Nitrogen-14 Quadrupole Coupling Constants in Propanedinitrile, $CH_2(CN)_2$, by Microwave Spectroscopy

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Nitrogen-14 quadrupole hyperfine structure has been resolved in the microwave spectrum of propanedinitrile, $CH_2(CN)_2$. Measurements between 5 and 30 GHz by Fourier transform and Stark modulation spectroscopy have been analysed. The general matrix elements for nuclear quadrupole interaction in molecules containing two equivalent coupling nuclei have been derived as simple formulae.

The quadrupole coupling constants determined for the inertial axis system of $CH_2(CN)_2$ are $\chi_{aa} = -2.368(28)$ MHz, $\chi_{bb} = 0.318(20)$ MHz, and $\chi_{cc} = 2.050(20)$ MHz. These values are used to establish that the electric field gradient tensor at nitrogen is cylindrically symmetric about the C ≡ N bond with a value of $\chi_{CN} = -4.09(4)$ MHz, close to values found for other organic cyanides.

1. Introduction

Several small molecules containing the $-C \equiv N$ group have been studied by microwave spectroscopy [1, 1a]. In these studies the CN bond length shows a remarkably small range close to 1.158 Å [2]. More interestingly in the asymmetric top molecules the CN internuclear axis is found to be bent by a few degrees from the X–CN internuclear axis:

$CH_2(CN)_2$	1.9(2)°	[3, 4]
CH_3CH_2CN	1.3(2)°	[5, 6]
$S(CN)_2$	5.0(2)°	[7]
NF_2CN	6.1(2)°	[8]
PF_2CN	8.8(8)°	[9].

The question arises whether the chemical bond strictly coincides with the internuclear axis, i.e. the question: Is a bent bond involved? The quadrupole coupling at the nitrogen nucleus provides a means of examining the triple bond environment in such cases.

The microwave spectrum of propanedinitrile (malononitrile) $CH_2(CN)_2$, has been extensively studied in the laboratory [10–13] as well as being detected from interstellar space in the comet Kohoutek [14]. Our structural studies of $CH_2(CN)_2$, to be published elesewhere [4], support the earlier findings; the purpose of this paper is to report the first measurements of nitrogen quadrupole coupling in $CH_2(CN)_2$.

Analysis of nuclear quadrupole fine structure involving two equivalent nuclear spins ($I \geqq 1$) has been performed for many molecules; for example CH_2Cl_2 [15, 16], Cl_2O [17], $CSCl_2$ [18], SCl_2 [19], CH_2Br_2 [20], $COBr_2$ [21], $S(CN)_2$ [7], $CO(CN)_2$ [22], 1,2,5-thiadiazole [23] and several other ring compounds [24–27]. Earlier references to the necessary theory can be found in the paper by Robinson and Cornwell [28]. In the present paper we give a simpler formulation of matrix elements of the appropriate quadrupole interaction Hamiltonian.

2. Experimental

A commercial sample of $CH_2(CN)_2$ (Aldrich Chemical Company) was used in the studies. Microwave transitions above 18 GHz were measured at Bristol, using a conventional 100 kHz Stark modulated spectrometer employing klystron and BWO sources (see Figure 1). At a later stage ten transitions below 18 GHz were measured under the very high resolution of microwave Fourier transform spectroscopy [29–31] at Kiel (see for example Figure 2). The Stark modulated measurements were made at room temperature while the Fourier transform work was carried out at −20 °C. The pressures were 10 mTorr and below 1 mTorr respectively.

