A preliminary study of the vibrational and N.M.R. spectra of trifluoromethyl isocyanide

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Abstract—Variable temperature n.m.r. spectra and ambient-temperature gas-phase near i.r., far i.r. and Raman spectra are reported for the molecule trifluoromethyl isocyanide. In each case, the results are regarded as preliminary to more extensive studies of this unstable material. On the basis of a simplified Urey-Bradley force field, calculations of force constants have been made from normal mode frequencies derived from the vibrational spectra.

INTRODUCTION

The compound trifluoromethyl isocyanide $(CF_3 \cdot NC)$, although structurally simple, has only recently been prepared [1, 2]. Unfortunately, the material has low stability to polymerization and to isomerization to the cyanide, particularly at ambient temperatures, and few physical measurements have been made on it. Molecular dimensions have not been determined and very little spectroscopic data has been reported [2].

The present paper is a preliminary study of ambient temperature i.r. and Raman spectra of the gaseous substance and of the low temperature ¹⁹F n.m.r. spectrum of a solution of the isocyanide in trichlorofluoromethane. There are strong grounds for more extensive investigations, particularly of the vibrational spectra, and it is hoped that the present report will provide a background for such The vibrational spectra an extension. of trifluoromethyl cyanide [3, 4] methyl isocyanide [5, 6] and methyl cyanide [6] have all been previously reported; data on trifluoromethyl isocyanide would seem to fill an obvious gap for this group of compounds.

PREPARATION OF TRIFLUOROMETHYL ISOCYANIDE

Trifluoromethyl isocyanide was prepared by the method described by BANKS, HASZELDINE, STEVENSON and WILLOUGHBY [2], viz., by fluorideinitiated decomposition of the butenoyl fluoride $CF_3 \cdot N : CF \cdot COF$, obtainable via thermolysis of the alternating copolymer trifluoronitrosomethane with trifluoroacryloyl fluoride; the latter fluoride was prepared from chlorotrifluoroethane by a wellestablished, but complicated, five-stage synthesis [7]. 3.3 moles of CF_2 : CFCl culminated in only 2.6 mmoles of CF_3 ·NC.

$$nCF_3 \cdot NO + nCF_2 : CF \cdot COF \xrightarrow{250K} [N(CF_3) \cdot O \cdot CF_2 \cdot CF(COF)]_n$$

$$[N(CF_{3}) \cdot O \cdot CF_{2} \cdot CF(COF)]_{n} \xrightarrow[830 \text{ KF}]{} \longrightarrow$$
$$n CF_{3} \cdot N : CF \cdot COF + n COF_{2}$$
$$CF_{3} \cdot N : CF \cdot COF \xrightarrow[720 \text{ KF}]{} CF_{3} \cdot NC + COF_{2}$$

The isocyanide and coproduct carbonyl fluoride have very similar boiling point (ca 190 K) and could not be separated by fractional condensation *in vacuo* [2].

The isocyanide could be freed from carbonyl fluoride by storing the mixture in the presence of a molecular sieve (type 4A) at low pressure (2.7 kPa initially) and room temperature but this also resulted in a significant reduction of the amount of isocyanide [8].

¹⁹F MAGNETIC RESONANCE SPECTRUM

The ¹⁹F spectrum of a mixture of the isocyanide and carbonyl fluoride dissolved in trichlorofluoromethane (15% w/w of the composite solutes) was obtained over the temperature range 191 to 313 K in a Varian HA100 Spectrometer, operating at 94.1 MHz. The spectrum associated with CF_3 ·NC is shown for a few selected temperatures in Fig. 1. The absorption is characteristic of a set of magnetically equivalent nuclei spin-coupled to a

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Fig. 1. ¹⁹F, 94.1 MHz spectra of CF₃·NC in CFCl₃ at (a) 301 K, (b) 278 K, (c) 262 K, (d) 237 K, (e) 217 K, and (f) 191 K.

single ¹⁴N nucleus in an electronic environment of near-spherical symmetry [9, 10]. At 191 K, there is a single band 51.2 ppm to high field of the $CFCl_3$ solvent. Increasing the temperature to about 210 K resulted in a splitting of the band into a 1:1:1 triplet, a structure which was more clearly resolved at higher temperatures. This well-known phenomenon, associated with decreased efficiency of ¹⁴N quadrupolar relaxation at increasing temperatures, has been observed previously with non-fluorinated isocyanides [11-13]. At temperatures above about 270 K, there was a reduction in intensity associated with homopolymerization of the isocyanide (to a yellow solid). (Indeed this homopolymerization was a constant problem in the manipulation of the isocyanide and, had sufficient material been available, would have posed severe limitations to vibrational spectroscopic investigations at ambient temperatures and at higher pressures than those used in the present work.) Over the temperature range 191-303 K, the chemical shift varied very little (in relation to the solvent): 51.2 to 51.5 ppm. The ¹⁴N—¹⁹F coupling constant modulus as measured by the triplet splitting in the range 260 to 280 K was 15.0 Hz.

