

*Studies in Spectroscopy. Part VII.\* Spectroscopic Evidence for  
Molecular-compound Formation with Iodine Cyanide.*

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Iodine cyanide acts as a weak Lewis acid and forms molecular compounds with neutral-molecule Lewis bases such as alcohols, ethers, nitriles, carbonates, ketones, amides, amines, and halogen compounds. Solvent-solute interaction is demonstrated by ultra-violet and infra-red spectroscopic studies, and the nature of the molecular compound is discussed. The relative basicities of certain of the neutral-molecule bases towards iodine cyanide can be assessed. Both iodine and iodine cyanide produce distinct changes in the infra-red spectra of the stronger Lewis bases, but only weak complex formation takes place with cyanogen bromide. Compound formation cannot be detected between iodine or iodine cyanide and benzene or hex-1-ene by infra-red spectroscopy although these solvents markedly change the ultra-violet spectra of iodine.

THE formation of molecular complexes between iodine, bromine, iodine monochloride, or iodine monobromide (Lewis acids) and organic compounds such as aromatic hydrocarbons, ethers, alcohols, or ketones (Lewis bases) has been established by use of ultra-violet spectroscopy (see Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703; Mulliken, *ibid.*, 1950, **72**, 600; 1952, **74**, 811); Glusker, Thompson, and Mulliken (*J. Chem. Phys.*, 1953, **21**, 1407) interpreted small changes in the infra-red spectra of electron-donor solvents containing iodine as due to complex formation. Molecular-complex formation was recently postulated (Part V, *J.*, 1953, 2622) to explain the marked effect of solvent on the ultra-violet spectra of polyfluoro-iodo-compounds such as heptafluoroiodopropane. The present paper presents ultra-violet and infra-red spectroscopic studies which indicate that complex formation or marked solvent-solute interaction occurs with iodine cyanide, a compound which contains iodine linked to carbon and shows distinct similarity to heptafluoroiodopropane.

Fairbrother (*J.*, 1950, 180) presented clear evidence from measurement of dielectric polarisation that iodine cyanide undergoes a polarisation in an electron-donor solvent similar to that shown by molecular iodine. He found its dielectric polarisation to be substantially higher in dioxan, diisobutylene, or benzene than in carbon tetrachloride. In these solvents it was substantially non-conducting and would thus be expected to have a normal molecular weight. Fairbrother also concluded that solvent-solute interaction

\* Part VI, *J.*, 1954, 691.

occurred from the ultra-violet light absorption of iodine cyanide in carbon tetrachloride, diisobutylene, and dioxan, since there was a displacement towards the shorter wave-lengths in the electron-donor solvents. These spectroscopic studies were limited by the type of apparatus used, since only absorption of long wave-length ( $>260\text{ m}\mu$ ) could be recorded. Gillam's earlier study (*Trans. Faraday Soc.*, 1933, 29, 1132) also showed no maximum in the absorption curve of iodine cyanide down to  $240\text{ m}\mu$ .

In the present work the ultra-violet spectra of solutions of iodine cyanide have been examined over a much wider range. In light petroleum or in cyclohexane solution, it shows a maximum near  $242\text{ m}\mu$  (Table 1, Fig. 1), and observation of the position or the disappearance of this when iodine cyanide is dissolved in other solvents enables complex

TABLE 1. Ultra-violet spectra of iodine cyanide.

Solvent	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$	$\lambda_{\text{min}}$	$\epsilon_{\text{min}}$	Solvent	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$
Light petroleum ....	242	150	214	65	Bu <sup>t</sup> Cl .....	229	270
cycloHexane .....	241	170	215	70	(C <sub>6</sub> F <sub>6</sub> ) <sub>2</sub> O .....	225	— *
SiCl <sub>4</sub> .....	244	180	—	—	BF <sub>3</sub> ·Et <sub>2</sub> O .....	225 †	220
Bu <sup>n</sup> Cl .....	232	240	—	—	CF <sub>3</sub> ·CH <sub>2</sub> ·OH .....	224 †	180

\* Saturated solution at 20°.

† Minimum below  $210\text{ m}\mu$ .

