MOLECULAR PARAMETERS AND BOND STRUCTURE. PART 8.¹ ENVIRONMENTAL EFFECTS ON ν (C=N) BOND STRETCHING FREQUENCIES

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SUMMARY

The vibrational frequencies associated with the characteristic bands arising from C=N bonds have been determined for a number of nitriles in different phases and in various solvents. Some dependence is found on the molecular environment of the C=N vibrator.

Frequency assignments are given for cyanogen, cyanogen bromide and *cis*and *trans*-1-cyano-1,3-butadiene.

INTRODUCTION

Studies on organic cyanides have in the past led to controversy as to whether the compounds have a nitrile or isonitrile structure². A similar problem was encountered in the case of monosubstituted acetonitriles for which three possible structural isomers were postulated at various times. These were

X·CH ₂ ·C≡N	X·CH=C=NH	X·C≡C·NH ₂
Nitrile	Ketimine	Aminoacetylene

A variety of physico-chemical studies including IR^3 , electron diffraction⁴, and electronegativity⁵ have now proved conclusively that these compounds have the nitrile structure and that the two σ -bonds associated with the carbon atom are colinear.

In molecular orbital terms the molecules can be formulated as in Fig. 1, in which the arrows indicate the direction and sense of the CN bond moment and the

Fig. 1. Electronic structure of $X \cdot CN$ molecules.

atomic dipole. As the group X varies, changes are to be expected in the bond order and ionic character of the CN bond. For a particular group X, variations in CNbond character may also be induced by altering the environment of the molecule, e.g. by change of phase or by dissolving the nitrile in different solvents.

This work was undertaken to see whether changes in C=N bonds could be detected by measurement of v(C=N) bond stretching frequencies in a number of environments. In addition, the IR spectra in various phases of cyanogen, cyanogen bromide and 1-cyano-2,3-butadiene were obtained since they have not previously been studied extensively.

EXPERIMENTAL

(i) Materials

Acetonitrile and monochloracetonitrile, laboratory reagents from the British Drug Houses Ltd., and propionitrile, isopropyl cyanide (or isobutyronitrile) and tert-butyl cyanide (2,2-dimethylpropionitrile or pivalonitrile), pure samples from Koch Light Laboratories Ltd., were dried over phosphoric oxide and fractionally distilled at ca. 760 mm immediately before use.

A sample of cyanogen bromide from Eastman Organic Chemicals was purified by vacuum sublimation immediately prior to use. At water pump pressure (12 mm Hg) slow sublimation occurred at $\sim 20^{\circ}$.

Cyanogen iodide was obtained from Nutritional Biochemicals Corporation, Cleveland, Ohio. Due to its great tendency to decompose, it was kept under refrigeration until immediately before use, and no purification was attempted.

A pure sample of a cis-trans mixture of 1-cyano-1, 3-butadiene from Koch Light Laboratories Ltd., had begun polymerising to a dark brown highly viscous liquid. However, distillation of this under water pump pressure gave two quite well separated samples. The first, a colourless liquid, boiled below room temperature and was collected in a liquid air trap. Its spectrum showed the presence of about 90 % of the cis isomer. The second fraction, also colourless, was collected at $21-24^{\circ}$ and proved to be mainly the trans form. Better separation than this was attempted by repeated fractional distillation under reduced pressure but proved unsuccessful. Polymerisation and interconversion of these samples were arrested by refrigeration.

A pure sample of fumaronitrile from K and K Laboratories Inc., was purified by recrystallisation from benzene.

Cyanogen was prepared by Janz's method⁶. It was collected in a trap cooled to -80° with dry ice in chloroform and carbon tetrachloride. The trap was then connected to a stainless steel cylinder, the system evacuated and the cyanogen transferred for storage purposes by immersing the cylinder in liquid air and slowly withdrawing the trap from its freezing bath.

Solvents

Laboratory reagent samples of tetrachloroethylene and carbon tetrachloride – spectroscopic quality – were obtained from BDH and were dried with anhydrous calcium chloride and filtered before use. Chloroform, also from BDH, was dried with anhydrous sodium sulphate and filtered.

