439. *Infrared Spectra of Nitriles and Their Complexes with Boron Trichloride.*

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The infrared spectra of a number of aliphatic and aromatic nitriles and their boron trichloride complexes have been measured in various solvents. The CN stretching frequencies are 80 ± 9 cm.$^{-1}$ greater in the complexes than in the free nitriles. The intensities of the CN stretching absorptions are virtually independent of solvent in the complexes (and are substantially greater than in the free nitriles), but are profoundly influenced by solvent in the free nitriles. The structural implications of the results are discussed.

Spectroscopic examination of organic nitriles has previously revealed that the C≡N stretching vibration is responsible for absorption in the 2250 cm.$^{-1}$ region, and that electron-releasing groups attached to the carbon atom of the nitrile group cause an increase in frequency.[1] The intensity of the CN absorption band, as measured by the integrated areas, showed large variations both with substituent (*e.g.*, aryl $\gg$ alkyl) [2] and solvent,[3,4] and the effect of solvent was interpreted in terms of solvent–nitrile association. The CN stretching frequencies in a number of complexes (with boron trifluoride and trichloride, titanium tetrachloride, and stannic chloride) of nitriles were recently reported and it was shown that these were higher than in the parent nitriles.[5]

In a previous paper [6] we described the preparation and reactions of a number of 1 : 1 complexes between nitriles and boron trichloride and we now report their infrared spectra, with variation of the solvent and hydrocarbon radical of the nitrile.

$$\text{(I)}\ \mathrm{R{-}C{\equiv}N{:}BCl_3} \qquad\qquad \mathrm{R{-}CCl{=}N{-}BCl_2}\ \text{(II)}$$

Comparison of Nitrile Frequencies in Free Nitriles and Their Complexes.—The results of measurements in methylene chloride solution are shown in Table 1. It has previously been demonstrated that neither solvent nor concentration significantly influences the position of the CN stretching frequency in free nitriles,[3] and the same applies also to their complexes with boron trichloride. Thus when benzene or chloroform was used as solvent, the position of the band was the same, within experimental error, as that recorded in Table 1 for R = Bu, Ph, or *p*-substituted Ph, but occurred at 2299 cm.$^{-1}$ for R = $CH_2{:}CH$ in benzene. Values of the CN stretching frequency in paraffin mulls of RCN,BCl_3 were: Bu^n, 2315; $CH_2{:}CH$, 2304; Ph, 2294; *p*-$Cl{\cdot}C_6H_4$, 2304; and *p*-$MeO{\cdot}C_6H_4$, 2278 cm.$^{-1}$. In the complexes, the band at ~2300 cm.$^{-1}$ is the strongest in the spectrum (excluding the 700 cm.$^{-1}$ region).

The important conclusions seem to be: (i) that the complexes still possess a nitrile group and therefore have structure (I) and not (II) (which represents them as products of addition across the triple bond); and (ii) that complex formation with boron trichloride invariably causes the nitrile band to shift to higher frequency (80 ± 9 cm.$^{-1}$).

It appears that co-ordination of nitriles with acceptors other than boron trichloride also increases the nitrile stretching frequency [*e.g.*, acetonitrile complexes with boron tribromide (ν_{CN} at 2320 cm.$^{-1}$), trichloride (at 2325 cm.$^{-1}$), and trifluoride (2359 cm.$^{-1}$),[5] titanium tetrachloride (1 : 2 MeCN) (ν_{CN} at 2304 cm.$^{-1}$), and stannic chloride (1 : 2 MeCN) (at 2303 cm.$^{-1}$); and nitrile oxides [7]] and this is surprising because it might have been expected that co-ordination would cause lowering of bond order and hence lengthening of

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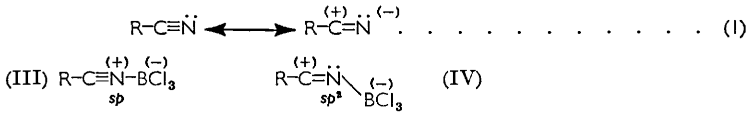
[1] Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334.
[2] Skinner and Thompson, *J.*, 1955, 487.
[3] Mander and Thompson, *Trans. Faraday Soc.*, 1957, **53**, 1402.
[4] Thompson and Steel, *Trans. Faraday Soc.*, 1956, **52**, 1451.
[5] Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.
[6] Gerrard, Lappert, and Wallis, preceding paper.
[7] Califano, Moccia, Scarpati, and Speroni, *J. Chem. Phys.*, 1957, **26**, 1777.