Solvent	$\lambda = 260$	Values of $\epsilon$ for $\lambda$ as named						$\lambda_{\text{inf.}} \ddagger$	$\epsilon_{\text{inf.}}$
		250	240	230	220	210	170		
MeOH .....	55	80	125	200	310	470	—	—	
EtOH .....	—	90	140	225	340	—	215	380	
Pr <sup>i</sup> OH .....	80	110	165	250	360	—	—	—	
HO·CH <sub>2</sub> ·CH <sub>2</sub> ·OH	97	133	197	291	405	528	—	—	
CH <sub>2</sub> Cl·CH <sub>2</sub> ·OH ...	77	111	168	244	339	460	—	—	
CH <sub>3</sub> ·CN .....	83	114	157	258	413	775	—	—	
(CH <sub>3</sub> ) <sub>2</sub> CO <sub>2</sub> .....	70	87	122	188	237	—	240—248	110	
Dioxan .....	85	121	193	331	540	—	—	—	
CH <sub>3</sub> ·CH·CH <sub>2</sub> ·O ...	79	112	160	223	354	—	—	—	
Et <sub>2</sub> O .....	76	108	160	233	310	495	—	—	
Pr <sup>n</sup> Cl .....	111	130	170	219	280	—	—	—	
Pr <sup>i</sup> Cl .....	117	154	215	274	310	—	—	—	

‡ These inflections are only slight.

formation to be clearly demonstrated. By analogy with the results for heptafluoroiodopropane and similar compounds recorded in Part V, the spectrum of iodine cyanide in light petroleum or cyclohexane is taken as essentially the same as that of iodine cyanide vapour, *i.e.*, to be the spectrum when solvent-solute interaction is negligible. Silicon tetrachloride is a non-polar solvent similar to carbon tetrachloride, but with the advantage that it is transparent to ultra-violet light at much shorter wave-lengths; the spectrum of iodine cyanide in silicon tetrachloride is thus very similar to that in light petroleum.

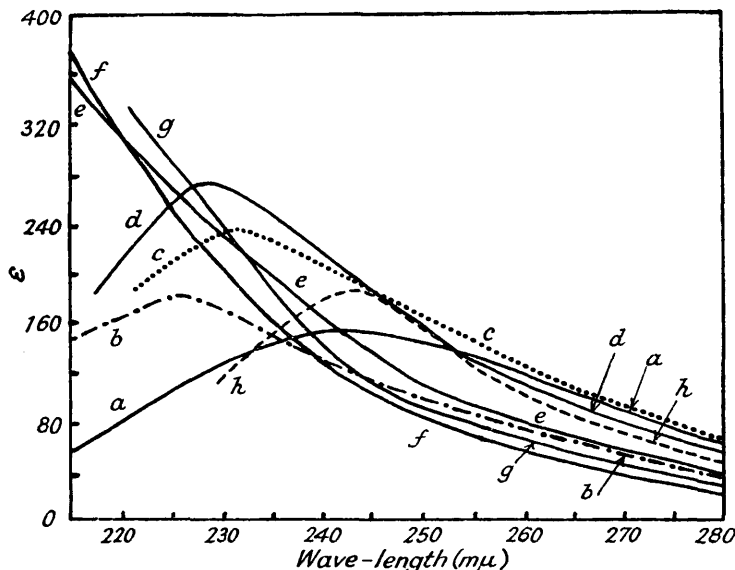
The other solvents used reveal solvent-solute interaction, and this is attributed to molecular-complex formation between iodine cyanide and a neutral-molecule base B, of the 1 : 1 or possibly the 1 : *n* donor-acceptor type. Iodine cyanide acts as a neutral-molecule Lewis acid by virtue of the incompletely satisfied electronegativity of its iodine atom, just as heptafluoroiodopropane, containing the strongly electronegative C<sub>3</sub>F<sub>7</sub> group, acts as a weak Lewis acid (cf. N≡C ← I and C<sub>3</sub>F<sub>7</sub> ← I). The donated electron in the structure Ψ[B<sup>+</sup>-(ICN)<sup>-</sup>] is derived from a lone pair of electrons in B (ROH, OR<sub>2</sub>, RCl, RCN, R<sub>2</sub>CO), and it is suggested that the wave-functions are mainly of the [(ICN)·(B)] van der Waals type [*e.g.*, R<sub>2</sub>O<sup>+</sup>-(I-CN)<sup>-</sup>] with formation of a weak covalent bond between (ICN)<sup>-</sup> and the odd electron of B<sup>+</sup>. Resonance in the excited state could involve structures similar to those suggested by Mulliken for iodine complexes and postulated in Part V for complexes involving heptafluoroiodopropane and other polyhalogeno-iodo-compounds.