Some attempts were made to analyse the band shapes of the resolved triplets in terms of (a) a temperature-dependent quadrupolar relaxation time (T_1) and an infinite transverse nonquadrupolar relaxation time (T_2') [14] and (b) a temperature-dependent T_1 and a finite but temperature-independent T_2 [15]. Unfortunately, the signal-to-noise ratio was insufficient to give precise results for such spectral characteristics as central maximum to outer maximum and central maximum to minimum ratios. With increasing temperature, the former should decrease and the latter should increase. This was not always found to be the case, but the deviations were ascribed to large random errors. Nevertheless, it was clear that analysis was not possible on the basis of infinite T_2' . There is clear scope here for a more extensive study of band-shape dependence on temperature, using (a) more concentrated solutions and/or (b)computer-of-average-transients (CAT) techniques.

INFRARED AND RAMAN SPECTRA-RESULTS AND ANALYSIS

Near i.r. spectra of gaseous CF_3 ·NC were recorded at ambient temperatures (*ca* 290 K) on Perkin–Elmer 257 and 621 Spectrophotometers, operating in the ranges 4000–625 and 4000– 300 cm⁻¹, respectively. 10 cm cells with NaCl (257) or KBr (621) windows were employed and gas pressures were in the range 70–6600 Pa. Figure 2



Fig. 2. Infrared spectrum of CF_3 ·NC (* grating change at 630 cm^{-1}).

comprises a complete 621 spectrum at 4 kPa and also a lower pressure 257 recording of the absorption around 1200 cm⁻¹ (70 Pa). Bands due to possible impurities are indicated in the Fig. 2. A scale-expanded 257 recording of the band system centred around 2130 cm⁻¹ is displayed in Fig. 3.

The structure in the 2130 cm⁻¹ band, assigned as the isocyanide stretching fundamental (ν_1) is too coarse to be associated with rotational fine structure. On the basis of a postulated structure, in which the F-C, F₃C-N and F₃CN-N bond lengths are 134, 142 and 117 pm, respectively, and the FCF angle is 108° (by analogy with CF₃·CN [16] and CH₃·NC [17]), the rotational constants (considered here as vibrationally invariant) are A = $B = 0.226 \text{ cm}^{-1}$, $C = 0.189 \text{ cm}^{-1}$ for ${}^{12}\text{C}{}^{19}\text{F}_3 \cdot {}^{14}\text{N}{}^{12}\text{C}$ (with about 98% abundance). The transition being a parallel one should then be associated with P and R branches with component separation of about $0.4-0.5 \text{ cm}^{-1}$ and a fairly sharp Q branch; unresolved P and R structure should result in a P-Rmaximum separation of about 20 cm⁻¹ at ambient temperatures [16]. The band at 2130 cm^{-1} band shows quite different features consisting of evenlyspaced maxima; to shorter wavenumber of the 2126 cm^{-1} —the third maximum from high wavenumber-the intensities diminish quite rapidly. There is no such tail on the high wavenumber side; a marked shoulder on this side of the 2138 cm⁻¹ component has the appearance of an unresolved R branch. The observed structure is analogous to that previously described by Brown and Sheppard for acetylenes and cyanides [19] and ascribed to "hot (or upper state) bands" [20], ν_1 + $m\nu_n - m\nu_n$. The components in the present band are assigned as the Q branches of bands corresponding to a single n and a variety of m. The mode ν_n , being necessarily one of low frequency, is assigned as ν_8 , doubly-degenerate CNC (E) bending. On the basis of a vibrational term value to second order in vibrational quantum numbers,



Fig. 3. Infrared band centered around 2130 cm^{-1} .