(ii) Instruments

All the spectra were measured with a Grubb Parsons GS2A double-beam spectrophotometer equipped with a 1200 lines/inch grating and a KBr/CaF₂ foreprism. The accuracy of the wavelength scale is about ± 1 cm⁻¹ between 5 and

TABLE 1

IR SPECTRUM OF CYANOGEN (cm⁻¹)

Liquid	Solid	Vapour	Assignment
3686 (vw)			
3600 (vw)			
3007 (vw)		3010 ¹³	$v_2 + v_3 = 3000$
2964 (vw)			
2920 (vw)			
2850 (vw)			
2663 (s)	2668 (s)	2663°	$v_3 + v_4 = 2670$
2566 (m)	2581 (m) 2569 (m)	2563°	$v_1 + v_5 = 2576$
2339 (s)			
(2336 Raman ¹⁰)		(2330 Raman ⁹)	v_1
2158 (vs)	2163 (s)	2150°	v_3
2132 (vw)		213113	$v_{3}^{(13C)}$
2089 (vw)		2093°	$v_1 - v_5 = 2096$
1713 (s)	1714 (m)		- ·
1614 (vw)			
1420 (vw)			
1384 (vw)	1387 (vw)		
1365 (m)	1367 (w)		
1262 (vw)	1261 (vw)		$2\nu_4 + \nu_5 = 1264$
1225 (m)	1226 (w)		
1181 (vw)	1184 (vw)		
1092 (vw)	1088 (vw)	109013	$v_2 + v_5 = 1100$
(860 Raman ¹⁰)		(848 Raman ⁹)	V ₃
791 (vs)	791 (w)		-
766 (s)	754 (m)		
741 (vs)	744 (m)	732°	$v_4 + v_5 = 746$
(756 Raman ¹⁰)			
659 (w)			
612 (w)	•	618 ⁹	$v_2 - v_5 = 620$
529 (w)			· · · · · · · · · · · · · · · · · · ·
(512 Raman ¹⁰)		(506 Raman ⁹)	VA
		240°	v_5

(vw: very weak m: medium vs: very strong).

T/	VB	LE	2
-			

Vapour	Liquid	Solid	Assignment
	3646 (vw)		
	3551 (vw)		
2888 (vw)	2962 (vw)	2964 (vw)	
2871 (vw)	2903 (vw)	2914 (vw)	$\nu_3 + 2\nu_2 = 287$
2779 (m) 2763 (m)	2760 (m)	2764 (w)	$v_3 + v_1 = 2753$
2534 (s)			
2528 (m)	2540 (m)	2550 (vw)	$v_3 + v_3 = 2532$
2523 (m)	· ·		
2204 (vs)			
2188 (vs)	2185 (vs)	2186 (m)	ν_3
		2158 (vw)	$v_{3}(^{15}N)$
	2137 (w)	2138 (w)	$v_{3}(^{13}C)$
·	1705 (m)	1717 (vw)	
	1652 (w)	1652 (vw)	
	1364 (w)		
	1281 (m)	1281 (vw)	
1255 (vw) 702 (vs)	1225 (w)		
695 (vs)	730 (s)	754 (vw)	$2\nu_2$
686 (vs)			
577 (w)	568 (s)	567 (11)	
564 (w)	541 (m)	507 (W)	ν1
	346 (vs)	357 (s) 346 (s)	ν_2

IR FREQUENCIES CS CYANOGEN BROMIDE (cm⁻¹)

(vw: very weak m: medium s: strong).

15 μ and correspondingly better in the higher orders. Five or more values for the CN-band frequencies consistent to within 0.5 cm⁻¹ were obtained in this work.

Wavelength calibration of the instrument was made by using the rotationvibration lines of the ammonia fundamental at 1213-753 cm⁻¹. Measurements of 15 or so of the fine structure bands were compared with values obtained from standard calibration tables⁷. As the wavelength scale employed on the instrument is linear, calibration in the first order automatically ensures calibration in the other orders.

In Tables 1 and 2 the frequencies of the observed bands in the vapour-, liquid- and solid-state spectra of cyanogen and cyanogen bromide are collected.

The absorption bands found for *cis*- and *trans*-1-cyano-1,3-butadiene are given in Table 3. The spectra indicated that complete separation of the isomers had not been achieved. In Table 4 are gathered together the v(CN) frequencies for different phases and in solution.

