The ^{14}N Nuclear Quadrupole Coupling in E- and Z-C-Cyanomethanimine; its Prediction from Restricted Hartree-Fock Wave Functions and its Experimental Determination by High Resolution Microwave Spectroscopy

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The ^{14}N hyperfine multiplets of low-J rotational transitions of the E and Z isomers of $HN=CH-C\equiv N$, produced by flash pyrolysis from $(CH_3)_2N-C\equiv N$ as precursor, were observed and analysed. The quadrupole coupling constants determined are (c-axis perpendicular to the molecular plane):

		X_{aa}/MHz	X_{bb}/MHz	X_{cc}/MHz
E	$H-N=CH-C\equiv\mathbb{N}$	−4.160 (10)	+1.658 (31)	+2.502 (31)
E	$H-\mathbb{N}=CH-C\equiv N$	+0.764 (11)	−4.459 (24)	+3.695 (24)
Z	$H-N=CH-C\equiv\mathbb{N}$	−4.078 (21)	+1.581 (42)	+2.497 (42)
Z	$H-\mathbb{N}=CH-C\equiv N$	−4.171 (21)	+0.401 (32)	+3.770 (32)

The observed hfs multiplets were predicted with reasonable accuracy from RHF/6-311G** field gradients, once the latter had been scaled appropriately to compensate partly for the typical errors in the RHF-wave functions. The hitherto unmeasured ^{14}N hyperfine multiplets of the related pyruvonitriles, $H-N=C(CH_3)-C\equiv N$, are predicted.

Introduction

Recently the microwave spectra of the two isomers of C-cyanomethanimine, $HN=CH-C\equiv N$, have been reported for the first time by Takamo et al. [1, 2]. From these pioneering studies the rotational constants, a set of centrifugal distortion constants and the components of the molecular electric dipole moments are known for both molecules. In view of the interest in these two "$HC\equiv N$ dimers" as potential interstellar molecules we decided to try to resolve and to analyse the narrow hyperfine structure of the rotational transitions. It is caused by the interaction of the two ^{14}N nuclear quadrupole moments with the local intramolecular electric field gradients. Knowledge of this hyperfine structure should be of great help in confirming the assignment of interstellar absorption or emission lines.

Since we intended to prepare the C-cyanomethanimines along the same route as reported in [2], i.e. by pyrolysis of $(CH_3)_2N-C\equiv N$, a left over from our previous studies of N-cyanoformimine, $H_2C=N-C\equiv N$ [3], we knew that the C-cyanomethanimines would be produced only in small quantities as minor byproducts, and we anticipated serious signal to noise problems, especially in the case of Z-C-cyanomethanimine with its smaller dipole moments. Therefore, in the hope to facilitate the detection and first assignment of the hyperfine satellites, we carried out quantum chemical calculations in order to predict the field gradients and thereby the nuclear quadrupole coupling constants from the electronic wavefunctions and the nuclear configuration. We describe these quantum chemical calculations in the first section of the present contribution. As a byproduct, a linear correlation was found between the experimental quadrupole coupling constant perpendicular to the molecular plane, X_{cc}, and the out-of plane electron density at the nitrogens, which we find interesting to report. In the second section we describe the experiment and the analysis of the observed hyperfine splittings. In the final section we use our new experience to predict the hitherto unknown hyperfine structure in the rotational spectra of the related pyruvonitriles.

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Theoretical Studies

From the work of Huber ([4] and references cited therein) it is known that the accurate prediction of nitrogen nuclear quadrupole coupling is not easy. It requires large basis sets for the immediate vicinity of the nucleus and configuration interaction (CI) may play an important role. This is especially true in the case of "sp^2-hybridized" nitrogens such as the imine-nitrogens in the C-cyanomethanimines. Ab initio calculations of such complexity were clearly out of reach in our study. On the other hand it appears to be possible to predict the quadrupole coupling constants with useful accuracy already from RHF wave functions constructed from fairly small basis sets, if an empirical conversion factor is used to convert the calculated field gradients to the experimentally accessible quadrupole coupling constants [5] (see also the discussion in [6] pages 795 through 797). Such a conversion factor is basis set and method dependent and partially compensates for the typical deficiencies in the wave function. In the present investigation we even went one step further and determined separate conversion factors for the imine nitrogen and for the nitrile nitrogen. To this end we did run the RHF-routine from the Gaussian 86 program package [7] for a set of imines and of nitriles with experimentally known structures and nuclear quadrupole coupling constants. The 6-311G** basis was used throughout. We have published the imine results recently (see Table 13 in [6]). The corresponding nitrile results are presented now in Table 1. The rigid nuclear frame approximation was used for all these calculations with the microwave structures as input data wherever available. Vibrational corrections were neglected.

We recall that the field gradients and the quadrupole coupling constants are related through

$$X_{aa} = eQ\langle 0|V_{aa}|0\rangle h^{-1} = -eQ(e\,q_{aa}/a_0^3)\,h^{-1} \qquad (1)$$

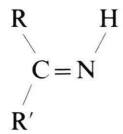
(and cyclic permutations).

Here e is the absolute value for the electron charge, Q the nuclear quadrupole moment ($Q(^{14}N) = 1.99(2)\ 10^{-30}\ m^2$, [8]), $\langle 0|V_{aa}|0\rangle$ the vibronic ground state expectation value for the second derivative of the intramolecular Coulomb potential taken in a-direction at the position of the nucleus, q_{aa} is the corresponding field gradient calculated in atomic units, h Planck's constant, and a_0 Bohr's radius for the hydrogen atom.