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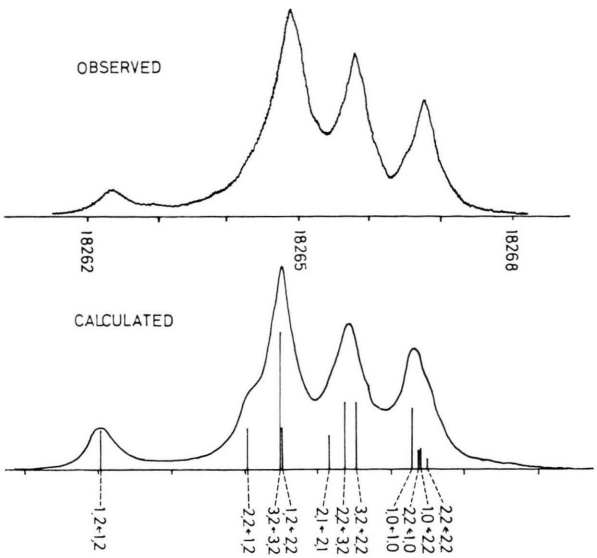
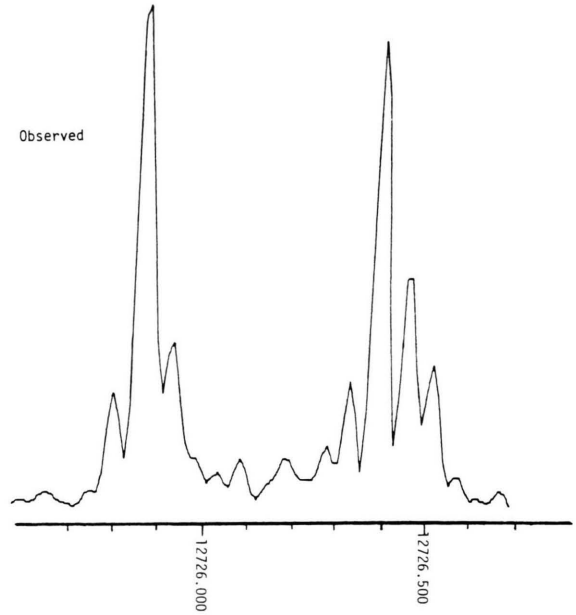


Fig. 1. Observed spectrum of quadrupole splitting in the $1_{01} \rightarrow 1_{10}$ transition of $CH_2(CN)_2$ with Stark modulation. Calculated pattern has been obtained with nitrogen quadrupole coupling constants $\chi_{aa} = -2.368$ MHz and $\eta = 0.7311$ using a half-width at half-height = 0.2 MHz.



3. Theory and Spectroscopic Analysis

Quadrupole fine structure arising from two equivalent nitrogen-14 nuclei has been measured for the transitions given in Table 1. The total Hamiltonian may be written as

$$H = H_R + H_Q\,, \tag{1}$$

where H_R is the rotational energy operator, and H_Q is the quadrupole interaction Hamiltonian for two nuclei given by

$$H_Q = H_{Q_1} + H_{Q_2}\,. \tag{2}$$

It is convenient for the evaluation of the interaction Hamiltonian to express (2) as the sum of two scalar products of irreducible tensor operators [32–34]*:

$$H_Q = \mathbf{V}_1^{(2)} \cdot \mathbf{Q}_1^{(2)} + \mathbf{V}_2^{(2)} \cdot \mathbf{Q}_2^{(2)}\,. \tag{3}$$

For two nuclei with identical quadrupole coupling the appropriate vector coupling scheme is $I_1 + I_2 = I$ and $I + J = F$. The Hamiltonian of (2) and (3) can then be expressed in terms of the reduced matrix elements using Wigner 6-j symbols [35].

* The sign of [34] Chapt. 7.2 is used.

