Quadrupole Coupling in 4-Fluoro-benzonitrile. A Microwave Fourier Transform Study

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The ^{14}N quadrupole hfs coupling has been studied in Para-fluoro-benzonitrile using the high resolution microwave Fourier transform spectrometer constructed at Kiel University. If interpreted within a simplified MO treatment, the data show that the out-off-plane p-electron density at the Nitrogen nucleus is appearently larger than the in-plane density, contrary to the prediction of a CNDO/2 calculation.

Unaware of a previous study by B. Bak and coworkers [1] we have assigned and analysed the vibronic ground state rotational spectrum of Para-fluoro-benzonitrile, using the high sensitivity/high resolution microwave Fourier transform spectrometer developed by H. Dreizler and coworkers [2, 3, 4, 5] to record the spectrum. In view of the fact that Bak et al. did not resolve the ^{14}N hyperfine structure of the rotational transitions, we present our results in the following note.

The sample, white cristals at room temperature, was obtained from Aldrich Chemie, Steinheim (purity > 99%). The X- through K-band spectrum (8 to 25 GHz) was recorded at cell temperatures between − 25 °C and − 39 °C and at sample pressures below 1 mTorr. The sample proved stable in the brass waveguide absorption cells. (Bak and coworkers used a flow system.)

In total 111 different rotational transitions, most split by the ^{14}N quadrupole hfs interaction, were analysed in detail. In Table 1 we give a small portion of the recorded spectrum, showing the complete set of $J = 4$ to $J = 5$ transitions and some selected $J = 12$ to $J = 13$ transitions. The complete list is available upon request [6]. In Fig. 1 we present the 9063.5 MHz to 9064.2 MHz region of the spectrum in order to demonstrate the typical resolution and signal to noise ratio obtained in the present investigation.

The spectrum was analysed by an iterative treatment of the centrifugally distorted rotor (program ZFAP4 written by Typke [7]) and the hfs interaction (program HT1NQ, written by Herberich [8]) similar to the procedure described in [9]. The resultant rotational constants and ^{14}N quadrupole coupling constants are given in Table 2. Also given for comparison are the ^{14}N quadrupole coupling constants observed in Benzonitrile [10] and Cyanoacetylene [11]. It is quite obvious, that by substitution to the aromatic ring, the quadrupole coupling tensor of the C≡N group has lost the cylindrical symmetry usually found in small organic molecules [12], and we will try to discuss the observed asymmetry in terms of p-electron densities at the N nucleus.

If one analyses the observed quadrupole coupling tensor within a simplified molecular orbital theory in which the intramolecular electric field gradient at the N nucleus is assumed to be essentially determined by the integrals involving the atomic p-orbitals centered at the N nucleus, the following expression for the coupling constants is obtained [13]:

$$\chi_{aa} = (e\, q_{n,1,0}\, Q/h)\,[P_{aa} - \tfrac{1}{2}(P_{bb} + P_{cc})] \qquad (1)$$

(and cyclic permutations). In (1) $e\, q_{n,1,0}\, Q$ represents the quadrupole coupling contribution of an electron in the atomic Nitrogen p-orbital ($n = 2$ for Nitrogen), and $P_{aa} = 2 \sum_n c^2_{n,p_a}$ etc. represent the p-electron densities at the Nitrogen nucleus with the sum running over all doubly occupied orbitals and c_{n,p_a}

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Table 1. Some of the recorded hyperfine multiplets (MHz) of Para-fluorobenzonitrile. The experimental resonance frequencies result from a line profile simulation taking into account dispersion/absorption overlap. They differ up to 6 kHz from the peak frequencies in the raw data of the Fourier transform spectra. $\bar{\nu}_m$ are the hypothetical center frequencies [16] of the measured hyperfine multiplets to which the rotational constants and centrifugal distortion constants were fitted. $\Delta\nu_{exp}$ are the measured hyperfine splittings to which the quadrupole coupling constants were fitted. $\Delta\nu_{calc.}$ are the corresponding splittings calculated from the optimized molecular parameters given in Table 2. A mean square deviation of 8 kHz was obtained for the $\bar{\nu}_m$'s and a mean square deviation of 8 kHz was obtained for the $\Delta\nu_{exp}$'s [6]. To our opinion especially the latter value indicates that the lineshape analysis should be further improved.