Table 1. Nitrile ^{14}N nuclear quadrupole coupling constants, χ_{gg} (in MHz), and RHF/6-311G** field gradients, q_{gg} (in atomic units, a.u.), for a set of nitriles. From a least squares fit, the best value for the conversion factor from the RHF field gradients to the experimental quadrupole coupling constants follows as $f_{nitrile} = -4.003\,(24)$ [MHz/a.u.]. The standard deviation of the fit is 82 kHz. The references for the structures (first) and for the experimental coupling constants (second) are given below the names of the compounds.

		q/a.u.	χ_{obs}/MHz	χ_{calc}/MHz
acetonitrile	*aa*	1.044699	−4.2253 (7)	−4.188
[19] [14]	*bb*	−0.522356	2.1127 (4)	2.094
monofluoro-	*aa*	0.923323	−3.704 (3)	−3.665
acetonitrile	*bb*	−0.491328	1.892 (4)	1.933
[20] [20]	*cc*	−0.431995	1.812 (4)	1.732
	ab	0.543611		
difluoro-	*aa*	1.099975	−4.373 (9)	−4.410
acetonitrile	*bb*	−0.614913	2.399 (9)	2.465
[21] [21]	*cc*	−0.485063	1.974 (9)	1.944
	ac	−0.614913		
trifluoroaceto-	*aa*	1.192282	−4.656 (15)	−4.780
nitrile [21] [21]	*bb*	−0.596141	2.328 (8)	2.390
propionitrile	*aa*	0.830252	−3.309 (33)	−4.183
[22] [23]	*bb*	−0.319503	1.265 (13)	2.135
	cc	−0.510749	2.044 (20)	2.047
	ab	−0.539019		
cisallyl-	*aa*	0.471817	−1.763 (34)	−1.891
cyanide	*bb*	0.041214	−0.284 (35)	−0.165
[24] [25]	*cc*	−0.513031	2.047 (35)	2.057
	ab	−0.766701		
propargyl-	*aa*	0.560692	−2.2558 (22)	−2.390
cyanide	*bb*	−0.062282	0.2102 (29)	0.252
[26] [26]	*cc*	−0.498411	2.0456 (29)	2.138
	ab	0.744187		
malononitrile	*aa*	0.604097	−2.368 (28)	−2.235
[27] [28]	*bb*	−0.101180	0.318 (20)	0.200
	cc	−0.502917	2.050 (20)	2.035
	ab	0.752353		
N-cyano-	*aa*	0.799533	−3.251 (8)	−3.205
formimine	*bb*	−0.247533	0.842 (17)	0.991
[29] [3]	*cc*	−0.552000	2.409 (17)	2.210
	ab	−0.350476		
d-acrylonitrile	*aa*	0.934463	−3.8373 (39)	−3.740
[30] [31]	*bb*	−0.447774	1.7218 (32)	1.792
	cc	−0.486689	2.1155 (32)	1.948
	ab	−0.406384		

As can be seen from Table 13 in [6], it appears to be possible to predict the quadrupole coupling constants for C-substituted imines,



(with R ≙ H_3C-, $H_2C=CH-$, H−, R′ ≙ H−, and with R ≙ F−, R′ ≙ F−), within better than 100 kHz if

a factor, $f_{\text{imine}} = -3.957\,(35)$ [MHz/a.u.], is used to convert from the RHF/6-311G** q-values to the coupling constants. The predictions get less accurate if R ≙ N≡C− or if the imino group carries an electronegative substituent at the nitrogen nucleus itself, such as for instance in $H_2C{=}N{-}OH$, $H_3C{-}CH{=}N{-}OH$, and $F_2C{=}N{-}F$. In the cases the uncertainty in the prediction rises to 300 kHz. Finally, for N-methyl derivatives such as $H_2C{=}N{-}CH_3$ or $H_3C{-}\ CH{=}N{-}CH_3$, our experience tells that the prediction should be better than 200 kHz.

For the nitriles,

$$R{-}C{\equiv}N$$

(with R ≙ H−, H_3C-, and H_2XC- (where X ≙ F−, HC≡C−, N≡C−)), a slightly larger conversion factor, $f_{\text{nitrile}} = -4.003\,(24)$ [MHz/a.u.], typically leads to predictions with an uncertainty below 100 kHz. For R ≙ O=N−, O=CH−, $H_2C{=}N-$, N_3- (as in cyanogenazide), the uncertainties in the predictions of the quadrupole coupling constants rise to approximately 250 kHz. In Table 2 we present some typical results.

According to (1), the conversion factors introduced would correspond to ^{14}N nuclear quadrupole moments of only $1.684\ 10^{-30}$ m^2 and $1.704\ 10^{-30}$ m^2, respectively, i.e. to values which are about 15% lower than the currently accepted value (see above). Apparently the RHF field gradients are typically too large in value. In other words: the true wave functions correspond to slightly more spherical electron densities in the immediate vicinity of the nuclei.

Table 2. Comparison between experimental quadrupole coupling constants (in MHz) for nitrile nitrogen and coupling constants (in MHz) calculated from RHF/6-311G** field gradients. The empirical conversion factor, $f_{\text{nitrile}} = -4.003$ [MHz/a.u.] (compare Table 1), was used for the conversion from the RHF field gradients to the coupling constants. The references for the structures (first) and for the experimental values (second) are given below the names of the compounds.