the CN bond, with consequent decrease in the nitrile stretching frequency. This argument is supported by analogy with carboxylic esters,[8] amides,[9] and ketones,[10] where the donors are the carbonyl groups and a substantial decrease in the carbonyl frequency on co-ordination is noted (*e.g.*, $CH_3{\cdot}CO_2Et$ has $\nu_{C=O}$ at 1740 cm.$^{-1}$, but $CH_3{\cdot}CO_2Et,BCl_3$ at 1563 cm.$^{-1}$).[8]

A number of explanations may be offered. First, that the band at ~2300 cm.$^{-1}$ does not arise solely from the CN stretching frequency, but represents a coupling of CN and BN (or TiN, SnN, or ON) modes as was assumed [11] to account for the higher C≡C frequency observed for disubstituted acetylenes R·C⋮C·R′ than for their monosubstituted analogues R·C⋮CH. However, we consider this proposal unlikely because of the wide separation in frequencies of CN and BN (and even more so, of TiN and SnN) stretching modes. Secondly, owing to a mass effect, the nitrile frequency would be expected to rise as between free nitrile and a complex, but this would produce only a very small increase and nothing of the order of 80 cm.$^{-1}$.[12] We therefore suggest that in the complexes the CN bond order is in fact higher than in the free nitriles. This is based on the following hypothesis: in the free nitriles, the CN bond is approximately intermediate between a double and a triple bond [see scheme (1)]; [13] on the other hand, such mesomerism [*i.e.*, involving (III) and (IV)] is not possible in the complex because of the very different geometry of (III) and (IV). Thus, in simplified terms, in (III) and (IV) the nitrogen atoms are regarded as *sp* (linear) and *sp*^{2} hybridised (∠CNB, 120°) and of the two structures, (III) is taken as substantially representing the structure of the complexes. In support, there is available the complete structural analysis (*X*-ray) of the acetonitrile–boron trifluoride complex.[14] This shows ∠CCN = 180°, ∠CNB = 180°, and ∠NBF = 103°. Further, the CN bond distances in acetonitrile (1·16 Å) and the boron trifluoride complex (1·13 Å) indicate that co-ordination

TABLE 1. *The* CN *stretching frequencies of free nitriles and their complexes in methylene chloride.*

R in RCN or RCN,BCl$_3$	Nitrile frequencies (cm.$^{-1}$) RCN	RCN,BCl$_3$	Δν	R in RCN or RCN,BCl$_3$	Nitrile frequencies (cm.$^{-1}$) RCN	RCN,BCl$_3$	Δν
Et	2247	2328	81	Ph	2229	2304	75
Pr^n	2248	2328	80	*p*-$NO_2{\cdot}C_6H_4$	2237	2313	76
Bu^n	2246	2335	89	*p*-$Cl{\cdot}C_6H_4$	2235	2310	75
n-C_5H_{11}	2256	2328	72	*p*-$Me{\cdot}C_6H_4$	2230	2305	75
CH_2:CH	2230	2313	83	*p*-$MeO{\cdot}C_6H_4$	2227	2302	75
$Ph{\cdot}CH_2$	2255	2344	89				



shortens bond length and hence increases bond order (although the difference between the two lengths is only just outside the quoted mean deviations). The spectroscopic results on the three boron halide complexes of acetonitrile also appear to support our view: the nitrile frequencies in the complexes increase in the order $BBr_3 < BCl_3 < BF_3$, which is the same order as for the complexes $CH_3{\cdot}CO_2Et,BX_3$.[8]

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[8] Lappert, Paper presented at the International Conference on Co-ordination Chemistry, London, 1959.

[9] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2144.

[10] Chalandon and Susz, *Helv. Chim. Acta*, 1958, **41**, 697; Terenin, Filimonow, and Bystrow, *Z. Elektrochem.*, 1958, **62**, 180.

[11] Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 12.

[12] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 173; Whiffen, *Chem. and Ind.*, 1957, 193.

[13] Pauling, Springall, and Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927.

[14] Hoard, Owen, Buzzell, and Salmon, *Acta Cryst.*, 1950, **3**, 130.

