862. *Spectroscopic Studies. Part V.*[1] *The Spectra and Structure of Monohalogenoacetonitriles*

By R. G. Jones and W. J. Orville-Thomas

The infrared spectra of a closely related series of acetonitriles have been obtained between 5000 and 500 cm.$^{-1}$. An analysis of the fine structure obtained for two fundamentals of fluoroacetonitrile, and of band contours in other cases, shows that the molecules have the nitrile structure, $XCH_2\cdot CN$ (X = halogen) and not the alternative ketimine structure $XCH = C = NH$.

Frequency assignments have been made and structural details deduced in each case.

The spectroscopic data have been used to calculate thermodynamic values for $FCH_2\cdot CN$ and $ClCH_2\cdot CN$.

The lower members of the nitrile family are neutral liquids, soluble in water, with which, according to one author, they can form hydrogen bonds.[2] A review of their physical properties reveals rather anomalous boiling points, in keeping, perhaps, with an ability to form hydrogen bonds. Table 1 summarises the molecular weights and boiling points of some nitriles, compared with the corresponding data for molecules in which the nitrile groups are replaced by chlorine. The chlorine atom has approximately the same mass and electronegativity as the nitrile group, and possesses the same potential for hydrogen bonding. Chemically, nitriles are very reactive, and their unsaturated nature is illustrated by numerous addition reactions.

Table 1

Boiling points of $XCH_2\cdot CN$ and $XCH_2\cdot Cl$ molecules

Molecule	Mol. wt.	B. p.	Molecule	Mol. wt.	B. p.
$CH_3\cdot CN$	41	82°	$CH_3\cdot Cl$	50	−24°
$F\cdot CH_2\cdot CN$	59	80	$F\cdot CH_2\cdot Cl$	68	−9
$Cl\cdot CH_2\cdot CN$	75	126	$Cl\cdot CH_2\cdot Cl$	84	40
$Br\cdot CH_2\cdot CN$	120	150	$Br\cdot CH_2\cdot Cl$	129	69

Monosubstituted acetonitriles can be formulated as C_2H_2NX. There are three possible structural isomers, which may be discussed in the light of the known properties. They

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[1] Part IV, E. W. Jones and W. J. Orville-Thomas, *J.*, 1964, 5853.

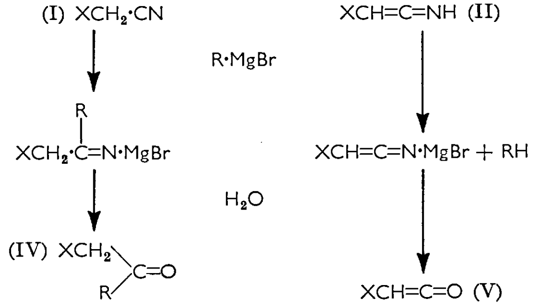
[2] I. L. Finar, " Organic Chemistry," Longmans, London, 1964, p. 249.

are:

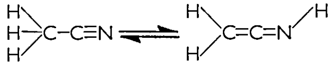
$X{-}CH_2{-}C{\equiv}N$ (I) Nitrile $\quad$ $X{-}CH{=}C{=}NH$ (II) Ketimine $\quad$ $X{-}C{\equiv}C{-}NH_2$ (III) Aminoacetylene

The possible structures are all unsaturated. The ketimine and the amino acetylene molecules would obviously give sodium salts, and the nitrile molecule might if the methylene group is sufficiently reactive, *e.g.*, in nitromethanes.[3] In deciding between the three possible structures chemical evidence alone is almost conclusive.

Nitriles undergo hydrolysis to give an acid and ammonia. This, together with the neutral properties of these compounds, suggests that structure (III) may be eliminated. Structure (II), however, survives, since the unsaturated nature of the nitrogen atom may well result in a neutral molecule. Hydrolysis would yield a substituted ketene and ammonia, the ketene reacting immediately with excess of water to give the acid. There is chemical evidence that many nitriles exhibit tautomerism in reacting with a Grignard reagent:



The ketone (IV) is the predominant product of the reaction but an acidic by-product provides evidence for the reaction sequence (II)—(V). The chemical evidence therefore leads to the conclusion that both structures (I) and (II) exist in a tautomeric equilibrium:



(I; X = H) (II; X = H)

in which (I) is the more stable form.

This view, however, is not wholly supported by physical evidence. Evidence in favour of structure (I) is provided by the microwave spectra of some nitriles. The molecular parameters obtained from these studies are listed in Table 2. An examination of these

TABLE 2

Molecular dimensions of $XCH_2{\cdot}CN$ molecules (bond lengths, r, in Å)

Molecule	r(CX)	r(CH)	r(CC)	r(CN)	$\widehat{HCH}$	$\widehat{CCX}$	Ref.
$CH_3{\cdot}CN$	1·112	1·112	1·458	1·157	109·27°	—	4
$ClCH_2{\cdot}CN$ ...	1·767	1·070	1·472	1·158	—	111° 24′	5
	1·782	1·088				111° 29′	6
$CN{\cdot}CH_2{\cdot}CN$...	1·49	1·09	1·49	1·17	109° 28′		7
$FCH_2{\cdot}CN$ ...	1·38	1·07	1·47	1·16	109·5°	110°	Assumed *
$BrCH_2{\cdot}CN$ ...	1·91	—	1·47	1·16	—	112	Assumed *
$ICH_2{\cdot}CN$	2·10	—	1·47	1·16	—	113	Assumed *

* The assumed dimensions have been transferred from similar molecules such as the dihalogenated methanes.

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[3] J. Yarwood and W. J. Orville-Thomas, *J.*, 1963, 5991.

[4] L. F. Thomas and E. I. Sherrard, *Trans. Faraday Soc.*, 1955, **51**, 619.

[5] J. Graybeal, *J. Chem. Phys.*, 1960, **32**, 1258.

[6] K. Wada, Y. Kikuchi, C. Matsumura, E. Hirota, and Y. Morino, *Bull. Chem. Soc. Japan*, 1961, **34**, 337.

[7] A. Tramer and K. L. Wierzchowski, *Bull. Acad. polon. Sci., Ser. Sci. chim., geol. geog.*, 1957, **5**, 335.

figures proves quite conclusively that nitriles of structure (I), with a triply bound CN bond with a characteristic length close to 1·16 Å, have a physical existence.†

The uncertainty as to whether structures (I) and (II) exist in tautomeric equilibrium or not prompted the infrared-spectroscopic investigation of monohalogeno-acetonitriles described in this Paper.