The transition wavenumber for $\nu_1 + m\nu_8 - m\nu_8$ is

$$\bar{\nu} = \omega_1 + \sum_i (\frac{1}{2} x_{1i} d_i) + \frac{3}{2} x_{11} + m x_{18}$$
(1)

where ω_1 and x_{11} are the vibrational wavenumber and the anharmonicity for the CN—C stretching mode, ν_1 , and x_{1i} (for $i \neq 1$) are interactive anharmonicities involving this mode and mode *i* of degeneracy d_i . It should be noted that the summation (taken over all modes including i = 1) includes $\frac{1}{2}x_{11}$ and x_{18} . Assuming that Equation 1 may be applied to *Q* maxima, comparison with the observed structure—highest wavenumber = 2138 cm⁻¹, mean spacing of 4 most intense maxima = 5.8 cm⁻¹ gives

$$\omega_1 + \sum_i \left(\frac{1}{2}x_{1i}d_i\right) + \frac{3}{2}x_{11} = 2138 \text{ cm}^{-1}$$
$$x_{18} = -5.8 \text{ cm}^{-1}.$$

Except for the high wavenumber shoulder on the 2138 cm^{-1} component, *P* and *R* branches are supposed to contribute to a general "continuum" underlying the *Q* maxima.

The intensity distribution of Q branches should reflect the vibrational wavenumber for the CNC bending mode. The weighted Boltzmann factor (on a harmonic basis) for occupancy of states with mquanta of this mode is $(m+1) \exp(-mhc\omega_8/kT)$. The observed pattern suggested a value for ω_8 in the region 100-200 cm⁻¹—successive Boltzmann factors for (a) $\omega_8 = 100 \text{ cm}^{-1}$:1, 1.24, 1.14, 0.96,..., (b) $\omega_8 = 150 \text{ cm}^{-1}$:1, 0.97, 0.71, 0.46,..., (c) $\omega_8 = 200 \text{ cm}^{-1}$:1, 0.76, 0.42, 0.24,...; the underlying "continuum" made accurate comparison impossible.

The far i.r. spectrum of $CF_3 \cdot NC$ was kindly obtained by Dr P. N. BRIER of the Faculty of Science, University of Manchester, using a Grubb Parsons cube interferometer and a cell provided with polyethylene windows. The gas pressure was about 2 kPa. The spectrum, produced by Fourier transformation of the interferogram, is shown in Fig. 4, at a resolution of 4 cm^{-1} . A band with maximum at 145 cm^{-1} , and assigned as the ν_8 CNC bending fundamental, is clearly shown. A value of 145 cm^{-1} for ω_8 (not corrected for anharmonicity) is compatible with the structure of the 2130 cm⁻¹ band.

The Raman spectrum of the gas at a pressure of 13 kPa was kindly recorded by Dr V. FAWCETT of the University of Bradford using a Spex 1401 Double Monochromator and a Spectraphysics Argon Ion Laser. Because of the low gas pressure used, the scattering was rather weak and in some aspects



Fig. 4. Far i.r. spectrum of CF₃·NC.

not very conclusive. The material also showed signs of chemical change in the laser beam, probably isomerization to the cyanide and/or polymerization. Excitation was performed both at 514.5 and 488.0 nm and the polarization of the significant Raman bands was tested. On the negative side. there was no clear indication of a Raman shift of 145 cm^{-1} (with either excitation)—weak scattering here may have been obscured by the Rayleigh scattering, nor was there any significant scattering at (Stokes) shifts around 1200 cm^{-1} where the i.r. absorption is so strong. However, on the positive side, Raman bands were observed at 845 and 2135 cm^{-1} , these apparently being the respective analogues of a weak i.r. band at 838 cm^{-1} and of the i.r. absorption around 2130 cm^{-1} (and previously described). Both Raman lines were polarized, indicating maximum symmetry for associated normal nodes.

The CF₃·NC molecule is of C_{3v} symmetry and has 12 normal modes, four of which are of A_1 symmetry and the remainder comprise 4 double degenerate pairs of symmetry *E*. The situation is exactly as in the related molecules CH₃·CN, CH₃· NC and CF₃·CN for which the normal mode vibrational wavenumbers are shown in Table 1; in the main, these are uncorrected for anharmonicity, i.e., they are fundamental wavenumbers. The Table also includes (*a*) an approximate description of the mode, although substantial delocalization is known to occur in some of these [4], and (*b*) a tentative "extrapolation" to CF₃·NC, i.e., without reference to the present observations, and based entirely on mode localization and transference of group

Table 1. Vibrational wavenumbers^{*} for $CH_3 \cdot CN$, $CH_3 \cdot NC$ and $CF_3 \cdot CN$ with tentative extrapolation to $CF_3 \cdot NC$