As the strength of the neutral-molecule base increases, the absorption maximum of iodine cyanide is shifted further to the blue, and in many cases lies below 200—210  $\text{m}\mu$  which is the limit of the instrument used (Table 1, Fig. 1). In the relatively strong neutral-molecule bases, methanol, ethanol, and isopropanol, iodine cyanide shows only general absorption or an ill-defined inflection. Its solutions in ethylene glycol or 2-chloroethanol

similarly show only general absorption. Trifluoroethanol is distinctly less basic than ethanol (Haszeldine, *J.*, 1953, 1757), and the spectrum in this solvent is displaced towards that in light petroleum (Table 1). Comparison of the shifts relative to the maximum in light petroleum gives an approximate measure of the relative basicities of the alcohols towards iodine cyanide:  $\text{MeOH} > \text{EtOH} > \text{Pr}^i\text{OH} > \text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH} > \text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} > \text{CF}_3\cdot\text{CH}_2\cdot\text{OH}$ .

Ethers are powerful Lewis bases, and ethyl ether, dioxan, and propylene oxide displace the maximum of dissolved iodine cyanide to approximately the same extent as the alcohols. In a perfluoro-ether such as  $(\text{C}_4\text{F}_9)_2\text{O}$  the electronegative perfluoroalkyl groups substantially prevent the lone pairs of electrons on the oxygen atom from being used in complex formation, *i.e.*, the perfluoro-ether is a very weak Lewis base. Iodine cyanide is only slightly soluble in perfluoro-*n*-butyl ether, but a saturated solution shows a distinct maximum in the spectrum, showing that at best only extremely weak complex formation is taking place.

FIG. 1. Ultra-violet absorption spectrum of iodine cyanide in: (a) light petroleum, (b) trifluoroethanol, (c) *n*-butyl chloride, (d) *tert*-butyl chloride, (e) ethyl ether, (f) methanol, (g) isopropanol, and (h) silicon tetrachloride.



The spectrum of iodine cyanide in ethyl ether shows no absorption maximum; if a stronger Lewis acid than iodine cyanide is added to the ether it should displace the iodine cyanide from its ether complex and the spectrum of the solution should approach that of iodine cyanide in an inert solvent such as *cyclohexane*. This can be demonstrated by use of boron trifluoride, and iodine cyanide in boron trifluoride-ether shows a maximum at 225  $m\mu$ .

Dimethyl carbonate shows complex formation with iodine cyanide, and here the complex could be either of two types, or both: involving the MeO groups as in the ether complexes, or the carbonyl group [*e.g.*,  $(\text{MeO})_2\text{C}=\text{O}^+-(\text{I}-\text{CN})^-$ ].

As demonstrated earlier with heptafluoroiodopropane, the butyl chlorides can act as weak Lewis bases, and with iodine cyanide give weak complexes  $(\text{Bu}^n\text{Cl})_2(\text{ICN})$  and  $(\text{Bu}^t\text{Cl})_2(\text{ICN})$ , involving a lone pair of electrons on the chlorine atom. When dissolved in *n*- or *iso*-propyl chloride, iodine cyanide shows an inflection near 230  $m\mu$ , again suggesting weak complex formation through the chlorine atoms.

The formation of a molecular complex between iodine cyanide and acetonitrile may be inferred from the absence of an absorption maximum (Table 1). Here complex formation may occur through the nitrogen atom or, more plausibly, through the electrons of the triple bond.

Dilution of a solution of iodine cyanide in a Lewis-base solvent such as ethanol by light petroleum moves the absorption maximum back to the longer wave-length. This effect is shown in Fig. 2 and Table 2. The weak inflection observed with pure ethanol as solvent becomes a maximum whose intensity drops steadily as it moves to longer wave-length. There is an isosbestic point *ca.* 240  $\mu$ , and these results are consistent with the formation

