref
RO (R = alkyl)	RO	406–425	485–510	CH_3COCH_3 CH_3SOCH_3 ROH CH_3CN	2, 5, 30, 103
H (R = alkyl)	RO	424–430	495–510	ROH	30, 113
H	CN	437	555	$CHCl_3$	64, 115
H	HO	445–450	475–485	H_2O CH_3SOCH_3–H_2O	5
H	$(R)_2N$–	448–452	525–538	CH_3SOCH_3	2, 50
H	$(R)_2C(NO_2)$	450–456	543–558	CH_3SOCH_3	36
H	$(R)_3C-C(=O)-C(R)_2$	460–470	552–572	RCOR CH_3OH CH_3SOCH_3	52, 53
H (R = alkyl)	RS	460–474	550–580	CH_3OH CH_3SOCH_3 $CH_3CON(CH_3)_2$	67
H	^-O_3S	462–474	525–550	H_2O CH_3SOCH_3–H_2O	66, 115

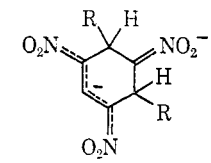
sponsible contains 2 equiv of amine per equivalent of aromatic, and in aprotic solvents is probably formed[49,50] as in eq 5.

As the concentration of base is increased in solutions of 2,4,6-trinitrocyclohexadienate complexes, the characteristic double maximum in the visible diminishes in intensity, and a new single absorption appears at about 500 ± 20 nm. This behavior is observed with solutions of trinitrocyclohexadienate complexes formed from 1,3,5-TNB and OH^-–H_2O,[103,127] CH_3O–CH_3OH,[112] SO_3–H_2O,[66,90] and C_2H_5S–CH_3OH.[67] Pmr spectra of the solutions (section II.B) have shown that such changes result from addition of a second equivalent of base to give the propenide complex **44a**. Addition of a third equivalent of base can occur at very high concentrations to yield **45** which is colorless.[90,128,129] HMO calculations are consistent with this observation, as the $C{=}NO_2^-$ function in **45** is predicted to have no visible maxima, and the dinitropropenide function in **44a** is predicted to have one (section III). Structure **44a** is also supported by the isolation of crystalline salts like **18**, which have a single visbile maximum at 500 ± 10 nm.[61] The propenide complex **44g** was reportedly isolated as the dipotassium salt and characterized by infrared.[130] The visible spectrum was reported as identical with that of **6a**. This is a puzzling result. The lower melting point of **44a** (98–100°) relative to **6a** (140–143°)[130] is also unexpected. The

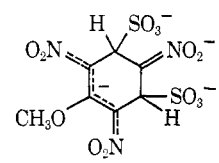


6a

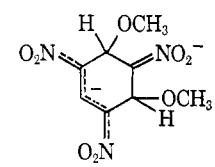
19h



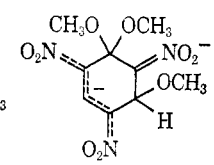
44a



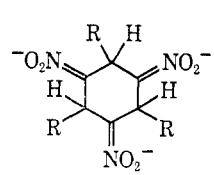
44c



44g



44h



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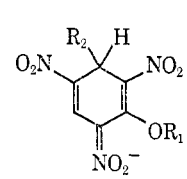
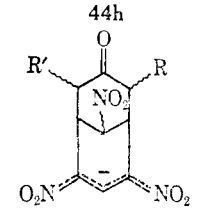


20o



18

propenide complexes **44h** and **44c** are formed from 2,4,6-TNA in the presence of high concentrations of methoxide[51,112] and sulfite.[66] These have absorption maxima at 480 and 430 nm, respectively. In dilute solutions of picryl ether and base, two isomeric trinitrocyclohexadienate complexes, **19h** and/or **20o**, can form; these have been characterized by pmr when R_2 is CH_3O,[48,51,69] CH_3COCH_2,[75] SO_3^-,[50] CCl_3,[65] and CN.[77] The visible spectra which have been reported are mainly those of **19h**. Some workers have suggested that the visible

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(129) T. Abe, *Bull. Chem. Soc. Jap.*, **32**, 339 (1959).
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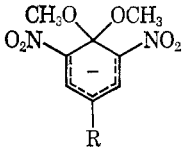
Table X

Visible Absorption Maxima of Substituted and Unsubstituted Dinitrocyclohexadienates

62

R_1	R_2	R_3	λ_{max}, *nm*	*Solvent*	*Ref*
CH_3O	CH_3O	H	493–505	CH_3SOCH_3 $CH_3CON(CH_3)_2$ CH_3OH	75, 118
H	CH_3COCH_2	H	480–580	ROH H_2O ROR CH_3SOCH_3 $CH_3NCON(CH_3)_2$ Pyridine	114, 119
CH_3O	CH_3O	CN	469–478	CH_3OH	118, 176
CH_3O	CH_3O	CH_3O	530	CH_3OH	118
CH_3O	CH_3O	CH_3	518	CH_3OH	118
CH_3O	CH_3O	CO_2^-	505	CH_3OH	118

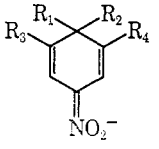


63

R	λ_{max}, *nm*	*Solvent*	*Ref*
H	568	CH_3OH	118
CN	531–535	CH_3OH	85, 118
CH_3	626	CH_3OH	118
CO_2^-	588	CH_3OH	118

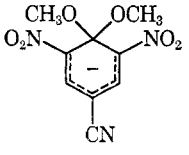
Table XI

Visible Absorption Maxima of Substituted and Unsubstituted Mononitrocyclohexadienates



64

R_1	R_2	R_3	R_4	λ_{max}, *nm*	*Solvent*	*Ref*
CH_3O	CH_3O	CN	CN	400	CH_3OH	86
F	N_3	H	H	397[a]	$CH_3CON(CH_3)_2$	120



39c

λ_{max}, *nm*	*Solvent*	*Ref*
480	CH_3OH	86

[a] This result could not be repeated.

spectra of these isomers might be significantly different and have made structural assignments on this basis.[3,131] These assignments were proven incorrect, as the predicted structures **19h** (R_2 = CN, R_1 = CH_3[3] and R_2 = CH_3COCH_2, R_1 = C_6H_5[131]) were later shown to be the corresponding isomers **20o**, or a mixture of both **19h** and **20o**,[75,77] by pmr (*vide supra*). Visible spectra of **19h** (R_2 = CH_3O) and **20o** (R_2 = SO_3^-) are quite similar, except that the λ_{max} of **20o** appears at longer wavelength. This difference has been attributed to characteristics of sulfite, and not the position of attack, as the 1,3,5-TNB–sulfite complex has a longer wavelength maximum than 1,3,5-TNB–oxygen base σ complexes.[5]

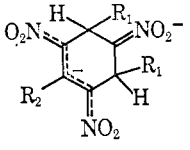
b. From Picramides

Visible spectra of picramides in basic solution are usually composite absorptions resulting from various species.[132] A multiplicity of processes are possible, including proton abstraction from nitrogen, addition at C-1 (not observed), addition at C-3, and twofold addition at C-3 and C-6. The absorption maxima for σ complexes of N,N-dimethylpicramide with methoxide, hydroxide, and sulfite and for N-methylpicramide with sulfite, are summarized[66,132] in Table XII. Base addition and proton abstraction are competing processes in strongly basic solutions of picramides containing a

Table XII

Visible Maxima of Picramide σ Complexes

20



44

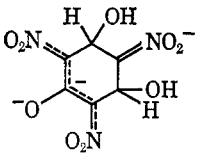
R_1	R_2	λ_{max}, nm: 20	44	Solvent	Ref
SO_3^-	CH_3NH	418	402	H_2O	66
SO_3^-	$(CH_3)_2N$	420	417	H_2O	66
CH_3O	$(CH_3)_2N$	480[a]	420[a]	CH_3OH	132
HO	$(CH_3)_2N$	Not formed	420	H_2O	132

[a] The spectra are complicated by absorptions of N,N-dimethylpicramide (λ_{max} 370 nm) and products from subsequent displacement reactions.

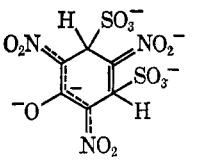
labile NH proton (section II.B). There is no pmr evidence for C-1 addition.

c. From Picric Acid

In the presence of base, picric acid forms picrate anion (λ_{max} 360 nm) which complicates interpretation of σ-complex absorptions. At high base concentration, addition of hydroxide to C-1 of picrate anion was proposed,[133] but kinetic studies[134] and pmr spectra[5] have provided evidence for **44i** (λ_{max} 390 nm). A similar absorption is observed in aqueous solutions of picric acid and sulfite, which has been attributed[5] to **44e**. At high concentrations of methoxide, methanolic solutions of picric acid have an absorption at 394 nm, which probably results from a dimethoxy complex analogous to **44i**.[135] Early workers[136] probably obtained 1:1 complexes between picric acid and carbanions, but these were not well characterized. Reaction of picric acid with acetone in basic solution yields two products (by chromatography) which have absorptions at 395 and at 410, 485 nm, respectively.[137] Oxidation of the latter yields 3-acetonylpicric acid,[137] evidence that the colored product may have been an acetonate–picric acid σ complex.



44i



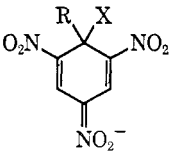
44e

d. From Other Substituted Trinitrobenzenes

2,4,6-Trinitrotoluene and 2,4,6-trinitrobenzaldehyde form σ complexes with sulfite in aqueous solution, λ_{max} 465 and 485 nm, respectively[115,138] (the low-energy maximum in each case is broad). In strong base, 2,4,6-trinitrotoluene has two maxima at 370 and 510 nm, attributed to 2,4,6-trinitrobenzyl anion.[139,140] There has been some discussion as to the efficacy of α-hydrogen exchange in 2,4,6-trinitrotoluene in basic solution,[33,108,141] a process which should occur if 2,4,6-trinitrobenzyl anion forms readily.[142] Pmr measurements, which would confirm the type of interaction, are hindered by formation of radicals.[51] The importance of α-hydrogen exchange will be clarified by studies of 2,4,6-trinitrotoluene-(CD_3) in $C_2H_5O^-$–C_2H_5OH, currently in progress.[143] Evidence now available suggests that colors produced in strong base (*i.e.*, alkoxide) result from 2,4,6-trinitrobenzyl anion, perhaps with concurrent formation of σ complexes, the relative amount of each depending on the solvent and base. With relatively weak bases like sulfite and cyanide, color undoubtedly results from σ-complex formation. The absorptions at 462 and 532 nm observed in acetone solutions of 2,4,6-trinitrotoluene and base[144–146] have been attributed to acetonate σ complexes. 2,3,4- and 2,4,5-trinitrotoluene have maxima at 430, 550, and 630 nm in such alkaline media, which could result from similar structures.[146]

The visible spectra of a series of 1-X substituted 2,4,6-TNB's (X = CO_2H, $CO_2C_2H_5$, Cl, CH_3, CH_2CH_2OH, and $CH_2CH_2OCOCH_3$) in alkaline acetone show maxima at 457 ± 8 and 528 ± 28 nm, attributed to a mixture of **19i** and **20p** (R = CH_3COCH_2).[147] Pmr evidence supports **20p**. Alkaline

(131) M. Kimura, *Chem. Pharm. Bull. Jap.*, **17**, 858 (1969).
(132) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1697 (1964).
(133) T. Abe, *Nature*, **187**, 234 (1960).
(134) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1722 (1964).
(135) C. H. Rochester, *ibid.*, 2404 (1965).
(136) M. Jaffe, *Z. Physiol. Chem.*, **10**, 399 (1886).
(137) M. Kimura, *Chem. Pharm. Bull. Jap.*, **3**, 81 (1955).
(138) H. Muraour, *Bull. Soc. Chim. Fr.*, **35**, 367 (1924).
(139) E. F. Caldin and G. Long, *Proc. Roy. Soc., Ser. A*, **228**, 263 (1955).
(140) J. A. Blake, M. J. B. Evans, and K. E. Russell, *Can. J. Chem.*, **44**, 119 (1966).
(141) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).
(142) K. G. Ship and L. A. Kaplan, *J. Org. Chem.*, **31**, 857 (1966).
(143) A. R. Norris, personal communication.
(144) S. S. Gitis and A. Ya. Kaminskii, *Zh. Org. Khim.*, **2**, 1811 (1966).
(145) S. S. Gitis and T. Krosovskii, *J. Gen. Chem. USSR*, **29**, 2612 (1959).
(146) T. Urbanski, S. Kwiatkowska, and W. Kutkiewicz, *Bull. Acad. Polon. Sci.*, **7**, 397 (1959); *Chem. Abstr.*, **54**, 21997*d* (1960).
(147) M. Kimura, *Chem. Pharm. Bull. Jap.*, **3**, 75 (1955).


19i


20p

solutions of N-nitropicramide also have visible spectra characteristic of σ complexes.[129]

The visible spectra of a series of 1-X, 1,3-X_2 and 1,3,5-X_3 substituted TNB's (X = F, Cl, Br, I, NO_2, CH_3, C_6H_5, 1,3-$(CH_3)_2$, and 1,3,5-Cl_3) in liquid ammonia have been reported.[148] Initially, all these compounds have spectra with maxima at 440 ± 25 and 509 ± 34 nm, probably resulting from σ-complex intermediates. Upon standing, the spectra of those compounds in which X is labile change to those of the corresponding picramide (X = NH_2).

In alkaline pyridine solution, alkyl-substituted 2,4,6-TNB's show the characteristic double maxima of anionic σ complexes.[149] Interestingly, the two maxima tend to coalesce as the bulk of the alkyl group increases. This has been attributed to steric compression in **20q**, which forces NO_2 groups *ortho* to the alkyl group out of the ring plane (Table XIII). When the NO_2 group bonded to C-2 is completely

Table XIII

Effect of Steric Compression on the Visible Maxima of Substituted 2,4,6-Trinitrocyclohexadienate[149]

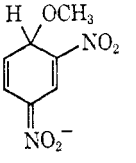

20q

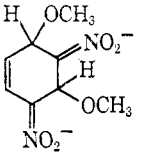
R	λ_{max_1}, *nm*	λ_{max_2}, *nm*
H	439	518
CH_3CH_2	443	513
$(CH_3)_2CH$	456	502
$(CH_3)_3C$	...	504

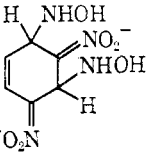
orthogonal to the ring, only a single visible maximum is expected, analogous to dinitrocyclohexadienate complexes (*vide infra*).

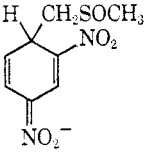
e. From Dinitrobenzenes

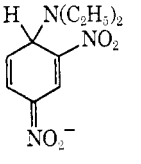
Removing an *ortho* NO_2 group from 2,4,6-trinitrocyclohexadienate complexes results in a predicted[25] high-energy shift of the two visible maxima; the one at low wavelength appears in the ultraviolet. In addition, the calculated stabilization energy of the complex decreases from 2.12 to 1.73 eV.[25] These calculations are in accord with observations that 1,3-DNB reacts with alkoxide to yield, in part, the 1,3-DNB radical anion, whereas 1,3,5-TNB yields only σ complexes.[51,82] Although pmr characterization of 1,3-DNB–methoxide ion solutions is hindered by radical formation, the intense maximum at 516–520 nm probably results from the major product, **62a**. Stable σ complexes formed from carbanions and 1,3-DNB have been isolated and characterized by pmr,[88,114] and these do show a visible maximum between 500 and 600 nm. A very unstable complex, **62b**, containing 2 equiv of methoxide per equivalent of 1,3-DNB, has been isolated;[130] it exhibits a maximum at 520 nm. The structural assignment is not conclusive, however. The related complex, **62c**, was reported to form in strongly basic solutions of hydroxylamine but it was not characterized by pmr.[150]

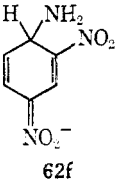

62a


62b


62c


62d

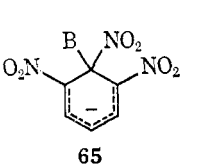

62e

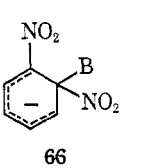

62f

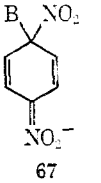
The possibility that color formation in alkaline solutions of 1,3-DNB results from 1,3-DNB anion has been ruled out by deuterium-labeling studies.[151] The increased rate of solute ring-proton solvent exchange with increasing basicity at low base concentration (methanolic methoxide) is terminated when 1,3-DNB is completely converted to its colored form, which is unreactive in exchange. Comparisons with visible spectra of σ complexes prepared from 2,4-DNA (*vide infra*) support the conclusion that color resulting from 1,3-DNB and methoxide is due to **62a**.