EFFECTS ON v(C=N) bond stretching frequencies

TABLE 3

Trans	Assignment	Cis
4670 (vw)		4724 (vw)
4448 (vw)		4515 (vw)
4284 (vw)		4340 (vw)
4235 (vw)	· · ·	4206 (vw)
4196 (vw)		4153 (vw)
4050 (vw)		
3092 (vw)		3115 (w)
3074 (s)	CH stretching (CH ₂)	3071 (s)
3006 (m)	CH stretching (-CH=CH-)	3031 (m)
2965 (w)		2989 (m)
2921 (w)		2967 (w)
2849 (w)		2922 (w)
2526 (vw)		
2500 (vw)		2693 (w)
2451 (vw)		2465 (vw)
2304 (vw)		2277 (w)
2214 (vs)	v(CN) stretch	2227 (vs)
2162 (w)		2087 (vw)
1872 (w)	2(CH ₂) out of plane deformation	1935 (w)
		1712 (m)
1626 (vs)	C=C stretch	1690 (s)
1572 (vs)	C=C stretch	1607 (m)
1420 (vs)	(CH ₂) in plane deformation	1413 (vs)
1359 (vs)	CH in plane deformation (-CH=CH-)	1359 (m)
1297 (s)	CH in plane deformation (-CH=CH ₂)	1297 (m)
1225 (m)		1227 (m)
1140 (w)		1148 (w)
1001 (vs)	C=C twist	1092 (m)
940 (vs)	CH₂ out of plane deformation (-CH=CH-)	970 (vs)
881 (w)		871 (m)
778 (vs)	CH out of plane	779 (vs)
668 (vs)	deformation (CH=CH)	686 (vs)

IR FREQUENCIES OF cis- AND trans-1-CYANO-1,3-BUTADIENE (cm⁻¹)

TABLE 4

EFFECT OF ENVIRONMENT ON THE CN BAND FREQUENCY. SUMMARY OF RESULTS (cm⁻¹; accuracy: ± 0.2 cm⁻¹)

Compound	Vapour	Liquid	Soln. in CCl4	Soln. in C ₂ Cl ₄	Soln. in CHCl ₃
$\overline{\operatorname{CH}_3 \cdot \operatorname{CN}}$	2267.0	2252.5	2255.0	2255.4	2255.7
CH ₃ ·CH ₂ · CN	2265.0	2247.2	2249.2	2249.6	2249.9
(CH ₃),CH · CN	2264	2245.3	2247.4	2247.8	2246.5
$(CH_{3})_{3}C \cdot CN$	2254	2234.5	2235.8	2236.6	2235.3
CICH. · CN	2266.0	2260.4	2260.4	2260.7	2261.4
BrCN	2196.0	2185.1	2188.4	2187.8	2188.5
ICN	÷.,		2168.1	2168.2	2166.6
trans-NC \cdot CH=CH \cdot CN		1			2240.4
cis-CH ₂ =CH·CH=CH · CN		2226.9			
trans-CH2=CH-CH=CH · CN		2214.6			

FREQUENCY ASSIGNMENT

(a) Cyanogen

Work on the IR absorption spectrum of gaseous cyanogen has already been published^{8,9}. The Raman spectrum of liquid cyanogen has also been measured¹⁰. No other measurement on the liquid state has been reported.

From classical stereochemistry as well as from consideration of the electronic structure, the cyanogen molecule in the ground state is expected to be linear and symmetric. This is confirmed by electron diffraction measurements¹¹. Hence, C_2N_2 has symmetry D_h . From group theoretical consideration it follows that there are three non-degenerate fundamental vibrations, two of which are symmetric and one antisymmetric with respect to the point of inversion, a further two degenerate vibrations being respectively symmetric and antisymmetric. According to D_h selection rules, all the antisymmetric fundamentals are IR-active while the symmetric ones are Raman active.

The problem of assigning the observed frequencies to definite modes of vibration has caused some deliberation in the literature⁸. The assignment given in Table 1 agrees with that of Herzberg¹².

The only fundamental that is active in the IR and within the range of the available instruments is v_3 , the asymmetric CN stretch at 2158 cm⁻¹ in the liquid. As usual, this is somewhat higher than that of the vapour phase. The weak band at 2132 cm⁻¹ is probably due to the asymmetric stretch of the N=¹²C-¹³C=N molecule.