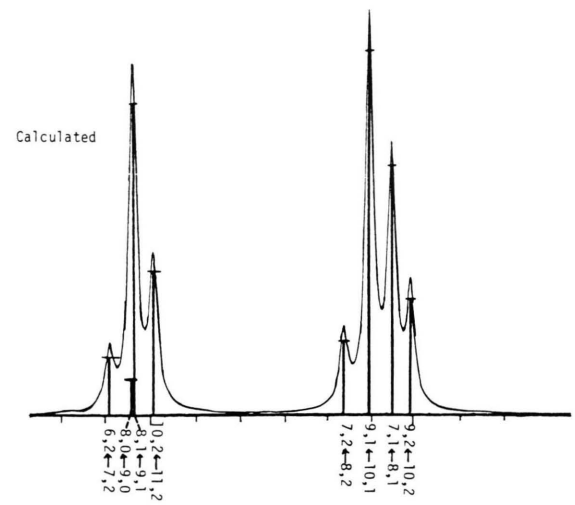


Fig. 2. Nitrogen quadrupole hyperfine structure of the $9_{19} \rightarrow 8_{26}$ transition of $CH_2(CN)_2$. – *Upper chart:* observed MWFT spectrum recorded with the following experimental conditions: A range of 1.1 MHz out of a 25 MHz-scan of the rotational spectrum of $CH_2(CN)_2$. Power spectrum, sample interval: 20 ns, 1280 K cycles, 1024 data points supplemented by 3072 zeros, microwave polarising frequency: $\nu_{MW} = 12716$ MHz; pressure: $p = 0.06$ mTorr, temperature: $T = -22$ °C. – *Lower chart:* calculated spectrum with $\chi_{aa} = -2.368$ MHz, $\eta = 0.7311$ and half-width at half-height = 25 kHz, frequency markers every 100 kHz.

Table 1. Observed rotational transitions of $CH_2(CN)_2$ in the ground vibrational state showing ^{14}N quadrupole hyperfine structure. Transitions below 18 GHz have been measured with microwave Fourier transform spectroscopy and those above with 100 kHz Stark modulation spectroscopy. The calculated hyperfine structure has been obtained using the constants of Table 2.

J	K_-	K_+	J'	K'_-	K'_+	F	I	F'	I'	Observed/ MHz	Obs-calc/ MHz	Weight	ν_0/MHz
4	0	4	3	1	3	5	1	4	1	5 045.964	−0.001	1.000	5 045.966
						5	2	4	2	5 046.133	0.059	0.0	
						4	1	3	1	5 045.902	−0.012	1.000	
						3	1	2	1	5 046.073	0.013	1.000	
5	0	4	4	1	4	7	2	6	2	11 176.075	0.009	1.000	11 176.115
						6	1	5	1	11 176.137	−0.003	1.000	
						6	2	5	2	11 176.249	0.000	1.000	
						5	0	4	0	11 175.988	0.002	1.000	
						5	2	4	2	11 176.296	−0.003	1.000	
						4	2	3	2	11 176.009	−0.003	1.000	
						3	2	2	2	11 175.906	−0.002	1.000	
6	0	6	5	1	5	8	2	7	2	17 413.510	0.012	1.000	17 413.574
						7	1	6	1	17 413.606	−0.007	1.000	
						6	2	5	2	17 413.832	0.024	0.0	
						6	1	5	1	17 413.439	−0.011	1.000	
						5	1	4	1	17 413.682	0.006	1.000	
						4	2	3	2	17 413.332	−0.038	0.0	
6	2	5	7	1	6	8	2	9	2	10 932.037	−0.005	1.000	10 931.994
						7	2	8	2	10 931.928	0.004	1.000	
						6	0	7	0	10 932.065	−0.006	1.000	
						6	2	7	2	10 931.864	0.007	1.000	
						5	2	6	2	10 932.011	0.001	1.000	
						4	2	5	2	10 932.098	−0.001	1.000	
8	2	6	9	1	9	10	2	11	2	12 715.941	0.017	1.000	12 716.248
						9	1	10	1	12 716.400	−0.010	1.000	
						9	2	10	2	12 716.518	0.015	1.000	
						8	1	9	1	12 715.879	0.001	1.000	
						7	1	8	1	12 716.464	0.003	1.000	
						7	2	8	2	12 716.336	−0.015	1.000	
						6	2	7	2	12 715.812	−0.011	1.000	
9	2	7	10	1	10	11	2	12	2	9 381.507	0.015	1.000	9 381.820
						10	2	11	2	9 382.072	0.002	1.000	
						9	0	10	0	9 381.450	0.004	1.000	
						9	2	10	2	9 382.554	−0.005	1.000	
						8	2	9	2	9 381.916	−0.014	1.000	
						7	2	8	2	9 381.397	−0.002	1.000	
10	1	9	9	2	8	11	1	10	1	9 870.236	−0.004	1.000	9 870.183
						11	2	10	2	9 870.294	0.005	1.000	
						10	1	9	1	9 870.040	−0.004	1.000	
						9	1	8	1	9 870.270	0.002	1.000	
11	1	10	10	2	9	13	2	12	2	17 062.213	−0.009	1.000	17 062.346
						12	2	11	2	17 062.464	0.010	1.000	
						11	2	10	2	17 062.644	0.007	1.000	
						10	2	9	2	17 062.368	−0.008	1.000	
12	3	10	13	2	11	14	2	15	2	14 090.479	0.005	1.000	14 090.436
						13	2	14	2	14 090.398	−0.003	1.000	
						12	2	13	2	14 090.344	−0.002	1.000	
13	3	10	14	2	13	15	2	16	2	14 897.554	−0.015	1.000	14 897.675
						14	2	15	2	14 897.746	0.002	1.000	
						13	2	14	2	14 897.916	0.013	1.000	
1	1	0	1	0	1	3	2	3	2	18 264.850	−0.047	0.001	18 265.339
						3	2	2	2	18 265.860	−0.103	0.001	
						2	2	3	2	18 265.860	0.040	0.001	
						2	2	1	0	18 266.790	0.011	0.001	
						1	0	2	2	18 266.790	−0.004	0.001	
						1	0	1	0	18 266.790	0.102	0.001	

Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	F	I	F'	I'	Observed/ MHz	Obs-calc/ MHz	Weight	ν_0/MHz
2	1	1	2	0	2	4	2	4	2	18 594.980	−0.341	0.0	18 595.616
						3	1	3	1	18 595.720	−0.043	0.001	
						3	2	3	2	18 596.250	0.044	0.001	
						2	1	2	1	18 594.980	−0.119	0.001	
						1	1	1	1	18 596.250	0.118	0.001	
3	1	2	3	0	3	5	2	5	2	19 098.380	−0.135	0.001	19 098.763
						4	2	4	2	19 099.230	0.094	0.001	
						3	2	3	2	19 098.380	0.041	0.001	
						3	0	3	0	19 099.230	−0.232	0.0	
4	1	3	4	0	4	6	2	6	2	19 785.130	−0.025	0.001	19 785.387
						5	1	5	1	19 785.540	0.037	0.001	
						4	1	4	1	19 785.130	0.062	0.001	
						3	1	3	1	19 785.540	−0.075	0.001	
8	1	7	8	0	8	10	2	10	2	24 655.440	−0.035	0.001	24 655.720
						9	1	9	1	24 655.880	0.038	0.001	
						8	1	8	1	24 655.440	0.011	0.001	
						7	1	7	1	24 655.880	−0.014	0.001	
9	1	8	9	0	9	11	2	11	2	26 496.230	0.017	0.001	26 496.466
						10	2	10	2	26 496.510	−0.168	0.001	
						9	2	9	2	26 496.230	0.065	0.001	
						8	2	8	2	26 496.510	−0.026	0.001	
						7	2	7	2	26 496.230	0.112	0.001	
10	1	9	10	0	10	12	2	12	2	28 626.200	−0.001	0.001	28 626.465
						11	1	11	1	28 626.600	0.003	0.001	
						10	1	10	1	28 626.200	0.039	0.001	
						9	1	9	1	28 626.600	−0.041	0.001	
2	1	2	1	0	1	4	2	3	2	28 732.600	0.052	0.001	28 732.492
						3	2	3	2	28 731.760	0.090	0.001	
						3	2	2	2	28 732.600	−0.135	0.001	
						2	0	2	2	28 733.840	−0.154	0.001	
						2	0	1	2	28 731.760	0.147	0.001	
4	2	2	5	1	5	6	2	7	2	29 039.320	−0.035	0.001	29 039.775
						5	1	6	1	29 040.030	0.045	0.001	
						4	1	5	1	29 039.320	0.079	0.001	
						3	1	4	1	29 040.030	−0.090	0.001	
5	1	4	5	0	5	7	2	7	2	20 667.710	−0.007	0.001	20 667.945
						6	2	6	2	20 668.120	−0.076	0.001	
						5	2	5	2	20 667.710	0.077	0.001	
						5	0	5	0	20 668.530	0.006	0.001	
1	1	1	0	0	0	3	2	2	2	23 498.800	0.048	0.001	23 498.784
						2	1	1	1	23 498.800	0.000	0.001	
						1	1	1	1	23 498.800	0.096	0.001	
						0	1	1	1	23 498.800	−0.143	0.001	

