The Rotational Spectra of Fluorinated Acetonitriles; ^{14}N-nuclear Quadrupole Hyperfine Structures Measured with a Microwave Fourier Transform Spectrometer

W. Kasten and H. Dreizler
Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel, BRD

Brian E. Job* and John Sheridan
Department of Chemistry, University of Birmingham, U.K. and School of Physical and Molecular Sciences, University College of North Wales, Bangor, Wales, U.K.

Z. Naturforsch. **38a,** 1015–1021 (1983); received June 3, 1983

The microwave spectra of CF_3CN, CH_2FCN, CHDFCN, CD_2FCN and CHF_2CN have been measured and analysed. The nuclear quadrupole hyperfine splittings due to ^{14}N have been measured by Microwave Fourier Transform spectroscopy. The nuclear quadrupole coupling constants, transformed to the bonding axis systems of the $C-C\equiv N$ groups, are shown to be in accord with structural predictions of the p-electron populations at the nitrogen atom.

I. Introduction

Detailed microwave spectroscopic data for fluorinated acetonitriles have previously been confined to the fully fluorinated symmetric top CF_3CN [1, 2]. A preliminary summary of the rotational spectra of monofluoro acetonitrile, CH_2FCN, was given some time ago by Job and Sheridan [3], whose measurements form the starting point of the present study. Graybeal and Roe [4] reported findings in close agreement with this work. Measurements on this substance were extended by Job [5] to improve resolution of the ^{14}N-nuclear quadrupole hyperfine splittings, which were shown to accord with a coupling tensor no longer symmetric with respect to the $C-C\equiv N$ line. Job [5] also reported rotational constants for CHDFCN and CD_2FCN, and for difluoro acetonitrile, but did not resolve nuclear quadrupole splittings for these molecules.

A main objective in such studies was the possible measurement of the effect of fluorine substitution on the ^{14}N-nuclear quadrupole tensors, and it was clear from the work summarised above that the resolution of conventional microwave spectrometers was insufficient to yield such information. Accordingly, we have extended studies of CF_3CN, CH_2FCN and CHF_2CN by the methods of Microwave Fourier Transform Spectroscopy (MWFT) where the resolution is such that new details of the small ^{14}N coupling effect in a number of molecules have been recently measured [6, 7]. The present MWFT measurements have yielded ^{14}N-nuclear quadrupole coupling constants of the required precision and have also allowed some refinements of the remaining spectroscopic constants.

II. Experimental

The fluoroacetonitriles were made by dehydration of the corresponding amides with phosphorus pentoxide [8, 9]. For CH_2FCN and CF_3CN, commercial samples of the amides were available, while difluoroacetamide was made in the standard way from ethyl difluoroacetate and ammonia.

All samples were fractionated before use.

It was not possible [5] to obtain the deuterated species CHDFCN and CD_2FCN by exchange between CH_2FCN and D_2O under alkaline conditions, since hydrolysis of the nitrile was too rapid for any to be recovered in the deuterated forms [10]. Accordingly, [5] chloroacetonitrile was first deuterated by treatment with a D_2O/H_2O mixture containing a little sodium carbonate, at 20 °C for 24 h. The nitrile was then separated, dried and the chlorine replaced by fluorine by treatment with anhydrous KF in dimethyl formamide at 100 °C. Measurements were made on the resulting mixture of CHDFCN and CD_2FCN finally fractionated.

---

* Present address: Heavy Chemicals New Science Group, I.C.I. plc Runcorn, Cheshire, U.K.

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie, Universität Kiel, Olshausenstr. 40–60, 2300 Kiel, Germany.

0340-4811 / 83 / 0900-1015 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

Table 1. Measured lines and N-hfs ν_{exp} [MHz] of CF_3CN. ν_{calc} [MHz] by (1) and first order hfs perturbation. Measuring accuracy 5 kHz, $\nu_{exp}-\nu_{calc}$ [kHz].