It has been found impossible to assign the band that occurs at 2339 cm⁻¹ in the liquid spectrum with any certainty. Due to the method used for its preparation, the cyanogen could have contained some carbon dioxide as impurity even though stringent precautions were taken for its exclusion; the antisymmetric CO stretch of CO₂ has a vapour-phase frequency value of 2330 cm⁻¹. It is interesting to note that this band was not observed in the solid spectrum. This could be due to the fact that the CO₂ had escaped during solidification. The fact that no absorption, or at least very little, was seen in the region of 667 cm⁻¹ where CO₂ usually absorbs extremely strongly due to its bending vibration seems, however, to throw doubt on this assignment of the 2339 cm⁻¹ band. Another cause for an absorption in this region could be the symmetric stretch, v_1 , of the cyanogen molecules. This vibration would be expected to be IR-inactive but some relaxation of the symmetry rules sometimes occurs in condensed phases due to intramolecular interaction. The disappearance of the band in the solid spectrum may indicate that the site symmetry in the liquid and solid phases is different.

Values of the frequencies of the fundamentals other than v_3 are taken from the literature^{9,10,13} and it is seen from Table 1 that the frequencies for the combination bands calculated using these values are in good agreement with experiment.

According to the literature the bending vibration, v_5 , has proved to be the most difficult to assign. Most workers^{8,9} have taken v_5 as 240 cm⁻¹ whereas others¹⁴ have taken it to be at 732 cm⁻¹. Certainly, very strong bands are seen in this region - three bands occur in the liquid spectrum at 791, 766 and 741 cm⁻¹. Other workers⁹ have found three bands in this region for gaseous cyanogen. On careful purification they found that one of these bands disappeared and this was then said to be due to HCN impurity. The other two bands were then assigned as Pand R branches of a parallel band. As v_5 is a perpendicular type vibration its connection with the frequency was thus disproved. Further reasons for not accepting 732 cm^{-1} as v_5 were that anomalous values were obtained for the bending force constants, and also combination bands were found to be more reasonably accounted for with v_5 at 240 cm⁻¹. Unfortunately, due to the limitations of our spectrometer, we were not able to record the band at 240 cm^{-1} . It is a fact that the three bands in the 700-800 $\rm cm^{-1}$ region persist in the liquid and solid spectra obtained in this study so that the assignment of two of these bands as P and Rsub-bands of $(v_4 + v_5)$ must be wrong. Also, the assignment of one of these bands as being due to HCN impurity must be in error as no vibrations occur in our spectra in the other regions¹² where HCN usually absorbs, viz., 1412, 2116, 2800 cm⁻¹.

It is clear therefore that more extensive work will have to be done on cyanogen in order to clarify this point. If v_5 has a value of ~ 750 cm⁻¹, then the combination band $2v_4 + v_5$ should be at around 1750 cm⁻¹. This may explain the band that occurs at 1714 cm⁻¹. The sharp band at 1260 cm⁻¹ would then be $v_4 + v_5$ (= 1256 cm⁻¹) and the band which other workers have reported at 240 cm⁻¹ would be the difference band $v_5 - v_4$ (= 244 cm⁻¹).

(b) Cyanogen bromide

Although the pure rotational and vibration-rotational spectra of BrCN have been extensively studied^{15, 16} no work has so far been done on this substance in the liquid phase. The spectrum of liquid BrCN held at a carefully regulated temperature just above its melting point was obtained in addition to the spectra of the solid and gaseous phases. The frequencies and tentative assignments are listed in Table 2.

A linear triatomic molecule such as BrCN, of symmetry $C_{\infty v}$, has four degrees of vibrational freedom. The bending vibration is doubly degenerate. Three fundamental frequencies will therefore exist, all of which appear in the IR spectrum.

Complication of the IR spectrum of BrCN is expected because of the two naturally occurring isotopes of bromine, ⁷⁹Br and ⁸¹Br. These have nearly equal abundance and so give rise to two sets of spectra which are nearly but not quite coincident.

The very strong low-lying band at 346 cm^{-1} in the spectrum of liquid BrCN is easily assigned to the doubly-degenerate bending mode, v_2 . The band

at 2185 cm⁻¹ which shows parallel structure in the vapour spectrum is obviously the CN stretching mode, v_3 . It follows that the band at 2540 cm⁻¹ is the combination $v_3 + v_2$.