TABLE 3

Raman * and infrared spectra (cm.$^{-1}$) of fluoroacetonitrile

Raman (liquid)		Liquid (capillary)		Infrared (liquid) (0·1 mm.)		Vapour		Assignment
				4442	(4)			3013 + 1448 = 4461
				4364	(2)			3013 + 1378 = 4391
				4225	(2)			2975 + 1249 = 4224
				4061	(2)			3013 + 1041 = 4054
				4021	(2)			2975 + 1041 = 4016
				3673	(3)			2257 + 1448 = 3705
				3167	(3)			2257 + 907 = 3164
3021	(1·5)	3012	(3)	3013	(8)	2992	(5)	A'' Fundamental
2983	(10)	2977	(5)	2975	(9)	2980 2962	(5)	A′ Fundamental
2895	(0)			2885	(4)			2 × 1448 = 2896
				2824	(3)			1448 + 1378 = 2826
				2484	(2)			2 × 1249 = 2498
		2452	(1)	2453	(4)			1447 + 1020 = 2467
2299	(0)			2295	(2)			1249 + 1041 = 2290
2266	(6)	2258	(2)	2258	(5)	2277 2269 2258	(5)	A' Fundamental
						2138 2130 2120	(2)	2 × 1071 = 2142
1585	(0)	1624	(3)	1625	(5)			1385 + 238 = 1623
1461	(1)	1451	(4)	1448	(9)	1476 1466 1457	(3)	A' Fundamental
1389	(0)	1378	(8)	1378	10)	1396 1385 1377	(7)	A' Fundamental
		1360sh	(4)	1361sh	(8)	1356 1344sh	(3)	2269 − 917 = 1352
1259	(0·5)	1248	(3)	1248	(7)	1297 1287 1277	(2)	
		1132sh	(4)	1131sh	(8)	1131	(5)	1385 − 238 = 1147
1054	(2)	1048	(9)	1050	(10)	1079 1071 1060	(9)	A' Fundamental
						1032 1019 1008	(5)	A'' Fundamental
922	(1)	911	(7)	910	(9)	930 917 911	(7)	A' Fundamental
				790	(5)	780 772 760	(2)	1019 − 238 = 781
				688	(6)	667 653	(2)	457 + 191 = 648
575	(0·5)			563		556 544	(2)	1019 − 457 = 562
457	(0)			485	(2)			2 × 238 = 476
357	(1)							2 × 191 = 382
238	(3)							A' Fundamental
191	(1)							A'' Fundamental

* The Raman spectra were recorded on the Cary 81 Raman spectrometer.

Figures in brackets indicate relative strengths.

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† This, however, does not prove that nitriles exist solely in this form since the absorption lines of the alternative tautomer (II), with its quite different moments of inertia, would lie at very different frequencies and might not have been observed.

EXPERIMENTAL

Materials.—*α-Fluoroacetonitrile and α-chloroacetonitrile.* These were prepared by dehydration of the respective amides with phosphorus pentoxide, and were purified by repeated distillation from fresh phosphorus pentoxide. The main impurity was the amide in each case, but spectroscopic evidence showed that the amount of impurity was very small.

The boiling points were recorded as follows: α-fluoroacetonitrile, 80°; (lit.,[8a] 80°) α-chloroacetonitrile, 126°; (lit.,[8b] 126—127°).

α-Bromoacetonitrile and α-iodoacetonitrile. These compounds were prepared by the addition of dry α-chloroacetonitrile to saturated solutions of potassium bromide and sodium iodide, respectively, in dry methanol. Excess of the solid inorganic salt was used in each case to increase the yields of the required products.

TABLE 4

Raman and infrared spectra (cm.$^{-1}$) of monochloroacetonitrile

Cheng (R)		Liquid			Vapour		Assignment
		Zeil (i.r.)	This work				
		4434	4412	(1)			1424 + 3013 = 4437
			4241	(1)			2968 + 1272 = 4240
		4211	4183	(1)			3013 + 1184 = 4197
		3916	3917	(1·5)			932 + 3013 = 3945
		3641					
		3509	3491	(2)			2261 + 1272 = 3533
		3390	3367	(2·5)			359 + 3013 = 3372
		3180	3190	(2·5)			198 + 3013 = 3211
3014	(1)	3013	3013	(9)	3016	(2)	A'' Fundamental
2966	(5)	2966	2968	(8·5)	2987 2970	(3)	A' Fundamental
		2857	2850	(1·5)			2 × 1424 = 2848
2759		2759	2747	(1)			2968 − 200 = 2768
		2660	2693	(1·5)			1424 + 1272 = 2696
		2611	2608	(2)			2968 − 359 = 2608
		2532	2529	(2)			2 × 1272 = 2544
		2451	2450	(2)			1184 + 1274 = 2458
			2317				
2258	(8)	2254	2261	(4·5)	2272 2266 2258	(3)	A' Fundamental
		1818	1811	(2·5)			2 × 907 = 1814
		1680	1694	(3·5)			2968 − 1272 = 1696
		1620					1420 + 200 = 1620
		1613	1614	(4)			904 + 739 = 1643
		1587					1273 + 350 = 1623
			1459	(6)			2 × 739 = 1478
1416	(1)	1420	1424	(8·5)	1446 1428	(3)	A' Fundamental
		1273	1272	(8)	1282 1272	(8)	A' Fundamental
1269	(1)	1259	1256sh	(5·5)	1265 1244sh 1237	(2)	907 + 359 = 1262
1180	(½)	1178	1184	(3)	1186	(2)	A'' Fundamental
1025	(0)	1026			1033	(1)	
		983	981	(3)	972	(3)	2261 − 1272 = 989
932	(0)	932	932	(9)	94 936 927	(6)	A' Fundamental
			907	(4·5)	909 900	(3)	A' Fundamental
742	(8)	741	739	(10)	756 749 740	(9)	A' Fundamental
683	(½)				668 654	(1)	1424 − 739 = 685 or 2 × 330
494	(1)	491	488	(3)			1424 − 932 = 492 or 2 × 250
424	(0)						
351	(2)	359					A' Fundamental
206		198					A'' Fundamental

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[8] (*a*) P. Sensi and G. G. Gallo, *Gazzetta*, 1955, **85**, 224; (*b*) Steinkopf, *Ber.*, 1908, **41**, 2541.

TABLE 5

Infrared spectrum (cm.$^{-1}$) of monobromoacetonitrile

Liquid		Vapour		Assignment
3925	(1)			2973 + 940 = 3913
3670	(2)			3021 + 648 = 3669
3560	(2)			
3195	(3)			2259 + 940 = 3199 or 3021 + (190) = 3211
3021	(9)	3033 3016	(4)	*A''* Fundamental
2973	(8)	2988 2971	(7)	*A'* Fundamental
2313	(2)			2 × 1167 = 2334
2259	(5)	2264	(3)	*A'* Fundamental
2089	(1)			1167 + 940 = 2334
1409	(9)	1427 1421	(4)	*A'* Fundamental
1286	(4)			2 × 648 = 1296
1214	(7)	1232 1217	(6)	*A'* Fundamental
1167	(4)	1168	(4)	*A''* Fundamental
940	(7)	948 941 936	(5)	*A'* Fundamental
860	(4)	859	(3)	*A''* Fundamental
648	(8)	658 644	(5)	*A'* Fundamental
574	(4)			2 × (290)
(290)				*A'* Fundamental
(190)				*A'* + *A''* Fundamental

