The Microwave Spectra and Nitrogen Quadrupole Coupling Constants of Cyano- and Isocyano-pentafluorobenzene

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The microwave spectra of cyano-pentafluorobenzene, C_6F_5CN, and isocyano-pentafluorobenzene, C_6F_5NC, have been assigned by molecular beam microwave Fourier transform spectroscopy. The ^{14}N nuclear quadrupole coupling constants have been determined for both isomers.

Introduction

The nuclear quadrupole coupling in free molecules provides a means of probing the electric field gradient (efg) at the site of a quadrupolar nucleus (i.e. a nucleus with spin $I > 1/2$) [1]. The ^{14}N nucleus with $I = 1$ is therefore suited to investigate the substitutional effect on its electronic environment, for example in cyanides (R–CN) and isocyanides (R–NC). Whereas the efg at the nitrogen nucleus in cyanides is dominated by the nitrogen lone pair and only shows a moderate dependence upon substitution, the effect on the efg at an isocyanide nitrogen is more pronounced. The only aromatic isocyanide that has been investigated with microwave spectroscopy to date is phenylisocyanide (C_6H_5NC) [2, 3]. In line with a systematic study of the fluorine substitution effect on the efg in isocyanides, we decided to investigate isocyano-pentafluorobenzene which has recently become available [4–6]. Among the aromatic cyanides so far investigated with microwave spectroscopy are cyanobenzene (benzonitrile) [7–9], 1-cyano-2-fluorobenzene [10–12], 1-cyano-3-fluorobenzene [12, 13], 1-cyano-4-fluorobenzene [10, 12, 14] and cyano-pentafluorobenzene [15]. For comparison, we reinvestigated the microwave spectrum of the latter compound to resolve the quadrupole hyperfine splittings.

Experimental

The molecular beam microwave Fourier transform spectrometer used in this investigation has been described elsewhere [16, 17]. The liquid sample was placed directly in front of the pulsed valve and helium at a pressure of 1.2 bar was used as carrier gas for the supersonic jet expansion. Cyano-pentafluorobenzene was obtained commercially and used without further purification. A pure sample of isocyano-pentafluorobenzene was kindly provided by D. Preugschat and D. Lentz of the Free University of Berlin.

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Assignment

Cyano-pentafluorobenzene

No rotational transitions of cyano-pentafluorobenzene could be detected at frequencies calculated from the rotational constants of Sharma and Doraiswamy [15]. A subsequent frequency sweep resulted in a reassignment of the rotational spectrum. We succeeded in measuring 14 rotational transitions, of which five showed a fine structure attributed to ^{14}N nuclear quadrupole coupling (Table 1). The derived rotational constants within the rigid rotor approximation are listed in Table 3 (column b), the quadrupole coupling constants are given in Table 4.

Isocyano-pentafluorobenzene

A guess on the structure of isocyano-pentafluorobenzene yielded preliminary rotational constants and a calculated spectrum. After the first few lines had been found and assigned, a total of 39 rotational transitions were measured. Three lines showed a hyperfine structure due to the ^{14}N nucleus. The line frequencies are listed in Table 2, the rigid rotor rotational constants are given in Table 3 (column a) and the quadrupole coupling constants in Table 4.

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Table 1. Rotational transitions of cyano-pentafluorobenzene and ^{14}N nuclear hyperfine structure. J, K_-, K_+, and J', K'_-, K'_+: quantum numbers of the lower and upper energy level; F, F': quantum numbers for the hyperfine component; ν_{obs}: experimental line frequency or calculated centerfrequency of a hyperfine multiplett (GHz); ν_{hfs}: observed frequency of hyperfine components (GHz); $\delta\nu$: difference between calculated and observed frequency of the hyperfine component (kHz); δ: difference between observed and calculated rigid rotor frequency (kHz).

J' K'_- K'_+ ← J K_- K_+	F' F	ν_{hfs}	$\delta\nu$	ν_{obs}	δ
8 0 8 ← 7 0 7				7.458 541 7	−11
8 1 8 ← 7 1 7				7.458 508 1	−22
9 1 8 ← 8 1 7				9.215 724 7	−1
	8 ← 7	9.215 731 8	−1		
	9 ← 8	9.215 697 1	−1		
	10 ← 9	9.215 742 3	−1		
9 2 8 ← 8 2 7				9.215 110 2	−1
	8 ← 7	9.215 117 6	−1		
	9 ← 8	9.215 082 3	0		
	10 ← 9	9.215 127 9	1		
9 3 7 ← 8 3 6				10.095 467 1	5
	8 ← 7	10.095 480 9	−1		
	9 ← 8	10.095 431 1	1		
	10 ← 9	10.095 487 3	0		
10 0 10 ← 9 0 9				9.213 293 5	−2
10 1 10 ← 9 1 9				9.213 293 5	−2
	9 ← 8	9.213 293 1	3		
	10 ← 9	9.213 283 6	−1		
	11 ← 10	9.213 301 9	−1		
10 4 7 ← 9 4 6				11.848 449 8	−1
11 0 11 ← 10 0 10				10.090 706 1	−1
11 1 11 ← 10 1 10				10.090 706 1	−1
	10 ← 9	10.090 706 0	2		
	11 ← 10	10.090 697 9	−1		
	12 ← 11	10.090 713 0	−1		
12 0 12 ← 11 0 11				10.968 121 2	6
12 1 12 ← 11 1 11				10.968 121 2	6
13 0 13 ← 12 0 12				11.845 540 2	15
13 1 13 ← 12 1 12				11.845 540 2	15