DMSO solutions of diethylamine and 1,3-DNB or substituted 1,3-DNB are highly colored (λ_{max} 577 nm for 1,3-DNB). The color has been attributed to diethylammonium salts of complexes like **62d**;[152] structure **62e** is more probable. In liquid ammonia, 1,3-DNB forms a colored complex, probably **62f**, with a λ_{max} at 564 nm.[148]

Generally, 1,2- and 1,4-DNB's as well as 1,2,3-TNB's do not give stable σ complexes on treatment with base. Addition to a substituted ring position occurs preferentially, yielding **65**, **66**, or **67**, followed by rapid loss of nitrite.[18,153] Early workers obtained colored solutions from aldehydes and ketones, 1,2-DNB, and alkali, but the nature of the species responsible was not known.[154] Free radicals may


65

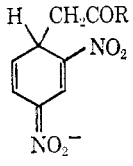

66


67

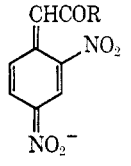
be present,[2] in addition to transient σ complees.

(148) R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 161 (1962).
(149) E. Liss and K. Lohmann, *Chem. Ber.*, **89**, 2546 (1956).
(150) S. S. Gitis, A. I. Glaz, V. V. Grigoriev, A. Ya. Kaminskii, A. S. Martynenko, and P. I. Saukov, *Zh. Org. Khim.*, **3**, 1617 (1967).
(151) M. R. Crampton and V. Gold, *J. Chem. Soc. B*, **6**, 498 (1966).
(152) J. P. Heotis and J. W. Cavett, *Anal. Chem.*, **31**, 1977 (1959).
(153) R. Schaal and J. C. Latour, *Bull. Soc. Chim. Fr.*, **9**, 2172 (1964).
(154) R. Truhaut, *J. Pharm. Chim.*, **25**, 216 (1937); *Chem. Abstr.*, **31**, 7363 (1937).

Observation of color resulting from addition of alkali to acetone solutions of 1,3-DNB was first reported by Janovsky[155] in 1886. Subsequently called the Janovsky reaction, it has been used as a test for active methylenes. Structure **62g** (R = CH_3), formed in alkaline acetone,[88,156] is representative of a wide variety of similar complexes formed from aldehydes[157] and ketones.[2,157] In acetone **62g** (R = CH_3)



62g



62h

has a visible maximum at ~570 nm which shifts to 540 nm in water, and 587 nm in DMSO.[156] The complexes formed in the Janovsky reaction are produced in a large excess of alkaline acetone (or other ketonic substrate). When excess nitro aromatic is used, the results are quite different.[158] The initially formed σ complex is oxidized to the conjugate base of a 2,4-dinitroalkyl ketone, **62h**.[156,159-161] This structure is supported by recovery of 3-nitroaniline from the reaction solution,[160] and by pmr spectra of the colored product.[156] In addition, both the conjugate base, **62h**, and the σ complex, **62g**, have distinctly different spectral characteristics. While λ_{max} for **62g** is solvent dependent, it is essentially independent of the ketonic moiety. On the other hand, absorption maxima for the conjugate base, **62h**, are solvent independent but vary considerably with changes in R. This is expected, as R is part of the conjugated system of **62h** but not **62g**. Visible maxima for a series of such complexes prepared from 1,3-DNB and various ketones are shown in Table XIV.[114,156,159]

Table XIV

Visible Maxima of 1,3-DNB Complexes and Conjugate Bases[114,156,159]

Ketone	62g λ_{max}, nm	62g Solvent	62h λ_{max}, nm	62h Solvent
Acetophenone	585	Acetone	514	Ethanol
Propiophenone	589	Acetone	540	Ethanol
Methyl ethyl ketone	576	Acetone	500	Ethanol
Methyl propyl ketone	570	Acetone	440	Ethanol
Methyl benzyl ketone	573	Acetone	550	Ethanol
Diethyl ketone	573	Acetone	460	Ethanol
Cyclohexanone	578	Acetone	532	Ethanol
Cyclopentanone	582	Acetone	514	Ethanol
Acetone	570	Acetone	490	Ethanol
Acetone	587	CH_3SOCH_3	498	CH_3SOCH_3
Acetone	580	Pyridine	500	Pyridine
Acetone	563	Cellosolve	494	Cellosolve
Acetone	536	Methanol	485	Methanol
Acetone	540	Water	487	Water

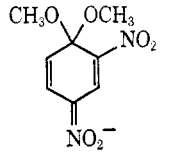
(155) J. V. Janovsky and L. Erb, *Ber.*, **19**, 2155 (1886).
(156) M. Kimura, K. Meiji, N. Masahiro, O. Noboru, and K. Masahiko, *Chem. Pharm. Bull. Jap.*, **16**, 634 (1968).
(157) T. Canback, *Farm. Revy*, **48**, 153 (1949); *Chem. Abstr.*, **43**, 4650g (1949).
(158) W. Zimmerman, *Z. Physiol. Chem.*, **223**, 257 (1935).
(159) R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 1131 (1962).
(160) T. J. King and C. E. Newall, *J. Chem. Soc.*, 367 (1962).
(161) O. Neunhoeffer, K. Thewalt, and W. Zimmerman, *Z. Physiol. Chem.*, **323**, 116 (1961).

The reactions of diketones and ketoesters with 1,3-DNB and base have been described qualitatively.[162] These substrates presumably yield complexes analogous to **62g**. The early literature dealing with reactions of 1,3-DNB with compounds containing active methylenes was reviewed in 1949.[157]

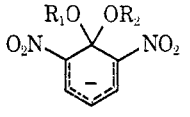
f. From Substituted Dinitrobenzenes

The visible spectra of **33a** and **33f** ($R_1 = R_2 = CH_3$), formed from 2,6- and 2,4-DNA and methoxide, have maxima at 503 and 568 nm, respectively. At higher methoxide concentrations, the 503-nm maxima for **33a** disappears and a new absorption appears at 302 nm, probably from 2,4-dinitrophenolate anion.[69]

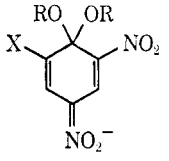
Each of the complexes **68** and **69** (R = CH_3 and C_2H_5, X = CH_3O, Cl, CO_2NH_2, CO_2CH_3, and CN), has two visible maxima.[118,163] The high-energy band occurs from 350 to 400 nm



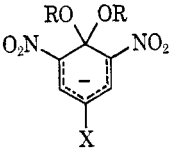
33a



33f



68



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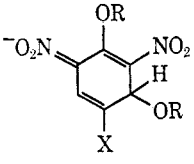

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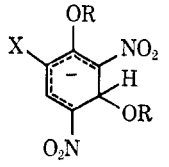

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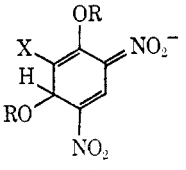


72

in both **68** and **69**. The low-energy band occurs from 480 to 530 nm in structures like **68**, and from 535 to 612 nm in structures like **69**. These differences parallel calculated differences in energy of the first and second charge-transfer transitions of 2,4- and 2,6-dinitrocyclohexadienate complexes.[25] The low-energy bands of both **68** and **69** shift to higher energy as the electronegativity of X increases.

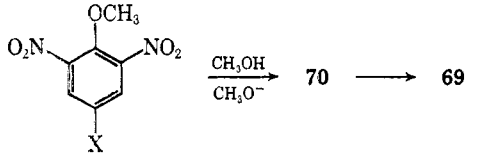
Stopped-flow spectrophotometric studies provide some tenuous evidence for initial base attack at an unsubstituted position prior to formation of **68** and **69**, which could yield the kinetically favored complexes **70**, **71**, and **72**.[92] Such behavior is analogous to that of 2,4,6-TNA where initial attack occurs at C-3. All the proposed complexes **70**, **71**, and **72** rapidly rearrange ($t_{1/2}$ ~ 5–20 sec) to the more thermodynamically stable **68** and **69**. The spectral changes accompanying these proposed transformations in methanolic methoxide are summarized in Table XV. There are no pmr spectra to substantiate the structures of **70**, **71**, and **72** except in the case of **72** (X = CN).[27]

Interestingly, in highly concentrated solutions of methoxide, **68** (X = CN) adds a second equivalent of base to yield **73**, which has a maximum at 370 nm.[23] The structure of **73** is

(162) M. Ishidate, T. Sakaguchi, and S. Hirokawa, *J. Pharm. Soc. Jap.*, **70**, 439 (1950).
(163) F. Terrier and F. Millot, *C. R. Acad. Sci., Ser. C*, **268**, 809 (1969); *Chem. Abstr.*, **70**, 105626g (1970).

Table XV

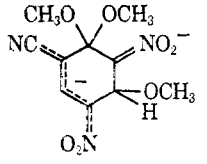
Visible Maxima (λ_{max}, nm) of Isomeric Complexes Formed from Unsubstituted and Substituted Dinitroanisoles and Methoxide[92]



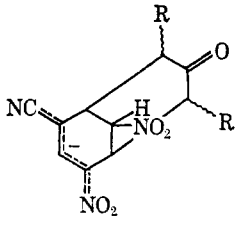
X = CN	460	540
X = F	485	640
X = H	488	595

X = CN	495	480	475
X = Cl		505	497

supported by the isolation and pmr characterization of **74** which exhibits a visible maximum at 374 nm.[61]

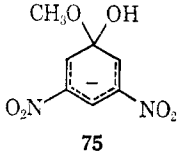


73



74

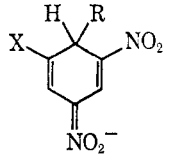
A dilute solution of 3,5-DNA in 0.02 *N* sodium hydroxide–methanol solution forms a transient colored intermediate, λ_{max} 425–520 nm. Structure **75** was tentatively proposed, since 3,5-dinitrophenolate anion is the sole product of the reaction.[164] Addition of methoxide to concentrated solutions



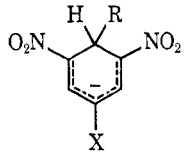
75

of 3,5-DNA in DMSO produces radicals which hinder pmr characterization of the species responsible for the color.[52] This result is expected, as the α substituent effect of methoxyl[18] (see section IV) favors production of a complex with the least stabilization energy of the three possible 1,3-dinitrocyclohexadienate anions.[25]

Visible spectra of basic solutions of 1,3-DNB's containing electron-withdrawing and -donating substituents in the 5 position have been reported.[165] The presence of electron-withdrawing substituents facilitates formation of the complexes, which have in some cases been isolated. Generally, two visible maxima are observed in basic solutions of 1,3-dinitro-5-substituted benzenes.[116] The one at high energy has been attributed to **76** and that at low energy to **77**. Structural assignments based solely on visible spectra of mixtures are of limited value without supporting evidence, however. Many papers reporting the absorption maxima of solutions of base and polynitro aromatics have appeared during the past three decades; these contain very little structural information.[126,129,146,147,152,166–176]

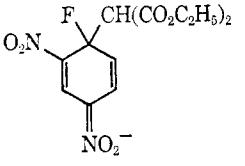


76

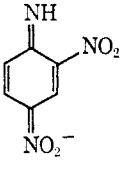


77

2,4-Dinitrofluorobenzene reacts with diethyl malonate and triethylamine to yield the crystalline complex **78**, with a maximum at 510 nm.[177] 2,4-Dinitroaniline loses an N–H proton in base to give the anion **79**,[69] λ_{max} 515 and 383 nm. At very high base concentration, there is evidence for addition to **79** to yield a doubly charged anion, λ_{max} 326 nm.[135]



78



79

g. From Nitrobenzene

There is no direct evidence for stable σ complexes resulting from the reaction of nitrobenzene and base. Several bases, such as potassium hydroxide,[178,179] potassium amide,[180] ammonia,[181] lithium piperidide,[182] dimethyloxosulfonium methylide,[183] and *t*-butylmagnesium chloride,[184] have been added to nitrobenzene. Colors are produced in certain instances,[178–180] but σ complexes have never been isolated. In one instance, a broad absorption at 300–550 nm which develops in strongly basic solutions of nitrobenzene was attributed to base addition.[185] Usually, rearranged substitution products, or products

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(165) M. Akatsuka, *Yakugaku Zasshi*, **80**, 375 (1960).
(166) S. S. Gitis, A. Ya. Kaminskii, and A. M. Varlamova, *Zh. Org. Khim.*, **4**, 484 (1968).
(167) S. S. Gitis and A. Ya. Kaminskii, *ibid.*, **4**, 504 (1968).
(168) S. S. Gitis, G. M. Oksengendler, and A. Ya. Kaminskii, *Zh. Obshch. Khim.*, **29**, 2983 (1959); *Chem. Abstr.*, **54**, 13028*g* (1960).
(169) G. Sollazzo, *Boll. Chim. Farm.*, **72**, 913 (1933); *Chem. Abstr.*, **28**, 5758 (1934).
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(171) T. Canback, *Sv. Kem. Tidskr.*, **58**, 101 (1946); *Chem. Abstr.*, **40**, 6060 (1946).
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(180) F. W. Bergstrom and J. S. Buehler, *J. Amer. Chem. Soc.*, **64**, 19 (1942).
(181) E. Havinga, *Tetrahedron Lett.*, **48**, 5957 (1966).
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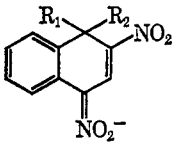
(185) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967).

Table XVI

Visible Maxima of Naphthalene Complexes



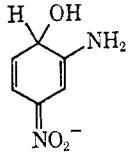
50

R_1	R_2	λ_{max_1}, *nm*	λ_{max_2}, *nm*	*Solvent*	*Ref*
$-OCH_2CH_2O-$		500	360	CH_3OH	84, 122
H	CH_3COCH_2	520		CH_3COCH_3	122
CH_3O	CH_3O	495 (505)	350	CH_3OH	91, 92
n-BuNH	C_2H_5O	527	360	CH_3SOCH_3	188
O_2NCH_2	H	538		CH_3SOCH_3	36

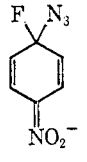
resulting from attack on the NO_2 group, are obtained. These may result from transient high-energy σ-complex intermediates. Since 4-nitrocyclohexadienate complexes are predicted to have a lower stabilization energy than any of the di- or trinitro complexes[25] (except for the 3,5-dinitro isomer), it is not surprising that they are not isolable.

h. From Substituted Nitrobenzenes

Nitroanilines lose an NH proton in basic solution, and addition may occur to the resulting anion at very high base concentrations.[81,185] In 17 *M* sodium hydroxide, a broad absorption at 433 nm, attributed to a complex of hydroxide and the conjugate base of *p*-nitroaniline,[186] was later shown to result from a solvent-shifted absorption for the conjugate base. Addition to *p*-nitroaniline has been shown to occur in solutions of sodium hydroxide and liquid ammonia.[81] *m*-Nitroaniline is much less acidic, and hydroxide addition yields **80**, λ_{max} 300–350 nm.[185]



80

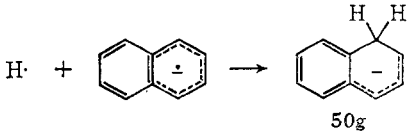


81

Addition of azide to 4-fluoronitrobenzene in dry dimethylformamide was reported to yield **81**, λ_{max} 397 nm, but this result could not be repeated.[120]

2. *Naphthalene σ Complexes*

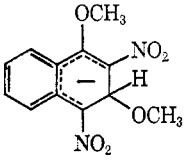
Most interestingly, the visible spectrum of **50g** has been reported to have a maximum at ~437 nm ($\epsilon \simeq$ 10,000) in tetrahydrofuran.[187] Since NO_2 groups are absent, this absorption is not a charge-transfer transition (section III) and must result from locally excited states of the π system. Replacing the hydrogens on C-2 and C-4 of naphthalene with



50g

(186) C. H. Rochester, *Trans. Faraday Soc.*, **59**, 2820 (1963).
(187) S. Bank, T. A. Lois, and M. C. Prislopski, *J. Amer. Chem. Soc.*, **91**, 5407 (1969).

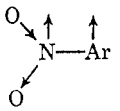
NO_2 groups enhances the stability of σ complexes which form by nucleophilic attack at C-1. The visible maximum moves to lower energy and may now result from charge transfer between the ring and NO_2 groups. The visible and near-ultraviolet maxima for several naphthalene σ complexes (**50**) are listed in Table XVI.[36,75,84,91,92,188] Addition at C-3 is not observed by pmr[91] but has been proposed to account for a transient intermediate detected by stopped-flow spectrophotometric techniques.[92] The proposed structure, **82**, has a maximum absorption at 505 nm with a shoulder at 550–600 nm.