TABLE 6

Infrared spectrum (cm.$^{-1}$) of monoiodoacetonitrile

Capillary		Liquid (0·1 mm.)		Vapour (8 mm.)		Assignment
4406	(3)	4408	(5)			3024 + 1403 = 4427
4156	(2)	4154	(4)			3024 + 1155 = 4179
4125	(2)	4123	(4)			2967 + 1155 = 4122
3826	(2)	3825	(4)			3024 + 802 = 3826
3654	(3)	3652	(7)			1403 + 2251 = 3654
3571	(3)	3569	(8)			2967 + 594 = 3561
3192	(4)	3192	(6)			2251 + 940 = 3191
3024	(9)			3037	(2)	*A''* Fundamental
2967				2993 2976	(2)	*A'* Fundamental
2796	(2)	2796	(4)			2 × 1403 = 2806
2655	(1)	2655	(3)			1403 + 1275 = 2687
2544	(1)	2544	(2)			1403 + 1155 = 2558
2305	(2)	2305	(4)			2 × 1155 = 2310
2251	(8)	2250	(10)			*A'* Fundamental
2199	(2)	2198	(5)			1275 + 940 = 2219
		2094	(1)			1155 + 940 = 2095
1729	(5)	1730	(8)			944 + 802 = 1746
1437	(3)	1437	(6)			944 + 594 = 1438
1403	(8)	1400	(10)	1432 1417	(3)	*A'* Fundamental
1275	(4)	1280	(9)	1269	(4)	*A'* Fundamental
1155	(6)	1150	(10)	1172 1159	(8)	*A''* Fundamental
1097	(3)	1100	(8)	1101		2251 − 1155 = 1096
1060	(2)	1063	(6)			
944	(6)	942	(10)	952 939	(3)	*A'* Fundamental
		888	(1)			
802	(5)	802	(9)	803	(2)	*A''* Fundamental
712	(2)	714	(5)	690	(2)	2967 − 2251 = 716
		646	(3·5)			
599	(5)	595	(9)	599 589 586	(4)	*A'* Fundamental
482	(2)	482	(5)			2 × (245)
(245)						*A'* Fundamental

The nitriles were isolated by fractional distillation under reduced pressure of the supernatant layer from the reaction vessel.

The boiling point of α-bromoacetonitrile was 150° at 760 mm. and 46° at 13 mm. The main impurity, which was present in significant amounts, was α-chloroacetonitrile.

The boiling point of α-iodoacetonitrile was 182°/720 mm. (decomp.) and 78° at 14 mm. The impurity in α-iodoacetonitrile was iodine, but this did not affect the spectrum observed. It was removed by washing the nitrile with a solution of sodium thiosulphate.

The boiling points observed were in excellent agreement with those in the literature.[8a,b]

Instruments.—The spectra (Tables 3—6 and Figures 1—4) of liquid capillary films, of liquid films 0·1 mm. thick, and of the vapours of these substances were recorded between 5000 and 500 cm.$^{-1}$ on a Grubb–Parsons GS-2A spectrometer. For convenience the fundamentals are collected together in Table 7.

RESULTS

Structure of the Nitrile Molecule.—It has already been argued on the basis of chemical evidence that the nitrile molecule may have either structure (I) or the ketimine structure (II), or be a tautomeric mixture of the two. In order to decide between these two possible models, it is sufficient to consider only those vibrations that involve principally a hydrogen atom and a second, much heavier, atom. These fundamental vibrations may be considered to be localised and to have characteristic frequency ranges as follows: model (I) two bands near 3000 cm.$^{-1}$ arising from the asymmetric and symmetric CH_2 stretching modes, ν_a-(CH_2) and ν_s-(CH_2) of the monosubstituted nitriles; model (II) a ν(NH) band near 3400 cm.$^{-1}$ and a ν(CH) band, from the =CH group, near to 3020 cm.$^{-1}$.

TABLE 7

Vibrational frequency assignment of $XCH_2{\cdot}CN$ molecules (frequency in wave-numbers)

Vibration type	$FCH_2{\cdot}CN$		$ClCH_2{\cdot}CH$		$BrCH_2{\cdot}CN$		$ICH_2{\cdot}CN$		Approx. description
	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour	
A′	2977	2971	2966	2979	2971	2979	2960	2984	$\nu_s(CH_2)$
A′	2258	2269	2261	2266	2259	2264	2245	—	ν(CN)
A′	1453	1466	1424	1437	1409	1426	1408	1425	$b_s(CH_2)$
A′	1381	1385	1274	1272	1210	1224	1155	1165	$w(CH_2)$
A′	911	917	932	936	940	940	944	945	ν(C–C)
A′	1041	1071	740	749	643	651	594	589	ν(C–X)
A′	(395)	(390)	(354)	—	(290)	—	(254)	—	b(CCX)
A′	238 *	(270)	206 *	—	(190)	—	—	—	bip(CCN)
A″	3012	2992	3013	3016	3021	3033	3024	3037	$\nu_a(CH_2)$
A″	1248	1287	1180	1186	1167	1168	1100	1101	$tw(CH_2)$
A″	—	1019	907	900	960	861	802	802	$r(CH_2)$
A″	191 *	(160)	206 *	—	(190)	—	—	—	bop(CCN)

Interpolated values in parentheses.

* Raman.

The NH stretching fundamental would be expected to give rise to a fairly broad band in the liquid phase because of hydrogen bonding. The 3-μ region therefore provides a sensitive probe for the theory that an equilibrium exists between the two structures. In all cases, no broad associated band was found near 3400 cm.$^{-1}$, this proves that the nitriles in the liquid state contain little if any of the ketimine tautomer. In each case studied, two sharp absorption bands were found near 3000 and 2950 cm.$^{-1}$; these obviously arise from a methylene group, and hence it is assumed in the subsequent discussion that the nitriles have the XCH_2CN structure (I). Confirming this view, a band was found near to 2250 cm.$^{-1}$ in the spectra of all molecules; this band is assigned to the ν(C≡N) vibration.

The dimensions of $ClCH_2{\cdot}CN$ and of $CH_3{\cdot}CN$ have been calculated from the moments of inertia obtained from microwave studies on various isotopic species.[4–6] As the other molecules have not been studied, it was assumed that the dimensions were identical with those for $ClCH_2{\cdot}CN$ together with the following values for r(CX); 1·38(F), 1·91(Br), and 2·10(I).

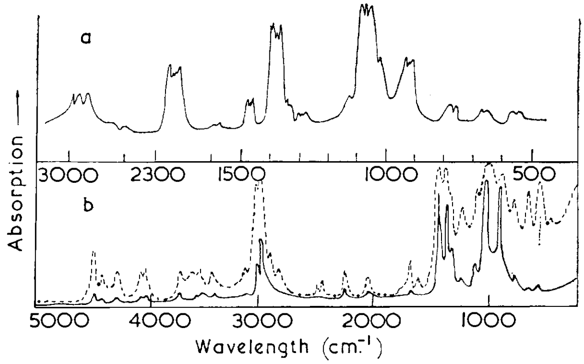

FIGURE 1. Infrared spectrum of monofluoroacetonitrile: (a) vapour (8-cm. cell); (b) liquid; (——) capillary film, (– – – –) 0·1 mm.