$J'-J$	K	$F'-F$	ν_{exp}	ν_{calc}	$\nu_{exp}-\nu_{calc}$
2−1	0	3−2	11782.223	11782.223	0
		2−1	11782.117	11782.123	−6
		1−0	11780.960	11780.959	+1
		2−2	11780.717	11780.726	−9
		1−1	11784.454	11784.451	3
	±1	3−2	11782.384	11782.382	2
		2−1	11780.928	11780.935	−7
		1−0	11783.846	11783.845	1
		1−1	11782.100	11782.099	1
3−2	0	4−3	17673.203	17273.208	−5
		3−2	17673.141	17673.153	−12
		2−1	17672.928	17672.920	8
	±1	4−3	17673.243	17673.241	2
		3−2	17672.816	17672.826	−10
		2−1	17673.243	17673.241	2
	±2	4−3	17673.355	17673.342	13
		2−1	17671.844	17671.846	−2
		3−3	17673.355	17673.342	13

Table 2. Measured lines and N-hfs ν_{exp} [MHz] of CHF_2CN. The calculated lines $\nu_{unsplit}$ [MHz] and ν_{exp} for unresolved lines were used for the centrifugal distortion analysis. $\Delta\nu_{exp}$ [MHz] and $\Delta\nu_{calc}$ [MHz] experimental and calculated hfs splittings.

$J'_{K'_-K'_+}-J_{K_-K_+}$	$F'-F$	ν_{exp}	$\nu_{unsplit}$	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
$2_{02}-1_{01}$	3−2	14233.268			
				0.079	0.070
	2−1	14233.189			
			14233.176	1.122	1.130
	1−0	14232.067			
				0.184	0.182
	2−2	14231.883			
$2_{11}-1_{10}$	1−0	15368.260			
				1.322	1.317
	3−2	15366.938			
			15366.667	0.773	0.771
	2−2	15366.165			
				0.593	0.592
	2−1	15365.572			
$2_{12}-1_{11}$	1−0	13341.037			
				1.427	1.432
	3−2	13339.610			
			13339.345	0.642	0.635
	2−2	13338.968			
				0.717	0.720
	2−1	13338.251			
$3_{22}-3_{12}$	3−3	16232.117			
				1.160	1.155
	4−4	16230.957	16231.250		
				0.397	0.404
	2−2	16230.560			
$4_{13}-4_{14}$	3−3	10074.518			
				0.038	0.035
	5−5	10074.480	10074.445		
				0.136	0.138
	4−4	10074.344			
$4_{23}-4_{13}$	4−4	14378.988			
				0.725	0.725
	5−5	14378.263	14378.455		
				0.196	0.187
	3−3	14378.067			
$5_{24}-5_{14}$	5−5	12200.333			
				0.495	0.497
	6−6	12199.838	12199.972		
				0.111	0.101
	4−4	12199.727			
$6_{25}-6_{24}$	6−6	9833.960			
				0.351	0.348
	7−7	9833.609	9833.705		
				0.071	0.060
	5−5	9833.538			
$7_{25}-7_{26}$	6−6	10903.255			
				0.021	0.024
	8−8	10903.234	10903.180		
				0.179	0.168
	7−7	10903.055			
$8_{26}-8_{27}$	9−9 7−7	16032.603	16032.451	0.186	0.177
	8−8	16032.417			
$9_{37}-9_{27}$	9−9	17829.300			
				0.329	0.336
	10−10	17828.971	17829.070		
				0.037	0.038
	8−8	17828.934			
$10_{38}-10_{28}$	10−10	14269.735			
				0.264	0.267
	11−11	14269.471	14269.550		
				0.030	0.027
	9−9	14269.441			
$3_{30}-3_{22}$		32066.89			
$4_{31}-4_{23}$		32428.79			
$5_{32}-5_{24}$		33203.54			
$6_{33}-6_{25}$		34643.56			
$7_{34}-7_{26}$		37066.10			
$4_{32}-4_{22}$		30669.00			
$5_{33}-5_{23}$		29248.98			
$7_{35}-7_{25}$		24464.42			
$8_{36}-8_{26}$		21296.34			
$10_{47}-10_{37}$		35818.00			
$11_{48}-11_{38}$		32008.03			
$1_{10}-0_{00}$		14081.61			
$2_{20}-1_{10}$		33159.08			
$2_{21}-1_{11}$		34052.28			
$2_{11}-1_{01}$		22271.32			
$3_{03}-2_{02}$		21060.67			
$3_{12}-2_{11}$		22969.78			
$5_{05}-4_{04}$		33866.46			
$5_{15}-4_{14}$		32908.27			
$5_{14}-4_{13}$		37794.49			