	O=N−C≡N [32] [32]		OHC−C≡N [33] [34]		N_3−C≡N [35] [36]	
	exp.	calc.	exp.	calc.	exp.	calc.
χ_{aa}	−3.92	−3.953	−4.330 (19)	−4.331	−2.27 (4)	−2.269
χ_{bb}	1.08	0.899	1.531 (14)	1.402	1.15 (7)	1.331
χ_{cc}	2.84	3.054	2.799 (29)	2.929	1.12 (11)	0.938
χ_{ab}		−1.344		1.477		2.496
	F−C≡N [37] [38]		H−C≡C−C≡N [39] [40]		C≡N−C≡N [41] [41]	
	exp.	calc.	exp.	calc.	exp.	calc.
χ_{aa}	−2.67 (5)	−2.796	−4.3320 (46)	−4.3446	−3.7811 (2)	−3.738

Having used the simple Townes/Dailey model [9] in the past for the interpretation of observed nuclear quadrupole coupling constants in terms of electron densities at the quadrupole nuclei, we also tried to correlate the experimental out of plane quadrupole coupling constants, X_{cc} (c-axis perpendicular to the heavy atom plane), to the p_c-electron densities at the nitrogen nuclei, i.e. to the π-densities. Within this model, and using the language of quantum chemistry, the quadrupole coupling constants are predicted from the p-electron densities, P_{pa}, P_{pb}, and P_{pc}, by [10]

$$X_{cc} = -(10\ \text{MHz})\,[P_{pc} - (P_{pa} + P_{pb})/2] \qquad (2)$$

(and cyclic permutations).

With the triple zeta basis used here fo the RHF calculation, we have to be slightly more specific about what we mean by p-density. The triple zeta basis contains three p_c-type valence orbitals at each nitrogen nucleus, $2p_c$, $3p_c$, and $4p_c$, rather than only one, and for the correlation to X_{cc} we have simply used the sum of their three Mulliken populations, i.e. $P_{pc} = P_{2pc} + P_{3pc} + P_{4pc}$, as global p_c-density. The results are given in Table 3. They are also shown pictorially in Figure 1. Apparently they contrast with an earlier observation of Hinchliff et al., who have stated that the experimental quadrupole coupling constants would not correlate to the p-densities [11]. The reason for this discrepancy is most likely due to the fact that here we have been looking at families of somehow related molecules, while they have made a general statement. The molecules considered here do indeed have something in common. Within each family their average RHF in-plane p-densities, i.e. the values $P_{\text{in plane}} = (P_{pa} + P_{pb})/2$, are essentially the same.

We are now in the position to make two predictions for the quadrupole coupling constants in Z- and E-C-cyanomethanimine. The first prediction is based on the RHF/6-311G** field gradients and on our empirical conversion factors for the imine and nitrile nitrogens. The structures from [12] were used as input data for these RHF-calculations. The field gradients lead to predictions for the complete ^{14}N nuclear quadrupole coupling tensors, including the off-diagonal elements X_{ab}. The second prediction is based on the linear correlations shown in Figure 1. It only predicts the out of plane components of the coupling tensors, $X_{cc,\,\text{imine}}$ and $X_{cc,\,\text{nitrile}}$, respectively. We present both

Table 3. Global ^{14}N p-electron densities, defined as the sum of the Mulliken population densities of the three p-type valence orbitals of the 6-311 G** basis, $P_{Pc}=(P_{2Pc}+P_{3Pc}+P_{4Pc})$, (and cyclic permutation $c\rightarrow a\rightarrow b$) and the experimental values for the out-of-plane ^{14}N quadrupole coupling constants for a set of imines and nitriles. P_{Pc} and χ_{cc} closely follow linear correlations (compare Fig. 1). Note, however, that the sum of the in-plane densities, $(P_{Pa}+P_{Pb})$, is approximately constant within each set.

Molecule	Electron density		χ_{cc}/MHz	
	out-of-plane P_{Pc}	in-plane $(P_{Pa}+P_{Pb})$	calc.	obs.
Imines				
H−N=CH−C≡N (E)	1.041	2.552	3.785	3.695 (24)
H−N=CH−C≡N (Z)	1.045	2.582	3.760	3.770 (32)
$H-N=CH_2$ [42] [43]	1.106	2.558	3.376	3.582 (2)
$H-N=CH-CH=CH_2$ (TS) [44] [6]	1.142	2.552	3.149	3.157 (5)
$H-N=CH-CH=CH_2$ (TA) [44] [6]	1.143	2.598	3.142	3.105 (2)
$H-N=CH-CH_3$ (cis) [45] [6]	1.148	2.538	3.111	3.058 (3)
$H-N=CH-CH_3$ (trans) [45] [6]	1.150	2.546	3.098	3.054 (3)
Nitriles				
O=N−C≡N	0.962	2.460	2.922	2.84
OHC−C≡N	0.976	2.452	2.775	2.799 (29)
H−N=CH−C≡N (E)	1.021	2.452	2.304	2.502 (31)
H−C≡C−C≡N	1.034	2.426	2.167	2.161 (5)
N≡C−CH_2−C≡N	1.043	2.412	2.073	2.050 (20)
C≡N−C≡N	1.051	2.412	1.989	1.891 (2)
$CH_2F-C\equiv N$	1.071	2.400	1.780	1.813 (4)
F−C≡N	1.104	2.410	1.434	1.335 (5)
$N_3-C\equiv N$	1.139	2.394	1.067	1.12 (11)