We obtain

$$(F\,M_F\,J\,\tau\,I\,I_1\,I_2 \mid H_Q \mid F\,M_F\,J'\,\tau'\,I'\,I_1\,I_2)$$
$$= (-1)^{J'+I+F} \begin{Bmatrix} J & J' & 2 \\ I' & I & F \end{Bmatrix}$$
$$\cdot [(J\,\tau \parallel \mathbf{V}_1^{(2)} \parallel J'\,\tau')\,(I\,I_1\,I_2 \parallel \mathbf{Q}_1^{(2)} \parallel I'\,I_1\,I_2) + (J\,\tau \parallel \mathbf{V}_2^{(2)} \parallel J'\,\tau')\,(I\,I_1\,I_2 \parallel \mathbf{Q}_2^{(2)} \parallel I'\,I_1\,I_2)]\,. \quad (4)$$

The Wigner-Eckart theorem is then used to express the reduced matrix elements in terms of the nuclear quadrupole moment, $e\,Q$, and the field gradient along the direction of J, $q_{J\tau}$. The matrix elements of

the interaction Hamiltonian are thus given by

$$\begin{aligned}
&(F\,M_F J\,\tau\,I\,I_1 I_2\,|\,H_{Q_1}+H_{Q_2}|\,F\,M_F J'\,\tau'\,I'\,I_1 I_2)\\
&=(-1)^{F+I-J}\sqrt{(2I+1)\,(2I'+1)}\begin{Bmatrix} J & J' & 2\\ I' & I & F\end{Bmatrix}\begin{pmatrix} J' & 2 & J\\ J & 0 & -J\end{pmatrix}\\
&\cdot\frac{1}{4}\left[(-1)^{I'-I_1+I_2}\,e\,Q_1\,q_{J\tau}(1)\begin{Bmatrix} I_1 & I_1 & 2\\ I' & I & I_2\end{Bmatrix}\begin{pmatrix} I_1 & 2 & I_1\\ I_1 & 0 & -I_1\end{pmatrix}\right.\\
&\left.+(-1)^{I'+I_1-I_2}\,e\,Q_2\,q_{J\tau}(2)\begin{Bmatrix} I_2 & I_2 & 2\\ I' & I & I_1\end{Bmatrix}\begin{pmatrix} I_2 & 2 & I_2\\ I_2 & 0 & -I_2\end{pmatrix}\right] \qquad (5)
\end{aligned}$$

with

$$\begin{aligned}
\frac{eQ_i}{2}&=\langle I_i\,M_{I_i}=I_i\,|\,\mathbf{Q}^{(2)}_{i,0}\,|\,I_i\,M_{I_i}=I_i\rangle\\
&=(-1)^{2I_i}\begin{pmatrix} I_i & 2 & I_i\\ I_i & 0 & -I_i\end{pmatrix}(I_i\,\|\,\mathbf{Q}^{(2)}_i\,\|\,I_i)
\end{aligned}$$

and

$$\begin{aligned}
\frac{q_{J\tau}(i)}{2}&=\langle J\,\tau\,M_J=J\,|\,\mathbf{V}^{(2)}_{i,0}\,|\,J'\,\tau'\,M_J=J\rangle\\
&=(-1)^{J'+J}\begin{pmatrix} J' & 2 & J\\ J & 0 & -J\end{pmatrix}(J\,\tau\,\|\,\mathbf{V}^{(2)}_i\,\|\,J'\,\tau')\\
&\qquad\qquad i=1,2\,.
\end{aligned}$$

The round brackets denote Wigner 3-*j* symbols [36] and the curved brackets Wigner 6-*j* symbols.