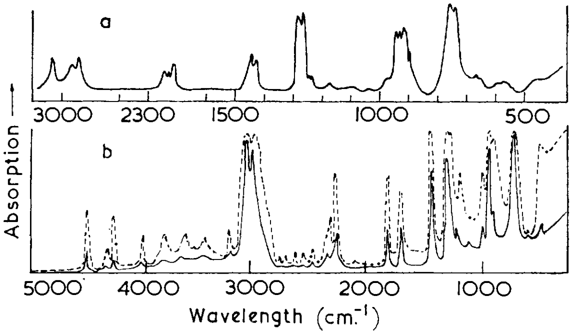

FIGURE 2. Infrared spectrum of monochloroacetonitrile: (a) vapour (8-cm. cell); (b) liquid; (——) capillary film, (– – – –) 0·1 mm.

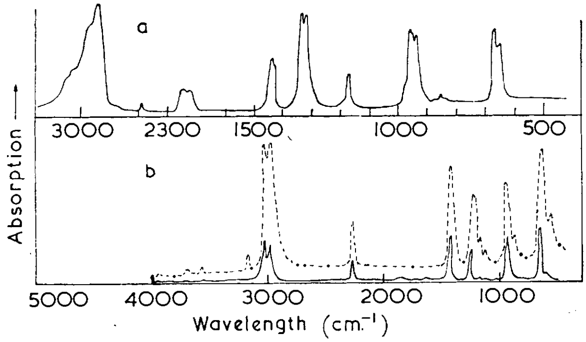

FIGURE 3. Infrared spectrum of monobromoacetonitrile: (a) vapour (8-cm. cell); (b) liquid; (——) capillary film, (– – – –) 0·1 mm.

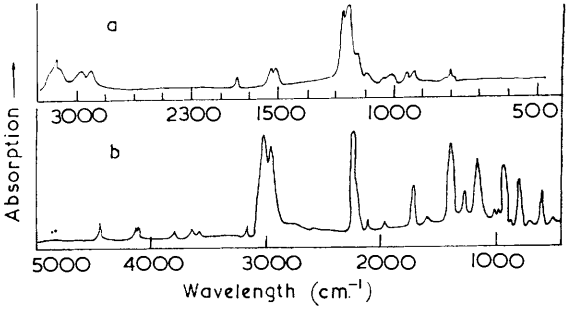

FIGURE 4. Infrared spectrum of monoiodoacetonitrile: (a) vapour (8-cm. cell); (b) liquid (capillary film)

TABLE 8

Calculated moments of inertia ($\times 10^{40}$ g. cm.^{2}) and rotational constants (cm.$^{-1}$)

Molecule	I_A	A	I_B	B	I_C	C
$FCH_2{\cdot}CN$	22·99	1·218	185·4	0·151	194·9	0·144
$ClCH_2{\cdot}CN$	33·07	0·847	267·9	0·104	295·7	0·095
$BrCH_2{\cdot}CN$	37·33	0·750	391·9	0·071	424·0	0·066
$ICH_2{\cdot}CN$	40·90	0·685	501·6	0·056	537·2	0·052

Calculated molecular parameters

Molecule	$I(\times 10^{40}$ g. cm.$^2)$	β	S	$\Delta\nu(P, R)$ (cm.$^{-1}$)
$FCH_2{\cdot}CN$	190·1	7·27	1·114	18·7
$ClCH_2{\cdot}CN$	281·8	7·52	1·110	15·9
$BrCH_2{\cdot}CN$	408·0	9·92	1·088	13·8
$ICH_2{\cdot}CN$	519·4	11·70	1·076	12·5

Vibrations of the $XCH_2{\cdot}CN$ *Molecule.*—At the most, these molecules have one plane of symmetry and therefore belong to the point group C_s. There are twelve fundamental vibrations distributed between two symmetry species:

$$\Gamma = 8A' + 4A''$$

The vibrations involve a change in dipole moment parallel to the symmetry plane for class A' modes and perpendicular for class A'' vibrations.

The fundamentals can be approximately described as follows: asymmetric and symmetric CH_2 stretching modes, ν_a and $\nu_s(CH_2)$, CH_2 bending, b, wagging, w, rocking, r, and twisting, tw(CH_2) modes, three skeletal stretching modes, ν(CX), ν(CC) and ν(CN), two bending-in-plane skeletal modes, bip(CCX) and bip(CCN) and one bending-out-of-plane, bop(CCN), vibration.

All the vibrations are infrared- and Raman-active.

Frequency Assignment.—As aids to frequency assignment, in this work emphasis is laid on (i) the use of fine-structure and contours of vapour phase absorption bands and (ii) comparison with the spectra of related molecules.

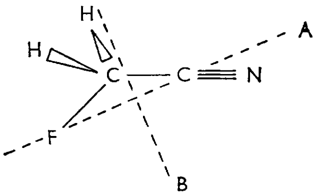

FIGURE 5. Principal axes for monofluoroacetonitrile

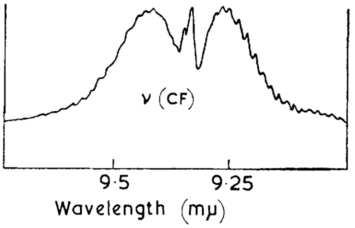

FIGURE 6. Fine structure of the ν(CF) band

(i) *Fine structure and band contours.* Modern commercial grating spectrometers enable spectroscopic studies of moderately high resolution to be carried out as a routine operation.

From the molecular parameters listed in Table 2, the values given in Table 8 are calculated for the moments of inertia * and the rotational constants for the $XCH_2{\cdot}CN$ molecules (Figure 5). Since $I_A \neq I_B \neq I_C$ the molecules are asymmetric rotors. The values obtained, however, show that, to a first approximation, the molecules are prolate symmetric tops (*i.e.*, $I_B \approx I_C \gg I_A$).

During the vapour-phase investigations fine structure was observed in two bands only, and these were centred near 920 and 1073 cm.$^{-1}$ in the spectrum of $FCH_2{\cdot}CN$. The appearance of the bands is shown in Figure 6 and the frequencies of the sub-band maxima are listed in Tables 9 and 10.

The substitution of a fluorine for a hydrogen atom in $CH_3{\cdot}CN$ changes the molecule from a symmetric to a slightly asymmetric top in which the three moments of inertia are different. The least axis is therefore inclined to the linear CCN grouping (Figure 5) and there are three sets of selection rules depending upon whether change in dipole moment during a vibration is

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* The methylene groups have been treated as point masses in calculating the moments of inertia of these molecules, in all except the monofluoroacetonitrile.