The MWFT measurements were made at Kiel in a spectrometer already described [11, 7]. Sample pressures were 0.5 to 0.05 mTorr and the cell temperature was −60 °C. The measurements by Job and Sheridan at the University of Birmingham were made with a conventional spectrometer with Stark effect modulation at 100 kHz, selected transitions being partially resolved into hyperfine patterns in a simple video spectrometer.

III. Results and Analysis

The measured frequencies and their assignments are listed in Table 1−3 for CF_3CN, CH_2FCN and CHF_2CN respectively. The resolution obtainable in the MWFT instrument is illustrated by the hyperfine multiplet reproduced in Figure 1.

The spectrum of CF_3CN was analyzed with the symmetric top Hamiltonian including centrifugal distortion [12].

$$H = BP^2 + (A - B)P_z^2 - D_J P^4 - D_{JK} P^2 P_z^2 - D_K P_z^4 . \tag{1}$$

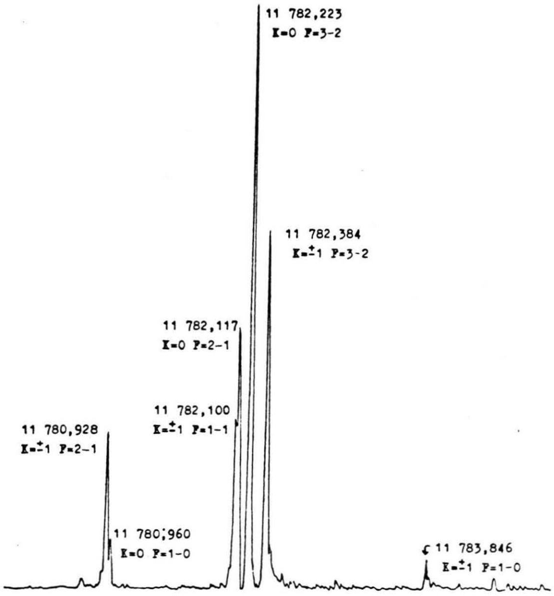

Fig. 1. $J = 2-1$ transition of CF_3CN, frequencies MHz, polarizing frequency 11 785 MHz, sample interval 50 ns, 1024 data points supplemented by 3072 zeros prior to Fourier-Transformation, $5 \cdot 10^5$ average cycles, spectral point distance 5 kHz, pressure 0.2 mTorr, temperature −60 °C.

Table 3. Measured lines and N-hfs of CH_2FCN, CHDFCN and CD_2FCN, see Table 2.

(a) Species CH_2FCN

$J'_{K'_-K'_+}-J_{K_-K_+}$	$F'-F$	ν_{exp}	$\nu_{unsplit}$	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
$1_{01}-0_{00}$	0−1	9122.847			
				1.665	1.662
	2−1	9121.182	9120.995		
				1.113	1.113
	1−1	9120.069			
$2_{12}-1_{11}$	1−0	17802.058			
				1.175	1.175
	3−2	17800.883	17800.658		
				1.155	1.151
	2−1	17799.728			
$6_{15}-6_{16}$	7−7 5−5	9268.249			
			9268.239	0.029	0.026
	6−6	9268.220			
$7_{16}-7_{17}$	8−8 6−6	12353.857	12353.849	0.025	0.026
	7−7	12353.832			
$8_{17}-8_{18}$	9−9 7−7	15876.543	15876.534	0.026	0.026
	6−6	15876.260			
$2_{02}-1_{01}$		18237.46			
$2_{11}-1_{10}$		18683.22			
$3_{03}-2_{02}$		27344.39			
$3_{13}-2_{12}$		26697.99			
$3_{12}-2_{11}$		28022.22			
$4_{04}-3_{03}$		36437.78			
$4_{14}-3_{13}$		35591.89			
$4_{13}-3_{12}$		37357.53			
$9_{18}-9_{19}$		19833.65			
$10_{1,9}-10_{1,10}$		24221.38			
$11_{1,10}-11_{1,11}$		29034.57			
$12_{1,11}-12_{1,12}$		34266.98			
$1_{10}-1_{01}$		32237.88			
$2_{11}-2_{02}$		32684.16			
$3_{12}-3_{03}$		33362.27			
$4_{13}-4_{04}$		34282.28			
$5_{14}-5_{05}$		35457.44			