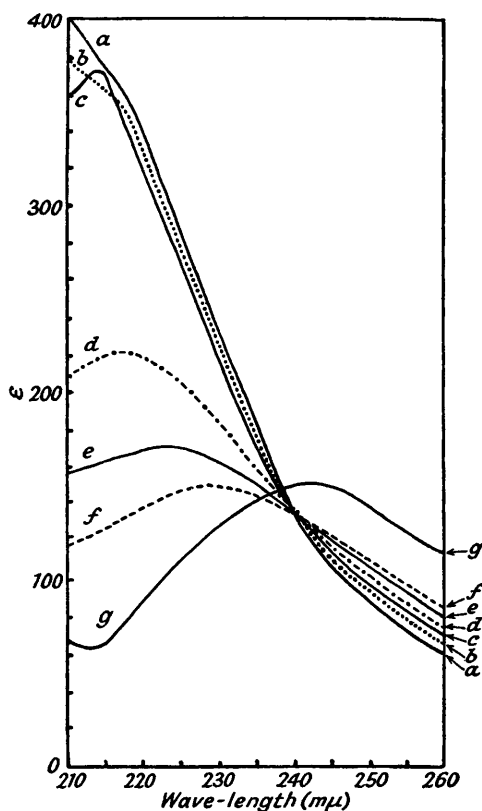


FIG. 2. Ultra-violet spectrum of iodine cyanide in ethanol-light petroleum.

	Ethanol	Light petroleum
a .....	100%	—
b .....	1	5
c .....	1	10
d .....	1	100
e .....	1	200
f .....	1	500
g .....	—	100%

of a molecular compound in solution; the marked effect of 0.2% and 0.5% by volume of ethanol on the spectrum of iodine cyanide in light petroleum is particularly noteworthy.

*Infra-red Spectra.*—The marked variation of the ultra-violet spectra of solutions of iodine or iodine cyanide might be expected to be reflected in the infra-red spectra of the

TABLE 2. *The effect of mixed solvents.*

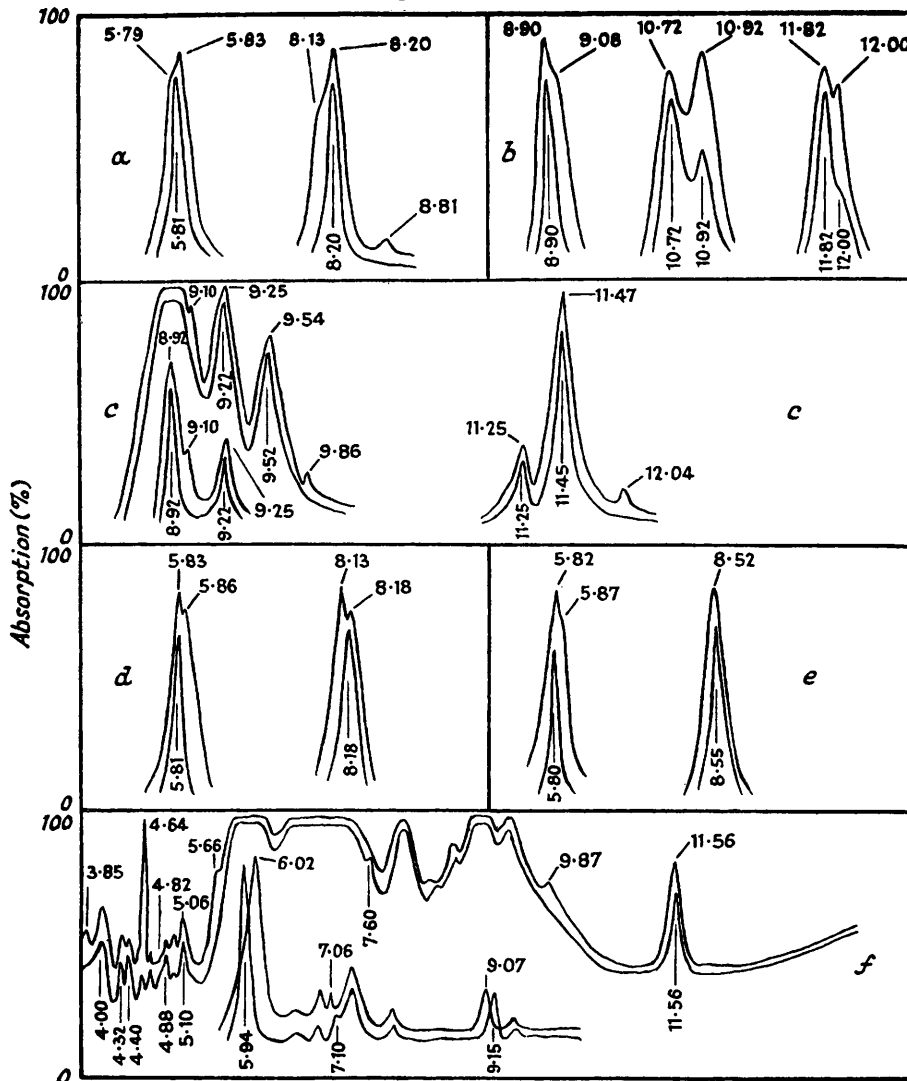
Solvent		
EtOH-petrol *	1 : 1	Infl. 210—214 $\mu$ , $\epsilon$ 380
	1 : 2	„ 211—214 $\mu$ , $\epsilon$ 370
	1 : 5	„ 215 $\mu$ , $\epsilon$ 360
	1 : 10	Max. 214 $\mu$ , $\epsilon$ 365
	1 : 100	Max. 217 $\mu$ , $\epsilon$ 220
	1 : 200	Max. 224 $\mu$ , $\epsilon$ 170
	1 : 500	Max. 230 $\mu$ , $\epsilon$ 150
100% EtOH	Infl. 210—215 $\mu$ , $\epsilon$ 380	
100% Petrol	Max. 242, $\epsilon$ 150; min. 214, $\epsilon$ 65	