TABLE 9

Observed fine structure for ν(CF) fundamental of $FCH_2{\cdot}CN$

Observed ν_0 sub.	Assignment	Observed ν_0 sub.	Assignment	Observed ν_0 sub.	Assignment	Observed ν_0 sub.	Assignment
1113·4	${}^{R}Q_{20}$	1093·7	${}^{R}Q_{10}$	1071·8	${}^{P}Q_{1}$	1051·6	${}^{P}Q_{11}$
1111·6	${}^{R}Q_{19}$	1091·6	${}^{R}Q_{9}$	1069·6	${}^{P}Q_{2}$	1049·4	${}^{P}Q_{12}$
1109·9	${}^{R}Q_{18}$	1089·5	${}^{R}Q_{8}$	1067·7	${}^{P}Q_{3}$	1047·0	${}^{P}Q_{13}$
1107·6	${}^{R}Q_{17}$	1087·2	${}^{R}Q_{7}$	1065·9	${}^{P}Q_{4}$	1044·8	${}^{P}Q_{14}$
1105·6	${}^{R}Q_{16}$	1085·2	${}^{R}Q_{6}$	1064·2	${}^{P}Q_{5}$	1042·5	${}^{P}Q_{15}$
1103·9	${}^{R}Q_{15}$	1083·2	${}^{R}Q_{5}$	1062·0	${}^{P}Q_{6}$	1040·5	${}^{P}Q_{16}$
1101·7	${}^{R}Q_{14}$	1081·1	${}^{R}Q_{4}$	1060·1	${}^{P}Q_{7}$	1038·4	${}^{P}Q_{17}$
1099·8	${}^{R}Q_{13}$	1079·2	${}^{R}Q_{3}$	1058·1	${}^{P}Q_{8}$	1036·1	${}^{P}Q_{18}$
1097·7	${}^{R}Q_{12}$	1077·5	${}^{R}Q_{2}$	1055·9	${}^{P}Q_{9}$	1033·9	${}^{P}Q_{19}$
1095·7	${}^{R}Q_{11}$	1075·5	${}^{R}Q_{1}$	1053·7	${}^{P}Q_{10}$	1032·0	${}^{P}Q_{20}$
						1029·9	${}^{P}Q_{21}$

TABLE 10

Observed fine structure for ν(CC) fundamental of $FCH_2{\cdot}CN$

Observed ν_0 sub.	Assignment	Observed ν_0 sub.	Assignment	Observed ν_0 sub.	Assignment	Observed ν_0 sub.	Assignment
950·1	${}^{R}Q_{15}$	932·3	${}^{R}Q_{7}$	918·5	${}^{P}Q_{1}$	900·3	${}^{P}Q_{9}$
948·0	${}^{R}Q_{14}$	930·6	${}^{R}Q_{6}$	916·8	${}^{P}Q_{2}$	898·6	${}^{P}Q_{10}$
944·6	${}^{R}Q_{13}$	928·7	${}^{R}Q_{5}$	914·8	${}^{P}Q_{3}$	896·3	${}^{P}Q_{11}$
943·0	${}^{R}Q_{12}$	927·1	${}^{R}Q_{4}$	912·3	${}^{P}Q_{4}$	894·3	${}^{P}Q_{12}$
940·1	${}^{R}Q_{11}$	925·0	${}^{R}Q_{3}$	910·6	${}^{P}Q_{5}$	891·8	${}^{P}Q_{13}$
938·6	${}^{R}Q_{10}$	924·0	${}^{R}Q_{2}$	907·6	${}^{P}Q_{6}$	889·5	${}^{P}Q_{14}$
936·0	${}^{R}Q_{9}$	922·0	${}^{R}Q_{1}$	905·1	${}^{P}Q_{7}$	887·2	${}^{P}Q_{15}$
933·0	${}^{R}Q_{8}$			902·7	${}^{P}Q_{8}$	884·6	${}^{P}Q_{16}$

parallel to the axis of least, intermediate, or greatest inertia. The corresponding bands are called *A*-, *B*-, and *C*-bands, respectively.

From the rotational constants given in Table 8 the following spacings are expected for $FCH_2{\cdot}CN$:

A-bands: *P*, *R* components separated by 0·14 cm.$^{-1}$, central *Q*-branch.

B-bands: *Q*-sub-bands separated by about 2 cm.$^{-1}$ no central *Q*-branch.

C-bands: *Q*-sub-bands separated by about 2 cm.$^{-1}$, strong central *Q*-branch.

These values indicate that with the spectrometer used in this work the *Q*-sub-band structure of *B*- and *C*-bands should be resolved, but that only the contours of *A*-bands will be obtained. An examination of Figure 6 shows that the bands have a *P*, *Q*, *R* envelope on which is superimposed a *Q*-sub-band fine structure with an average spacing of slightly more than 2 cm.$^{-1}$ (Tables 8 and 9). Hence, both bands are hybrid (*A*/*B*) in character. The 1072 cm.$^{-1}$ band has a more prominent central *Q*-branch than that of the 920 cm.$^{-1}$ band; *i.e.*, it has more *A*-character. The subsequent assignment of these bands to the ν(CF) and ν(CC) stretching modes is in complete accord with this analysis.

Fine-structure analysis. For a near-symmetric top the frequencies of the fine-structure components are given by:

$$\nu = \nu_0 + [A' - B'] \pm 2[A' - B']K + [(A' - B') - (A'' - B'')]K^2 \qquad (1)$$

where the plus sign is taken for the *R*-branch ($\Delta K = +1$) and the minus sign applies to the *P*-branch ($\Delta K = -1$). The primed constants refer to the excited state, the double-primed constants to the lower state; ν_0 is the band centre.

The simplest way of determining rotational constants is to fit the sub-band maxima to equation (1). For greater (up to ten-fold) accuracy the method of combination differences was employed in this work.

From the usual relationships, graphs of the $\Delta_2F(J,K)$ functions against *K* were plotted and the slopes obtained by a least-squares treatment. (Figure 7). The results obtained indicate that the resolution (as expected) was not great enough to obtain accurate rotational constants for the molecule in the ground and upper state of the vibrational transition. The average value obtained experimentally for $(A'' - B'')$ is 1·04 cm.$^{-1}$, whilst that calculated from the moments of inertia assumed above is 1·07 cm.$^{-1}$ It seems therefore that the value assumed for the bond lengths and bond angles are slightly in error. The values are near enough, however, to confirm the correctness of the initial assumption that the molecule has structure (I).

Unresolved band contours. Apart from the two bands of $FCH_2 \cdot CN$ dealt with above, no fine structure was resolved. In many cases, however, the resolution was sufficient to provide the contours or envelopes of the bands, so that it was possible to decide whether a particular band was primarily *A*, *B*, or *C* in type.

It is possible to predict, in an approximate fashion, the band contours for particular vibrations on the basis of the following assumptions:

(*a*) The transition moment accompanying the stretching or bending of a bond, in localised vibrations, takes place parallel to the bond for stretching modes, and perpendicular to it for bending modes.