(b) Species CHDFCN and CD_2FCN

$J'_{K'_-K'_+}-J_{K_-K_+}$	ν_{exp} CHDFCN	ν_{exp} CD_2FCN
$4_{04}-3_{03}$	35886.95	35354.47
$4_{14}-3_{13}$	35005.94	34477.06
$4_{13}-3_{12}$	36865.64	36344.96
$1_{11}-0_{00}$	36640.78	31718.69
$1_{10}-1_{01}$	27119.06	23329.55
$2_{11}-2_{02}$	27590.24	23803.65
$3_{12}-3_{03}$	28308.34	24528.00
$4_{13}-4_{04}$	29286.84	overlapped
$5_{14}-5_{05}$	30543.03	26795.67
$6_{15}-6_{06}$	32098.24	28384.24

For the asymmetric top molecules CHF_2CN and CH_2FCN the Hamiltonian of van Eijck [13, 14] was used:

$$\begin{aligned} H = {} & B P_x^2 + C P_y^2 + A P_z^2 \\ & - D'_J P^4 - D'_{JK} P^2 P_z^2 - D'_K P_z^4 \\ & - \delta_J (P^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P^2) \\ & - 2 R'_6 (3 (P_x^2 P_y^2 + P_y^2 P_x^2) - P_x^4 - P_y^4) . \qquad (2) \end{aligned}$$

In the expressions (1) and (2) above the symbols have their usual meanings. Where resolution of hyperfine structure was obtained, this was analysed by first order treatment [12, 15] to give the nuclear quadrupole coupling constants and the unperturbed frequencies ν_{unsplit}. All fitting procedures were repeated until no further changes in the derived parameters were observed.

For the deuterated species $CHDFCN$ and CD_2FCN the smaller numbers of data were analysed by less elaborate means [5, 16, 17] in which smaller constants such as D'_J and δ_J were taken to be the same as those derived from a similar analysis for the parent species. It is perhaps worth noting that the values of the distortion constant D'_{JK} in fluoroacetonitrile are very sensitive to deuterium substitution. A negative value of D'_{JK} in CH_2FCN parallels findings for molecules with similar inertial properties, such as CH_2FCCH [18] or CH_3CH_2CCH [19], but deuteration changes D'_{JK} towards a positive value, which is attained in CD_2FCN.

Tables 4–6 summarize the final values of the rotational and centrifugal distortion constants, while Table 7 gives the results of the nuclear quadrupole analyses, in which only the lines measured in the MWFT instrument were used. It was checked that the energy levels of CHF_2CN and CH_2FCN are such that no lines of these substances within the range of the spectrometer are sensitive to χ_{ac} or χ_{ab} respectively.

Table 4. Rotational and centrifugal distortion constants of CF_3CN from an analysis of the lines of Table 1. σ mean square deviation of the fit. $|(B, D_J)|$ magnitude of highest correlation coefficient. Conversion factor 505 376 MHz amu Å^2. Standard errors are given.

B	[MHz]	2945.5349 (13)
D_J	[kHz]	0.52 (11)
D_{JK}	[kHz]	5.98 (80)
σ	[kHz]	7
$\lvert(B, D_J)\rvert$		0.95
I_b	[amu Å^2]	171.5749 (1)

Table 5. Rotational and centrifugal distortion constants of CHF_2CN from an analysis of the lines of Table 2, see also Table 4. σ is relatively high as the measuring accuracy of the two sets of lines are different. $|(C, D'_J)|$ magnitudes of highest correlation coefficient.