C-Br absorptions usually occur¹⁷ in the region 600-500 cm⁻¹. The band at 568 cm⁻¹ has therefore been assigned to v_1 . The stronger band at 730 cm⁻¹ is then the overtone $2v_2$. The levels v_1 and $2v_2$ lie relatively close together and it has been suggested¹⁶ that they may undergo Fermi resonance since they belong to the same symmetry species. From the spectra it is deduced that Fermi resonance appears to be more pronounced in the solid than in the gaseous state.

Assignments of these main bands agree with those made previously by Freitag and Nixon¹⁶ although the band centres differ somewhat.

In addition to these main bands there are a few weak ones that are easily assigned. A band centred at 2137 cm⁻¹ on the low-frequency side of the main v_3 band is due to the v_3 vibration of the isotopic molecule Br¹³CN. In the solid spectrum an additional shoulder to the main v_3 band at 2158 cm⁻¹ is assigned to the ¹⁵N isotopic band.

Instead of the expected P, Q, R structure for the combination band $v_3 + v_2$ at 2528 cm⁻¹ in the vapour phase a series of sharp peaks is observed, these being about 5 cm⁻¹ apart. The most prominent peaks at 2534, 2528 and 2523 cm⁻¹ are probably the Q branches of $v_3 + v_2$ and of hot bands such as $v_3 + 2v_2 - v_2$. The less intense peaks below 2523 cm⁻¹ are then the P and R branches of these bands. The irregularities observed in the band envelope of $2v_2$ in the vapour phase may also be due to hot bands.

An interesting observation is the strong shoulder on the high-frequency side of the v_2 peak of solid BrCN. It has been reported¹⁶ that the closely related molecule ClCN has a linear chain structure of space group D_{2h} with two molecules per unit cell at -30° (~ 10° below its melting point). If this were the case with BrCN the v_1 and v_3 vibrations of the free molecule should give rise to one active component in the crystal while the v_2 mode should give two components. The greater half-band width of the v_2 mode in the solid as compared with liquid BrCN suggests that this is occurring and that the packing in the crystal is of the linear chain form at the temperature used, 25°. Freitag and Nixon¹⁶ observed no splitting of this band at -180° ; their suspicion that the crystal structure has changed at such low temperatures seems to be justified. The fact that the parallel bands v_1 and v_3 are very weak in the solid spectrum indicates that the dipole moment change is greatly reduced because of coupling with neighbouring molecules.

(c) Cis- and trans-1-cyano-1,3-butadiene

The isomers of this substance were separated by careful fractional distillation under reduced pressure. Once obtained they proved, by their spectra, to be quite stable provided they were kept under refrigeration between runs. The trans isomer polymerises within a few hours if left at room temperature; the structure of the dimer initially formed has been discussed by Snyder and Poos¹⁸ and established as



The report of Snyder et al.¹⁹ of the instantaneous dimerisation of the trans isomer could be due to some impurity acting as a catalyst. The frequencies observed are given in Table 3. A molecule such as this, containing 11 atoms, will have 27 vibrational degrees of freedom. As cyanobutadiene is most probably planar, some of the in-plane and out-of-plane fundamental vibrations will be almost degenerate but, nevertheless, the spectra are expected to be complicated. The spectral region investigated is confined to $2-15 \mu$ so that it is not expected that all vibrational bands have been obtained. Only a partial assignment is therefore attempted.

As expected, the spectra of both species show a strong nitrile absorption at around 2220 cm⁻¹. The v(CN) frequency of *cis*-cyanobutadiene is found to be slightly higher than that of the trans isomer. This can be easily explained by a study of the molecular structures of these two isomers, namely



The π -system in the trans isomer is more nearly linear than in the cis so that improved conjugation would be expected²⁰. If this were the case the CN bond should be weaker in the trans isomer and its frequency lower, as is found experimentally.

Bands that occur in the 3000 cm^{-1} region are easily assigned as being due to the various CH stretching modes. The C=C stretching vibrations appear at 1607 and 1690 cm⁻¹ (cis) and 1572 and 1626 cm⁻¹ (trans) – their intensities are considerably enhanced by the conjugation of the double and triple bonds¹⁷. The C=C twist of the vinyl groups appears at 1092 cm⁻¹ (cis) and 1001 cm⁻¹ (trans). The vinyl CH₂ wag appears at 970 and 940 cm⁻¹ in the cis and trans isomers respectively, and their first overtones fit very well the bands found at 1935 and 1872 cm⁻¹. The two strong bands at around 700 cm⁻¹ have been assigned as hydrogen out-of-plane deformations.