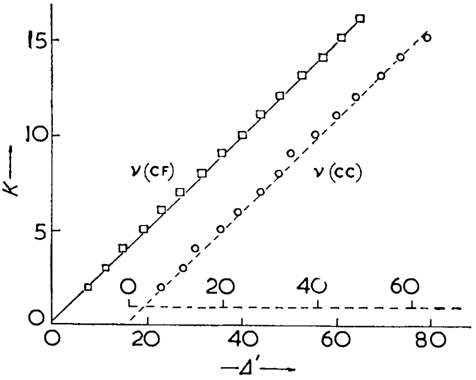

FIGURE 7. Combination differences for the ν(CC) and ν(CF) bands

(*b*) The resultant transition moment in vibrations involving more than two atoms is the vector sum of the contributing bond-transition moments.

On this basis, hybrid *A*/*B* contours * are predicted for the $w(CH_2)$, $tw(CH_2)$, ν(CX) and ν(CN) bands, whilst hybrid *B*/*A* contours are to be expected for the $\nu_s(CH_2)$, $b(CH_2)$, ν(CC), bip(CCX), and bip(CCN) bands. *C*-Type bands are predicted for the $\nu_a(CH_2)$, $r(CH_2)$, and bop(CCN) vibrations in which the transition moment changes in a direction perpendicular to the plane of symmetry, *i.e.*, parallel to the *C*-axis.

Band contours can also be used in a more quantitative fashion. Since the molecules approximate to symmetric tops, the separation $\Delta\nu(P,R)$ between the points where the *P* and *R* branches have maximum intensity is given by: [9]

$$\Delta\nu(P,\ R) = [S(\beta)/\pi][kT/I]^{\frac{1}{2}}$$

where $S(\beta) = 0{\cdot}721/(\beta + 4)^{1{\cdot}13}$, $\beta = (I - I_A)/I_A$, and $I = (I_B + I_C)/2$.

The *P*–*R* separations calculated for parallel or *A*-type bands are given in Table 12. In the

TABLE 11

Observed rotational constants of $F{\cdot}CH_2CN$

	νCF	νCC		νCF	νCC
$(A'_v - B'_v)$	1·026	1·052	$(A'_v - B'_v) - (A''_v - B''_v)$ *	−0·008	0·006
$(A''_v - B''_v)$	1·034	1·046	$(A'_v - B'_v) - (A''_v - B''_v)$ *	−0·008	−0·014

TABLE 12

P, *R* separations in parallel bands of $XCH_2 \cdot CN$ molecules

Molecule	$\Delta\nu(P,\ R)$	$w(CH_2)$	$tw(CH_2)$	Observed (CX)	(CC)	(CN)
$FCH_2 \cdot CN$	18·7	19 ± 1	20 ± 1	18·5 ± 1	18·4 ± 1	18·5 ± 1
$ClCH_2 \cdot CN$	15·9	17 ± 1	—	16 ± 1	16 ± 1	15 ± 1
$BrCH_2 \cdot CN$	13·8			14 ± 1	14 ± 1	
$ICH_2 \cdot CN$	12·5	—	13 ± 1	13 ± 1	13 ± 1	—

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* The symbol *A*/*B* indicates that the *A* component is more prominent than *B*; that is, the transition moment changes in a direction more nearly parallel to the *A* axis than to the *B* axis.

[9] S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, 1933, **43**, 197.

subsequent discussion any band that has the appropriate $\Delta\nu(P, R)$ separation is assigned to a class A' vibration in which the transition moment is parallel to the plane of symmetry of the molecule (Tables 3—6).

(ii) *Comparison with spectra of related molecules.* Of the four molecules of this series, monochloroacetonitrile is the only one that has received concentrated attention by spectroscopists. The Raman spectrum was first recorded by Cheng,[10] and more recently by Zeil,[11] who attempted a frequency assignment of the fundamental modes. Herman [12] included monofluoroacetonitrile in the study of the Raman spectra of some fluoro-compounds. Infrared studies on monochloroacetonitrile have been carried out by Cheng and Lecomte,[13] by Eukomoto,[14] and by Zeil.[11]

For convenience the assignment has been divided into two sections:

(*a*) the bands associated with the vibrations of the XCCN skeleton, and

(*b*) the vibrational modes of the methylene group.

The observed frequencies are given in Tables 3—6, and in Table 7 where the fundamentals are gathered together for comparison.

(a) *Skeletal modes.* The heavy-atom skeleton has three stretching modes, ν(CN), ν(CC), and ν(CX), and three bending modes, bip(XCC), bip(CCN), and bop(CCN).

CN-*Stretching modes.* ν(C≡N) bands occur in a well-defined region near 2250 cm.$^{-1}$. Such bands were observed in the vapour phase in all cases, excpt monoiodoacetonitrile. Presumably this band is very weak in this compound, and the cell path-length was too short at the temperature of observation (165°); at higher temperatures, the substance decomposed rapidly. In the liquid state, the corresponding bands were found for all four molecules.

The band contours in the vapour phase were found to be hybrid A/B in type as predicted. The observed P, R separations are remarkably close to those calculated from the assumed dimensions (Table 12).

CC-*Stretching modes.* Sheppard and Simpson, in a review of the characteristic regions of absorptions of branched paraffinic chains, give the region between 1300 and 650 cm.$^{-1}$ as characteristic of the skeletal stretching vibrations.[15] The assignments made for ν(CC) frequencies in ethyl halides [16-18] suggest a value close to 960 cm.$^{-1}$, whilst the corresponding figures for aceto- and malono-nitrile [19,20] suggest a lower value of 920 cm.$^{-1}$ for ν(CC). Strong bands, with the expected hybrid A/B contour and P, R separation of 13—18 cm.$^{-1}$ were found close to 930 cm.$^{-1}$ for all molecules and are therefore assigned to the ν(CC) modes. The liquid-state frequencies were almost identical with those obtained in the vapour phase.[21]

CX-*Stretching modes.* The position of these bands is subject to considerable fluctuation as the result of interactions with neighbouring groups; this is especially the case with the lighter halogens, fluorine and chlorine, in which the mass of the halogen involved does not differ much from the rest of the carbon skeleton. In all cases, the absorption bands are expected to be strong. Using, as a guide, the frequencies found for carbon–halogen stretching vibrations in the methyl halides we assign the bands centred at 1071 (F), 749 (Cl), 651 (Br), and 589 cm.$^{-1}$ (I), with an A/B contour, to the ν(CX) modes.

Skeletal bending modes. The frequencies of the skeletal bending vibrations are expected to be low. For example, the b(CCX) bands in C_2H_5X molecules are found at 415 (F), 335 (Cl), 292 (Br), and 262 cm.$^{-1}$ (I), whilst b(CCN) modes give rise to bands varying from 361 (CH_3CN) to 163 cm.$^{-1}$ in $Cl_3C{\cdot}CN$.