If for two equivalent nuclei we substitute $e\,Q_1\,q_{J\tau}(1)=e\,Q_2\,q_{J\tau}(2)=e\,Q\,q_{J\tau}$ and $I_1=I_2(\equiv I_0)$ in (5), the matrix elements are reduced to

$$\begin{aligned}
&\langle F\,M_F J\,\tau\,I\,I_0\,I_0|\,H_{Q_1}+H_{Q_2}\,|\,F\,M_F J\,\tau\,I\,I_0\,I_0\rangle\\
&=W_{Q_0+Q_0}(I_0,I)\\
&=(-1)^{2F}\,2\,e\,Q\,q_{J\tau}\frac{\{\frac{3}{4}\,C\,(C+1)-I\,(I+1)\,J\,(J+1)\}}{J\,(2J-1)\,(2I-1)\,(2I+3)}\\
&\cdot\frac{\{\frac{3}{4}\,(I^2+I-1)-I_0\,(I_0+1)\}}{I_0\,(2I_0-1)} \qquad (6)
\end{aligned}$$

and

$$\begin{aligned}
&\langle F\,M_F J\,\tau\,I\,I_0\,I_0|\,H_{Q_1}+H_{Q_2}\,|\,F\,M_F J\,\tau\,I+2\,I_0\,I_0\rangle\\
&=(-1)^{2F}\frac{3}{16}\,e\,Q\,q_{J\tau}\frac{[(F+I+J+3)\,(F+I+J+2)\,(F-I+J)\,(F-I+J-1)]^{1/2}}{(2I+3)\,[(2I+5)\,(2I+1)]^{1/2}}\\
&\cdot\frac{[(F+I-J+2)\,(F+I-J+1)\,(-F+I+J+2)\,(-F+I+J+1)]^{1/2}}{J\,(2J-1)}\\
&\cdot\frac{[(I+2I_0+3)\,(I+2I_0+2)\,(2I_0-I)\,(2I_0-I-1)]^{1/2}}{I_0\,(2I_0-1)}\,, \qquad (7)
\end{aligned}$$

where

$$C=F\,(F+1)-I\,(I+1)-J\,(J+1)\,.$$

Elements with $\Delta I=1$ are zero.

Equation (6) may be compared with the diagonal matrix element $W_{Q_0}(I)$ of the quadrupole interaction Hamiltonian for a single coupling nucleus with the spin I:

$$\begin{aligned}
&W_{Q_0+Q_0}(I_0,I)\\
&=(-1)^{2I}\frac{4\,I\,\{\frac{3}{4}\,(I^2+I-1)-I_0\,(I_0+1)\}\,W_{Q_0}(I)}{(2I+3)\,I_0\,(2I_0-1)} \qquad (8)
\end{aligned}$$

where $W_{Q_0+Q_0}(I_0,I)$ and $W_{Q_0}(I)$ are the diagonal elements for two equivalent coupling nuclei with spin I_0 and total spin I and a single one with spin I respectively. For $CH_2(CN)_2$ $I_0=1$ and the expressions derived for the quadrupole energies agree with those given in reference [23].

A computer program has been written to calculate quadrupole splittings based on (6) and (7). Ten highly resolved transitions measured by Fourier transform spectroscopy have been combined with eleven transitions measured by Stark spectroscopy.

A total of 94 quadrupole components have been analysed by least squares fitting in terms of $e\,Q\,q_{aa}=\chi_{aa}$ and the asymmetry parameter $\eta=(\chi_{bb}-\chi_{cc})/\chi_{aa}$ (see Table 2!). As shown in Table 1 the Stark spectrometer measurements have been included in the fit with a small weighting

Table 2. Rotational and quadrupole coupling constants of $CH_2(CN)_2$. The rotational constants A, B and C are from [12]. σ: standard deviation of the fit, $|(\chi_{aa},\eta)|$: correlation between χ_{aa} and η; least squares errors in brackets as one standard deviation in units of the last digit.