DISCUSSION

It has been reported²¹ that the C=N bond stretching frequency is independent of the environment surrounding the molecule. An examination of Table 4

shows that this is not so since not only does v(CN) change as one goes from one molecule to another (as expected) but that, for a particular molecule, v(CN) depends upon the phase and in solution varies with solvent.

In each case the highest frequency is found in the vapour phase whilst the lowest recorded frequencies are for the liquids – the solution values lie between these extremes. In the vapour phase v(CN) for the alkyl compounds (except tertbutyl) is almost constant. Oddly enough this is so even for chloroacetonitrile where the presence of the nearby polar CCl bond would be expected to alter the frequency from that found in acetonitrile. In the liquid phase a decrease in v(CN) is observed ranging from 6 cm⁻¹ (ClCH₂ · CN) to 20 cm⁻¹ in (CH₃)₃C · CN. Rather smaller decreases are found in solution and for a particular molecule v(CN) changes but little with change of solvent.

Two main effects are usually taken into account when attempting an explanation of the changes that occur in the characteristic vibrational frequency arising from a particular bond situated in different molecules. These are the inductive effect of an electrophilic group on the α -carbon atom, and secondly the possibility of the formation of delocalized π -bonding involving groups conjugated with the C=N bond.

The inductive effect of chlorine in $ClCH_2 \cdot C = N$ decreases the ionic character of the CN bond, i.e. the effective net charges on the C and N atoms become smaller. This means that the attractive force between these bonded atoms becomes less and hence the bond length increases slightly leading to a smaller value for the force constant which is mirrored in a lower frequency for v(CN). Since the diminution in frequency is small then the change in ionic character in the bond must also be small.

When the halogen atom is directly attached to the CN group, as in cyanogen bromide, the perturbation on the CN group is much stronger and more complicated. It is seen that in such compounds the v(CN) frequency is actually displaced to lower frequencies with respect to that of acetonitrile. This can be explained as being due to delocalization of π -electrons leading to a decrease of bond order in the CN link and an increase in the CBr bond. There are two further factors which would have a similar weakening effect on the CN bond.

A model of BrCN shows that the bromine atom has such a large covalent radius that its effect would be felt on the nitrogen atom. Bromine has a large number of completed inner shells of electrons so that there is a high charge density around it which would tend to repel the charge cloud of the nitrogen. This would give rise to a repulsion between the ends of the molecule tending to lengthen the CN bond thereby weakening it and reducing its frequency. If this were really the mode of action then we would expect a greater effect from the more massive iodine than from bromine; this is in fact observed, v(CN) of ICN being even lower than that of BrCN.

Finally the polar $C \leftrightarrow Br$ bond induces a moment in the CN bond whose

sense is $C \leftrightarrow N$; this opposes the "natural" moment of the CN bond thus reducing its value, decreasing the C to N attraction and increasing the length of the bond.

The frequency of the nitrile group in acetonitrile is decreased slightly on passing to propionitrile and is further decreased when more of the hydrogens are displaced by methyl groups. This is in line with the greater electron repelling effect of methyl than of hydrogen. It is interesting to note that a linear relationship exists between the inductive power of the substituent group as given by the Taft

TABLE 5

values of taft substituent constant, σ^* , for various substituents and the corresponding $\Delta \nu$ (CN)

Substituent	σ^{*22}	$\nu(CN)_{comp} - \nu(CN)_{CH_3CN} (cm^{-1})$		
		Vapour	Soln. in CCl _s	
CH ₃ -	0	0	0	
CH ₃ ·CH ₂ -	-0.100	-2.0	5.8	
(CH ₃) ₂ ·CH-	-0.190	-3.0	7.6	
(CH ₃) ₃ C-	-0.300	-13.0	-19.2	
CICH ₂ -	1.05	-0.1	5.4	
I-	2.38		13.1	
Br	2.80	29.0	33.4	



Fig. 2. Plot of $[\nu(CN)_{compound} - \nu(CN)_{acctonitrile}]$ vs. Taft's substituent constant, σ^* . (() vapour; (Δ) soln. in CCl₄.

substituent constant σ^* and the frequency displacement (see Table 5 and Fig. 2). This relation does not hold however for substituents of different kind; for example, the point corresponding to monochloroacetonitrile is far removed from this line.