$J_{K-K_+} - J'_{K'-K'_+}$	$F-F'$	ν_{exp}	$\bar{\nu}_m$	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
$5_{41} - 4_{40}$	6− 5	9015.013			
$5_{42} - 4_{41}$	5− 4	9013.867	9014.718	1.146	1.133
	4− 3	9015.347		1.480	1.471
$5_{23} - 4_{22}$	6− 5	9064.988			
	5− 4	9064.678	9064.895	0.309	0.307
	4− 3	9065.020		0.341	0.338
$5_{05} - 4_{04}$	6− 5	8942.889	8942.870		
	5− 4			0.079	0.073
	4− 3	8942.810			
$5_{32} - 4_{31}$	6− 5	9019.356	9019.180		
	5− 4	9018.701		0.655	0.648
	4− 3	9019.506		0.803	0.806
$5_{14} - 4_{13}$	6− 5	9351.026			
	5− 4	9350.919	9350.979	0.107	0.091
	4− 3	9350.961		0.042	0.038
$5_{33} - 4_{32}$	6− 5	9018.387			
	5− 4	9017.731	9018.203	0.656	0.648
	4− 3	9018.537		0.806	0.805
$5_{15} - 4_{14}$	6− 5	8635.560			
	5− 4	8635.470	8635.522	0.090	0.088
	4− 3	8635.514		0.044	0.046
$5_{24} - 4_{23}$	6− 5	9000.354	9000.264	0.300	0.298
	5− 4	9000.054		0.331	0.328
	4− 3	9000.385			
$13_{12\,1} - 12_{12\,0}$	14−13	23434.152			
$13_{12\,2} - 12_{12\,1}$	13−12	23433.562	23433.975	0.590	0.595
	12−11	23434.219		0.657	0.657
$13_{10\,3} - 12_{10\,2}$	14−13	23438.060			
$13_{10\,4} - 12_{10\,3}$	13−12	23437.647	23437.935	0.413	0.414
	12−11	23438.109		0.462	0.455
$13_{11\,2} - 12_{11\,1}$	14−13	23435.859			
$13_{11\,3} - 12_{11\,2}$	13−12	23435.361	23435.709	0.498	0.500
	12−11	23435.916		0.555	0.552

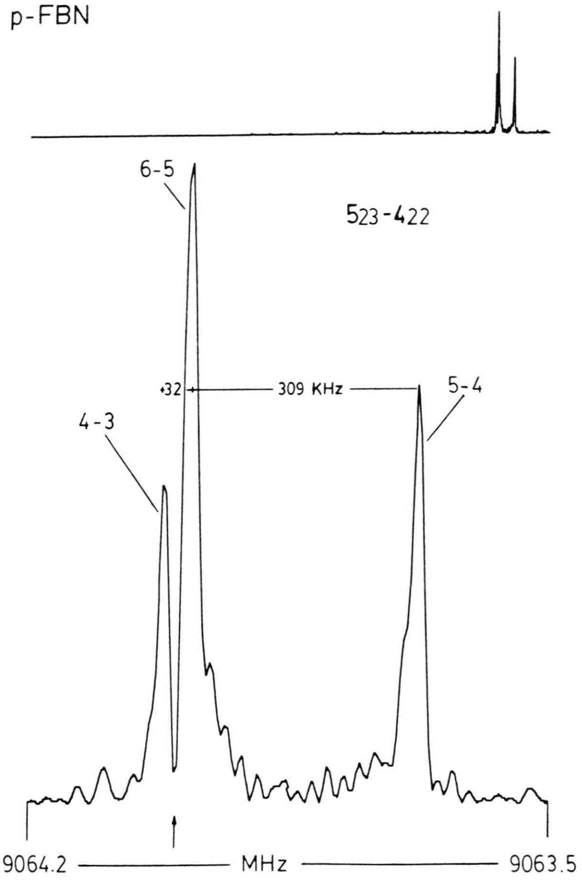

Fig. 1. 10 MHz range (top) and enlarged 700 kHz portion (bottom) in the region of the $5_{23}-4_{22}$ rotational transition of Para-fluorobenzonitrile. Experimental conditions were: $p < 0.2$ mTorr, $T = -26\,°C$, duration of polarizing pulse: 50 ns, carrier frequency of pulse: 9064.0 MHz (indicated by vertical arrow), sampling: 1024 data points taken per decay at time intervals of 50 ns, 3072 zeros added prior to Fourier transformation. Note the wiggles at the bottom. They indicate that the signal had not yet completely decayed to zero at the end of digitization.

the LCAO coefficient for the p_a-orbital in the n-th molecular orbital.

With $e\,q_{n,1,0}\,Q$ clearly negative [14], Eq. (1), combined with the experimental coupling constants from Table 2 indicates that the electron density in the out of plane p-orbital is larger than in the in-plane p-orbital. This finding is contrary to a prediction based on a CNDO/2 calculation with Bak's preliminary structure [15] as input data (see Fig. 2 and Table 3). It certainly would be of interest to carry out an ab initio calculation for the field gradient, possibly taking into account the vibrational ground state averaging.

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Table 2. Rotational constants, centrifugal distortion constants and nuclear quadrupole coupling constants determined from the hfs patterns of 111 rotational transitions. Watson's S-reduction and the I^r-representation was used in the centrifugal distortion routine (compare also [17]). Also given for comparison are the ^{14}N quadrupole coupling constants found in Benzonitrile and in Cyanoacetylene.