A/MHz	20 882.7537(8)
B/MHz	2 942.3003(16)
C/MHz	2 616.7225(16)
χ_{aa}/MHz	−2.368(28)
η	0.7311(83)
σ/kHz	3.4
$\|(\chi_{aa},\eta)\|$	0.92

reflecting the lower resolution and precision of that work; nevertheless the inclusion of these transitions gives a significant improvement in the accuracy of the coupling constants derived. The weighting factors adopted are not critical and a very satisfactory fit to the patterns has been obtained, see Table 1 and Figs. 1 and 2.

The fit shows that a first order treatment is sufficient. So off-diagonal elements in J have been neglected. The second-order quadrupole perturbation terms in χ_{ab} have been tried but do not improve the fit; these terms are insignificant because no appropriate near-degeneracies occur. Such is the quality of the present fit that it has not been thought worthwhile to include spin-rotation terms in the analysis.

Assignment of the F components in the patterns was made by comparison of synthesized and observed spectra using a curve plotter. Experimental half-widths were used in the calculations. In calculating relative intensities it was important to consider the nuclear spin statistical weights. $CH_2(CN)_2$ has C_{2v} symmetry with three pairs of equivalent nuclei; one pair of fermions and two pairs of bosons. The total wavefunction has to change sign for the symmetry operation of rotation of 180° about the b-axis. For the ground vibronic state the ratio of statistical spin weights is 15:21 comparing rotational transitions with $(K_- + K_+)$ even for the upper and lower energy level to transitions with $(K_- + K_+)$ odd. When the nitrogen quadrupole splitting of a single rotational transition is considered, these weights are divided as follows: If $(K_- + K_+)$ is even for both levels, we get a ratio of 5:9:1 for the $I = 2$, 1 and 0 states respectively; for $(K_- + K_+)$ being odd the ratio is 15:3:3. Thus the statistical weights have a pronounced effect on the nitrogen-14 patterns. Moreover for the $(I = 0, 2)$-states for $J = F$, the mixing of wavefunctions through the $\Delta I = 2$ matrix element (Eq. (7)) has to be taken into account to obtain the correct frequencies and relative intensities.

4. Discussion

The analysis yields the quadrupole coupling constants at the nitrogen nuclei in the inertial principal axis system. These values may be used to test the cylindrical symmetry of the electric field gradient tensor along the C ≡ N bonds. Assuming this cylindrical symmetry to exist, the three χ_{gg} values allow three independent values of χ_{CN} to be derived from the equation

$$\chi_{gg} = \tfrac{1}{2}(3\Phi_g^2 - 1)\,\chi_{CN}\,, \tag{9}$$

where Φ_g is the direction cosine relating the C ≡ N axis with the inertial principal axis $g = a$, b and c. χ_{cc} leads directly to $\chi_{CN} = -4.10(4)$ MHz, and taking $\Phi_b = \cos 58.0°$ from the structure determination [4] χ_{aa} and χ_{bb} give values of $\chi_{CN} = -4.09(5)$ and $-4.04(25)$ MHz respectively. The excellent agreement among these values for χ_{CN} firmly establishes that the electric field gradient tensor at nitrogen is cylindrically symmetry about the C ≡ N bond within the accuracy of the hyperfine measurements. The average value of χ_{CN} obtained, $-4.09(4)$ MHz, is very close to the values found for CH_3CN ($\chi_{CN} = -4.21(2)$ MHz [37]), CH_3CH_2CN ($\chi_{CN} = -4.14(4)$ MHz [5, 6, 38]) and other organic cyanides.

The quadrupole coupling results for $CH_2(CN)_2$ are very interesting in view of the structural result [3, 4] that the C ≡ N groups are bent away from each other by 4°. Both the C ≡ N bond length {1.156(2) Å [4]} and the local bonding symmetry about the nitrogen atom appear to be practically unchanged by the angular distortion. The chemical bonding of the cyano group is relatively unaffected by the hydrocarbon group to which it is attached, strengthening arguments about the localised nature of the bonding in the C ≡ N linkage. The situation is very different in $S(CN)_2$ where appreciable asymmetry in the quadrupole coupling about the CN bond is found [7]. This finding together with the short SC bond length is taken as an indication for a significant π-back bonding with sulphur.

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