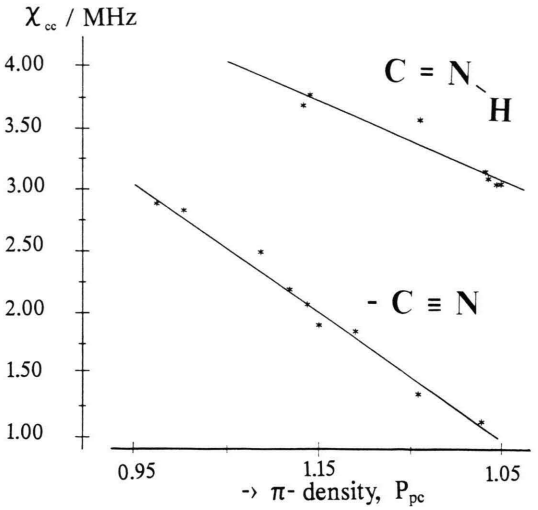


Fig. 1. Correlation between the out-of-plane RHF/6-311 G** p-electron densities (π-densities), $P_{pc}=(P_{2pc}+P_{3pc}+P_{4pc})$, and the experimental out-of-plane coupling constants, X_{cc}, for the set of imines and nitriles presented in Table 3. X_{cc} and P_{pc} closely follow a linear relation given by

$X_{cc}/\mathrm{MHz}=10.3_{457}-6.3_{021}\cdot P_{pc}$ for the imines (above)

and

$X_{\infty}/\mathrm{MHz}=13.0_{058}-10.4_{820}\cdot P_{pc}$ for the nitriles (below).

The standard deviation of the fits is 81 kHz. The slope for the imines (−6.3 MHz) differs considerably from the value of −10 MHz [14], which has been recommended for use with the Townes/Dailey model (see (2) in the text, while that for the nitriles (−10.4 MHz) agrees well.

sets of predicted quadrupole coupling constants in Table 4.

From the values in Table 4 we expect the hfs multiplets of low-J rotational transitions to spread over a frequency range of one to three MHz. In the a-type transitions, whose hfs patterns largely depend on the X_{aa} value, the splitting is predominantly caused by the nitrile nitrogen in both isomers.

Experimental and Analysis

For the experimental studies we have used the flash pyrolysis flow system described earlier [6]. The precursor, dimethylcyanamide, $(CH_3)_2N-C\equiv N$, was pyrolysed immediately in front of the S-band waveguide microwave absorption cell. The quartz tube used for pyrolysis had an inner diameter of 1 cm. The heated zone had a length of 20 cm. A fairly rapid flow was maintained, corresponding to a total pressure of about 10 mTorr at the entrance hole of the waveguide cell and of about 1 mTorr at the exit slit. The effective length of the waveguide cell, as determined by the length of the Stark-septum, was 180 cm. The cell was cooled to a wall temperature of about −50 °C by methanol from a kyromat flowing through a cooling jacket. Phase stabilized backward wave oscillators were used as radiation sources. 8 kHz square wave Stark-effect modulation and lock- in detection as well as computer averaging were used for noise suppression.

When the oven temperature was raised, the absorption lines originating from the precursor molecules disappeared around 800 °C, indicating the onset of thermal cracking processes. Yet no C-cyanomethanimine absorptions could be detected in this tempera-

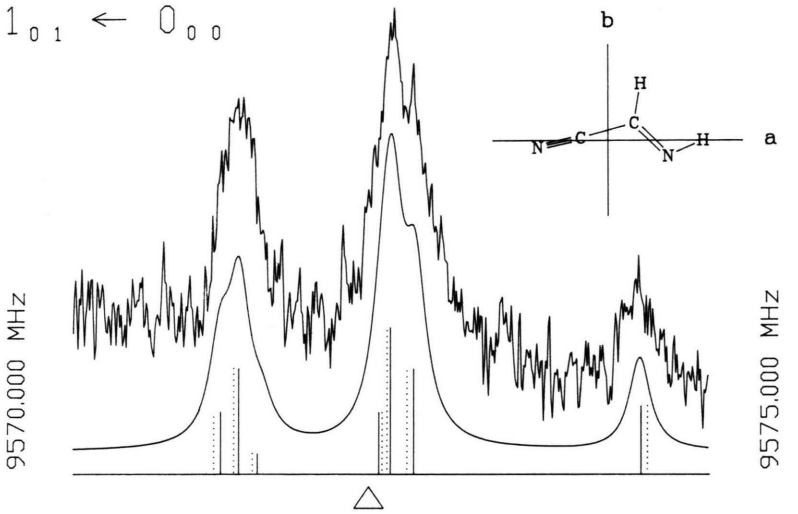


Fig. 2. ^{14}N nuclear quadrupole hfs-pattern of the $1_{01} \leftarrow = 0_{00}$ μ_a-type rotational transition of E-C-cyanomethanimine, a trace product in the pyrolysis of dimethylcyanamide. The lower curve represents a simulation based on the experimental quadrupole coupling constants (see Table 7). The dotted bar spectrum was calculated from the RHF-prediction (see Table 5). The triangle indicates the intensity weighted center frequency of the transition. The insert shows the orientation of the principal inertia axes system with respect to the nuclear frame. From [2] the electric dipole moments are: $\mu_a = 3.25$ D (and $\mu_b = 2.51$ D, respectively). For the analysis of such noisy signals compare for instance [43].