\* Petrol = light petroleum, b. p. 60—80°.

solutions. Ham, Rees, and Walsh (*Nature*, 1952, **169**, 11; *J. Chem. Phys.*, 1952, **20**, 1336) failed to observe any change in the infra-red spectrum of benzene, mesitylene, or ethyl ether when these solvents were saturated by iodine, however, although very marked changes in ultra-violet spectra are well established. Ham *et al.* concluded that solvent

complexes did not exist in these cases, particularly since pyridine, which gives a well-defined crystalline compound with iodine, shows a marked change in infra-red spectrum when iodine is added. Glusker *et al.* (*loc. cit.*) in a recent preliminary note subsequently reported that pyridine and the picolines gave distinct new bands in the infra-red when

FIG. 3. Infra-red spectra. (The upper curve of each pair represents the solution spectrum, and the lower the pure solvent spectrum.)



(a) Iodine in ethyl ether.

(b-f) Iodine cyanide in (b) ethyl ether, (c) dioxan, (d) acetone, (e) ethyl methyl ketone, and (f) dimethylformamide.

saturated by iodine; no change in spectrum could be detected when carbon disulphide, acetonitrile, benzene, toluene, or the xylenes were used as solvents. Small but definite effects were observed, however, when iodine was dissolved in ether, dioxan, tetrahydrofuran, ethyl acetate, or in certain ketones (*e.g.*, acetone). Mention was also made of studies with iodine cyanide, but no details were given.

The results of Ham *et al.* for benzene have also been confirmed during the present work

since, with the resolving power available with a sodium chloride prism, no change in infra-red absorption spectrum can be observed when benzene is saturated with iodine. This is somewhat surprising in view of the marked changes in ultra-violet spectrum of iodine when dissolved in benzene. Hex-1-ene solutions of iodine also failed to show changes in infra-red spectra. Solvent-solute interaction has been detected, however, with solutions of iodine in dry acetone, and this confirms the earlier observations by Glusker *et al.* and their interpretation of them. Small but distinct changes are apparent (Fig. 3), and in particular the C:O stretching vibration at  $5.81 \mu$  in pure acetone is moved to  $5.83 \mu$  with a shoulder at  $5.79 \mu$  in the spectrum of the iodine solution; this clearly reveals that the iodine, bonded to the carbonyl-oxygen atom, is modifying the C:O vibration. More detailed infra-red studies have been made with iodine cyanide, since this is more soluble in many organic solvents, and these also strongly support the concept of solvent-solute compound formation. Compound formation does not occur with carbon disulphide, chloroform, tetrachloroethylene, benzene, hex-1-ene, or formamide. It occurs with ethyl ether, dioxan, acetone, ethyl methyl ketone, and, particularly, dimethylformamide and *n*-butylamine.

A solution of iodine cyanide in ethyl ether shows a strong new band at  $9.08 \mu$  clearly caused by modification of the C—O—C vibration at  $8.90 \mu$  (Fig. 3). Dioxan solutions similarly show new bands at  $9.10$  and  $12.04 \mu$  (Fig. 3), again suggesting complex formation involving the oxygen and causing shifts in the normal C—O—C vibrations at  $8.92$  and  $11.45 \mu$ . These observations support the conclusions based on ultra-violet spectra.