	ω/cm^{-1}					
Normal mode	CH ₃ ·CN[6]	CH ₃ ·NC[5]	CF ₃ ·CN [4]‡	$CF_3 \cdot NC$ (extrapolated)		
(CH) stratab	2965.3	2965.8				
$A_1 CF $			1227.2	$1230 (\omega_2)$		
C=N stratah	2267.3		2275.0			
$A_1 \{ N \cong C \}$		2166.0		2170 (ω_1)		
$\{CH_3\}$	1400.0	1429				
$A_1 \{ CF_3 \}$ deform.			801.7†	800 (ω ₃)		
(C-C)	919.9		521.0†			
$A_1 \{ C-N \}$ stretch.		944.6		$500-700(?)(\omega_4)$		
_ (CH)	3009.0	3014.3				
$E_{\rm CF}$ stretch.			1214.3	1210 (ω ₅)		
$[CH_3]$	1454.0	1466.9				
$E\left\{ CF_3 \right\}$ deform.			618.3§	620 (ω ₇)		
(CH_3)	1041.0	1129.3				
$E\left\{ CF_{3}\right\}^{rock}$			462.7§	460 (ω ₆)		
_(CC==N),	361.0		196.0			
$E \left\{ C = N \cong C \right\}$ bend.		263		100–150 (?) (ω ₈)		

* From i.r. spectra of gases.

† and § Could be interchanged [3].

With mode descriptions from ref. 3.

characteristics from one molecule to another. Because of substantial difference of "corresponding" wavenumbers in the two cyanides, extrapolations for the A_1 C—N stretching and the E C—N=C bending modes are made very tentatively (on the basis of a fractional reduction when CH₃ is replaced by CF₃). Already assigned wavenumbers for ν_1 and ν_8 conform reasonably with the extrapolations. Other assignments, some of which must remain uncertain pending more detailed investigation, have been based upon Table 1, Raman polarization and band shape. Unfortunately the rotational constants of the molecule are too low to permit detailed rotational fine structure to be observed in the i.r. absorption and one can only utilize the general band envelope. For parallel transitions, principally A_1 fundamentals, one would expect J-structure only and this to appear as a sharp O branch with P and R envelopes having maxima separated by about 20 cm⁻¹ at ambient temperatures [16]. For perpendicular transitions in the form of E fundamentals, this structure should be repeated in accordance with the wavenumber formula [21]

$$\tilde{\boldsymbol{\omega}} = [\tilde{\boldsymbol{\omega}}_{J} + C(1 - 2\zeta_{i}) - B] \\ \pm 2[C(1 - \zeta_{i}) - B] |K''| \quad (2)$$

where $\tilde{\omega}_I$ are wavenumbers of corresponding Jstructure bands, e.g., the Q-branches, B(=A) and C are rotational constants assumed invariant of the vibrational state for the present purpose, |K''| is the modulus of the lower state K-quantum number,

and ζ_i is the Coriolis coupling constant for the E mode involved. With calculated B, C of 0.226 and 0.189 cm⁻¹ respectively, Equation 2 predicts a repetition of J-structure at intervals of between zero and 0.46 cm⁻¹ according to the value of ζ_i . In the absence of resolution of such structure, one would expect a general broadening of the parallel-type band.

An assignment of i.r. bands is shown in Table 2. Of the fundamental assignments, that for ν_6 is probably the most speculative, this differing significantly from the extrapolation of Table 1. The expected parallel structure is shown clearly in the bands at 838 and 550 cm^{-1} . The band at 760 cm^{-1} is noticeably broader and may thus be possibly described as typically perpendicular. The band at 616 cm^{-1} ought to be perpendicular and indeed is rather different in band envelope to the band at 550 cm^{-1} , for example. However, there is a sharp O-branch centre which would seem to suggest a value for the associated Coriolis coupling constant, ζ_7 of about -0.2 (this making the last term in Equation 2 equal to zero).

The bands at 1210 and 1240 cm^{-1} both show doublet structure in the lower pressure records. The explanation for this is not clear. Certainly the structure is very different from (a) the hot-band structure of the 2130 cm⁻¹ band, and (b) the POR branch structure characteristic of parallel bands. Fermi resonance (particularly with $2\omega_7$, A_1) and/or the presence of the isomeric cvanides are possibilities here.

$\bar{\nu}/\mathrm{cm}^{-1}$	Intensity	Assignment	$\bar{\nu}/\mathrm{cm}^{-1}$ Intensity		Assignment	
3330	w	$\omega_1 + \omega_2, \omega_1 + \omega_5$	1390]	m		
2960	w	$\omega_1 + \omega_2$	1380		w3 1 w4, w5 7 w81	
2850	w	$\omega_1 + \omega_6(?)$	1340	w	$\omega_2 + \omega_8$	
2670	UW	$\omega_1 + \omega_4$	1240**	vs	$\omega_5(+2\omega_7?)$	
2465		$(2\omega_2, 2\omega_5)$	1210**	vs	ω2	
2440 }	m	$\frac{1}{\omega_2 + \omega_5}$	1170¶	w	$\omega_4 + \omega_7$	
ل 2400		C 2 3 5			- /	
			1090	w	2ω4	
2300	vw	$\omega_1 + \omega_8$	838†	w	ω3	
2138*	5	ωı	760§	w	$\omega_6(?)$	
2040	w	$\omega_2 + \omega_3$	696	UW	$\omega_4 + \omega_8 (??)$	
1850	UW	$\omega_5 + \omega_7$	616	m	ω7	
1800	w	$\omega_4 + \omega_5$	550	w	ω ₄	
			155		ωg	