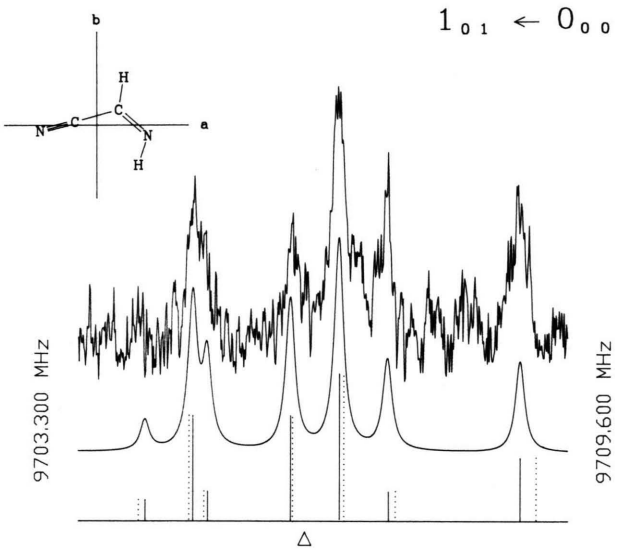


Fig. 3. ^{14}N nuclear quadrupole hfs-pattern of the $1_{01} \leftarrow 0_{00}$ μ_a-type rotational transition of Z-C-cyanomethanimine, produced as a trace product by pyrolysis of dimethylcyanamide at a temperature of 1100 °C. The lower trace shows a simulation and a bar spectrum. Both are based on the experimental quadrupole coupling constants (see Table 7). The dotted "bar spectrum" shows the corresponding RHF-prediction. Due to the smaller electric dipole moment, $\mu_a = 1.35$ D ($\mu_b = 0.4$ D) [2], and its higher ground state energy, a considerably larger number of averaging cycles had to be taken to obtain this signal to noise ratio.

Table 4. Predictions for the ^{14}N nclear quadrupole coupling constants in E and Z C-cyanomethanimine. The predictions are based on the RHF/6-311G** field gradients, the empirical conversion factors for the imine- and nitrile-nitrogens and (only for the out-of-plane components, χ_{cc}), on the empirical linear correlations between χ_{cc} and the global Mulliken population density in the nitrogen p-orbitals perpendicular to the molecular plane (see Figure 1).

	E-C-cyano-methanimine	Z-C-cyano-methanimine
Imine-^{14}N		
q_{aa}/a.u.	−0.168823	1.127870
χ_{aa}/MHz	0.668	−4.463
q_{bb}/a.u.	1.185739	−0.110368
χ_{bb}/MHz	−4.692	0.437
q_{cc}/a.u.	−1.016916	−1.017502
χ_{cc}/MHz	4.024	4.026
q_{ab}/a.u.	0.171310	0.338072
P_{Pc}	1.041	1.045
χ_{cc}/MHz	3.785	3.760
Nitrile-^{14}N		
q_{aa}/a.u.	1.037801	1.020173
χ_{aa}/MHz	−4.154	−4.083
q_{bb}/a.u.	−.0.416111	−0.411283
χ_{bb}/MHz	1.666	1.646
q_{cc}/a.u.	−0.621690	−0.608890
χ_{cc}/MHz	2.488	2.437
q_{ab}/a.u.	0.373724	0.425938
P_{Pc}	1.021	1.023
χ_{cc}/MHz	2.304	2.283

ture range. They started to show up only when the temperature was raised further to 1050 °C, and they were accompanied by strong absorption signals due to $H_3C-C\equiv H$ and $H_2C=NH$. This is perfectly in line with the reaction route proposed in [2]. The final recordings were carried out at an oven temperature of about 1100 °C.

In Figs. 2 and 3 we present recordings of the the hyperfine multiplets corresponding to the $1_{01} \leftarrow 0_{00}$ rotational transitions. The apparent similarity in the

Table 5. ^{14}N quadrupole hyperfine splittings in some low-J rotational transitions of E C-cyanomethanimine. The splittings are given with respect to the hypothetical center frequency, ν_0, in the absence of quadrupole coupling ($\Delta\nu = \nu - \nu_0$). The calculated splittings follow from the optimized coupling constants presented in Table 7. The following coupling scheme is used to designate the states. First the nitrogen spins are coupled to an intermediate spin I_{12}: $I_{12} = I_1 + I_2$ (the index 1 refers to ^{14}N of the nitrile group, 2 to the ^{14}N of the imine group). Second the intermediate spin is coupled to the rotational angular momentum: $F = J + I_{12}$.

$J'_{K^-K^+} - J_{K^-K^+}$ ν_0/MHz	F'	I'_{12}	F	I_{12}	Relative intensity	$\Delta\nu_{exp.}$ [MHz]	$\Delta\nu_{calc.}$ [MHz]	Δ [kHz]
$1_{01} - 0_{00}$	1	1	2	2	4.06	−1.183	−1.175	−8
	1	1	1	1	3.25		−1.175	
9572.344	1	1	0	0	1.70		−1.175	
	2	2	2	2	10.27	−1.016	−1.028	−12
	2	2	1	1	4.73		−1.028	
	3	2	2	2	21.00	0.174	0.170	4
	2	1	1	1	10.27	0.352	0.349	3
	2	1	2	2	4.73		0.349	
	1	2	2	2	4.83	2.078	2.095	−17
	1	2	1	1	3.54		2.095	
	1	2	0	0	0.63		2.095	
$2_{12} - 1_{11}$	1	2	1	2	2.54	−1.457	−1.473	16
	3	2	2	1	1.04		−1.473	
18773.328	2	2	1	0	2.88	−1.381	−1.396	15
	2	0	1	2	3.40	−1.246	−1.228	−18
	3	2	3	2	3.94	−1.068	−1.071	3
	3	2	2	2	7.62	0.165	0.171	−6
	4	2	3	2	16.20	0.303	0.303	0
	2	1	1	0	3.03	0.694	0.698	−4
	2	0	1	0	2.79	1.030	1.021	9
	2	0	2	2	2.16	2.158	2.163	−5
	2	1	1	1	2.47	2.229	2.228	1
	1	2	1	1	1.46	2.317	2.306	21
$2_{11} - 1_{10}$	2	1	2	2	2.52	−2.211	−2.212	1
	3	1	2	2	2.02	−1.807	−1.798	−8
19516.774	2	0	1	0	3.30	−1.067	−1.058	−9
	3	1	2	1	8.82	−0.811	−0.819	8
	3	1	3	2	1.76	−0.392	−0.379	−13
	2	1	1	1	2.24	−0.377	−0.369	−8
	3	2	2	2	6.49	0.080	0.079	1
	4	2	3	2	16.20	0.108	0.110	−2
	2	0	1	1	3.27	0.644	0.645	−1
	1	2	1	2	2.23	0.720	0.723	−3
	3	2	2	1	3.68	1.066	1.059	7
	0	2	1	2	1.19	1.396	1.393	3
	3	2	3	2	2.44	1.514	1.499	15
	2	2	1	1	1.30	1.722	1.726	−4