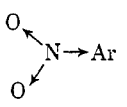
82

D. INFRARED SPECTRA

The infrared spectra of several anionic σ complexes have been reported.[2,64,90,91,115,119,189–194] A number of characteristic absorption frequencies are present; the most intense result from NO_2 stretching modes. A normal aromatic NO_2 group has strong absorptions at 1530–1550 and 1345–1350 cm^{-1} due to the asymmetric and symmetric stretching modes.[195] The N–O force constant, and hence the N–O bond order, determines to a large extent the overall force constant



asym



sym

for the asymmetric stretching vibration (the effect of N–C bond bending is negligible), whereas the symmetric mode is determined by both N–C and N–O force constants, and

(188) J. A. Orvik and J. F. Bunnett, *ibid.*, **92**, 2417 (1970).
(189) A. R. Norris and H. F. Shurvell, *Can. J. Chem.*, **47**, 4267 (1969).
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(193) L. K. Dyall, *ibid.*, 5160 (1960).
(194) L. K. Dyall, *Spectrochim. Acta*, **22**, 467 (1966).
(195) R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952).

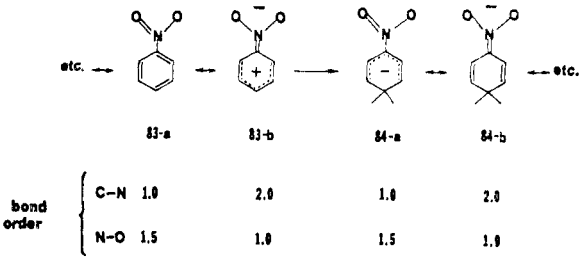
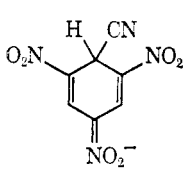
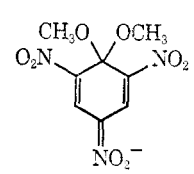


Figure 4. Bond orders in the canonical forms of a nitro aromatic and its corresponding 4-nitrocyclohexadienate σ complex.

hence both bond orders.[196] Conversion of an aromatic NO_2 group to one bearing partial negative charge in a σ complex is schematically illustrated in Figure 4. If the N–C bond bending contribution is negligible, then since **84b** contributes to the total structure of **84** to a greater extent than **83b** contributes to the total structure **83**, the N–O bond order in **84**, and hence the asymmetric absorption frequency, should decrease relative to that in **83**. The symmetric stretch depends upon both N–C and N–O bond orders. Since the bond order of two N–O bonds decreases and only the N–C bond order increases, in going from **83** to **84**, the symmetric absorption frequency might be expected to decrease also. This has in fact been observed in all the complexes studied. The N–O symmetric stretch in 2,4,6-TNA was reported to decrease from 1343 to 1291 cm^{-1} and the asymmetric stretch from 1552 to 1492 cm^{-1} on conversion to the 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate complex (**19a**).[192] The absorption at 1492 cm^{-1} could result from a ring vibration, however.[193] In 1,3,5-TNB, the asymmetric and symmetric NO_2 absorptions appear at 1550 and 1345 cm^{-1}, with extinction coefficients (chloroform) of 1740 and 1400 M^{-1} cm^{-1}, respectively.[189] In addition, a symmetric NO_2 deformation appears at 825 cm^{-1}, an in-plane bending vibration at 518 cm^{-1}, and an in-plane rocking vibration at 360 cm^{-1}.[189] When cyanide is added to a chloroform solution of 1,3,5-TNB, both the symmetric and asymmetric NO_2 absorptions diminish as two new peaks with similar extinction coefficients appear at 1235 and 1190 cm^{-1}. These reach maximum intensity at a 1:1 equivalent ratio of 1,3,5-TNB:cyanide and are attributed to the asymmetric and symmetric NO_2 stretching modes of **6g**.[189] The same changes occur when cyanide is added to a solution of 1,3,5-TNB-d_3 in chloroform.[189] The



6g



19a

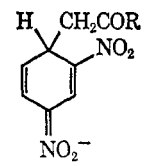
complex **6g** also has an absorption at 1495 cm^{-1} which might be assigned to the asymmetric NO_2 stretch analogous to the assignment made for **19a**.[192,193] The extinction coefficient of this peak is much smaller than would be expected for NO_2 vibrations, however, and the 1235-cm^{-1} band is thus a more likely assignment. Since the 4-NO_2 group delocalizes more negative charge than a 2- or 6-NO_2 group as shown by X-ray crystallography and HMO calculations, two different asymmetric and symmetric absorptions might be expected for a 2,4,6-trinitrocyclohexadienate complex. That only one of each has been assigned in all systems studied could mean that these absorptions are not resolved, or that other bands in the spectrum have been incorrectly assigned.

The infrared spectra of 1,1-dialkoxy σ complexes have been discussed in some detail.[2,83,84,91,192–194] These complexes exhibit a series of strong overlapping bands from 1225 to 1040 cm^{-1} and a weak band at 1010 cm^{-1}. Such absorption does not resemble that of the parent ethers but is similar to bands characteristic of ketals.[197] The bands at 1232–1195 and 1060–1010 cm^{-1} have been assigned to the asymmetric and symmetric C–O–C stretching frequencies.[83] An absorption at 1110 cm^{-1}, observed in the spiro σ complexes **33d** and **33e**, prepared from 1-(β-hydroxy)-2,4- and -2,6-dinitrobenzenes, has been assigned to the ketal function, as has a similar band at 1140 cm^{-1} for the spiro complex **50d**, prepared from 1-(β-hydroxyethoxy)-2,4-dinitronaphthalene.[84]

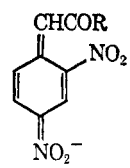
The out-of-plane C–H deformations in alkoxide complexes of picryl ethers have been assigned to absorptions at 750 and 910 cm^{-1}.[194] The C–H stretch at ~3090–3094 cm^{-1} is very weak in these complexes and was not reported in early work, where spectra were recorded in Nujol.[192]

The C–C stretching modes of 1,3,5-TNB have been assigned to absorptions at 1625 and 1443 cm^{-1}, with extinction coefficients (chloroform) of 330 and 60 M^{-1} cm^{-1}.[189] Conversion to **6g** results in replacement of these bands with an absorption at 1615 cm^{-1}, assigned to the C–C stretching mode in the complex. Cation absorptions obscure other bands associated with C–C stretch in **6g**.

The infrared spectrum of **62g** has absorptions at 1524 and 1348 cm^{-1}, assigned to the NO_2 asymmetric and symmetric stretch, and an absorption at 1719 cm^{-1} for the carbonyl.[114] As expected, the carbonyl in the conjugate base **62h** absorbs at 1610 cm^{-1}.[114]



62g



62h

The CN absorption of **6g** was reported to appear at higher frequency and with greater intensity than that for free cyanide (2320–2350 cm^{-1} complexed *vs.* 2060–2080 uncomplexed), but this assignment is now considered doubtful.[189] Absorptions from carbon dioxide were cited as complicating factors.

In bicyclopropenide complexes formed from 2,4,6-TNB, ketones, and amines (**18**), the anionic NO_2 asymmetric and symmetric stretch have been tentatively assigned to absorptions at 1420 and 1265 cm^{-1}.[59,198] In the carbomethoxynitropropenide and cyanonitropropenide complexes, **49** (X = CO_2CH_3 and CN), the anionic carbonyl and cyanide have absorptions at 1690 and 2180 cm^{-1}, respectively, compared to 1725 and 2285 cm^{-1} in methyl 3,5-dinitrobenzoate and 3,5-dinitrobenzonitrile.[61] These shifts parallel those observed with NO_2 groups in both bicyclic and monocyclic complexes.

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(197) E. Bergmann and R. Richards, *Recl. Trav. Chim. Pays-Bas*, **71**, 161 (1952).

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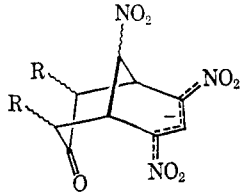
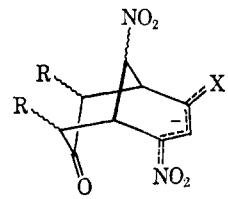


18



49

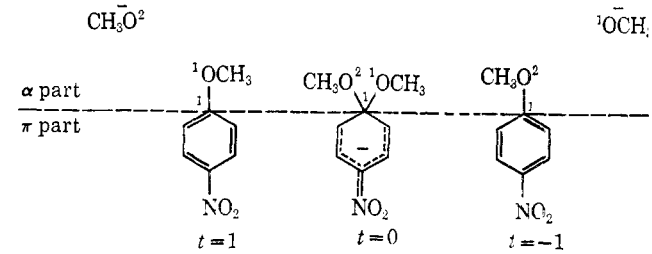
III. Molecular Orbital Calculations

As electrophilic and nucleophilic aromatic substitution processes each involve charge-delocalized σ-complex intermediates, it is not surprising that simple MO methods have proven useful in the study of structure and reactivity relationships in both kinds of reactions. Much of the work through 1961, concerned with MO treatments of electrophilic substitution, has been summarized by Streitwieser.[199] Simple MO treatments of nucleophilic aromatic substitution and related topics have been reported by several workers.[21,23-25,103,104,200-204] The material covered here will consider only those calculations which deal with formation and structural characterization of the intermediate complex.

Structure and stability of σ complexes, as well as electronic and pmr spectra, are qualitatively correlated by simple HMO techniques.[21,103,104] More detailed HMO treatments[23] and Pariser–Parr–Pople-type SCF calculations with configuration interaction[25] provide a more complete description of electronic structure. Application of simple HMO methods to the calculation of π-electron energy changes during σ-complex formation involves several gross approximations, in addition to the approximate nature of the method.[103,104] The calculations do not allow predictions of experimentally determined energy differences, but do show energy changes with alteration in structure, paralleling those obtained from thermodynamic and kinetic studies. One useful technique is to consider the complex a composite of σ and π parts and calculate the energy of each during a symmetrical substitution process, using resonance and coulomb integrals which are a function of a reaction parameter t, Scheme I (reaction scheme and parameters adapted from ref 103 with permission of the author).

The σ part is a linear combination of an atomic orbital on methoxyl and the p orbital on C-1 of the ring. The π part is a combination of all interacting p orbitals in the system. Initially ($t = 1$) there is no σ or π interaction of CH_3O-2 with C-1. As reaction proceeds to the complex, σ bonding between these atoms increases until the interaction is equal to that between CH_3O-1 and C-1. As this occurs, π interaction between C-1 and CH_3O-1, and between the ring and C-1, decreases and becomes zero in the complex. The interactions are reversed as CH_3O-1 is displaced. These changes are expressed by resonance and coulomb integrals which are a multiplicative function of the parameter t, and fixed values of α and β. Since the energy of the π or σ part

Scheme I



For $t = 1 \rightarrow 0$: $\beta_{\sigma_{C^1-O^2}} = (1 - t)0.5\beta_{\sigma_{C-C}}$
$\beta_{\pi_{C^1-O^1}} = t0.6\beta_{\pi_{C-C}}$, $\beta_{C^1-C} = t\beta_{C-C}$

For $t = 0 \rightarrow -1$: $\beta_{\sigma_{C^1-O^1}} = (1 + t)0.5\beta_{\sigma_{C-C}}$
$\beta_{\pi_{C^1-O^2}} = -t0.6\beta_{\pi_{C-C}}$, $\beta_{\pi_{C^1-C}} = -t\beta_{\pi C-C}$

where $\alpha_\sigma O = \alpha_\sigma C + 0.5\beta_{\sigma_{C-C}}$
and for CH_3O $\alpha_\pi O = \alpha_\pi C + 2\beta_{\pi_{C-C}}$
and for NO_2 $\alpha_\pi N = \alpha_\pi O = \alpha_\pi C + \beta_{\pi_{C-C}}$
and $\beta_{\pi_{C-N}} = \beta_{\pi_{N-O}} = \beta_{\pi_{C-C}}$

can be computed in units of β at any value of t by summation over all the occupied orbitals, a range of energy values can be obtained. These values are plotted against t for both the σ and π parts during methoxide displacements on 4-nitro-, 2,4-dinitro-, and 2,4,6-trinitroanisole, Figure 5 (adapted with permission of the author, from ref 103). The energy of the π part is a maximum in the complex where disruption of delocalization is greatest. The energy of the σ part is at a minimum in the complex, as both entering and leaving groups are covalently bound to the ring. Combination of the two parts can be accomplished by letting $\beta_\sigma = -6.36$ eV and $\beta_\pi = -3.0$ eV, respectively (Figure 5), which results in a qualitative reaction coordinate. As observed experimentally, the activation energy for complex formation decreases with increasing numbers of NO_2 groups. Since the change in energy of the σ part is assumed to be independent of the number of NO_2 groups (resulting from approximations inherent in the calculations), differences in activation energies for decomposition of the various complexes are proportional to differences in localization energies of the various π systems. These localization energies are determined to a large extent by the energy of the highest occupied orbital, as calculated energy changes for lower lying filled orbitals are insignificant. The energy of all the molecular orbitals at $t = 0$ (*i.e.*, for the complex) are shown in Figure 6 (adapted from ref 103 and 104, with permission of the author). The number of absorption maxima observed in the visible region is qualitatively predicted by the energy of transitions from the highest occupied to the lower unoccupied orbitals. Solvent effects, neglected in the calculation, are of considerable importance, and steric compression of the *ortho* NO_2 groups and C-1 substituents must be taken into account, as noncoplanarity of the π system will substantially affect the calculated energies. Models of σ complexes formed by attack of methoxide and ethoxide on C-1 of 2,4,6-TNA and 2,4,6-trinitrophenetole do show steric compression between the 2- and 6-NO_2 groups and the alkoxyls. This has been confirmed by X-ray studies.[21,22] Noncoplanarity resulting from such compression is taken into account by allowing the resonance integral β_{C-N} for the *ortho* NO_2 groups to be a function of ω, $\beta_{C-N} = (0.8 \cos \omega)\beta$, where ω is the dihedral angle between the ring plane and that of the NO_2 group.[23] As ω increases

(199) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.
(200) J. Murto, *Suom. Kemistilehti*, 38, 246 (1965).
(201) S. Carra, M. Raimondi, and M. Simonetta, *Tetrahedron*, 22, 2673 (1966).
(202) S. Nagakura, *ibid.*, 19, 361 (1963).
(203) L. S. Markova and A. F. Terpugova, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 11, 94 (1968); *Chem. Abstr.*, 70, 40813u (1969).
(204) P. Beltrame, P. L. Beltrame, and M. Simonetta, *Tetrahedron*, 24, 3043 (1968).