Intensities of the CN *Stretching Absorption Bands in Free Nitriles and Their Complexes.*— The results shown in Table 2 are expressed in terms of apparent extinction coefficients (ε_a), extrapolated to zero concentration. The significant conclusions appear to be: (i) the intensities of the nitrile bands in the complexes are much greater (approximately 5- and 7-fold increases in chloroform and benzene) than in the free nitriles; (ii) while the nitrile intensities in the free nitriles are much influenced by solvent (as has been noted before [3]), this is not the case with the complexes. The increase in band intensity with increasing solvent polarity (*e.g.*, in $CHCl_3$ greater than in CCl_4) has been attributed [3] to solvent–nitrile association and this view is consistent with both (i) and (ii). Thus co-ordination of boron trichloride with nitriles causes increases in CN band intensities quite out of proportion to those produced by possible solvent association, and furthermore solvent association (particularly hydrogen-bonding) with complexes is likely to be much more restricted than with free nitriles.

Although the solvents used in this investigation were carefully dried by conventional procedures (benzene over sodium, and chloroform by refluxing with phosphoric oxide), the solutions of the boron trichloride complexes nevertheless showed some slight hydrolysis, as indicated by the appearance of nitrile doublets in the spectra (a very strong band due to complex and a very weak band due to free nitrile), and this was more marked for the chloroform solutions than for those in benzene and was still more marked for solutions in methylene chloride. In view of this, the values for the apparent extinction coefficients in chloroform, shown in Table 2, should be regarded as minimal values and the factors $\varepsilon_{aCHCl_3}/\varepsilon_{aC_6H_6}$ are probably nearer to unity than is evident. Because of the hydrolytic susceptibility of the complexes, accurate measurements of extinction coefficients in a wider range of solvents were not pursued.

TABLE 2. *Apparent extinction coefficients of* CN *stretching bands in free nitriles and their complexes.*

	Apparent extinction coefficients of CN bands							
	in RCN			in RCN,BCl_3^-			$\varepsilon_{aRCN,BCl_3}/\varepsilon_{aRCN}$	
R in RCN or RCN,BCl_3	In $CHCl_3$	In C_6H_6	$\varepsilon_{aCHCl_3}/\varepsilon_{aC_6H_6}$	In $CHCl_3$	In C_6H_6	$\varepsilon_{aCHCl_3}/\varepsilon_{C_6H_6}$	In $CHCl_3$	In C_6H_6
Bu^n	31·6	18·6	1·70	143	148	0·97	4·5	8·0
Ph	76·2	52·6	1·45	465	520	0·89	6·1	9·9
p-$NO_2{\cdot}C_6H_4$ *	30·8	20·3	1·50	—	145	—	—	7·1
p-$Cl{\cdot}C_6H_4$	89	62·8	1·42	376	363	1·03	4·2	5·8
p-$Me{\cdot}C_6H_4$ ...	126	87·9	1·44	524	601	0·87	4·2	6·8
p-$MeO{\cdot}C_6H_4$ ...	173	115	1·50	822	872	0·94	4·7	7·6

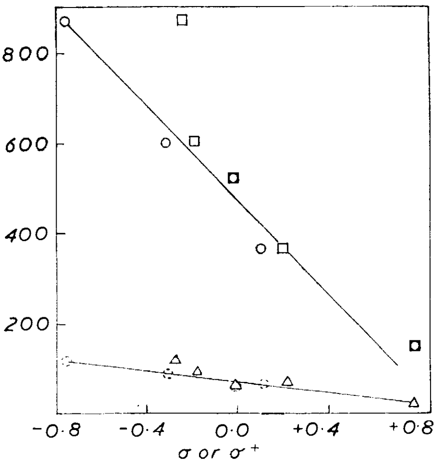
* The boron trichloride complex of *p*-nitrobenzonitrile was insufficiently soluble in chloroform to permit measurements of extinction coefficient in that solvent.

TABLE 3. *Apparent extinction coefficients of* CN *stretching bands of benzonitrile in various solvents.*

Solvent	CCl_4	$CHCl_3$	CH_2Cl_2	$CH_3{\cdot}NO_2$	C_6H_6	PhCl	$Ph{\cdot}NO_2$	Ph·OMe
ε_a	48	76·2	85·6	81·2	52·6	59·5	64·9	57·8

It was thought that if the increase in intensity of the nitrile band of a free nitrile through a range of solvents was attributable solely to dipole–dipole interaction this might provide a method of determining relative solvent polarities. Accordingly, the measurements of apparent extinction coefficients were extended (for benzonitrile), as shown in Table 3. It will be noted that the results do not agree even qualitatively with those obtained by other methods, although it is clear that the influence of substitution in the benzene ring is shown up for the aromatic solvents, with the order $NO_2 > Cl > MeO > H$, whilst for the aliphatic chlorinated solvents, the order $CH_2Cl_2 > CHCl_3 > CCl_4$ is not unreasonable. These orders are not independent of structure of the nitrile; thus the values for apparent extinction coefficients of free nitriles do not invariably show these to be higher in methylene chloride than in chloroform [in methylene chloride, RCN (ε_a): R = Bu^n (25·8); R = *p*-NO_2·C_6H_4 (31·6); R = *p*-Cl·C_6H_4 (85·8); R = *p*-Me·C_6H_4 (113); and R = *p*-MeO·C_6H_4 (126)]. Other workers have also pointed out recently that a complete correlation between solvent polarity and solvent influence on CN stretching intensities is not possible.[15]