Table 2. Assignment of i.r. bands

* Centered at $ca \ 2120 \text{ cm}^{-1}$ (see text); 2135 cm^{-1} in Raman. † 845 cm⁻¹ in Raman.

Possibly affected by Fermi resonance.
Possibly affected by Fermi resonance.
Underlying COF₂ (?) impurity band.
On edge of CF₃-CN impurity band.
On edge of 1210 cm⁻¹ band.

* Doublet means.

Valence coordinate	Non-bonding coordinate*	Force constant†/unit‡
1. FC stretch.		3.91
2. CN stretch.		4.80
3. N≇C stretch.		14.99
4. FCF deform.		2.27
5. FCN deform.		-1.01
6. CNC deform.		1.25
	7. FF stretch.	0.62
	8. FN stretch.	1.90

Table 3. Calculated Urey-Bradley force constants

*F-terminal C stretching force constants and intramolecular tension equated to zero.

 \dagger Quadratic for non-bonding coordinates; linear force constant equated to -10% of quadratic constants.

 $\pm 10^{2}$ N m⁻¹ for coordinates 1, 2, 3, 7, 8; 10^{-18} J rad⁻² for coordinates 4, 5, 6.

FORCE CONSTANT CALCULATIONS

The fundamental wavenumbers of Table 2 have been used (without anharmonicity correction) as approximations to normal mode wavenumbers in the calculation of force constants; for ω_3 , the Raman fundamental wavenumber (845 cm^{-1}) was used. With only eight normal mode frequencies and in the absence of (a) isotopic data, and (b) Coriolis coupling and centrifugal distortion constants, it was necessary to utilize a more restricted field than the general (harmonic) valence force field (requiring 20 valence and interaction force constants [4]). The Urey-Bradley (UB) [22] field was used here; this has been used for methyl cyanide previously [23, 24]. The full UB field would require 13 force constants (6 valence, 3 linear non-bonding, 3 quadratic non-bonded and 1 intramolecular tension), but this was reduced to 8 by (a) the Shimanouchi approximation [25] whereby each linear nonbonding force constant is set at -10% of the corresponding quadratic constant, and (b) equating the intramolecular tension and the F-terminal C nonbonding force constants to zero. The calculations

Wavenumber/cm ⁻¹					
Observed	Estimated "error"	Calculated			
(2138	1	2137.9			
1210	2	1210.1			
A_1					
845	4	845.3			
550	2	547.8			
(1240	2	1239.7			
760	10	759.5			
E_{1620}^{E}	4	622.8			
145	$\frac{1}{2}$	145.3			

Table 4. Comparison of observed and calculated normal mode wavenumbers

were performed on the University of Manchester Regional Computer Centre ICL 1906A–CDC 7600 Joint System using the GMAT, UBZM and FPERT programmes of SCHACHTSCHNEIDER [26]. An additional subroutine was added to UBZM to allow the use of two mutually perpendicular CNC bending coordinates in the chosen set of valence coordinates [27]. The postulated molecular geometry was as given on page 397. The results of the calculations are given in Tables 3, 4 and 5. The agreement between observed and calculated vibrational wavenumbers is good but there are some peculiar features in the potential energy distribution, particularly for the 145 cm⁻¹ mode.

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Table 5. Potential energy distribution

Wayanumbar/	Valence/non-bonding coordinate*							
cm ⁻¹	1	2	3	4	5	6	7	8
2138	0.000	0.109	0.824	0.002	-0.001	0.000	0.000	0.065
1210	0.212	0.464	0.074	0.336	-0.134	0.000	0.028	0.020
845	0.298	0.103	0.083	0.003	-0.001	0.000	0.109	0.405
550	0.136	0.027	0.020	0.509	-0.202	0.000	0.282	0.230
1240	0.621	0.000	0.000	0.335	-0.089	0.062	0.013	0.059
760	0.053	0.000	0.000	0.028	-0.139	0.739	0.019	0.301
620	0.183	0.000	0.000	0.485	-0.028	0.161	0.183	0.017
145	0.747	0.000	0.000	0.002	-5.507	0.039	0.056	5.663

* See Table 3 for coordinate descriptions.

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