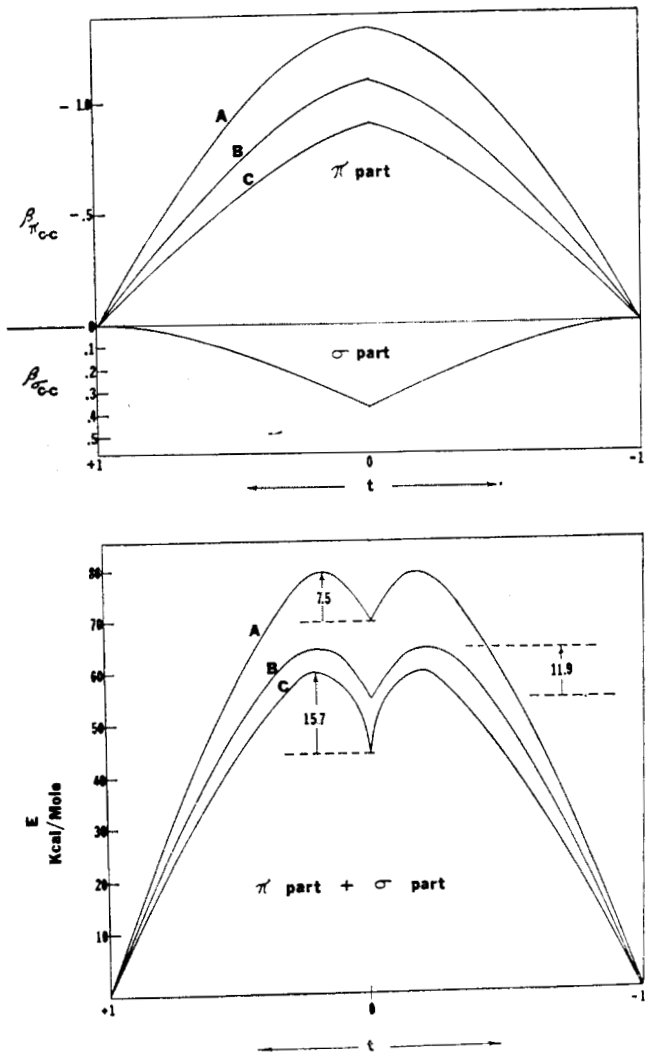
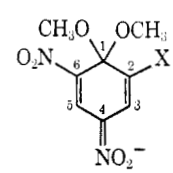


Figure 5. Change in the total electronic energy of the σ and π parts in the reaction of methoxide ion with (A) 4-nitroanisole, (B) 2,4-dinitroanisole, and (C) 2,4,6-trinitroanisole (adapted from ref 103 with permission of the author).

from 0° to 60°, the charge density, q, increases on C-3 and C-5 in both the starting aromatics and the complexes **19a**, **39a**, and **33a**. Figure 7. Inductive effects of the methoxyl groups and



19a (X = NO_2)
39a (X = CN)
33a (X = H)

methylene bridge in the complex can be included by use of atomic polarizabilities, but this causes little change in the relative charge distributions of the starting aromatic or the complex.[23] The total π populations for individual parts of the delocalized system are obtained by summation over the charge densities q, and these are illustrated for various starting aromatics and the corresponding σ complexes in Figure 7 (adapted from ref 23 with permission of the author). It should be noted that π-electron density is predicted to *decrease* in the

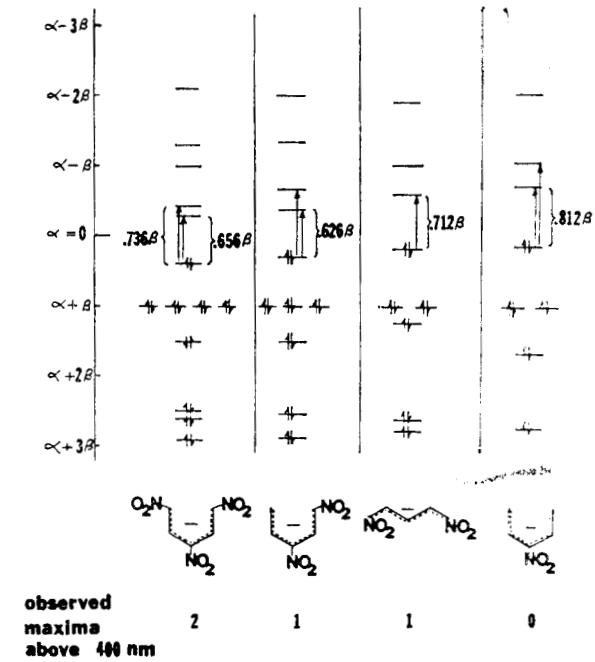


Figure 6. Orbital energy levels in nitrocyclohexadienate and nitropropenide σ complexes (adapted from ref 103 and 104 with permission of the author).

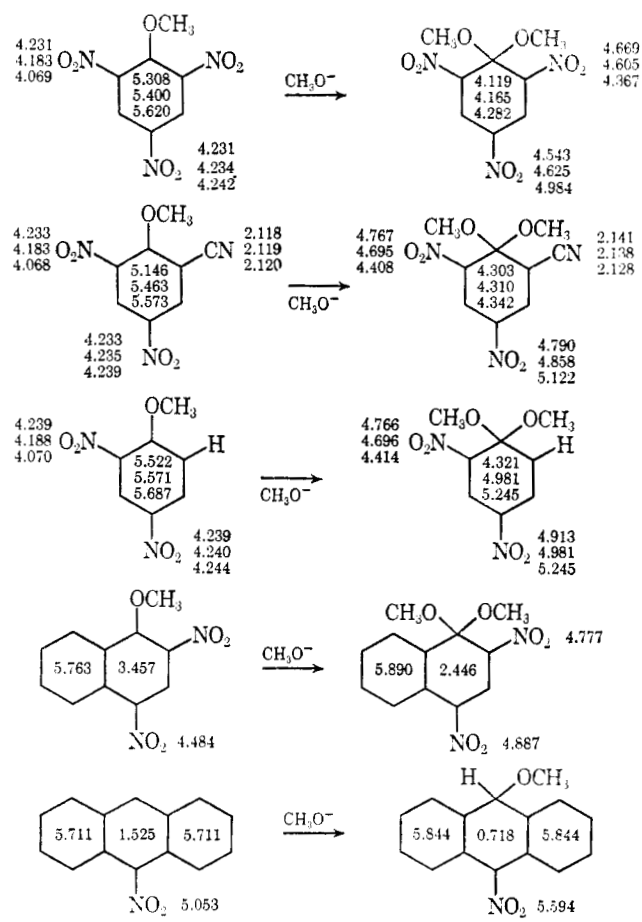


Figure 7. Electron populations for various nitro aromatics and their corresponding σ complexes with methoxide. Values from top to bottom represent dihedral angles of 0, 30, and 60° (for the bicyclic and tricyclic systems; only the value for ω = 0° was calculated). This figure is adapted from ref 23 with permission of the authors.

attacked ring on going from the starting aromatic to the complex. In monocyclic systems, the increased charge is accommodated by NO_2 groups in the fully conjugated ring. The former result is not supported by more extensive SCF calculation on these systems [25] (*vide infra*).

It has been pointed out[23] that if conjugation between the NO_2 groups and ring in cyclohexadienate σ complexes is considered zero, the π-electron system is an odd-numbered chain of linearly bound carbon atoms, resulting in a nonbonding orbital, ψ_{nb}, which is of greater energy than the highest unoccupied MO in the attached NO_2 group(s), ψ_a. In the starting aromatic, these energy relationships are reversed, and the highest occupied orbitals of the aromatic are bonding (and degenerate). These energy relationships are shown schematically in Figure 8 (adapted from ref 23 with permission of the author). The energy of the NO_2 acceptor orbital, ψ_a, drops to ψ_{c_1} and ψ_{nb} increases to ψ_{c_2} as the NO_2 and pentadienyl systems are allowed to interact. Allowing interaction between the NO_2 group and benzene causes ψ_a to increase to ψ_{A_2} and ψ_1 to drop to ψ_{A_1}. The electrons in the highest occupied orbital of pentadienyl anion will then occupy the lowest energy orbital in the complex, $\psi_{c_1} = \psi_a + K\psi_{nb}$ $(K < 1)$, and will be largely localized on the NO_2 function, whereas ring electrons in the starting aromatic will occupy the lowest energy orbital in the interacting system, $\psi_{A_1} = \psi_1 + \lambda\psi_a$ $(\lambda < 1)$, and will be largely localized in the ring.

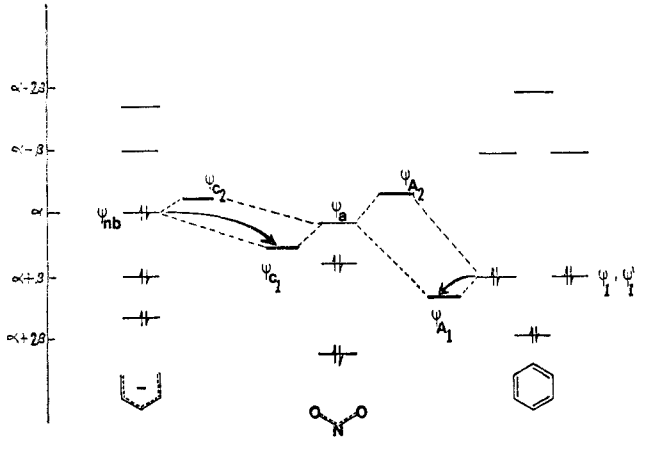


Figure 8. Orbital energies for interaction of a NO_2 group with pentadienyl anion and benzene (adapted from ref 23 with permission of the authors).

More sophisticated calculations, using the method of composite molecules and Pariser–Parr–Pople-type SCF calculations with configuration interaction, provide an interesting comparison.[25] In CM (composite molecule) calculations, the complex is formally separated into pentadienyl anion and NO_2 groups, and the MO's of each are used to construct a series of many electron configurations for the complete anion. These can be categorized into ground-state configurations, locally excited configurations, and charge-transfer configurations, Figure 9 (adapted from ref 25 with permission of the authors), where NO_2 is shown in the charge-transfer and locally excited configurations for only one NO_2 group. Other locally excited configurations, LE_{n_2}, LE_{n_3}, and charge-transfer configurations, CT_2 and CT_3, for additional NO_2 groups, are identical with LE_{n_1} and CT_1, respectively. The energies of the

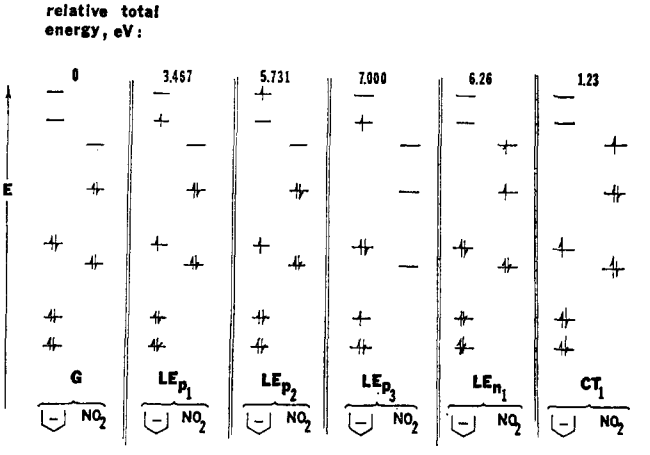


Figure 9. Electronic configurations of the pentadienyl and NO_2 parts of a nitrocyclohexadienate σ complex (adapted with permission of the authors from ref 25).

locally excited configurations for the pentadienyl anion were calculated by the VESCF method and those for the NO_2 groups were measured from the spectrum of nitromethane. The energy of the charge-transfer configuration was calculated from the difference in electron affinity of a NO_2 group and the calculated ionization potential of the pentadienyl anion. From the various excited and ground-state configurations a series of state wave functions, 0 to 4, were constructed and their energies computed. In the 2,4,6-trinitrocyclohexadienate anion, the state wave function 0 is composed mainly of ground-state configuration G (Figure 9), with smaller contributions from CT_1 and CT_2, whereas states 1, 2, and 3 are composed mainly of different combinations of charge-transfer configurations. The lowest transitions are $0 \rightarrow 1$, $0 \rightarrow 2$, and $0 \rightarrow 3$ in the 2,4,6-trinitrocyclohexadienate anion. Interestingly, these can be qualitatively represented by electronic excitation from the highest occupied SCF MO to the next three unoccupied levels (analogous to excitation from HMO 9 to 10, 11, and 12, Figure 6). The energies of the orbitals involved, and electron density shifts occurring during these transitions, are illustrated in Figure 10. The structural formulas approximately indicate the square of the SCF coefficients at each atom, with the ring plane taken as zero. The electronic properties of the several nitrocyclohexadienate anions, A–E, calculated by the method of composite molecules, are summarized in Table XVII (adapted from ref 25 with permission of the authors). These data are interesting in several respects. The predicted stabilization energy of D is quite low as expected, but the large stabilization energy of E is rather surprising, especially since a visible band is predicted at 500 nm. This is contrary to predictions resulting from simple HMO methods.[123] The first two bands predicted for A, B, and C are close to those observed experimentally (see section II. C). Of the ions A–E, A, B, and C have been isolated as crystalline salts. Substrates which might yield D (*i.e.*, 3,5-DNA and methoxide) produce free radicals. The pentadienyl anion ground state is lowered about 0.6, 0.0, and 1.0 eV by NO_2 substitution in the 1, 2, and 3 positions, respectively. These values are additive and parallel the squares of the coefficients of the highest occupied orbital in the anion. This relative order of stability is confirmed experimentally (section V). The ring-bond orders and total charge densities calculated by SCF and CM (composite molecule) methods for the ground state of a 2,4,6-trinitrocyclohexadienate anion are shown in

Table XVII

Charge Densities and Transition Energies for Nitrocyclohexadienate[a]

	A	B	C	D	E
Stabilization energy (eV)	2.121	1.736	1.111	0.004	0.832
Net charge					
Ring	−0.586	−0.594	−0.669	−0.995	−0.680
1-NO_2	−0.121 (2)	−0.189	−0.165 (2)	...	...
2-NO_2	...	...	...	−0.002 (2)	...
3-NO_2	−0.173	−0.217	...	...	−0.320
1st band, nm	534	490	768	2040	500
(eV)	(2.322)	(2.533)	(1.616)	(0.609)	(2.483)
2nd band, nm	386	327	379	1445	289
(eV)	(3.217)	(3.784)	(3.277)	(0.858)	(4.288)
3rd band, nm	263	214	...	...	...
(eV)	(4.711)	(5.802)	...	...	...

[a] Adapted from ref 25 with permission of the authors. The terminal carbon atom is labeled C-1 in structures A–D.

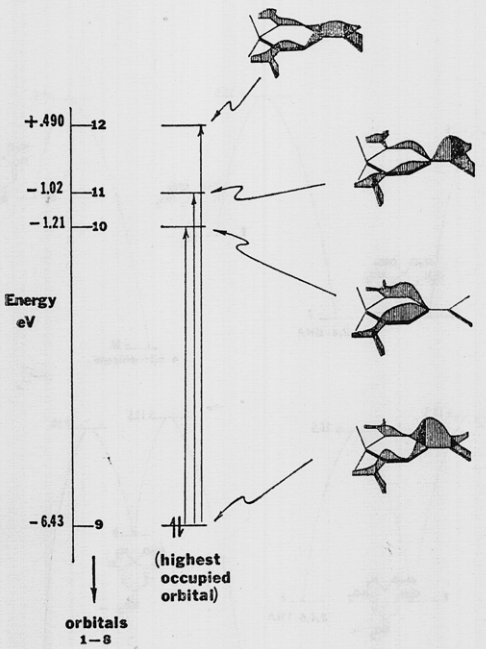


Figure 10. Energy levels and electron densities in 2,4,6-trinitrocyclohexadienate σ complexes.

Figure 11.[25] It is interesting to note that the SCF and CM methods predict a net negative charge density in the ring (−0.5859 and −0.2358, respectively). A net positive charge is predicted from the HMO data in Figure 7.[23] This discrepancy is most likely a result of approximations inherent in the HMO method.

IV. An Empirical Approach to Complex Stability

Miller has devised a semiempirical method for calculating the relative energies of reactants, activated complex, and intermediate σ complex along a reaction coordinate for aromatic nucleophilic substitution.[205–208] The method yields results

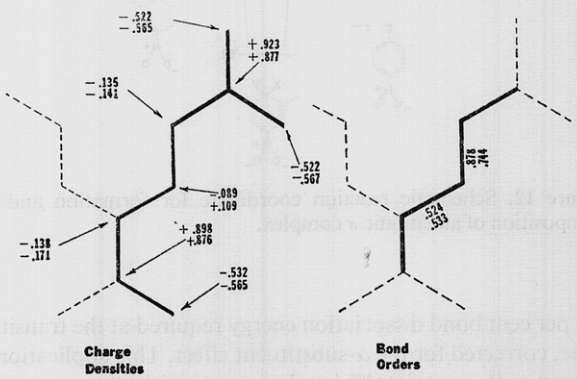


Figure 11. Charge densities and bond orders for a 2,4,6-trinitrocyclohexadienate anion. SCF and CM values are read from top to bottom.[25]

which are in agreement with a large body of experimental data and can be used to predict activation energies for many nucleophilic aromatic substitutions. The calculations are based on a hypothetical reaction coordinate constructed schematically as in Figure 12. The intermediate complex is taken as zero energy and the relative energies of the initial and final states are computed on the basis of energy changes accompanying bond breaking and formation, electron transfer, solvation and desolvation, and delocalization changes. Certain empirical corrections are applied which make the calculations internally consistent. Of particular importance for good agreement with experimental data is an effect attributed to electronegative substituents attached to the reaction center. Such an "α substituent" presumably causes a lowering of the energy of the transition state for nucleophilic attack. The energy levels of the activated complexes are calculated on the basis of a relationship between exo- or endothermicity of the reaction and

(205) J. Miller, *J. Amer. Chem. Soc.*, 85, 1628 (1963).
(206) K. C. Ho, J. Miller, and K. W. Wong, *J. Chem. Soc. B*, 310 (1966).
(207) D. L. Hill, K. C. Ho, and J. W. Miller, *ibid.*, *B*, 299 (1966).
(208) J. Miller, *Aust. J. Chem.*, 22, 921 (1969).