A	[MHz]	9985.938 (51)
B	[MHz]	4095.116 (30)
C	[MHz]	3081.427 (34)
D'_J	[kHz]	0.36 (75)
D'_{JK}	[kHz]	17.86 (89)
D'_K	[kHz]	−6.4 (49)
δ_J	[kHz]	0.28 (14)
R'_6	[kHz]	−0.20 (9)
$\varkappa$		−0.7063
σ	[kHz]	274
$\lvert(C, D'_J)\rvert$		0.88
I_a	[amu Å^2]	50.6088 (3)
I_b	[amu Å^2]	123.4094 (6)
I_c	[amu Å^2]	164.0071 (9)

IV. Fitting of Structure Parameters

Structure parameters for CF_3CN and CH_3CN have been well established [2, 12]. The structure consistent with the inertial information now obtained for the asymmetric molecules CHF_2CN and CH_2FCN were considered partly to establish their consistency within the series of compounds, and in particular to allow placement of the *a*-axes within probable structures as a preliminary to the transformation of the nuclear quadrupole coupling constants into the bond-axis systems (Section V below).

For CHF_2CN, with data for only the parent isotopic form, it was possible to fit only three parameters in an r_0-structure. As indicated in Table 8, six parameters were assumed from the known geometries in related structures and values were obtained as tabulated for r(C−F), ∢HCC and ∢FCC.

For CH_2FCN nine inertial constants were available (Table 6) and these were sufficient to fit only five structure parameters with three similar assumptions, as indicated in Table 9. A higher number of parameters was correlated.

The values given for the parameters in these molecules are essentially preliminary and approximate on account of the necessity of making assumptions. The findings, however, support the view that r(C−F) in the monofluoro derivative is about the same as r(C−F) in methyl fluoride [12], while the presence of two fluorine atoms in the former methyl group in CHF_2CN leads to a shorter r(C−F), this shortening being continued in CF_3CN [2]. These comparisons resemble findings in related cases [12].

Table 6. Rotational and centrifugal distortion constants of CH_2FCN, $CHDFCN$ and CD_2FCN from an analysis of the lines of Table 3. See also Tables 4 and 5. Assumptions in brackets. (0) assumed to zero as D'_K is correlated to A. A centrifugal distortion analysis for CH_2FCN in the mm-wave region is in progress [29].

	CH_2FCN	$CHDFCN$	CD_2FCN	
A	36577.42 (11)	31379.837 (85)	27524.067 (57)	MHz
B	4781.237 (23)	4725.974 (32)	4661.772 (21)	MHz
C	4339.679 (23)	4260.946 (16)	4194.616 (10)	MHz
D'_J	1.3 (8)	(1.3)	(1.3)	kHz
D'_{JK}	−67.1 (6)	−52.3 (127)	4.34 (861)	kHz
D'_K	(0)	(0)	(0)	kHz
δ_J	0.57 (5)	(0.57)	(0.57)	kHz
R'_6	0.05 (30)	(0.05)	(0.05)	kHz
$\varkappa$	−0.9726	−0.9657	−0.9600	–
σ	146	142	94	kHz
$\lvert(\delta_J, R'_6)\rvert$	0.99	–	–	–
$\lvert(B, D'_{JK})\rvert$	–	0.92	0.92	–
I_a	13.81661 (4)	16.10512 (4)	18.36124 (4)	amu Å^2
I_b	105.6998 (5)	106.9358 (8)	108.4086 (5)	amu Å^2
I_c	116.4547 (6)	118.6065 (4)	120.4821 (3)	amu Å^2

Table 7. Quadrupole coupling constants of acetonitriles in MHz. σ mean square deviation of the fit, $\overline{\Delta\nu}$ mean of hfs splitting in kHz, $\lvert(\chi^+, \chi^-)\rvert$ magnitude of correlation coefficient. The symmetry plane is *ac* for CHF_2CN, *ab* for CH_2FCN. – * influenced by accuracy of ∢CN, a.