4-Fluoro-benzonitrile	
A	5627.483 ± 0.087 MHz
B	972.395 ± 0.001 MHz
C	829.109 ± 0.001 MHz
$\varkappa$	− 0.940277
D_J	0.0140 ± 0.0020 kHz
D_{JK}	0.2396 ± 0.0117 kHz
D_K	31.6080 ± 32.9000 kHz
d_1	− 0.0030 ± 0.0009 kHz
d_2	− 0.0021 ± 0.0011 kHz
$\chi^+ = \chi_{bb} + \chi_{cc}$	4.1976 ± 0.0066 MHz
$\chi^- = \chi_{bb} - \chi_{cc}$	0.5927 ± 0.0145 MHz
χ_{aa}	− 4.1976 ± 0.007 MHz
χ_{bb}	2.3952 ± 0.012 MHz
χ_{cc}	1.8025 ± 0.012 MHz
Benzonitrile	
χ_{aa}	− 4.187 ± 0.07 MHz
χ_{bb}	2.301 ± 0.08 MHz
χ_{cc}	1.886 ± 0.08 MHz
Cyanoacetylene	
$e\,Q\,q(^{14}\mathrm{N})$	− 4.322 ± 0.0046 MHz

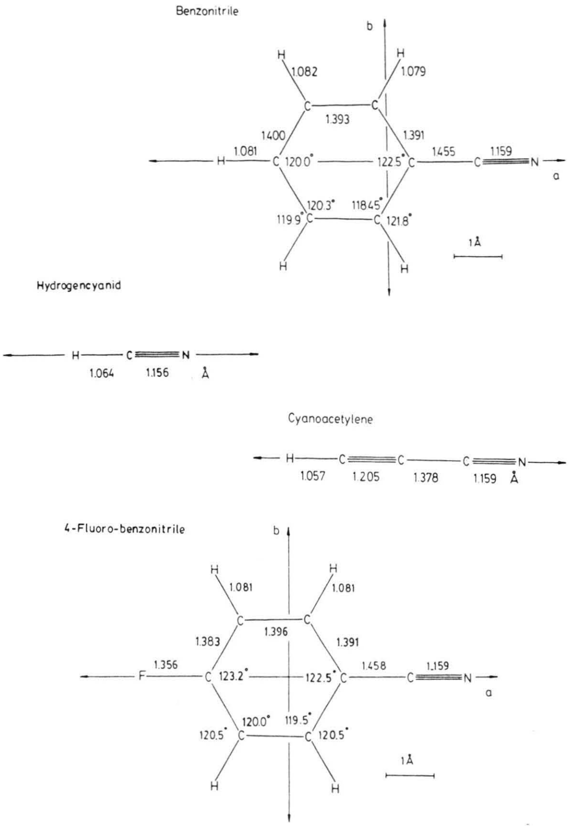

Fig. 2. Molecular structures which were used as input data for the semi-empirical CNDO/2 calculations of the p-electron densities.

Table 3. Comparison of the experimental ^{14}N quadrupole coupling constants of H−C≡N [18], HC≡ C−C≡N [11], 4-Fluorobenzonitrile (this work) and Benzonitrile [10] with the values calculated according to Eq. (1) from CNDO/2 wavefunctions. (Pople's original parametrisation was used.) For this calculation we have calibrated the $e\,q\,Q$-value of Eq. (1) using the H−C≡N values. (This leads to $e\,q\,Q = -15.58$ MHz.) While CNDO/2 predicts a smaller p-electron density in the out off plane p-orbital as compared to the in-plane p-orbital, the reverse density distribution follows from the experiment.

Molecule	Exp. coupling constants			CNDO/2 p-densities			
	χ_{aa}/MHz (χ/MHz) ≙ CNDO/2 calc.	χ_{bb}/MHz	χ_{cc}/MHz	$P_{\mathrm{p}_a \mathrm{p}_a}$	$P_{\mathrm{p}_b \mathrm{p}_b}$	$P_{\mathrm{p}_c \mathrm{p}_c}$	$P_{\mathrm{p}_c \mathrm{p}_c} - P_{\mathrm{p}_b \mathrm{p}_b}$ $(P_{\mathrm{p}_c \mathrm{p}_c} - P_{\mathrm{p}_b \mathrm{p}_b})$ exp.
Hydrogencyanid	− 4.709	2.354	2.354	1.3519	1.0496	1.0496	0 (0)
Cyanoacetylene	− 4.317 (− 4.494)	2.1585 (2.247)	2.1585 (2.247)	1.3546	1.0661	1.0661	0 (0)
Benzonitrile	− 4.187 (− 4.021)	2.301 (1.213)	1.886 (2.808)	1.3436	1.1196	1.0513	− 0.0683 (+ 0.0266)
4-Fluorobenzonitrile	− 4.1976 (− 4.018)	2.395 (1.326)	1.803 (2.692)	1.3417	1.1130	1.0545	− 0.0585 (+ 0.0380)

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