In the case of fumaronitrile, the CN groups are attached to opposite ends of the ethylenic bond and their electron attracting properties will tend to polarise the C=C bond in opposite directions. In the resonance hybrid therefore, the nitrogen atoms will be negatively charged with respect to the olefinic carbon atoms. This separation of charge is effectively relayed only to the α -carbon atom of the olefinic link and not to the β -atom as would be the case in the appropriate mononitrile. A higher nitrile frequency would therefore be expected, and is found; fumaronitrile shows an increase of about 10 cm⁻¹ in its CN frequency above that of acrylonitrile²⁰.

In order to explain the frequency displacements that occur in the same molecule when it is found in a different phase or environment, it is convenient to define a quantity, Δv , given by, $\Delta v = [v(CN)_{vapour} - v(CN)]$ of the particular environment].

TABLE 6

VALUES OF	[v(CN]	$v_{apour} - v(CN)_{iiquid or soln.}$](cm-	5
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Compound	Liquid	Soln. in CCl ₄	Soln. in C_2Cl_4	Soln. in CHCl ₂
$\overline{CH_{a} \cdot CN}$	14.5	12.0	11.6	11.3
$CH_3 \cdot CH_2 \cdot CN$	17.8	15.8	15.4	15.1
(CH ₃) ₂ CH · CN	18.7	16.6	16.2	17.5
(CH ₂) ₂ C · CN	19.5	18.3	17.4	18.7
CICH. · CN	5.6	5.6	5.3	4.6
BrCN	10.9	7.6	8.2	7.5

From Table 6 it is seen that the v(CN) frequency always decreases by quite an appreciable amount on passing from the vapour to the liquid state. This is probably due to the presence of some association²² in the liquid phase brought about by the polar nature of the CN group which causes the following orientation to be favoured:

 $N \leftrightarrow C-CH_3$ $CH_3-C \Rightarrow N$

The total moment $\mu(CN)$ is therefore reduced by induction and so will be the attraction of the atoms of the CN bond for one another; the bond will then be lengthened somewhat and its vibrational frequency reduced. If this is the reason for the frequency displacement it would be expected that the more polar the CN bond then the greater the force of association; in such cases, therefore, the induced moment would be greater and so also should be the effect of the phase change from vapour to liquid on the frequency $\nu(CN)$. This is in fact seen; from CH₃·CN to $(CH_3)_3C \cdot CN$ the polarity of the CN bond increases due to the effect of the electron-repelling CH₃ groups and, from Table 6, the frequency displacement also

EFFECTS ON v(C=N) BOND STRETCHING FREQUENCIES

increases in this order. (At this point it must be stated that the v(CN) values for $(CH_3)_2CH \cdot CN$ and $(CH_3)_3C \cdot CN$ in the vapour state are only approximate $(\pm 2 \text{ cm}^{-1})$. This is due to the fact that the pressure inside the gas cell available could not be raised much above atmospheric and at the temperature used, ~150°, the CN bands for these compounds showed no fine structure as did the others and were quite broad so that accurate frequency measurement was impossible). In ClCH₂·CN where the CN bond moment is smaller owing to the inductive effect of the CCl group so also is the frequency displacement.

Even though the shift in v(CN) on changing phase is quite considerable, the change that occurs in solution on changing solvent is relatively much smaller, but nevertheless recognisable. When the nitrile molecule is surrounded by solvent, molecular association with its own kind as previously envisaged becomes less likely so that the frequency is expected to rise with respect to that in the liquid. From Table 6 this is seen to happen in all cases. In general, the greatest frequency displacement occurs in solution in CCl₄, then in C₂Cl₄, and the least displacement occurs in solutions in CHCl₃. Hydrogen bonding, which intensity measurements²³ show to be present between nitriles and chloroform, will not explain this effect except in the cases of $(CH_3)_2CH \cdot CN$ and $(CH_3)_3C \cdot CN$ where a greater displacement is in fact observed in chloroform solution. The higher polarity of the CN bonds in these compounds probably facilitates hydrogen bonding to the hydrogen of chloroform and makes the hydrogen bond $XCN \cdot \cdot H \cdot CCl_3$ sufficiently strong to influence the frequency.