Acetone solutions reveal complex formation particularly clearly, since the carbonyl stretching vibration at  $5.81 \mu$  splits into two with a shift to longer wave-length ( $5.83$ ,  $5.86 \mu$ ), and a new band appears at  $8.13 \mu$ . Complex formation involving carbonyl oxygen is also revealed by similar shifts in the C:O bands of ethyl methyl ketone at  $5.80$  and  $8.55 \mu$ . Complex formation between ketones and iodine cyanide cannot be shown by ultra-violet spectroscopic studies, since the solvent itself has too powerful an absorption in the region of interest.

Complex formation cannot be detected with formamide, but dimethylformamide shows strong interaction with iodine cyanide. Band shifts and new bands are apparent in the infra-red spectrum (see Fig. 3), and in particular there is a marked change ( $0.08 \mu$ ) in the position of the carbonyl band suggesting that complex formation involves the carbonyl-oxygen atom rather than the amide-nitrogen atom.

In the examples given above the changes in infra-red spectra are minor though distinct, and the spectra are very similar to those of the pure solvent. An almost complete change in spectrum is produced when iodine cyanide is dissolved in butylamine and it is probable that the bond here tends to that of a true compound of the type  $[\text{BuNH}_2\text{I}]^+\text{CN}^-$  similar to that from pyridine and iodine.

The position of the C:N stretching vibration changes only slightly. This supports the postulate that complex formation occurs through the iodine atom of iodine cyanide; so does the failure of cyanogen bromide to change the infra-red spectrum of acetone significantly at concentrations comparable with those used for iodine cyanide; some indications—much weaker—of complex formation are given also with cyanogen bromide in dimethylformamide.

The infra-red and ultra-violet spectroscopic results reported above thus provide independent supporting evidence for the solvent-solute interaction with iodine cyanide first shown by Fairbrother.

#### EXPERIMENTAL

Iodine cyanide and iodine were purified by sublimation and thoroughly dried ( $\text{P}_2\text{O}_5$ ) *in vacuo*.

*Ultra-violet Spectra.*—A Unicam Spectrophotometer was used adjusted to give maximum sensitivity at low wave-lengths. Solvents were specially dried and purified and were transparent (*i.e.*, transmitted more than 40% of the light) at the wave-lengths studied. The light petroleum had b. p.  $60$ — $80^\circ$  before purification. Matched  $1.0$ ,  $0.5$ , or  $0.1$  cm. cells were used. The solvent ratios given in Table 2 are by volume.

*Infra-red Spectra.*—These were recorded with a Perkin-Elmer Model 21 with rock-salt optics. The pure dry solvent was first recorded for various cell thicknesses (usually 0.1 mm., 0.01 mm., and capillary film) so that both weak and strong bands could be observed. The spectrum of a saturated solution of iodine cyanide in the solvent was then recorded on the same sheet of paper with identical conditions and cell thicknesses as before. In this way minor shifts and changes in intensities could be detected and errors were reduced to a minimum. Shifts in wave-length of 0.01—0.02  $\mu$  were then significant and reproducible. The experiments were repeated at least once to ensure that the changes observed were real. The absolute accuracy of the wave-length calibration is  $\pm 0.01 \mu$ .

The curves in Fig. 3 are diagrammatic and not to scale. To make the changes in spectra clearer, the curves of solution and solvent have been separated, since on the actual recording the bands often overlap. Unless stated, the intensities of bands are nearly the same for solvent and solution.

A saturated solution of iodine in acetone shows the C:O stretching at 5.83  $\mu$  (cf. pure acetone 5.81  $\mu$ ) with a shoulder at 5.79  $\mu$ . New bands appear at 8.13  $\mu$  (strong side band) and 8.81  $\mu$ .

The positions of the C:N stretching vibration and the changes (new bands or shifts) in the infra-red spectra of various solvents when saturated with iodine cyanide are summarised below :

CS<sub>2</sub>: 4.61  $\mu$ . No change.

CHCl<sub>3</sub>: 4.61  $\mu$ . No change.

C<sub>2</sub>Cl<sub>4</sub>: 4.61  $\mu$ . No change.

Nujol mull: 4.62  $\mu$ . Iodine cyanide shows no other absorption in the region studied.