Table XVIII

Comparison of Miller's Calculated Energy Parameters for 1,1-Dimethoxycyclohexadienate Formation and Decomposition with HMO and Experimentally Determined Values[a]

Substituents	$\Delta H^* \sim (E_a)$ – formation			$\Delta H^* \sim (E_a)$ – decompn			E° (ΔH°)		
	Miller[205]	HMO[103]	Exptl[28]	Miller[205]	HMO[103]	Exptl	Miller[205]	HMO[103]	Exptl[28,212]
4-NO_2	25.5	78	...	9.5	7.5	...	16	70	...
2,4-$(NO_2)_2$	19.5	67	17	12.5	11.9	11.2	7	55	+3 (+6)
2,4,6-$(NO_2)_3$	14.0	60	9.5	16.0	15.7	~16	−2	43	−7.1 (−2.8)

[a] All values are in kilocalories.

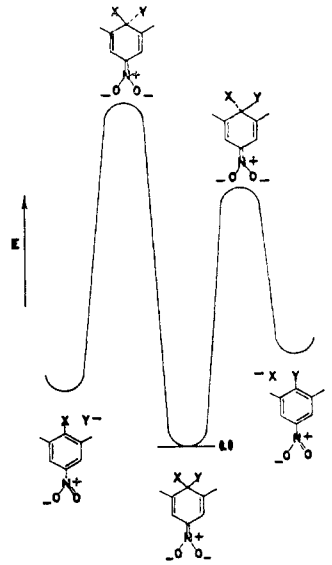


Figure 12. Schematic reaction coordinate for formation and decomposition of an anionic σ complex.

the per cent bond dissociation energy required at the transition state, corrected for the α-substituent effect. This application of Hammond's postulate[209] involves an empirically constructed plot of thermicity *vs.* per cent bond dissociation energy. The remarkable agreement with experimentally determined activation energies is adequate justification for such a procedure. The results apply to reactions occurring in methanol. Reaction coordinates for several systems relevant to this review are shown in Figure 13.[18,205,210] The reactions of 2,4,6-trinitro-, 2,4-dinitro-, and 4-nitroanisole are illustrative. The stability of the various complexes relative to starting aromatics increases with increasing numbers of NO_2 groups, as expected. This is reflected by decreasing activation energies for formation and increasing activation energies for decomposition. Changes in the former are predicted to be most important. These results are qualitatively in agreement with experimental results as the 2,4,6-trinitro- and 2,4-dinitrocyclohexadienate complexes are isolable, whereas the 4-nitrocyclohexadienate complex is not. The predicted activation energies for formation and decomposition are compared with those calculated by simple HMO methods,[103,211,212] and with experimentally determined values in Table XVIII. The calculated activation energies for decomposition are quite close to those determined experimentally. The calculated activation energies for formation are not in agreement with those predicted by HMO calculations. The latter discrepancy is undoubtedly a result of approximations in the HMO method (section III).

The reaction of methoxide with picryl azide is predicted to have an activation energy of 13.5 kcal and should lead to a reasonably stable complex (Figure 13). Both these predications have been verified.[76] The experimental activation energy is 13.4 kcal (determined in dimethylacetamide–acetonitrile), and the complex has been characterized by pmr.[56] Such close agreement is certainly fortuitous but does illustrate the utility

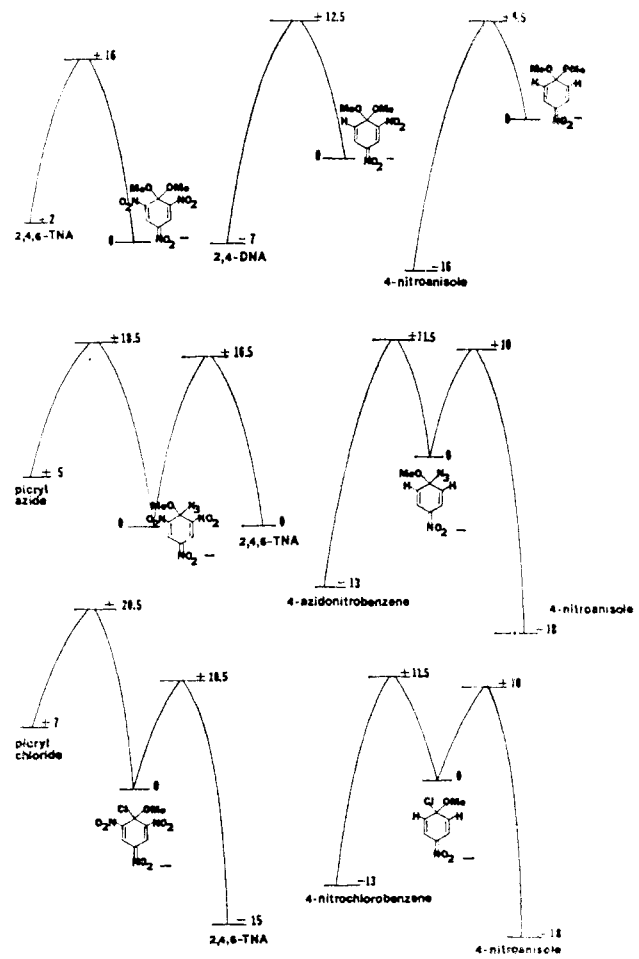


Figure 13. Calculated reaction coordinates for the formation and decomposition of several anionic σ complexes (adapted from ref 18 and 205 with permission of the author).

(209) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(210) Only relative energy differences within one reaction system should be compared with energy differences in another.

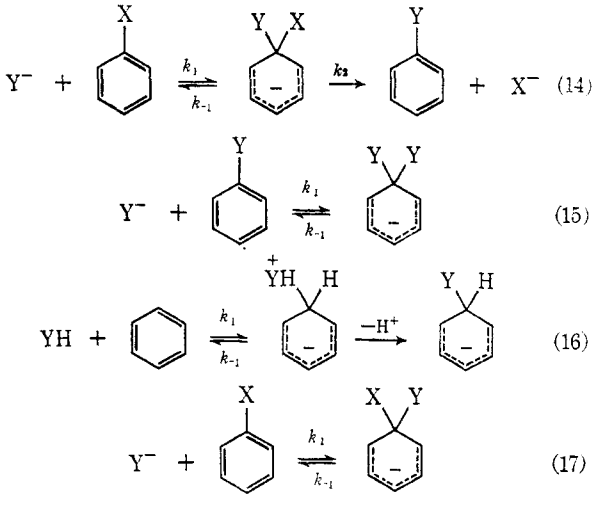
(211) The experimental values are only approximate. A detailed discussion of thermodynamic and kinetic studies is presented in section V.

(212) T. Abe, T. Kumai, and H. Arai, *Bull. Chem. Soc. Jap.*, 38, 1526 (1965).

of such predictive calculations. The complex prepared from picryl chloride and methoxide ion is predicted to be less stable than the methoxide–azide complex, and this is confirmed by experiment.[213] Both 4-azidonitrobenzene and 4-chloronitrobenzene react with methoxide to give 4-nitroanisole and the activation energies for these reactions are in good agreement with the predicted values.[205]

V. Thermodynamic and Kinetic Studies

The factors influencing anionic σ-complex stability have been studied extensively during the past few years. Recent systematic investigations have shown several interesting correlations between structure and stability. The impetus for much of this research was provided by the more general problem of aromatic nucleophilic substitution (eq 14), where the σ complex is a reactive intermediate rather than an addition product. The discussion presented here includes certain nucleophilic substitutions (eq 14), symmetrical exchange (eq 15), and nucleophilic additions (eq 16 and 17). Previous reviews of structure–reactivity relationships in aromatic nucleophilic substitution[13,16,18] are of course pertinent to a discussion of σ-complex stability. Those aspects discussed here pertain directly to complex structure and stability.



A. METHODS OF INVESTIGATION

Visible spectroscopy is commonly used to determine rate and equilibrium constants for reactions involving detectable anionic σ complexes. Equilibrium constants are usually determined by the method of Benesi and Hildebrand,[214] or by some modification of this method.[7] Rate constants have been determined using rapid mixing techniques[27,86] in conjunction with stopped-flow[188,215] and temperature-jump methods.[28,49] Radioactive exchange[216,217] and calorimetric experiments[218,219] have also proven useful. Equilibrium constants and rate constants for formation and decomposition of various anionic σ complexes, as well as the corresponding thermodynamic and kinetic parameters, are summarized in Tables XIX and XX. Individual systems are discussed below.

B. COMPLEX STABILITY

1. Polynitrocyclohexadienates and Related Complexes

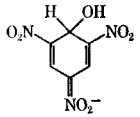
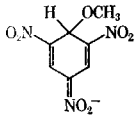
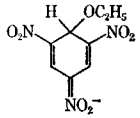
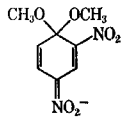
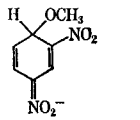
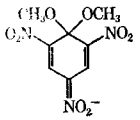
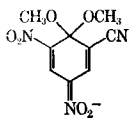
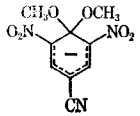
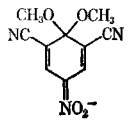
In various protic solvents, the equilibrium constants, K_{eq}, for formation of the 2,4,6-trinitrocyclohexadienate complexes **6a** and **6d** range from 3 to 15 l. mol^{-1} at 25–28°.[49,67,113,127] In DMSO, a dramatic increase in K_{eq} is observed.[65] This results in part from increased methoxide nucleophilicity in this solvent (*vide infra*). In methanol, formation of the methoxide complex **6a** is endothermic, and spontaneity results from a large positive entropy change.[218] In aqueous dioxane, in the presence of tetramethylammonium chloride, the equilibrium constant for **6d** is twice as large as when sodium chloride is used as the compensating electrolyte.[49] This is consistent with the observation, made earlier, that cations of low-charge density stabilize the activated complex for aromatic nucleophilic substitution, relative to the initial state.[223]

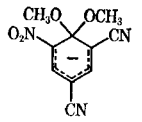
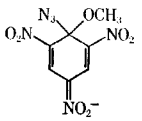
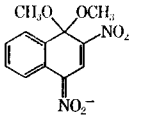
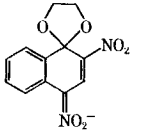
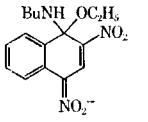
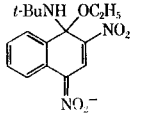
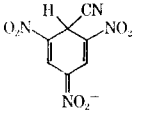
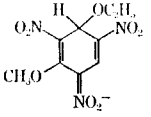
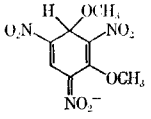
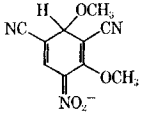
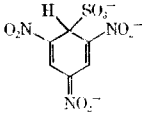
A dramatic reduction in stability occurs when an *ortho* NO_2 group is removed from **6a**. The equilibrium constant for formation of the 1-methoxy-2,4-dinitrocyclohexadienate complex (**62a**) in methanol has been reported as 5×10^{-7} l. mol^{-1}.[5] This value was probably determined by use of an acidity function[224] and is subject to the limitations of such a treatment.[5] In any case, the stability of **62a** is many orders of magnitude less than that of **6a**. Comparing stabilities of complexes such as **6a** and **62a** is difficult, as the experimental conditions necessary for equilibrium constant determinations vary considerably. If the starting aromatics are of similar free energy, based on the equilibrium values given in Table XIX, the free-energy difference between **6a** and **62a** is ~9 kcal. This represents the stabilizing effect of an *ortho* NO_2 group in this system. It is also the difference in stabilization energy, predicted by composite molecule calculations, between **6a** and **62a** as well as between **19a** and **33a** (section III). A similar free-energy difference is observed experimentally for the latter two complexes which differ only by an *ortho* NO_2 group. The 1,1-dimethoxy-2,4-dinitrocyclohexadienate complex (**33a**) has an equilibrium constant of about 10^{-3} l. mol^{-1} (Table XIX),[28,135] which is less than that of **6a** but greater than that of **62a**. The greater stability of **33a**, relative to **62a**, might result from reduction of steric compression between the coplanar, *ortho* NO_2 and methoxyl groups in 2,4-DNA, upon formation of **33a**.[21,22,113] Such steric compression is absent in the ground state of 1,3-DNB, and the driving force for complexation is thus diminished. The equilibrium constant for the 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate complex (**19a**) has been determined in several laboratories[27,97,111,212,217] and ranges from 2×10^3 to 20×10^3 l. mol^{-1}, depending on the

(213) R. C. Farmer, *J. Chem. Soc.*, 3425 (1959).
(214) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 71, 2703 (1949).
(215) R. Gaboriand and R. Schaal, *Bull. Soc. Chim. Fr.*, 8, 2683 (1969).
(216) H. Gore, D. F. C. Morris, and T. J. Webb, *Radiochim. Acta*, 6, 122 (1966).
(217) J. H. Fendler, *J. Amer. Chem. Soc.*, 88, 1237 (1966).
(218) J. W. Larson, J. H. Fendler, and E. J. Fendler, *ibid.*, 91, 5903 (1969).
(219) E. Buncel, A. R. Norris, W. Proudlock, and K. E. Russell, *Can. J. Chem.*, 47, 4129 (1969).
(220) A. R. Norris, *Can. J. Chem.*, 45, 2703 (1967).
(221) F. Cuta and E. Beranek, *Collect. Czech. Chem. Commun.*, 23, 1501 (1958).
(222) F. Terrier, P. Pastour, and R. Schaal, *C. R. Acad. Sci.*, 260, 5783 (1965); *Chem. Abstr.*, 63, 5001*f* (1965).
(223) C. A. Bunton and L. Robinson, *J. Amer. Chem. Soc.*, 90, 5965 (1968).
(224) The equilibrium constant found in ref 5 was referenced to 151 but no numerical value is found here.

Table XIX

Thermodynamic and Kinetic Data for Anionic σ Complexes[f]

		K_{eq}[a]	k_1[b]	k_{-1}[c]	T, °C	$\Delta H°$[d]	$\Delta S°$[e]	ΔH_1*[d]	$\Delta H_{-1}*$[d]	$\Delta S*_1$[e]	$\Delta S*_{-1}$[e]	*Solvent*	*Conditions*	*Ref*
6d		2.7			28							H_2O	0.03 *M* OH^-	127
		5.0	48	9.5	25							H_2O–dioxane	NaCl	49
		11.8	70	6.5	25							H_2O–dioxane	$(CH_3)_4N^+Cl^-$	49
6a		...			25	2.15	12.6					CH_3OH		218
		15.4			28							CH_3OH	0.8 *M* CH_3O^-	113
		20.8			40							CH_3OH	6×10^{-5} *M* TNB	113
		10^9			...							CH_3SOCH_3	Estimated	67
6b		1800										C_2H_5OH		5
		2070										C_2H_5OH		3
33a		2.7×10^{-4}	7.9×10^{-3}	28.7	25	5.6	2.7	6.8	11.2	−9.4	−12.1	CH_3OH	0.2 *M* CH_3O^-	28
		2.5×10^{-3}	1.9×10^{-3}	7.63	25	3.1	−1.3	6.1	13.0	−15.6	−14.3	CH_3OH	1.0 *M* CH_3O^-	28
			2.1×10^{-3}		25			6.8		−17.4		CH_3OH	0.02 *M* CH_3O^-	217
				42	25							CH_3OH	Infinite dil	28
		2.9×10^{-4}			25							CH_3OH	Extrapolation	135
62a		5×10^{-7}			25							CH_3OH		5
19a		2,260	4.55	2×10^{-3}	25	−2.8		9.5	12.3	−22.9	−29.6	CH_3OH	Dilute CH_3O^-	212
		7,700	4.0	5×10^{-4}	25							CH_3OH	10^{-3}–10^{-5} CH_3O^-	111
		17,000	17.3	1×10^{-3}	25			13.5	19.0	−9.4	−4.8	CH_3OH	10^{-2}–10^{-3} CH_3O^-	27
		21,000	7.17	4.8×10^{-4}	20							CH_3OH	10^{-4} CH_3O^-	97
				5×10^{-4}	25				18.8		−0.9	CH_3OH		217
						−4.9	3.0					CH_3OH		218
39a		2,600	18.8	7.2×10^{-3}	25			17.8	14.4	5.0	−20	CH_3OH	10^{-2}–10^{-3} CH_3O^-	86
		5,736	30.4	5.3×10^{-3}	25			17.1	15.6	3.8	−14	CH_3OD	10^{-2}–10^{-3} CH_3O^-	86
						−2.8	6.2					CH_3OH		218
39b		2.5			43							CH_3OH	Li^+ salt	85
		280	6.1	0.222	25			13.9	9.6	−10.4	−32.0	CH_3OH	10^{-2}–10^{-3} CH_3O^-	86
					25	−3.41	−0.40					CH_3OH		218
39d		34	12	0.373	25				14.6		−20.4	CH_3OH	10^{-2}–10^{-3} CH_3O^-	86
					25	−2.2	3.3					CH_3SOCH_3–CH_3OH		218
					25	>0						CH_3OH		218

39c		10	2.0	0.198	25				12.4		−22.0	CH_3OH	86
					25	−0.82	8.7					CH_3SOCH_3–CH_3OH	10^{-2}–10^{-3} CH_3O^-	218
19b								12.8		−0.4		DMF–CH_3CN	$(C_2H_5)_4N^+$ salt	76
50h		230	0.9	3.95×10^{-3}	25	−2.7		13.2	15.9	−17	−18	CH_3OH		91
50d		356	1.28	3.6×10^{-3}	25			11.8	20.0	−20	−5	CH_3OH		84
50i		540	31.8	5.9×10^{-2}	25.4	−19	−51		24.4		18	CH_3SOCH_3	$BuNH_3^+$ salt in 0.005 *M* $BuNH_2$, Cl^-	188
50j		~0.1	0.5	4.9	25							CH_3SOCH_3	*t*-$BuNH_3^+$ salt	188
6g		39			25.3	~0	7.2					CH_3OH	Ph_4As^+ salt	219
		1,265			25	−6.2	−8.7					C_2H_5OH	Ph_4As^+ salt	219
		1,470			25	−7.1	−10.0					*n*-C_3H_7OH	Ph_4As^+ salt	219
		10,000			25		−5.5					*i*-C_3H_7OH	Ph_4As^+ salt	219
		2,020			25	−7.2	−10.4					*n*-C_4H_9OH	Ph_4As^+ salt	219
		500,000			25	...	−25.0					*t*-C_4H_9OH	Ph_4As^+ salt	219
20c		117.5			−80	−3.3	−7.5	10.4	13.7			C_2H_5OH	Complex not structurally characterized	68
20a					25	−1.5						CH_3OH	Assumes $K_{eq} > 10^3$	86
40c					25	+3.05						CH_3SOCH_3–CH_3OH	Assumes $K_{1,1} \simeq K_{1,3}$	86
6k		225			25							H_2O		115
		250			20							H_2O		66
		267			25	−4	−2.3					H_2O	Ionic strength 0.144,	115
		512			25							H_2O	0.0 salt concn	221

[a] l. mol^{-1}. [b] l. mol sec^{-1}. [c] sec^{-1}. [d] kcal mol^{-1} (no distinction is made between E_a and ΔH). [e] Gibbs mol^{-1}. [f] Sodium salts unless indicated otherwise.