The Kirkwood-Bauer-Magat theory²⁴ predicts a solvent shift given by the relation

$$\Delta v/v = c(\varepsilon - 1)/(2\varepsilon + 1)$$

where c is a constant which depends on the dimensions of the solute molecule and on the details of the dipole model, and ε is the solvent dielectric constant. Tests of this relationship have been made by many workers^{25,26} and in general it has been found to work quite well for non-polar solvents. For polar solvents it was however found necessary to bring in additional concepts such as hydrogen bonding and molecular complexes. Dielectric constants of carbon tetrachloride, tetrachloroethylene and chloroform at 25° are 2.238, 2.30 and 4.806, respectively²⁷ so that the corresponding values of $(\varepsilon - 1)/(2\varepsilon + 1)$ are 0.225, 0.23 and 0.36. These values are seen to be roughly inversely proportional to the $\Delta v/v$ values of Table 7. The relation however is far from the linear one predicted from the KBM relation. It is nevertheless probably accurate to say that the effect on the v(CN) frequency in these solvents is mainly a bulk dielectric one. It is impossible to be sure of this fact of course because of the magnitude of the frequency shifts observed, these being much smaller for example than the corresponding ones for the C=O bond even though the change that occurs in going from vapour to liquid in both cases is about the same (c.f. ref. 28).

Bellamy has shown that the KBM relationship is unsatisfactory in explaining the observed medium shift of X=O stretching frequencies and that a better procedure is to plot the relative frequency shift, $\Delta v/v$, of the X=O absorption in any compound against the relative shifts of any other to give a straight line²⁸. The data obtained in this study were treated in this fashion and the results are shown in Table 7 and Fig. 3. Reasonable straight lines are obtained, varying in slope as follows:

$CH_3CH_2 \cdot CN$	0.84	$ClCH_2 \cdot CN$	0.09
$(CH_3)_2 CH \cdot CN$	0.90	BrCN	1.08
$(CH_3)_3C \cdot CN$	0.71		

TABLE 7

VALUES OF $[\nu(CN)_{vapour} - \nu(CN)_{soln.}]/\nu(CN)_{vapour}$ (×10³).

Compound	Liquid	Soln. in CCl ₄	Soln. in C ₂ Cl ₄	Soln. in CHCl ₃
CH ₃ · CN	6.397	5,294	5.118	4.985
CH ₃ CH ₃ · CN	7.857	6.976	6.798	6.667
(CH ₃) ₂ CH · CN	8.258	7.331	7.155	7.727
$(CH_3)_3 C \cdot CN$	8.650	8.074	7.718	8.294
CICH, CN	2.472	2.472	2.340	2.031
BrCN	4.962	3.461	3.735	3.416



Fig. 3. Plot of $\Delta \nu / \nu_{(compound)}$ vs. $\Delta \nu / \nu_{(acetonitrile)}$. (1) CH₃CH₂·CN, (2) (CH₃)₂CH·CN, (3) (CH₃)₃C·CN, (4) ClCH₂ · CN, (5) BrCN.

The individual sensitivities to solvent effects, as determined by the slopes of the lines, vary widely. The fact that a slope of unity is not obtained suggests that the frequency shifts are not solely dependent upon a single property of the solvent such as dielectric constant but that the properties of the solute molecules are also involved in some sort of solvent-solute dipolar association. The much weaker sensitivity of ClCH₂CN to solvent effect than that of the other compounds, as shown by the small slope of its line, in Fig. 3, may be explained by the fact that the CN bond in this compound is almost homopolar in nature²³.

The frequency displacement of a solute vibration is a complex function of the properties of both solute and solvent and it is only in special cases, such as in the highly-localised X-H vibrations, that one factor alone is sufficient to account for the greater part of the shift. It is probably true to say that the sensitivities of ν (CN) to solvent effects, however small, are a complex function taking into account the polarity and polarizability of the CN bond, the proton-accepting power of the CN group and the shape of the molecule.

The problem is thus complex and, owing to the smallness of the frequency shifts, the possible application of solvent shifts of the CN frequency in diagnostic work is very limited.

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