Table 6. As Table 5 but for Z C-cyanomethanimine.

$J'_{K^-K^+} - J_{K^-K^+}$ ν_0/MHz	F'	I'_{12}	F	I_{12}	Relative intensity	$\Delta\nu_{exp.}$ [MHz]	$\Delta\nu_{calc.}$ [MHz]	Δ [kHz]
$1_{01} - 0_{00}$	2	2	2	2	4.06	−1.438	−1.444	6
	1	0	0	0	6.14	−1.275	−1.259	−17
9706.263	1	2	0	0	2.86		−2.259	
	2	1	1	1	15.00	−0.213	−0.206	−7
	3	2	2	2	21.00	0.415	0.412	3
	1	1	1	1	9.00	1.035	1.031	4
	1	2	2	2	6.14	2.704	2.703	1
	1	2	0	0	2.86		2.703	
$2_{12} - 1_{11}$	2	2	2	2	2.66	−1.772	−1.784	12
	2	2	1	0	4.70	−1.740	−1.744	4
18971.398	3	2	2	2	4.94	−1.370	−1.358	−12
	1	1	0	1	2.91	−1.311	−1.326	15
	3	2	2	1	3.74	−0.914	−0.931	17
	3	2	3	2	3.92	−0.854	−0.848	−7
	3	1	2	2	4.10	−0.586	−0.584	−2
	3	1	2	1	8.22	−0.158	−0.157	−1
	4	2	3	2	16.20	0.546	0.547	−1
	2	0	1	1	4.62	1.248	1.240	8
$2_{02} - 1_{01}$	1	1	1	1	2.25	−2.057	−2.065	8
	1	2	1	2	2.76	−1.658	−1.669	11
19409.483	3	2	3	2	4.20	−1.583	−1.594	11
	2	0	1	2	5.01	−1.347	−1.346	−1
	2	2	1	0	5.66	−0.543	−0.541	−3
	2	2	2	2	2.99	−0.358	−0.356	−2
	3	1	2	1	12.60	−0.087	−0.089	2
	2	1	1	1	6.75	0.003	0.002	1
	4	2	3	2	16.20	0.176	0.178	−2
	3	2	2	2	8.40	0.264	0.262	2
	1	1	0	1	3.00	1.045	1.028	16
$2_{11} - 1_{10}$	3	1	2	2	3.73	−1.100	−1.094	−6
	3	2	2	1	4.64	−0.514	−0.513	−1
19854.322	3	1	2	1	7.84	−0.098	−0.097	−1
	4	2	3	2	16.20	0.455	0.455	0
	2	1	1	1	2.26	0.933	0.925	8
	2	0	1	1	4.04	1.148	1.147	1

signal to noise ratios is somewhat misleading since a considerably larger number of averaging cycles was used in the recording of the Z-species. The absorption signals form the Z-species had in fact much lower intensities than those from the E-species. This is probably mostly due to the difference in the electric dipole moments; in the Z-species the local dipoles associated with the lone pair and the nitrile group largely compensate. But the Z-species is also assumed to be higher in energy [12] and should thus be less populated. However, we have not attempted to study the intensities quantitatively in the present investigation. The observed hfs multiplets are presented in Tables 5 and 6.

In Figs. 2 and 3 we also show the positions of the hfs-satellites as predicted form our theoretical studies described in the previous section. They are presented as dotted-line bars. The close agreement with the observed spectra is quite pleasing.

The hfs multiplets were analyzed using our program SUZIQ.FOR (author O. Böttcher [13]). For the theoretical background of nuclear quadrupole coupling we refer to Chapt. IX in [14]. In our program the matrix of the effective Hamiltonian, which consists of the rigid rotor energy expression, supplemented by the potential energies of the two ^{14}N nuclear quadrupole

moments within the local intra molecular electric field gradients, is set up in a coupled basis in which the two nitrogen spins are first coupled to form an intermediate spin angular momentum:

$$I_{12}=I_1+I_2.$$

Then this intermediate spin angular momentum is coupled to the rotational angular momentum associated with the end over end rotation of the molecule:

$$F=J+I_{12}.$$

Matrix elements off-diagonal in the quantum number J are neglected in this program, a simplification which is feasible in the present application since no close degeneracies associated with neglected off-diagonal elements occur in our case.

In Table 7 we present the ^{14}N quadrupole coupling constants which result from a least squares fit to the hfs-splittings presented in Tables 5 and 6, respectively.

In both molecules the nitrogen coupling tensors follow the general rule that their principal axis, which corresponds to the largest negative coupling constant, points into the general direction of the lone pair, i.e. into the direction of the "sp-orbital" in the case of the nitrile nitrogen and into the direction of the non-bonded "sp^2-orbital" in the case of the imino nitrogen.