Table XX

Equilibrium Constants of Cyclohexadienate and Propenide Complexes[c]

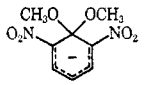
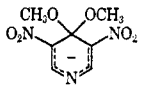
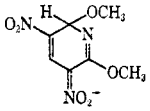
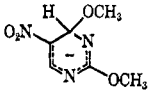
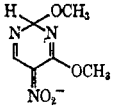
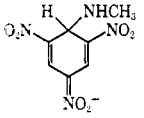
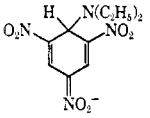
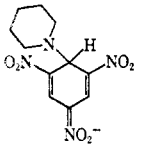
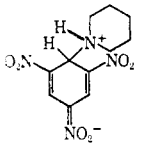
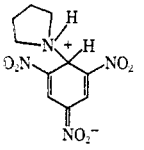
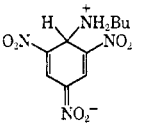
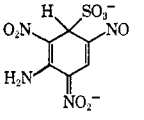
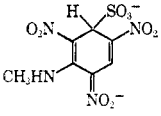
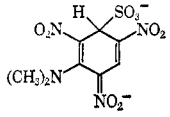
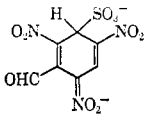
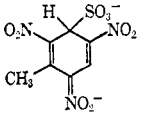
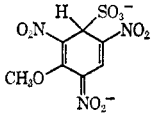
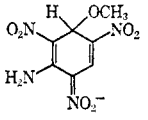
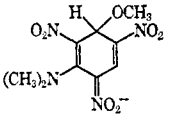
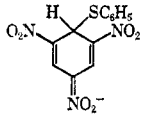
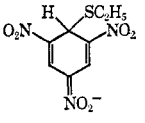
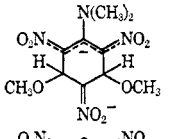
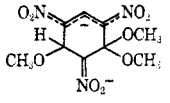
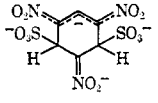
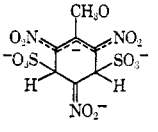
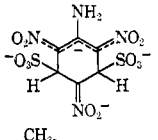
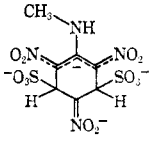
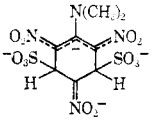
		K_{eq}[a,b]	*T*, °C	*Solvent*	*Comments*	*Ref*
33f		9.8×10^{-20}	25	CH_3OH	K^+ salt	222
52a		2770 4770	20 25	CH_3OH CH_3OH		97 85
51a		1.9	20	CH_3OH		95
54		2–3	27	CH_3SOCH_3	Approximate K_{eq}	98
53		2–3	27	CH_3SOCH_3	Approximate K_{eq}	98
(6e)[d]		2000	20	CH_3SOCH_3	$CH_3NH_3^+$ salt	50
(6e)[d]		13	20	CH_3SOCH_3	$(C_2H_5)_2NH_2^+$ salt	50
(6e)[d]		0.05	::	CH_3CN	 salt	105
(7)[d]		0.201	25	H_2O–dioxane	$k_f = 3000\ M^{-1}\ sec^{-1}$ $k_r = 14{,}900\ sec^{-1}$	49
(7)[d]		0.31	25	H_2O–dioxane	$k_f = 8100\ M^{-1}\ sec^{-1}$ $k_r = 2.5 \times 10^4\ sec^{-1}$	49
(7)[d]		6.2×10^{-3}	25	H_2O–dioxane	$k_f = 123\ M^{-1}\ sec^{-1}$ $k_r = 2 \times 10^4\ sec^{-1}$	49
(20k)[d]		10^4	20	H_2O		66
(20k)[d]		5.4×10^4	20	H_2O		66
(20k)[d]		5.4×10^4	20	H_2O		66

Table XX (Continued)

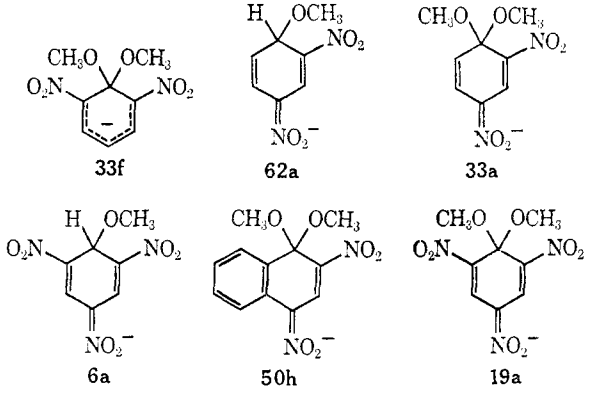
		K_{eq}[a,b]	T, °C	Solvent	Comments	Ref
		2150	25	H_2O	Structure assumed by analogy to cyanide complex	115
		5.6	25	H_2O	Structure assumed by analogy to cyanide complex	115
20g		210	20	H_2O		66
20h		38	25	CH_3OH		132
20j		7	25	CH_3OH		132
6l		1.95 8×10^{4}	20 20	CH_3OH CH_3SOCH_3		67
6m		3500	20	CH_3OH		67
44j		~1	25	CH_3OH		132
44h		1.3×10^{-4}	25	CH_3OH		135
(44d)[d]		0.5	20	H_2O	Zero ionic strength by extrapolation	66
(44d)[d]		58	20	H_2O	Zero ionic strength by extrapolation	66
(44d)[d]		1.05	20	H_2O	Zero ionic strength by extrapolation	66
(44d)[d]		110	20	H_2O	Zero ionic strength by extrapolation	66
(44d)[d]		2300	20	H_2O	Zero ionic strength by extrapolation	66

[a] $l.^{-1}$ mol^{-1}. [b] The equilibrium constants for the dinitropropenide complexes refer to formation from the corresponding trinitrocyclohexadienate complex. [c] Sodium salts unless indicated otherwise. [d] Numerical designation is that of a general structure of this type.

experimental conditions. The enhanced stability imparted to anionic σ complexes by a NO_2 group *para* to the tetrahedral ring carbon is evident when the equilibrium constants for **19a** and **33f** are compared. The latter has an approximate equilibrium constant of 10^{-19}.[222] If 2,6-DNA and 2,4,6-TNA are of similar free energy, the **19a**–**33a** stability difference, in terms of free energies, is over 30 kcal.[225] This is the order of magnitude predicted by composite molecule calculations[25] (section III) and by Miller's empirical method (section IV). A *para* NO_2 group is therefore about three times as effective in stabilizing a 1,1-dimethoxycyclohexadienate complex as an *ortho* NO_2 group. Greater effectiveness in the *para* position probably results from a steric barrier to coplanarity of the ring and *ortho* NO_2 group(s) in the complex, even though such a barrier should be much less than in both starting aromatics. These ideas are supported by X-ray crystallographic studies of the complexes.[21,22]

Extension of the aromatic system in the complex, as in **50h**, also enhances stability. The stabilizing effect, relative to **62a**, is about the same as an additional *ortho* NO_2 group.[28] The equilibrium constant for **50h** is 230 l. mol^{-1},[91] a free-energy difference of ~7.5 kcal from **33a**, again assuming similar free energies for the starting aromatics. The calculated difference in resonance energy between benzene and a cyclohexadienate complex is 10 kcal, whereas the calculated difference between naphthalene and its C-1 complex is 2 kcal.[226] The difference in these two values is close to the experimentally measured value of 7.5 kcal ($RT \ln K_{50h}/K_{33a}$).

The above comparisons are summarized by the following sequence of relative stabilities in methanol: **33f** < **62a** < **33a** < **6a** < **50h** < **19a**. The stabilization energies calculated by



molecular orbital theory[25] for **19a** or **6a**, **33a** or **62a**, and **33f** (section III) are substantiated by this stability sequence, as are Miller's calculations for **19a**, **33a** (Figure 13), and **50h**.[28] The structural feature most effective in complex stabilization is a *para* NO_2 group. Stability is also enhanced, but to a lesser extent, by an *ortho* NO_2 group or extension of the aromatic system, as in **50h**. Of least importance is dimethoxy substitution on C-1.

The equilibrium constant for **33a** in methanol increases significantly as the concentration of sodium methoxide increases.[28] This is a composite effect, resulting from an increase in k_1 and a decrease in k_{-1}. Both these rate constants are, to a first approximation, linearly dependent on ionic strength, which is equal to the sodium methoxide concentration in dilute solution. At higher concentrations, ion-pair formation complicates the situation. This is especially true for k_1, as in addition to influencing ionic strength, ion-pairing reduces methoxide nucleophilicity.[28]

Increased stability in the order **33a** < **50h** < **19a** is the result of an increase in k_1 and a decrease in k_{-1}. Structural changes in this sequence affect k_{-1} to a greater extent than k_1. Since **33a**, **50h**, and **19a** are structurally similar, activation entropy differences have been assumed small, and the rate constants have been assumed to reflect differences in activation enthalpies.[28] If a "correct" ΔH^*_{-1} is chosen for **19a** (16.2 kcal),[28] reasonable agreement is obtained between Miller's predicted activation parameters and those determined experimentally. Entropy effects do not cancel in other structually related systems, however,[27] and the assumption that they do for the series **33a**, **50h**, and **19a** is probably an oversimplification. Replacing a 2-NO_2 group in **19a** with a 2-cyano group causes both k_1 and k_{-1} for **39a** to be more entropy dependent than enthalpy dependent[27] (*vide infra*).

The entropies of activation for the unimolecular decomposition of all the 1,1-dialkoxy σ complexes listed in Table XIX are strongly negative.[227] This is consistent with a shift of delocalized charge in the σ complex to incipient methoxide ion in the activated complex. An increased solvation requirement at the transition state and a concomitant negative entropy of activation are then expected.[28]

The solvent deuterium isotope effect (methanol, methanol-O-*d*) on the equilibrium constants and rate constants for formation and decomposition of **33a** and **39a** have been reported.[27,28]

	K^H/K^D	k_1^H/k_1^D	k_{-1}^H/k_{-1}^D
33a	0.38	0.51	1.34
39a	0.45	0.6	1.36

The rate constants for formation of the complexes are considerably enhanced, whereas those for decomposition are smaller, in the deuterated solvent. The values are in the range of secondary isotope effects.[28] If a primary isotope effect is associated with a process in which methoxide is formally protonated as it leaves the complex, then these secondary effects indicate methoxide is only solvated at the transition state for decomposition. The more positive entropy of activation for the decomposition of **39a** in methanol-O-*d* relative to methanol (Table XIX) has been attributed to a higher structural order for the deuterated solvent.[27] The solvation requirement in going from **39a** to the activated complex for decomposition, where charge is being localized on incipient methoxide, is then expected to be less in methanol-O-*d*. A similar entropy difference has been observed for the decomposition of **39a** in water and deuterium oxide.[27] The rate of decomposition of **39a** in water,[27] like that of **19a**[228] and **50d**,[91] is strongly catalyzed by acid.

The spirocyclic σ complexes **21**, **33d**,[84,229] and **50d**[70,71,84] have relative stabilities which parallel their noncyclic analogs: **33d** < **50d** < **21**. The equilibrium constant for **50d** (Table XIX) is 50% higher than that for its dimethoxy analog **50h**.[84]

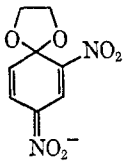
(225) This is only an approximation, as the error in values of the equilibrium constants for **33f** and **19a** are not taken into account.

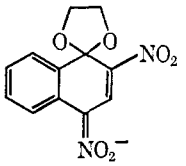
(226) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p 177.

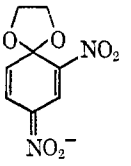
(227) The entropy of activation for the decomposition of **50i** is large and positive as it decomposes to neutral reactants with a concomitant decrease in solvation.[188]

(228) J. Murto and J. Vainionpää, *Suom. Kemistilehti B*, 39, 133 (1966).

(229) S. S. Gitis and A. Ya. Kaminskii, *J. Gen. Chem. USSR*, 30, 3771 (1960).

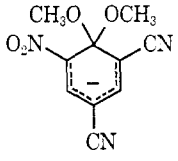

33d

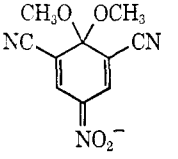

50d

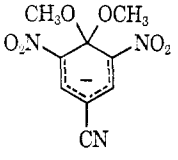

21

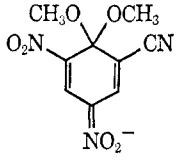
Similar increased stability might be expected for **33d** and **21** relative to **33a** and **19a**. The enhanced stability of **50d** is reflected by activation parameters for its formation and decomposition relative to those of **50h**. The latter has a higher enthalpy of activation for formation and a lower enthalpy of activation for decomposition than **50d**. This favors **50d** energetically but is partially compensated by entropy effects (Table XIX) which reflect increased order in **50d** relative to **50h**.