	CF_3CN	CHF_2CN	CH_2FCN	CH_3CN [21]
χ_+	4.656 (15)	4.373 (9)	3.707 (4)	4.2253 (7)
χ_-	0.000	0.424 (9)	0.071 (4)	0.000
χ_{aa}	−4.656 (15)	−4.373 (9)	−3.707 (4)	−4.2253 (7)
χ_{bb}	2.328 (8)	2.399 (9)	1.889 (4)	2.1127 (4)
χ_{cc}	2.328 (8)	1.974 (9)	1.818 (4)	2.1127 (4)
σ	7	6	2.2	3.4
$\overline{\Delta\nu}$	781	446	740	484
$\lvert(\chi_+, \chi_-)\rvert$	–	0.26	0.09	–
χ_{ac}, χ_{ab}	–	1.315*	−2.295*	–
χ_{xx}	2.328	2.236*	2.710*	2.1127
χ_{yy}	2.328	2.399	1.818	2.1127
χ_{zz}	−4.656	−4.635*	−4.528*	−4.2253

Table 8. Partial r_0-structure of CHF_2CN calculated with the rotational constants of Table 5. Assumptions in brackets.
The last two angles are derived from the fitted values.

r(C–N)	(1.158 (1)) Å[a]
r(C–C)	(1.459 (1)) Å[b]
r(C–H)	(1.092 (8)) Å[c]
r(C–F)	1.35 Å
∢ HCC	113.7°
∢ FCC	110.8°
∢ CCN	(180.0°)
∢ CCF/CCF	(120°)[d]
∢ CCF/CCH	(120°)[d]
∢ FCF	108.1°
∢ CN,a	11.3°[e]

[a] mean value and error from CH_3CN [22], C_2H_5CN [23], $(CH_3)_3CCN$ [24], CCl_3CN [25];

[b] from CH_3CN [22], C_2H_5CN, CCl_3CN [25], $NC{-}CH_2{-}CN$ [26];

[c] from CH_2F_2 [27], C_2H_5F [28], C_2H_5CN [23], $NC{-}CH_2CN$ [26];

[d] dihedral angles;

[e] angle between CN bond and *a*-axis.

V. Comparison and Interpretation of the Nuclear Quadrupole Coupling Constants

The nuclear quadrupole coupling constants χ_{aa}, χ_{bb} and χ_{cc} listed in Table 7 may be identified with the principal constants of the nuclear quadrupole coupling tensors only in the cases when the symmetry permits this, namely for CH_3CN and CF_3CN. For the asymmetric tops, only the measured coupling constants for the axes perpendicular to the molecular symmetry planes, χ_{cc} for CH_2FCN and χ_{bb} for CHF_2CN, are principal constants of the nuclear coupling tensors. To obtain estimates of the principal constants of the nuclear coupling tensors, we have made the usual transformation with the assumption that the C–C–N line will be a principal axis of the coupling tensor. In the light of experience with substances where this assumption has

Table 9. Partial r_0-structure of CH_2FCN calculated from nine rotational constants. For notes a, b, d, e, see Table 8. The last three angles are derived from the fitted values.

r(C–N)	(1.158 (1)) Å[a]
r(C–C)	(1.459 (1)) Å[b]
r(C–H)	1.09 Å
r(C–F)	1.38 Å
$\sphericalangle$ HCC	110°
$\sphericalangle$ FCC	111.2°
$\sphericalangle$ CCN	(180.0°)
$\sphericalangle$ CCH/CCH	117.5°[d]
$\sphericalangle$ CCF/CCH	121.2°[d]
$\sphericalangle$ HCH	106.9°
$\sphericalangle$ CN,a	19.7°[e]