We note that the Townes-Dailey model, (2), even though it could provide physical insight for understanding the linear correlations shown in Fig. 1, would have lead to poor predictions of the coupling constants. This may be checked by using the p-orbital populations presented in Table 3 and is left to the reader. On the other hand, comparison with Table 4 shows that the RHF-6-311 G** field gradients lead to an excellent prediction for the coupling constants of the cyano nitrogen. These predictions are well within the single experimental standard deviations! By contrast the predictions for the coupling constants of the imino nitrogens are much less accurate, even though the values are essentially predicted within the expected 300 kHz uncertainty range. This difference in the predictive power of the RHF-calculation probably reflects the fact that in the nitrile case the immediate neighbour is always the triply bonded C-atom. This makes the local electron configuration around the nitrogen less sensitive to different molecular environments farther apart, and thus also makes it easier to account for the deficiencies in the RHF-wavefunctions just by introducing a calibration factor.

As indicated above, the fair success of using the RHF field gradients for the calculations of the quadrupole coupling constants has prompted us to predict the yet unmeasured coupling constants in the related pyruvonitriles, $H-N=C(CH_3)-C\equiv N$. We describe our procedure in the final section of this contribution.

Table 7. Experimental ^{14}N nuclear quadrupole coupling constants in E- and Z-C-cyanomethanimine. The least squares program was written to fit $\chi_+=\chi_{bb}+\chi_{cc}=-\chi_{aa}$ and $\chi_-=\chi_{bb}-\chi_{cc}$. The individual components then follow from Poisson's equation: $\chi_{aa}+\chi_{bb}+\chi_{cc}=0$. N1 designates ^{14}N in the nitrile group, N2 designates ^{14}N in the imine group. Compare to Table 4 for the predicted values.

	E-isomer	Z-isomer
χ_+ (N1)	4.160 (10)	4.078 (21)
χ_- (N1)	−0.844 (29)	−0.916 (36)
χ_{aa} (N1)	−4.160 (10)	−4.078 (21)
χ_{bb} (N1)	1.658 (31)	1.581 (42)
χ_{cc} (N1)	2.502 (31)	2.497 (42)
χ_+ (N2)	−0.764 (11)	4.171 (21)
χ_- (N2)	−8.153 (21)	−3.369 (24)
χ_{aa} (N2)	0.764 (11)	−4.171 (21)
χ_{bb} (N2)	−4.459 (24)	0.401 (32)
χ_{cc} (N2)	3.695 (24)	3.770 (32)

Prediction of the ^{14}N Nuclear Quadrupole Coupling Constants in cis- and trans-Pyruvonitrile, $N\equiv C-C(CH_3)=N-H$, and in N-methylamine, $H_2C=N-CH_3$

For the prediction of the ^{14}N nuclear quadrupole coupling in the pyruvonitriles we followed a twofold route. First we used the known structures [15] to calculate the RHF-6-311 G** field gradients and we converted those to the corresponding experimental coupling constants by multiplication with our empirical conversion factors (see above). We present these results in Table 8. From our present experience we expect to have hit the cyano coupling constants by this procedure within better than 100 kHz. Much less accurate predictions are expected for the imino coupling constants.

For those we have therefore used an extrapolation, which makes partly use of RHF information, but which is largely based on our experimental results for the C-cyanomethanimines. It relies on two assumptions.

The first assumption is that the RHF field gradients, including the off-diagonal element, q_{ab}, are sufficiently accurate to calculate at least the orientation of the

Table 8. RHF-6-311 G** field gradients at the ^{14}N nuclei in E- and Z-C-cyanomethanimine and in N-methylmethanimine. The geometries of the nuclear frames were taken from the references given in brackets. For the conversion from the field gradients to the observable coupling constants we have used our empirical factors $f_{imine} = -3.957$ [MHz/a.u.] and $f_{nitrile} = -4.003$ [MHz/a.u.], respectively.

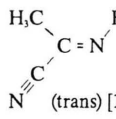
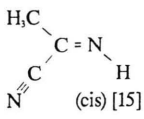
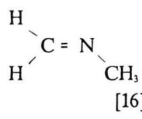
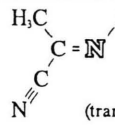
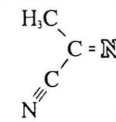
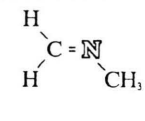
	 (trans) [15]	 (cis) [15]	 [16]
$^{14}N_{imino}$			
q_{aa}/a.u.	0.096 998	1.150 257	−0.289 243
q_{bb}/a.u.	0.870 840	−0.245 360	1.269 574
q_{cc}/a.u.	−0.904 837	−0.904 897	−0.980 331
q_{ab}/a.u.	0.691 111	−0.144 704	−0.058 394
X_{aa}/MHz	−0.384	−4.552	1.156
X_{bb}/MHz	−3.197	0.971	−5.024
X_{cc}/MHz	3.581	3.581	3.879
$^{14}N_{nitrile}$			
q_{aa}/a.u.	1.213 398	1.140 845	
q_{bb}/a.u.	−0.590 494	−0.502 909	
q_{cc}/a.u.	−0.622 904	−0.637 935	
q_{ab}/a.u.	−0.126 563	−0.150 138	
X_{aa}/MHz	−4.857	−4.565	
X_{bb}/MHz	2.363	2.012	
X_{cc}/MHz	2.494	2.553	

Table 9. Quadrupole coupling constants for the imino nitrogen in cis- and trans-pyrouvonitrile and in N-methylmethanimine as extrapolated by the increment method ($\Delta X_{cc} = -0.528$ MHz and $\Delta X_{lonr\,pair} = +0.352$ MHz for $H- \rightarrow H_3C-$ substitution at the imino C-atom). The extrapolations are based on the experimental coupling constants of the C-cyanomethanimine studied here and of N-methylethanimine studied by the Zürich group [16]. For the orientation of the quadrupole coupling tensors with respect to the nuclear frame, the RHF-field gradient tensors were used.