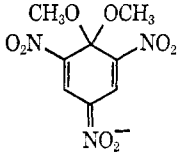
The effect of substituent electronegativity and orientation on 1,1-dimethoxy-2,4,6-trisubstituted cyclohexadienate stability is illustrated by the following sequence: **39c** < **39d** < **39b** < **39a** < **19a**.[27,85,86] The equilibrium constants for complex formation in methanol at 25° are 10, 34, 280, 2600, and 17,000


39c


39d

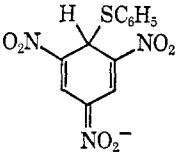

39b

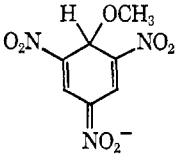

39a

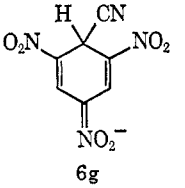

19a

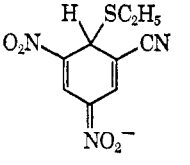
l. mol^{-1}, respectively, for **39c**, **39d**, **39b**, **39a**, and **19a**. The equilibrium constant ratios, K_{19a}/K_{39d} = 500 and K_{19a}/K_{39a} = 1700, illustrate the greater stabilizing effect of a NO_2 relative to a cyano group, especially in the *para* position. This is in accord with relative stabilities of the isomeric dinitrocyclohexadienates (*vide supra*), and with the greater effectiveness of a *para*, relative to an *ortho* NO_2 group, in methoxydehalogenations.[230,231] If the starting aromatics are of equal free energy, the difference in stability between **19a** and **39b**, as well as between **39a** and **39c**, is ~3.5 kcal. This is probably a good measure of the difference in stabilizing effect of a *para* NO_2 and *para* cyano group in 1,1-dimethocyclohexadienates, as the free-energy difference between the complexes and between the starting aromatics resulting from steric compression of *ortho* substituents should cancel. More information on comparative substitutent effects in these complexes will be available when the relative stabilities of 1,1-dimethoxy-2,4-dicyano- and 2,4,6-tricyanocyclohexadienates are determined.[232] Equilibrium constant differences between **19a**, **39a**, and **39b** result from larger changes in k_{-1} than in k_1 (Table XIX). The effect of increasing DMSO concentration in methanol on the rate of formation and decomposition of **39c** has been studied.[86] As expected, K_{39c} increases with increasing DMSO concentration, a result of both increasing k_1 and decreasing k_{-1}. The correlation between rate constants and DMSO concentration is linear and has been used to obtain extrapolated equilibrium constant values in methanol for complexes which are very unstable in this solvent.[86] Increased stability in highly concentrated DMSO solutions has been attributed to decreased hydrogen bonding power of DMSO.[86] It is well known that small anions of high-charge density are much less solvated in dipolar aprotic solvents like DMSO than in protic solvents. The nucleophilicity of methoxide in solutions of high DMSO concentration is thus enhanced, with a concomitant increase in k_1. The decrease in k_{-1} can be rationalized similarly, as the charge-delocalized anionic complex is better solvated in DMSO than in methanol, thus increasing its stability in the former solvent. It has been pointed out that these arguments are oversimplifications, as activity coefficient changes of reactants and activated complexes, solvent sorting, and ion-pairing have not been considered.[86] Studies of the formation of isomeric 1,1-and 1,3-dimethoxycyclohexadienates across the entire DMSO–methanol solvent range, and determination of activity coefficients for these species and for the activated complexes leading to them, are now in progress.[233] Similar solvent effects on the stability of the 1-cyano-2,4,6-trinitrocyclohexadienate complex (**6g**) have been observed. As the alcohol solvent gets progressively more hydrocarbon-like in character (*i.e.*, methanol, ethanol, 1-propanol, etc.) the stability of **6g** increases[219] (Table XIX). This is expected if cyanide ion is more strongly solvated by the lower molecular weight alcohols. The equilibrium constant for **6g** in *t*-butyl alcohol is over 10,000 times that in methanol. Very large equilibrium constants for **6g** are also observed in chloroform, acetone, and acetophenone,[220] but there is no simple relation between the magnitude of K_{6g} and solvent dielectric constant. A linear relationship between log K_{6g} and E_T has been observed for alcoholic solvents, but the significance of this relationship is not clear.[219]

Thiophenoxide, methoxide, cyanide, and thioethoxide adducts of 1,3,5-TNB in methanol have increasing stability in the following order (Tables XIX and XX): **6l** < **6a** < **6g** < **6m**.


6l


6a


6g

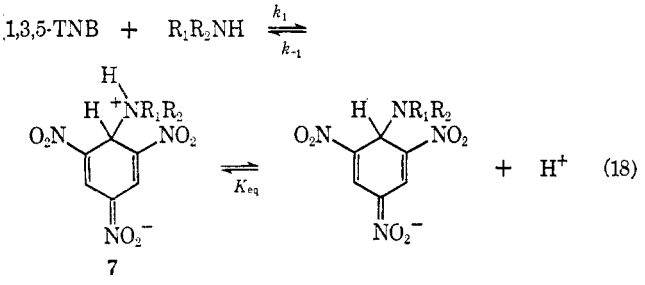

6m

This stability sequence can be taken as an approximate measure of the thermodynamic basicity[5,18] of these nucleophiles in this solvent. Relative acidity of the conjugate acids HSC_2H_5, HCN, etc., shows clearly that those factors influencing affinity for hydrogen are not simply related to those influencing affinity for aromatic carbon. When both modes of interaction can occur, as in picramide, the observed result is very much dependent on the nucleophile. With sulfur bases (sulfite and thio-

(230) J. F. Bunnett and R. J. Morath, *J. Amer. Chem. Soc.*, 77, 5051 (1955).
(231) W. Greizerstein and J. A. Brieux, *ibid.*, 84, 1032 (1962).
(232) These complexes have recently been mentioned in ref 27 and 86, but equilibrium constants were not reported.
(233) J. W. Larson personal communication.

alkoxide) only addition occurs, whereas with oxygen bases (methoxide and hydroxide) both addition and NH proton abstraction are observed (section II.B).

Addition of primary or secondary amines to 1,3,5-TNB initially yields a zwitterion, which then loses an alkylammonium proton to give the anionic complex (*vide supra*). The mechanistic aspects of these processes have been studied recently in some detail by a temperature-jump technique.[49] Earlier studies, carried out in DMSO, provided equilibrium constants for the interaction of 1,3,5-TNB with 2 equiv of amine to give the anionic complex as its alkylammonium salt.[50] Results for the methylamine and diethylamine complexes (**6e**), Table XX, indicate that decreased complex stability may be associated with increasing bulk of the N-alkyl group. Both these complexes are formed *via* zwitterionic intermediates which cannot be detected by pmr. The rates of formation and decomposition of zwitterions like **7** (Table XX) have been measured in aqueous dioxane[49] by determining



(18)

7

a relaxation time, τ, for reaction 18, where in a large excess of amine

$$\frac{1}{\tau} = k_1[R_1R_2NH] + k_{-1}\frac{[H^+]}{[H^+] + K_{eq}}$$

Plotting $1/\tau$ *vs.* $[R_1R_2NH]$ yields straight lines with slopes equal to k_1 and intercepts dependent on $[H^+]$, *i.e.*

$$1/(\text{intercept}) = k_{-1}^{-1} + K_{eq}/k_{-1}[H^+]$$

Plotting reciprocal intercepts *vs.* $[H^+]^{-1}$ gives new intercepts equal to k_{-1}^{-1} and slopes equal to K_{eq}/k_{-1}. The results for pyrrolidine, piperidine, and *n*-butylamine complexes (**7**) are shown in Table XXI.[49] It has been noted that the zwitterionic

Table XXI

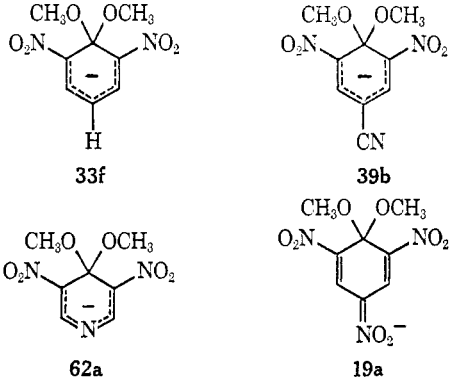
Equilibrium and Rate Constants for Amine–1,3,5-TNB Complex Formation in 90% Aqueous Dioxane

	k_1, M^{-1} sec^{-1}	$k_1 \times 10^4$, sec^{-1}	k_1/k_{-1}, $l.\ M^{-1}$	$K_{eq} \times 10^{11}$ $(R_1R_2NH_2^+)$	$K_{diss}{}^a \times 10^{11}$ $(R_1R_2NH_2^+)$
n-Butylamine	123	2	0.006	52.8	2.1
Piperidine	3000	1.5	0.2	1.5	0.76
Pyrrolidine	8100	2.5	0.3	2.1	0.50

[a] Determined in aqueous solution.[49]

n-butylammonium complex **7** (R_1 = H, R_2 = *n*-C_4H_9) is about 25 times more acidic than free butylammonium ion, K_{eq}/K_{diss} = 25, whereas the zwitterionic complexes of piperidine and pyrrolidine have K_{eq}/K_{diss} equal to 2 and 4, respectively. Increased acidity of the zwitterion has been attributed to the inductive effect of C-1, which may be electron deficient,[23] compensated to some extent by intramolecular hydrogen bonding with the *ortho* NO_2 groups, which weakens acid strength.[49,234,235]

The aza group is very effective in stabilizing negative charge in an anionic σ complex, as **52a** has an equilibrium constant in the range of 3000–5000 l. mol^{-1} in methanol at 25° (Table XX).[85,97] The relative stability of 1,1-dimethoxy-2,6-dinitro-4-substituted cyclohexadienate complexes is then **33f** < **39b** < **62a** < **19a**. The stability difference between **19a** and **52a** is



33f **39b**

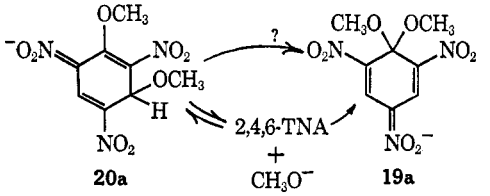
62a **19a**

small. It has been attributed to the greater effectiveness of NO_2 in delocalizing negative charge,[97] partially compensated by more effective solvation of the aza group.[97,236]

2. Isomeric Addition

During the past few years it has become clear that addition to an electron-deficient aromatic commonly occurs at both substituted and unsubstituted positions. The various factors which determine the mode of addition in any particular case are not completely understood. Steric compression, solvation of, and charge delocalization in the isomeric complexes, and in the transition states leading to them, are all important. These factors are in many instances interdependent, which makes it difficult to simply explain relative complex stability. Certain nucleophiles add to electron-deficient aromatics only at unsubstituted positions, whereas others add only at substituted positions. The position of attack is many times solvent dependent. The relative importance of various factors influencing the stability of isomeric complexes is now considered.

The pmr spectrum of 2,4,6-TNA and sodium methoxide in DMSO–methanol solution characterizes the rapid formation of **20a**, followed by slow conversion of **20a** to **19a**[5,51,69] (section II.B). This sequential process is very rapid in pure methanol and cannot be detected by pmr in this solvent.

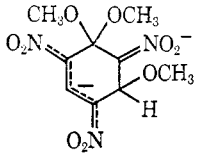


20a **19a**

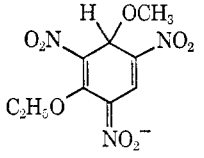
It has been detected by calorimetry in methanol, although no structural identification of **20a** was possible.[218] Formation of **19a** is catalyzed by increasing concentrations of methanol in

(234) M. Eigen, *Angew. Chem. Int. Ed. Engl.*, 3, 1 (1964).
(235) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p 181.
(236) G. Illuminati, G. Marino, and G. Sleiter, *J. Amer. Chem. Soc.*, 89, 3510 (1967).

DMSO and by methoxide ion.[51,69] There is no experimental evidence that **20a** is a direct precursor to **19a**. The least contrived sequence is one in which **19a** and **20a** are both in equilibrium with 2,4,6-TNA, although methoxide ion catalysis is suggestive of direct conversion through an intermediate like **44h**. Two reaction coordinates, illustrating the interconversion of **19a**, **20a**, and 2,4,6-TNA *in methanol*, have been considered.[5,98] These are reproduced schematically in Figure 14. The dotted curve is hypothetical but does approximate the experimental observations in methanol, where **20a** *cannot be observed* by pmr. If the transient species detected in methanol by calorimetry is **20a**, then the solid curve is more appropriate. This is supported by data which show attack at unsubstituted ring positions is usually faster than attack at substituted positions (see k_1 for complexes **6a**, **6g**, and **7** compared to **19a**, Table XIX). The solid curve has been derived using experimental values of the enthalpy of activation for the decomposition[217] and formation[27] of **19a**, and estimated parameters for **20a**.[5,68] Activation parameters for the latter complex were assumed similar to those for **20c**. In fact, **20c** has not been



44h



20c

characterized structurally in methanol, and although it probably does form from trinitrophenetole and methoxide as a precursor to the 1,1 complex, steric compression between the ethoxyl and *ortho* NO_2 groups should be considerably greater than in **20a**. Both curves in Figure 14 were constructed neglecting entropy effects. The assumption that reaction coordinates for formation of **20a** and **20c** are similar is thus tenuous. The present experimental evidence does suggest that **19a** is thermodynamically more stable than **20a** in methanol, where the latter is kinetically favored. The greater stability of **19a** has been attributed to steric compression in 2,4,6-TNA (resulting from coplanarity of the methoxyl and 2,6-NO_2 groups) which is released on formation of **19a**, but not on formation of **20a**.[69] This is supported by the relative stabilities of **19a** and **6a** (Table XIX). The activated complex **84**, leading to **19a**, has been assumed more strained than **85**, leading to **20a**, thus accounting for more rapid formation of the latter.[69] Solvent effects are considerable as the lifetime of **20a** in DMSO is greater than in methanol. This could result from a lower energy solvolytic route leading directly from **19a** to **20a** through some intermediate species resembling **86**. Differential solvation of the activated complex **84**, relative to **85**, might also be important. Since partial negative charge in the ring of **84** or **85** might tend to localize on the NO_2 group *para* to developing tetrahedral carbon, steric hindrance to solvation and to coplanarity of this group with the ring in **85**, caused by the adjacent methoxyl, will favor **84**. This would be especially

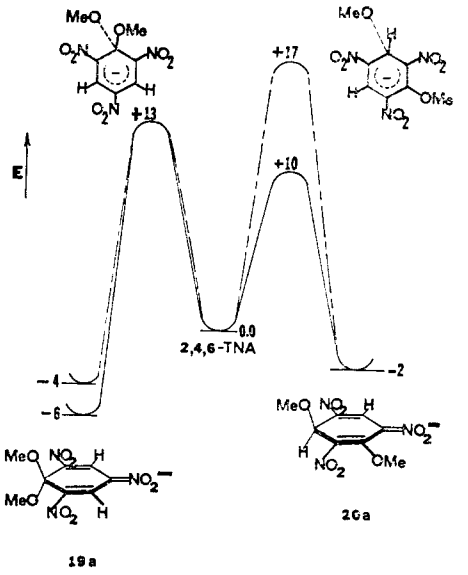
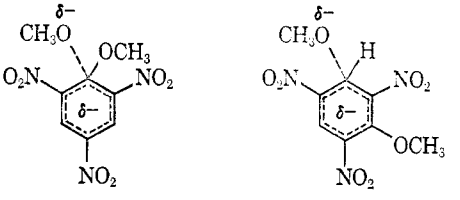
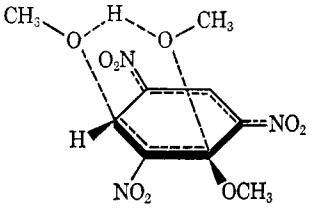


Figure 14. Reaction coordinate for interconversion of **19a** and **20a** in methanol.[98,5]

true in methanol, as the more localized the charge on *para* NO_2, the more effective methanol will be in providing for charge dispersal by solvation. Increasing concentrations of DMSO might then be expected to favor **85**, and hence **20a**.



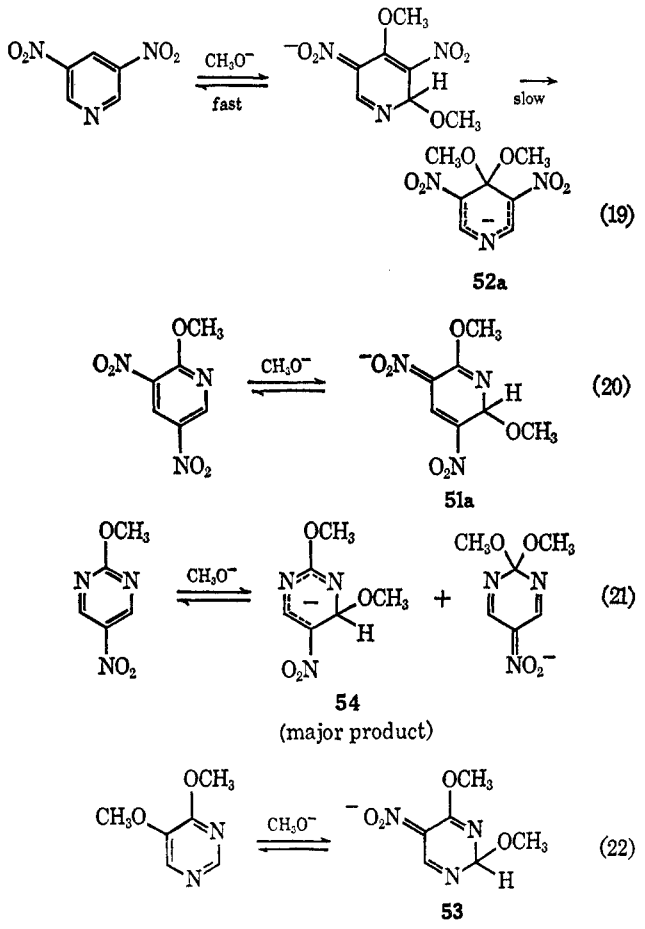
84 85



86

The less sterically hindered pyridine and pyrimidine complexes **53** and **54** are *more* stable than their 1,1-dimethoxy isomers in both methanol and DMSO.[98] The reactions of methoxide with methoxydinitropyridines[95,97,237] and methoxynitropyrimidines[98] in methanol–DMSO are summarized in eq 19–22. The reaction of methoxide with 4-methoxy-3,5-dinitropyridine is analogous to that of 2,4,6-TNA, and leads to **52a** as the thermodynamically most stable product. If the methoxyl in the starting aromatic is not flanked by two NO_2 groups, as in 2-methoxy-3,5-dinitropyridine, steric compression is absent, and the driving force provided by strain release upon complexation is not available. Attack thus occurs at C-6 to give **51a**. The 3-methoxyl in **51a** can assume a conformation *anti* to the adjacent NO_2 group, thus allowing for effective solvation of this function.