Correlation between Structure and Intensity of CN *Stretching Absorption Band in Complexes of Benzonitrile and its Derivatives.*—The plots of apparent extinction coefficients (in benzene solution) of CN stretching bands against Hammett's [16] σ or H. C. Brown and Okamoto's [17] σ^+ functions for benzonitrile and four *para*-substituted derivatives and their boron trichloride complexes are shown in the Figure. The σ^+ plots give fair approximation to linearity, whereas the σ plots show particularly pronounced deviations for the *p*-methoxy-compounds. Plots of intensities (the more accurate integrated areas being used rather than extinction coefficients) against Hammett σ functions for a series of substituted benzonitriles have previously been recorded,[3,4] but it was pointed out that the choice of these functions was inappropriate as the influence of substituents on the nitrile bond was akin to their influence in electrophilic aromatic substitution,[18] for which likewise the σ values show deviations, particularly noticeable for the *p*-methoxy-group. The σ^+ functions have been derived from solvolysis kinetics on substituted 1-methyl-1-phenylethyl chlorides and have proved widely applicable over a range of electrophilic aromatic substitution reactions and for others involving resonance interaction between an electron-deficient centre and the substituents.[17] Accordingly, our results show that the influence of structure on CN stretching intensities in nitriles and their complexes can be correlated to at least one independently derived structural parameter.



Plot of extinction coefficient (ε_a) *against the Hammett functions* [16,17] σ *and* σ^+.

Nitrile complexes: ○, σ^+; □, σ.
Free nitriles: ○, σ^+; △, σ.

BCl *Stretching Frequencies in Nitrile–Boron Trichloride Complexes.*—The absorption frequencies of strong bands assigned to BCl stretching modes are listed in Table 4 and samples were measured as paraffin mulls. The values for aryl derivatives are not recorded because of the strong aromatic absorption in the relevant region. These figures compare

TABLE 4. BCl *Stretching frequencies in* RCN,BCl_3.

R in RCN,BCl_3	Me	Pr^n	CH_2:CH
BCl stretching frequencies (cm.$^{-1}$)	777, 734, 712	778, 732, 711	778, 741, 714

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[15] Bayliss, Cole, and Little, *Spectrochim. Acta*, 1959, 12.
[16] Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.
[17] H. C. Brown and Okamoto, *J. Org. Chem.*, 1957, **22**, 485; *J. Amer. Chem. Soc.*, 1957, **79**, 1913.
[18] T. L. Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 794.

well with those obtained on amide–boron trichloride complexes (*e.g.*, ν_{BCl} in $CH_3{\cdot}CO{\cdot}NMe_2,BCl_3$ at 777, 753, and 713 cm.$^{-1}$).[9]

Experimental.—The complexes were prepared and purified as described earlier.[6]

Spectra were measured on a Grubb-Parsons S3A double-beam spectrometer, sodium chloride optics being used. Samples were taken as liquids, paraffin mulls, or in solution as stated. We estimate that the quoted frequencies are correct to ± 6 cm.$^{-1}$ and the apparent intensities to $\pm 10\%$. The extinction coefficients are not absolute because of the relatively high slit-width used and the low dispersion of sodium chloride.

The intensities were measured in standard cells of path-length 0·05 cm. for the nitriles and 0·0206 cm. for the complexes, with corresponding solvent-compensating cells. Extinction coefficients were determined by taking measurements at three concentrations, adjusted so as to give absorption of the nitrile band in the range 20—80%; the results were plotted and extrapolated to zero concentration. All the measurements were carried out at a mechanical slit-width of 0·08 mm., which was the lowest value at which the nitrile band showed no change in intensity with decreasing slit-width.

We thank Drs. L. A. Duncanson and N. Singer and Mr. H. A. Willis for valuable discussions, and one of us (J. W. W.) gratefully acknowledges having received a maintenance grant from Messrs. Albright and Wilson, Ltd.

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[*Received, September 16th,* 1959.]