For $FCH_2{\cdot}CN$, three weak bands are observed, at 772, 660, and 550 cm.$^{-1}$, in the vapour phase and four in the liquid phase at 790, 688, 563, and 485 cm.$^{-1}$. Quite clearly these values are too high to be bending fundamentals. Three weak Raman lines were observed at 191, 238,

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[10] H. C. Cheng, *Z. phys. Chem. (Leipzig)*, 1934, *B*26, 288.
[11] W. Zeil, *Z. phys. Chem. (Frankfurt)*, 1958, **14**, 230.
[12] M. Herman, *Ind. chim. belge*, 1951, **16**, 86.
[13] H. C. Cheng and J. Lecomte, *Compt. rend.*, 1935, **201**, 199.
[14] V. Eukomoto, *Sci. Reports Tohoku Univ.*, 1934, Ser. 1, **23**, 62.
[15] N. Sheppard and D. M. Simpson, *J. Chem. Phys.*, 1955, **23**, 582.
[16] N. Sheppard, *J. Chem. Phys.*, 1949, **17**, 79.
[17] D. C. Smith, R. A. Saunders, J. R. Nielson, and E. E. Ferguson, *J. Chem. Phys.*, 1952, **20**, 847.
[18] L. W. Daasch, C. Y. Liang, and J. R. Nielsen, *J. Chem. Phys.*, 1954, **22**, 1293.
[19] N. E. Duncan and G. J. Janz, *J. Chem. Phys.*, 1955, **23**, 434.
[20] F. Halverson and R. J. Francel, *J. Chem. Phys.*, 1949, **17**, 694.
[21] G. Herzberg, " Spectra of Polyatomic Molecules," 1945, Van Nostrand, New York.

and 457 cm.$^{-1}$. Since the C–C≡N grouping has cylindrical symmetry, it is reasonable to suppose that the bip and bop (CCN) vibrations have nearly the same frequency (cf. H·C≡N). The bands at 191 and 238 cm.$^{-1}$ are therefore thought to arise from these modes. The bip(CCF) mode is assigned to the 457-cm.$^{-1}$ band. Some of the other Raman lines and infrared bands can be interpreted as overtones and combinations of these fundamentals, thus strengthening the assignments.

The low-lying bands found for $ClCH_2·CN$ are listed in Table 4. The band observed at 424 cm.$^{-1}$ by Cheng was not observed in this work, and is presumably due to some impurity, as suggested by Zeil. The frequency of the b(CCCl) vibration in ethyl chloride, 325 cm.$^{-1}$, strongly suggests that the corresponding band for $ClCH_2·CN$ is that observed by Cheng at 354 and by Zeil at 359 cm.$^{-1}$. Two bending CCN vibrational bands are to be expected in the spectra, one A' bip mode and one A'' bop-band. They are expected to have similar frequencies and are both placed at 206 cm.$^{-1}$.

For $BrCH_2·CN$ no bands were observed below 570 cm.$^{-1}$. However, weak absorptions at higher frequencies can be explained by assigning the following values to the bending fundamentals, *viz.*, b(CCBr) $\sim$ 290 cm.$^{-1}$ and bip $\sim$ bop(CCN) $\sim$ 190 cm.$^{-1}$.

One weak band only was observed for $ICH_2·CN$; this, at 480 cm.$^{-1}$, is thought to be the first overtone of the b(CCI) band, which is therefore placed near 245 cm.$^{-1}$.

(b) *Methylene vibrations.* The vibrations associated with the CH_2 group can be divided into internal and external vibrations. The internal vibrations consist of the two stretching vibrations and the bending mode. These are internal vibrations to the extent that they would appear even if the group in question were isolated. The corresponding frequencies in hydrocarbons differ little from 2926, 2853, and 1440 cm.$^{-1}$, respectively. Two sharp bands were observed in the liquid- and vapour-phase spectra in the 3000-cm.$^{-1}$ region, and can be confidently assigned to the ν_a and $\nu_s(CH_2)$ modes. The frequencies are, however, higher than the average values quoted above. This is in line with the values found for dihalogenated methanes, $X·CH_2·Y$, where the frequencies are raised some 100 cm.$^{-1}$ from the hydrocarbon values.

The methylene group has four deformation vibrations, bending, b, wagging, w, twisting, tw, and rocking, r. In a recent publication, Jones and Orville-Thomas [22] have found relationships between the methylene deformation frequencies in $X·CH_2·Y$ molecules and the electronegativity product $\chi(X)\chi(Y)$. These correlations have been used to predict the frequencies in $XCH_2·CN$ molecules. Agreement between the predicted and the observed values is good, the average error being less than 2%.

Thermodynamic Properties.—Thermodynamic parameters can be calculated from spectroscopic data when the molecular moments of inertia and a complete frequency assignment are known. The experimental data are fairly complete for $FCH_2·CN$ and $ClCH_2·CN$ and preliminary estimates have been made for the heat capacity $C_p°$, the entropy $S°$, the free energy function, $(F° - E_0°)/T$, and the internal energy function, $(E° - E_0°)/T$.

The translational and rotational contributions to the thermodynamic functions have been calculated from equations given by Rossini *et al.*[23] The contributions from each fundamental vibrational mode are available by interpolation from tables.[24,25]

The calculated thermodynamic quantities for two temperatures are given in Table 13.

TABLE 13

Thermodynamic parameters

Molecule	Temp. (°K)	$Cp°$ (I)—(II)	$Cp°$ (III)	$S°$ (I)—(II)	$S°$ (III)	$-(F° - E_0°)/T$ (I)—(II)	$-(F° - E_0°)/T$ (III)	$(E° - E_0°)/T$ (I)—(II)	$(E° - E_0°)/T$ (III)
$FCH_2·CN$	300°	7·95	6·65	61·83	0·62	53·34	2·67	5·96	3·26
	400	7·95	8·80	64·11	0·40	55·63	3·99	5·96	4·38
$ClCH_2·CN$	300	7·95	7·91	63·40	1·25	55·21	2·33	5·96	3·54
	400	7·95	9·65	65·69	1·29	57·50	3·54	5·96	4·79

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[22] R. G. Jones and W. J. Orville-Thomas, *Spectrochim. Acta*, 1964, **20**, 291.

[23] D. Wagman, J. Kilpatrick, W. J. Taylor, K. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

[24] P. Torkington, *J. Chem. Phys.*, 1950, **18**, 1373.

[25] E. B. Wilson, jun., *Chem. Rev.*, 1940, **27**, 17.

DISCUSSION

The spectroscopic evidence presented above gives substantial support to the view that nitriles have the $XCH_2{\cdot}CN$ structure. The fine-structure analysis for the ν(CF) and ν(CC) bands of $FCH_2{\cdot}CN$ has provided an accurate check on the configuration of the molecule and of the assumed dimensions.