	 (trans)	 (cis)	
X_{aa}/MHz	−0.392	−4.135	1.429
X_{bb}/MHz	−2.775	0.968	−4.980
X_{cx}/MHz	3.167	3.242	3.551

imino quadrupole coupling tensor with respect to the nuclear frame and that this information can be used to infer the principal axes components of the coupling tensor from its measured diagonal elements with respect to the principal inertia axes system. For the transformation properties of the quadrupole coupling tensor under rotation cf. (5-63) through (5-69) in [18].

The second assumption is that it is a reasonable approximation to transfer the changes in the principal coupling constants of the imino nitrogen, which are observed in the pairs methanimine, $H_2C=NH$, on the one hand and in cis- and trans-ethanimine, $H_3C-CH=N-H$, on the other hand to other imines, where a proton at the carbon atom of the imino group is substituted by a CH_3-group. For the corresponding experimental coupling constants compare [6].

Proceeding that way we arrived at the coupling constants presented in Table 9. These extrapolated values are certainly more accurate than the values in Table 8. Personally we would trust them within better than 100 kHz. In Fig. 4 we present the corresponding predicted hfs-patterns for the $1_{01} - 0_{00}$ rotational transitions of both molecules.

For the prediction of the coupling constants in N-methylmethanimine we followed essentially the same procedure with the only difference that we have used the experimental coupling constants of N-methylethanimine determined earlier by the Zürich group [16] for the extrapolation. The corresponding coupling constants are given in Tables 8 (directly calculated from the RHF field gradients) and 9 (extrapolated from the N-methylethanimine values under the assumptions that the orientation of the coupling tensor with respect to the nuclear frame is accurately calculated by the RHF program and that the changes in the principal coupling constants that are observed in the pair methanimine ↔ethanimine are typical for $H- \leftrightarrow H_3C-$ substitutions at the imino C-atom and can be transferred to other pairs of molecules).

In the present case of N-methylmethanimine experimental coupling constants have been published earlier [17]. These older values are up to 470 kHz off our prediction. Since this could serve as a test for the validity of the assumptions on which our extrapolation was based, we suggest that the hfs-multipets should be restudied under higher resolution. We are convinced that our predictions should hit the coupling constants within 100 kHz and should thus be of great help in a future assignment and analysis of the hfs-multiplets in all three molecules.

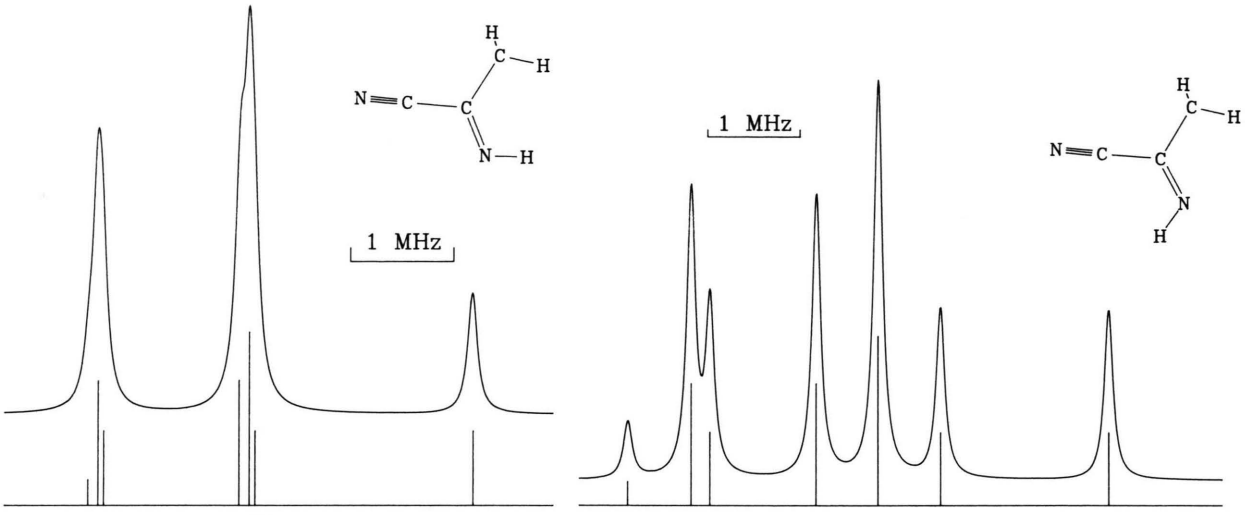


Fig. 4. Predictions of the ^{14}N nuclear quadrupole hfs-patterns of the $1_{01} \leftarrow 0_{00}$ rotational transitions of the pyruvonitriles. The predictions are based on the nitrile coupling constants presented in Table 8 and on the imino quadrupole coupling constants presented in Table 9. The spectral ranges are 5.40 MHz for the trans-species (left spectrum, imino hydrogen in trans position with respect to the nitrile group) and 7.04 MHz for the cis-species (right spectrum). For both isomers we only show the hfs-patterns of the A-species of methyl top internal rotation (no tunneling). Quite in general essentially the same pattern is expected for the E-species (tunneling), unless the barrier is very low, i.e. well below a value of $V_3 = 1$ kcal/mole.

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