(237) M. E. C. Biffin, J. Miller, A. G. Moritz, and D. B. Paul, *Aust. J. Chem.*, in press.

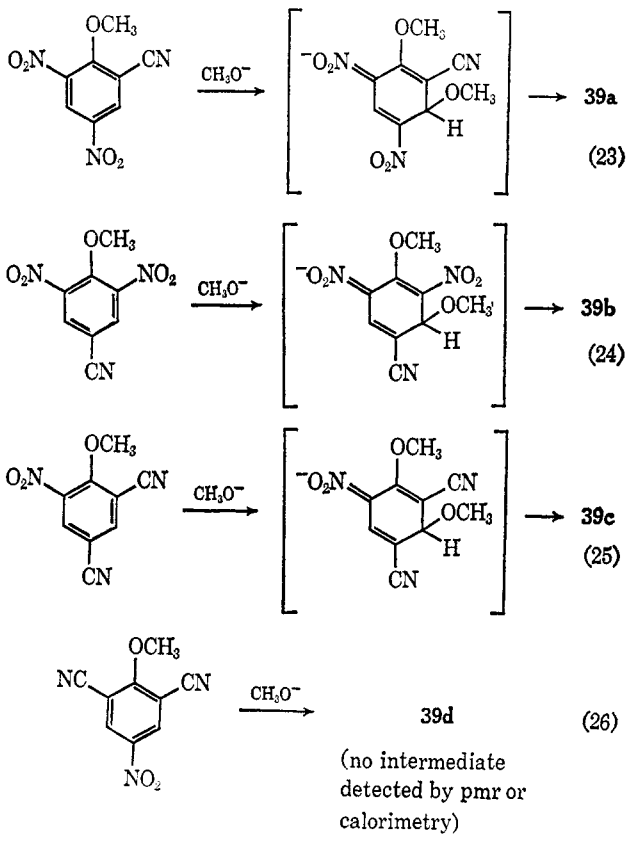


Isomeric complexes also result from attack of carbanions on 3,5-dinitrobenzonitrile[87] and from methoxide attack on 3,5-dinitropyridine,[237] but 5-nitropyrimidine yields only the complex resulting from attack at C-2.[98] The methoxynitropyrimidines add methoxide to give **53** and **54** as the main products.

Transient 1,3-dimethoxy complexes are also observed when methoxide is added to cyanodinitro- and dicyanonitroanisoles (eq 23–26). These are eventually converted to the thermodynamically more stable 1,1-dimethoxy complexes,[27,86] at a rate which is increased by increasing concentrations of methanol in DMSO. Arguments similar to those advanced to rationalize the formation and decomposition of the transient, **20a**, can also be extended to eq 23–26. The diminished steric requirement and electronegativity of a cyano relative to a NO_2 group complicate detailed interpretation. One point is clear. Transient 1,3 complexes which have a cyano or less electronegative group *para* to the tetrahedral ring carbon have not been detected by pmr or calorimetry.

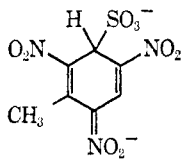
Preliminary reports of a transient σ-complex precursor to **33a**, detected by visible spectroscopy, must be considered quite tenuous, as no structural characterization has been made.[92]

In chloroform, attack of cyanide occurs at C-3 of 2,4,6-trinitrotoluene and C-1 of 2,4,6-trinitrobenzaldehyde.[77] Many aromatic substrates suffer attack *only* at unsubstituted positions. Methoxide attacks picramide and N,N-dimethylpicramide, and sulfite attacks 2,4,6-TNA, 2,4,6-trinitrotoluene, 2,4,6-trinitrobenzaldehyde, picramide, and substituted picramides, only at C-3 (section II.B). The preference for methoxide attack at C-3 of N,N,-dimethylpicramide has been explained on the basis of differential steric effects.[5] The transition state

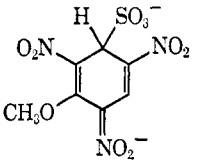


for formation of the C-1 adduct is assumed to be more strained than that for addition at C-3, to such an extent that even if the C-1 complex is thermodynamically more stable, it is not favored kinetically. The dimethylamino group is lost when methoxide attacks C-1, and the complex cannot be observed in any case.[69] Sulfite attack at C-3 in all the 1-substituted 2,4,6-trinitro aromatics may be a consequence of the formal negative charge on sulfite in the complex, a feature which distinguishes all the sulfite complexes from those formed from mononegative nucleophiles and favors their formation in aqueous solution. Anionic sulfite, in the complex and as a doubly charged anion, should have a much greater solvation requirement than methoxide or cyanide. Steric hindrance to attack at a ring-substituted position could be quite severe, as could hindrance to solvation of sulfite in the complex. Attack at an unsubstituted position may therefore be kinetically and thermodynamically favored. These arguments are oversimplified as coplanarity of the NO_2 groups and ring in the isomeric complexes and the solvation requirements of these groups have not been considered. In aqueous solution such effects should be quite important.

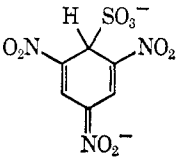
The equilibrium constant for the sulfite–1,3,5-TNB complex (**6k**) is ~200–500 l. mol^{-1} in aqueous solution (Table XIX). All the sulfite complexes are quite stable in water, as expected for doubly charged anions. In aqueous solution, the sulfite complexes of 2,4,6-trinitrotoluene, 2,4,6-trinitrobenzaldehyde, 2,4,6-TNA, and picramides have increasing stability in the following order: **87** < **20g** < **6k** < **88** < **20k-1** < **20k-2** < **20k-3**. The 2,4,6-trinitrotoluene–sulfite complex (**87**) is probably least stable because of the electron-donating methyl group. The rather large increase in stability of the 2,4,6-trinitrobenzaldehyde, picramide, and N-methylpicramide complexes may result, in part, from stabilization due to hydrogen bonding between a NO_2 group and the aldehydic or



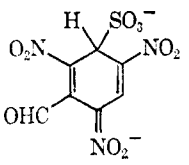
87



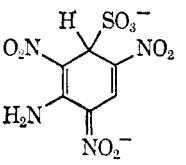
20g



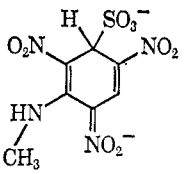
6k



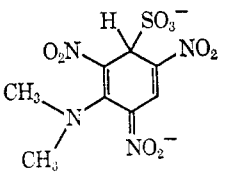
88



20k-1



20k-2

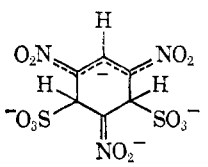


20k-3

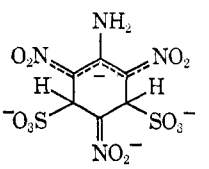
amino protons.[5] In the N,N-dimethylpicramide complex, and in the N-methylpicramide complex, increased stability has been attributed to steric hindrance, which tends to rotate the NO_2 groups out of the ring plane, facilitating sulfite addition at C-3.[5] This argument is not supported by the small equilibrium constant for **20j** in methanol (Table XX).

3. *Diadducts—The Propenide Complexes*

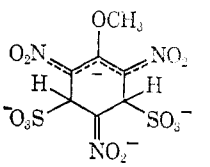
The stability of several complexes containing 2 equiv of sulfite or methoxide per equivalent of aromatic has been measured (Table XX). These complexes are formed most easily in protic solvents such as methanol and water. Since they contain more localized negative charge than 1:1 complexes, they are not well solvated in aprotic solvents like DMSO. Measurement of equilibrium constants for 1:2 complexes is difficult because high concentrations of nucleophile are necessary to convert a significant amount of aromatic substrate to complex. In addition, such equilibrium constants are strongly dependent on ionic strength, so that extrapolations to infinite dilution are necessary. Propenide complex stability increases with increasing size of the substituent attached to the central propenide carbon atom; **44b** < **44d-3** < **44c** < **44d-2** < **44d-3**.



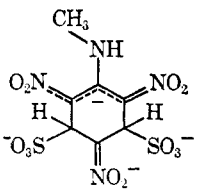
44b



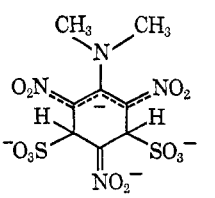
44d-3



44c



44d-2



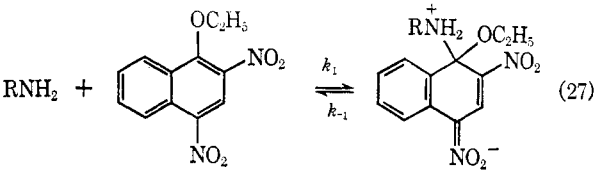
44d-1

This increase in stability has been attributed to increasing release of steric compression between the central propenide substituent and the *ortho* NO_2 groups on going from the starting aromatic to the 1:2 complex.[5] Such decreased steric compression is thought to arise from decreased ring coplanarity relative to the starting aromatic, resulting from extensive disruption of conjugation in the 1:2 complex. An argument more consistent with those presented to explain 1:1 sulfite complex stability would consider the propenide substituent as forcing the *ortho* NO_2 groups into a conformation which allows for more effective solvation of the adjacent sulfite. Stabilization gained in this way must more than compensate for destabilization resulting from diminished delocalization, caused by noncoplanarity of the propenide NO_2 groups.

4. *Formation and Decomposition of Observable σ Complexes in Aromatic Nucleophilic Substitution*

A good deal of evidence has been obtained from steady-state kinetic studies, which supports the conclusion that aromatic nucleophilic substitutions proceed through metastable intermediate σ complexes.[13, 15, 17, 238–240] In most cases the intermediate complex is not directly observed. Until recently, there has been no direct evidence as to whether the main intermediate in aromatic nucleophilic substitutions by amines is zwitterionic or the conjugate base of an initially formed zwitterion. Recent kinetic studies of the separately observable formation and decomposition of intermediate σ complexes in aromatic nucleophilic substitutions are of interest in this regard.[188, 215] Such intermediates have been detected by visible spectroscopy during substitution on 1-substituted 2,4-dinitronaphthalenes[188] and 2,4,6-trinitrobenzenes.[215]

In DSMO, evidence for the substitution sequence of eq 27–30 has been obtained.[188] The reaction occurs in two



(27)

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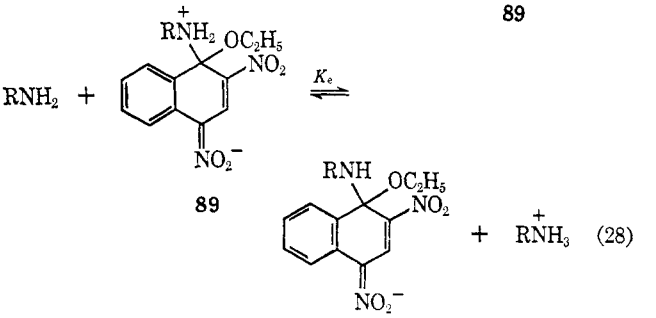
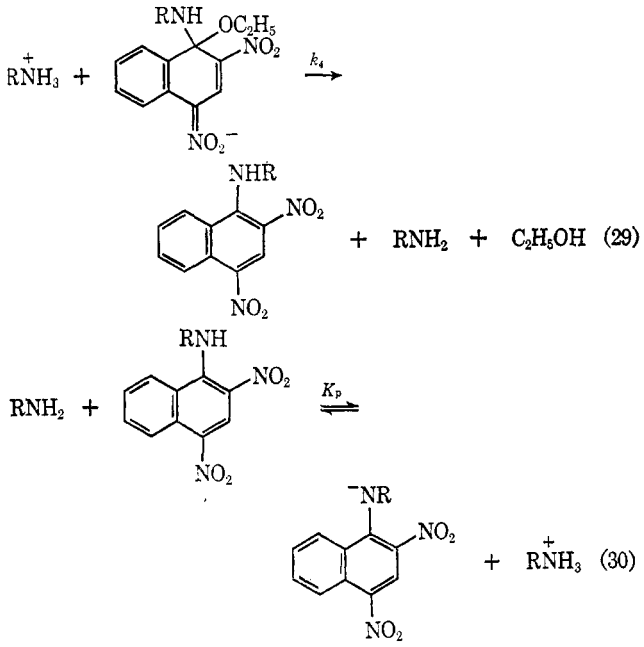


(28)

stages. Initially, the visible spectrum of the starting ether very rapidly changes to a spectrum characteristic of naphthalene σ complexes (section II.C). The change can be observed by stopped-flow spectrophotometry. It is followed by slow change to a spectrum characteristic of the conjugate base of a 2,4-dinitronaphthylamine. Both the equilibrium constants K_e and K_p, as well as the rate constants k_1 and k_4, have been

(238) J. F. Bunnett and J. H. Randall, *J. Amer. Chem. Soc.*, **80**, 6020 (1958).
(239) J. F. Bunnett and R. H. Garst, *ibid.*, **87**, 3879 (1965).
(240) J. F. Bunnett and G. T. Davis, *ibid.*, **82**, 665 (1960).

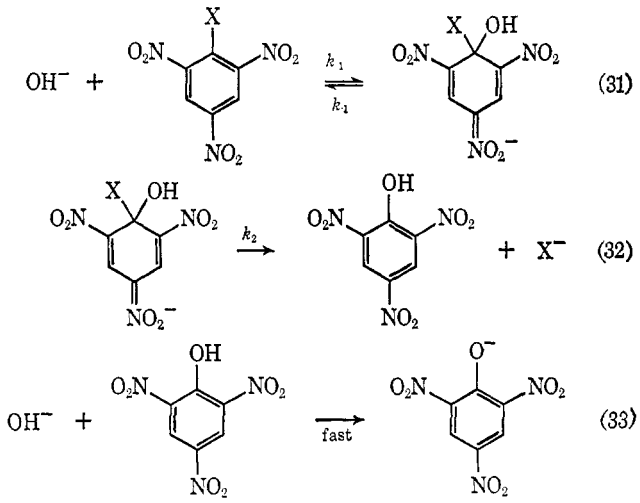


determined. An equilibrium constant K_i was defined as

$$K_i = (k_1/k_{-1})K_e = \frac{[\text{anionic complex}][\overset{+}{\text{R}}\text{NH}_3]}{[\text{starting aromatic}][\text{RNH}_2]}$$

The constant value of K_i ($\sim$540 M^{-1} for *n*-butylamine) at various concentrations of amine and alkylammonium ion indicates that the intermediate exists predominantly as the anionic complex and not its zwitterionic precursor. This is consistent with results obtained for 1,3,5-TNB–amine complexes in DMSO and in aqueous dioxane. Since the first stage of the reaction of amine with 1-ethoxy-2,4-dinitronaphthalene (eq 27 and 28) was found to be first order in amine and first order in starting aromatic, formation of the intermediate complex is not base catalyzed. This is in accord with steady-state kinetic studies of similar systems.

Under appropriate reaction conditions, transient σ-complex intermediates can be detected in the alkaline hydrolysis of picryl chloride and 2,4,6-TNA.[215] In the latter case, spectra characteristic of the intermediate 2,4,6-trinitrocyclohexadienate anion can be observed for about 30 sec before the yellow color of picrate anion appears. The kinetics of the process (eq 31, 32, and 33) have been studied using stopped-flow spectrophotometric methods. The rate constants k_1 and k_{-1} were reported to be much larger than k_2 under the experimental conditions used in the study, and the substitution was characterized as a rapid preequilibrium followed by a slow step. The visible spectrum of the intermediate complex exhibits the characteristic double maximum of anionic σ complexes (section II.C). A reaction scheme involving equilbration between the C-3 hydroxide adduct of picryl chloride or 2,4,6-TNA, and the corresponding parent aromatics, may be more appropiate, however. Hydroxide is undoubtedly a worse leaving group than chloride, and a mechanistic sequence in which $k_{-1} \gg k_2$ is unreasonable.[241]



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(241) The author thanks Professor C. Bernasconi for pointing out this discrepancy.