proved valid, we believe it justified here, although rarely applied to nitrogen couplings. The necessary angles of rotation for this transformation, $\sphericalangle$ (CN, a), are taken from the structures in Tables 8 and 9, and yield the χ_{xx} and χ_{zz} values listed for CH_2FCN and CF_2HCN in Table 7. These coupling constants are in the bond-axis systems, with χ_{yy} always referred to an axis perpendicular to the molecule symmetry plane. We may now seek to interpret and compare the χ_{xx}, χ_{yy} and χ_{zz} values for the four substances in terms of contributions of various mesomeric structures according to the approach of Townes and Dailey [12, 15, 20]. In all cases the χ_{zz} values show a dominance of the normal bonded structure C–C≡N. With the common assumption of sp orbitals on the N for the σ-bond and for the lone pair in this form, and a coupling of 10 MHz per unbalanced p-electron, the predicted χ_{zz} are numerically larger than observed. The lowering of the observed p-electron unbalance $(U_p)_z$ is attributable to small contributions of states which contain negatively charged N. These are of two types. In the first of these the balancing positive formal charge is either on the cyanide nitrogen or distributed elsewhere with retention of axial symmetry. Such forms are represented in Table 10 by $C{-}C^+{=}N^-$ and labelled type (a). The second type, labelled type (b) in Table 10, may be termed hyperconjugated forms in which the positive formal charge is on a hydrogen atom. For CH_3CN such forms clearly allow the axial symmetry of the electron distribution to be retained, but for CH_2FCN and CHF_2CN they introduce asymmetry into the coupling constants in the bond-axis system. This is shown in Table 10 by the p-electron populations N_x, N_y and N_z, which reflect the fact that the second lone pair on the nitrogen atom is in the p_x orbital for form (b) of CHF_2CN and in the p_y orbital for form (b) of CH_2FCN. The p-electron unbalances $(Up)_x$ etc. have then been calculated in the usual ways and also the coupling constants χ_{xx} etc. associated with each mesomeric form. The coupling of ^{14}N per unbalanced p-electron has been taken as 10 MHz for neutral N and 7.69 MHz for nitrogen with a negative formal charge. In the last column of the table, the percentage weights of each

Table 10. Interpretation of the N-hfs quadrupole coupling constants. N_g mean number of p-electrons $g = x, y, z$, $(U_p)_g$ = number of unbalanced p-electrons, χ^m_{gg} = quadrupole coupling constants of the mesomeric forms.

	Mesomeric forms	N_x	N_y	N_z	$(U_p)_x$	$(U_p)_y$	$(U_p)_z$	χ^m_{xx}	χ^m_{yy}	χ^m_{zz}	weight
Trifluoracetonitrile	$CF_3{-}C{\equiv}N$	1	1	3/2	0.25	0.25	−0.5	2.5	2.5	−5.0	93.1%
(a)	$CF_3{-}C^+{=}N^-$	3/2	3/2	3/2	0	0	0	0	0	0	6.9%
Difluoracetonitrile	$CHF_2{-}C{\equiv}N$	1	1	3/2	0.25	0.25	−0.5	2.5	2.5	−5.0	92.7%
(a)	$CF_3{-}C^+{=}N^-$	3/2	3/2	3/2	0	0	0	0	0	0	5.9%
(b)	$\genfrac{}{}{0pt}{}{H^+}{F_2}{\geq}C{=}C{=}N^-$	2	1	3/2	−0.75	0.75	0	−5.77	+5.77	0	1.4%
Monofluoracetonitrile	$CH_2F{-}C{\equiv}N$	1	1	3/2	0.25	0.25	−0.5	2.5	2.5	−5.0	90.6%
(a)	$CH_2F{-}C^+{=}N^-$	3/2	3/2	3/2	0	0	0	0	0	0	1.7%
(b)	$\genfrac{}{}{0pt}{}{F}{H_2^+}{>}C{=}C{=}N^-$	1	2	3/2	0.75	−0.75	0	5.77	−5.77	0	7.7%
Acetonitrile	$CH_3{-}C{\equiv}N$	1	1	3/2	0.25	0.25	−0.5	2.5	2.5	−5.0	84.5%
(a)	$CH_3{-}C^+{=}N^-$	3/2	3/2	3/2	0	0	0	0	0	0	15.5%
(b)	$H_3^+{-}C{=}C{=}N^-$										

mesomeric form which provide fits with the measured coupling constants in the bond axis systems are given.