The frequency assignment outlined above is in good agreement with that accepted for $X{\cdot}CH_2{\cdot}Y$ molecules. It also confirms the predictions of Nakagawa[26] that the order of frequencies of CH deformation modes in CH_3, CH_2, and CH groups is:

$$b_a(CH_3) > b(CH_2) > b_s(CH_3) > w(CH_3) > w(CH_2) > b(CH) > tw(CH_2) > r(CH_3) > r(CH_2)$$

Zeil[11] has given an alternative assignment for $ClCH_2{\cdot}CN$. The main differences are listed in Table 14. Zeil bases his assignment on correlations between the spectra of mono-, di-, and trichloro-acetonitrile, supported by Nielsen's work on 1,1,1-trifluoro-2-chloroethane.[27] In view of the great degree of internal consistency shown by the frequency assignments for all the halogenated acetonitriles (Table 7), it is believed that the assignment for $ClCH_2{\cdot}CN$ put forward here is superior to that of Zeil.

TABLE 14

Monochloracetonitrile bands (cm.$^{-1}$)

Mode	This work	Zeil
$b(CH_2)$	1424	1277
$w(CH_2)$	1274	(1026)R
$tw(CH_2)$	1180	1418
$r(CH_2)$	907	1186

R = Raman data.

The $XCH_2{\cdot}CN$ model having been adopted, it is not immediately apparent why the nitriles have such high boiling points in comparison with the compounds where the CN group is replaced by chlorine. It is obvious that the higher boiling points of the nitriles cannot be attributed to hydrogen bonding. An increase in boiling point however generally indicates a real or effective increase of molecular weight.

Hydrogen bonding increases molecular weights by causing the molecules to form aggregates. There are, however, other ways in which aggregates can be formed: one of the most important is by dipole–dipole interaction, which can be shown to give rise to a force of attraction between molecules that is proportional to the square of the dipole moment of the molecules. Since:

$$\chi(\mathrm{C}{:}sp^3) < \chi(\mathrm{C}{:}sp) < \chi(\mathrm{N}),$$

the dipoles are aligned H_3C +— $C \rightarrow N$.

Zhukova[28] has shown that the decrease in intensity of the ν(CC) and ν(CN) bands with increasing concentration in solvents such as carbon tetrachloride and benzene can be explained by dimerisation of the nitrile molecule as follows:

$$\begin{array}{ll} CH_3{-}C{\equiv}N & \\ & N{\equiv}C{-}CH_3 \end{array}$$

This view is contrary to that expressed by Murray and Schneider, who suggest that dipole interaction in nitriles appears to be unlikely since the mutual repulsions of the high charge-densities in the region of the CN triple bond would make it unfavourable.[29] It is, however, not necessary for the molecules to be aligned in a head-to-toe fashion for dimerisation to occur. The greater electronegativity of the nitrogen atom, together with the

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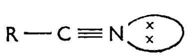
[26] I. Nakagawa, *J. Chem. Soc. Japan*, 1955, **76**, 540.

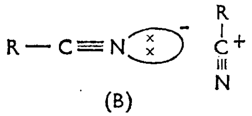
[27] J. R. Nicken, C. Y. Liang, and D. C. Smith, *J. Chem. Phys.*, 1953, **21**, 1060.

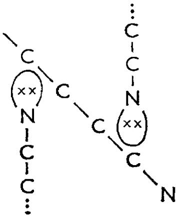
[28] E. L. Zhukova, *Optics and Spectroscopy*, 1958, **4**, 750.

[29] F. E. Murray and W. G. Schneider, *Canad. J. Chem.*, 1955, **33**, 797.

considerable electron charge-density in the lone-pair orbital of the nitrogen atom, results in an overall charge distribution which may be represented as in (A).


(A)


(B)


(C)

Nitriles form stable addition compounds with boron trifluoride, a typical vacant orbital acceptor.[30] The charge distribution can be represented as $R\overset{+}{C}\equiv\overset{-}{N}$. Hence, the dimerisation most probably takes place because the positively charged carbon acts as an acceptor to the lone pair of a second molecule (B).

Such a configuration (C) is in accord with the observed crystal structure of dicyanoacetylene,[31] which is an open, rather than a parallel, arrangement.

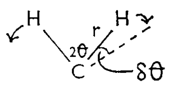
The closest approach is between the N-atom of one molecule and the innermost C-atoms of another.

This seems a reasonable mechanism for the formation of dimers in the liquid acetonitriles and hence explains their anomalous properties.

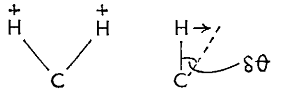
For the methylene deformation vibrations, the observed band intensities, expressed as a ratio of maximum extinction coefficients, $E_{\text{max.}}(\text{band})/E_{\text{max.}}\text{w}(CH_2)$, are:

	$FCH_2{\cdot}CN$	$ClCH_2{\cdot}CN$	$ICH_2{\cdot}CN$		$FCH_2{\cdot}CN$	$ClCH_2{\cdot}CN$	$ICH_2{\cdot}CN$
w(CH_2)......	1·0	1·0	1·0	r(CH_2)......	0·4	0·4	0·3
b(CH_2)......	0·3	0·4	0·3	tw(CH_2) ...	0·2	0·3	0·3

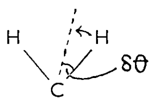
This order can be predicted, if it is assumed that the normal co-ordinates describing the vibrations involve changes in the HCH and HCX angles only. In these "ideal" circumstances, since the CH bond moment remains constant, the transition moments are proportional to the displacement of the hydrogen atoms from their equilibrium positions. From the forms of the vibrations, the following proportionality relations are easily derived:



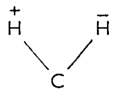
b(CH_2)
$(\delta\mu/\delta Q) \propto r.\delta\theta.\sin\theta$



w(CH_2)
$(\delta\mu/\delta Q) \propto r\,\delta\theta$



r(CH_2)
$(\delta\mu/\delta Q) \propto \delta\theta.\cos\theta$



tw(CH_2)
$(\delta\mu/\delta Q) \sim 0$

A normal co-ordinate treatment by Shimanouchi and Suzuki[32] on the related molecules XCH_2X (X = halogen) has shown that to a very good approximation $\Delta\theta \sim \Delta\phi$. If the same state of affairs holds in the $XCH_2{\cdot}CN$ molecules, then the predicted intensity order is w(CH_2) > b(CH_2) > r(CH_2) > tw(CH_2). The approximate agreement with the observed intensities is no more than expected, considering the much simplified model used. The fact that the tw(CH_2) vibration gives rise to an infrared absorption (the corresponding vibration is infrared-inactive in XCH_2X molecules) emphasises that there must be a

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[30] A. W. Laubengayer and D. S. Sears, *J. Amer. Chem. Soc.*, 1945, **67**, 164.

[31] R. B. Hannan and R. L. Collin, *Acta Cryst.*, 1953, **6**, 350.

[32] T. Shimanouchi and I. Suzuki, *J. Mol. Spectroscopy*, 1962, **8**, 222.

contribution to $\partial\mu/\partial Q$ from the twisting of the XC·CN grouping, *i.e.*, the normal co-ordinate is not localised within the CH_2 group.

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THE EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES,
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