H·CO·NH<sub>2</sub>: 4.65  $\mu$ . No change (low solubility).

C<sub>6</sub>H<sub>6</sub>: 4.63  $\mu$ . No change.

Hex-1-ene: 4.61  $\mu$ . No change.

Et<sub>2</sub>O: 4.62  $\mu$ . New weak band at 4.03  $\mu$ . Strong side band appears at 9.08  $\mu$ . 9.75- $\mu$  band (medium) shifts to 9.77  $\mu$ . 10.92- $\mu$  band shows a marked increase in intensity and is now stronger than the 10.72- $\mu$  band. The shoulder at 12.00  $\mu$  changes to a distinct sharp band with increase of intensity.

Dioxan: 4.63  $\mu$ . 4.05- $\mu$  band moves to 4.02  $\mu$ . New band (medium) appears at 9.10  $\mu$ . Distinct shifts of 9.22 and 9.52  $\mu$  bands to 9.25 and 9.54  $\mu$ . New band (medium) appears at 9.86  $\mu$  in place of weak shoulder. 11.45- $\mu$  band shifts to 11.47  $\mu$ . Strong new band appears at 12.04  $\mu$ .

COMe<sub>2</sub>: 4.63  $\mu$ . New bands (weak) at 3.80, 4.02  $\mu$ . Carbonyl band at 5.81  $\mu$  splits to give two strong bands at 5.83 and 5.86  $\mu$ . A new strong band appears at 8.13  $\mu$ , on the side of the 8.18  $\mu$  band.

COMeEt: 4.64  $\mu$ . 3.98  $\mu$  band moves to 4.05  $\mu$ . Carbonyl band at 5.80  $\mu$  moves to 5.82  $\mu$  and a strong side band appears at 5.87  $\mu$ . 8.55- $\mu$  band shifts to 8.52  $\mu$ .

H·CO·NMe<sub>2</sub>: 4.64  $\mu$ . New band (weak) at 3.85  $\mu$ . 4.00- $\mu$  band shifts to 4.02  $\mu$ . 4.32- and 4.40- $\mu$  bands (weak) have reversed relative intensities and appear at 4.34 and 4.39  $\mu$ . New band (weak) at 4.82  $\mu$ . 4.88- $\mu$  band decreases in intensity. 5.10- $\mu$  band shifts to 5.06  $\mu$ . New band (medium) at 5.66  $\mu$ . Carbonyl band at 5.94  $\mu$  moves to 6.02  $\mu$ . 7.10- $\mu$  band shifts to 7.06  $\mu$ . Band at 7.60  $\mu$  disappears. 9.15- $\mu$  band shifts to 9.07  $\mu$ . New band (medium) at 9.87  $\mu$ .

Bu<sup>n</sup>·NH<sub>2</sub>: 4.63  $\mu$ . Marked change in spectrum. Sharp doublet (medium) of N-H at 2.96, 3.03  $\mu$  becomes a single band at 3.17  $\mu$ . New bands (medium) at 3.77, 3.97  $\mu$ . 4.51- $\mu$  band has increased intensity. 4.76- and 5.85- $\mu$  bands disappear. 6.22- $\mu$  band shifts to 6.15  $\mu$ . New band (strong) at 6.67  $\mu$ . 7.92- $\mu$  bands increased in intensity. New bands at 8.55 and 8.75  $\mu$ . 8.90- $\mu$  band disappears. 9.20- $\mu$  band shifts to 9.30  $\mu$ . New bands (weak) at 9.57, 9.85  $\mu$ . 10.00-, 10.35- $\mu$  bands disappear. New strong doublet at 10.85, 11.00  $\mu$ . Broad band at 11.95  $\mu$  disappears. New band at 12.45  $\mu$ .

The following observations were made with cyanogen bromide :

Nujol mull: C:N 4.58  $\mu$ .

COMe<sub>2</sub> solution: C:N 4.59  $\mu$ . Carbonyl bands at 5.81  $\mu$  and 8.16  $\mu$  show no signs of broadening or of splitting. No new bands detected.

H·CO·NMe<sub>2</sub> solution: C:N 4.58  $\mu$ . 4.00- $\mu$  band shifts to 3.93  $\mu$ . Carbonyl band moves from 5.94 to 5.97  $\mu$ , and 9.15- $\mu$  band moves to 9.11  $\mu$ .