These percentages appear reasonably in accord with expectations on general chemical grounds. The contributions of forms (a) and (b) together fall progressively as F atoms replace hydrogen successively and increasingly withdraw electrons from the cyanide group. On the other hand the contributions of hyperconjugated forms of type (b) appear to increase in the sequence CHF_2CN, CH_2FCN and, presumably, CH_3CN. Hence we conclude that this approach by the Townes and Dailey method accounts satisfactorily for the observed coupling constants.

We thank the members of the group in Kiel, especially Dipl.-Phys. G. Bestmann and Dipl.-Chem. E. Fliege, the Deutsche Forschungsgemeinschaft and the Fonds der Chemie. The calculations were made at the Computer Center in Kiel. One of us (J. S.) is grateful to the Royal Society for assistance through the European Scientific Exchange Programme. The work at Birmingham was also supported by the Science Research Council through research grants and a Studentship to B. E. J., which are gratefully acknowledged.

[1] J. Sheridan and W. Gordy, J. Chem. Phys. **20,** 591 (1952).
[2] L. F. Thomas, J. S. Heeks, and J. Sheridan, Z. Elektrochem. **61,** 935 (1957).
[3] B. E. Job and J. Sheridan, Nature London **192,** 160 (1961).
[4] J. D. Graybeal and D. W. Roe, J. Chem. Phys. **37,** 2503 (1962).
[5] B. E. Job, Ph.D. Thesis, University of Birmingham, 1963.
[6] E. Fliege, G. Bestmann, R. Schwarz, and H. Dreizler, Z. Naturforsch. **36a,** 1124 (1981).
[7] G. Bestmann and H. Dreizler, Z. Naturforsch. **37a,** 58 (1982).
[8] H. Gilman and R. G. Jones, J. Amer. Chem. Soc. **65,** 1458 (1943).
[9] F. J. Buckle, R. Heap, and B. C. Saunders, J. Chem. Soc. **1949,** 912.
[10] A. Ya. Yakubovich, I. N. Belyaeva, A. P. Sergeev, O. P. Solov'eva, and V. P. Lavrishahev, Khim. Nauka: Prom. **4,** 679 (1959); Chem. Abs. **54,** 8618 (1960).
[11] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35a,** 392 (1980).
[12] W. Gordy and R. L. Cook, Microwave Molecular Spectra Interscience, New York 1970.
[13] B. P. van Eijck, J. Mol. Spectrosc. **53,** 246 (1974).
[14] Computing program by V. Typke, Z. Naturforsch. **26a,** 1775 (1971).
[15] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw Hill, New York 1955.
[16] S. R. Polo, Can. J. Phys. **35,** 880 (1957).
[17] S. C. Wait and M. P. Barnett, J. Mol. Spectrosc. **4,** 93 (1960).
[18] B. E. Job and J. Sheridan, Nature London **193,** 677 (1962).
[19] K. Bolton, P. A. Curnuck, N. L. Owen, and J. Sheridan, Nature London **212,** 1229 (1966).
[20] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17,** 782 (1949).
[21] D. Boucher, J. Burie, J. Demaison, A. Dubrulle, J. Legrand, and B. Segard, J. Mol. Spectrosc. **64,** 290 (1977).
[22] J. Demaison, A. Dubrulle, D. Boucher, J. Burie, and V. Typke, J. Mol. Spectrosc. **76,** 1 (1979).
[23] H. Mäder, H. M. Heise, and H. Dreizler, Z. Naturforsch. **29a,** 164 (1974).
[24] L. J. Nugent, D. E. Mann, and D. R. Lide, J. Chem. Phys. **36,** 965 (1962).
[25] J. G. Baker, D. R. Jenkins, C. N. Kenney, and T. M. Sugden, Trans. Faraday Soc. **53,** 1397 (1957).
[26] E. Hirota, J. Mol. Spectrosc. **7,** 242 (1961).
[27] E. Hirota, J. Mol. Spectrosc. **71,** 145 (1978).
[28] L. Nygaard, Spectrochim. Acta, **22,** 1261 (1966).
[29] A. Guarnieri, Private communication.