Table 2. Rotational transitions of isocyano-pentafluorobenzene and ^{14}N nuclear hyperfine structure. Explanation of symbols see Table 1.

J' K'_- K'_+ ← J K_- K_+	F' F	ν_{hfs}	$\delta\nu$	ν_{obs}	δ
7 1 6 ← 6 1 5				7.618 678 3	−7
	6 ← 5	7.618 682 6	0		
	7 ← 6	7.618 674 6	0		
	8 ← 7	7.618 678 8	0		
7 2 6 ← 6 2 5				7.611 875 6	−8
8 0 8 ← 7 0 7				7.611 590 7	−5
8 1 7 ← 7 1 6				8.510 090 2	−6
8 1 8 ← 7 1 7				7.611 570 0	−4
8 2 6 ← 7 2 5				9.436 502 5	−3
	7 ← 6	9.436 511 6	0		
	8 ← 7	9.436 490 9	0		
	9 ← 8	9.436 506 2	0		
8 2 7 ← 7 2 6				8.508 670 3	−7
8 3 6 ← 7 3 5				9.400 566 1	−9
9 0 9 ← 8 0 8				8.506 987 4	−3
9 1 9 ← 8 1 8				8.506 987 4	−3
9 1 8 ← 8 1 7				9.404 229 8	−5
9 2 7 ← 8 2 6				10.312 647 7	−3
	8 ← 7	10.312 650 4	−1		
	9 ← 8	10.312 642 3	0		
	10 ← 9	10.312 650 4	1		
9 2 8 ← 8 2 7				9.403 955 1	−5
9 3 7 ← 8 3 6				10.303 626 8	−6
10 0 10 ← 9 0 9				9.402 409 0	−3
10 1 10 ← 9 1 9				9.402 409 0	−3
10 1 9 ← 9 1 8				10.299 117 7	−3
10 2 8 ← 9 2 7				11.201 440 8	−2
10 2 9 ← 9 2 8				10.299 068 0	−4
10 3 8 ← 9 3 7				11.199 411 5	−2
10 4 7 ← 9 4 6				12.098 563 5	−2
11 0 11 ← 10 0 10				10.297 840 4	−1
11 1 11 ← 10 1 10				10.297 840 4	−1
11 1 10 ← 10 1 9				11.194 254 5	−3
11 2 9 ← 10 2 8				12.094 203 7	1
11 2 10 ← 10 2 9				11.194 243 6	−1
11 3 9 ← 10 3 8				12.093 780 6	2
12 0 12 ← 11 0 11				11.193 277 4	1
12 1 12 ← 11 1 11				11.193 277 4	1
12 1 11 ← 11 1 10				12.089 494 8	2
12 2 11 ← 11 2 10				12.089 494 8	2
12 2 10 ← 11 2 9				12.988 264 2	5
12 3 10 ← 11 3 9				12.988 181 1	5
13 0 13 ← 12 0 12				12.088 718 5	3
13 1 13 ← 12 1 12				12.088 718 5	3
13 1 12 ← 12 1 11				12.984 798 3	4
13 2 12 ← 12 2 11				12.984 798 3	4
14 0 14 ← 13 0 13				12.984 161 8	6
14 1 14 ← 13 1 13				12.984 161 8	6

Results

Spectra

In Table 3 the rotational constants of cyano- and isocyano-pentafluorobenzene are compared to the data of Sharma and Doraiswamy [15]. Column d lists their values, column c gives the results when their line frequencies are analyzed with the computer program used in this investigation, whereas in columns a and b the results of the present assignment and analysis are listed. The correctness of our assignment can be ascerted as follows: 1. The standard deviation in columns a and b is of the order of the experimental accuracy, whereas the previous data show a standard deviation of 1.5 MHz – much larger than the experimental accuracy of a continuous wave spectrometer used in the earlier study. 2. The rotational constant A is similar for both the cyanide and the isocyanide. As the change from the cyanide to the isocyanide is equivalent to an exchange of two nuclei on the principal axis a (see Fig. 1), a good approximation is that no change of the moment of inertia around this axis will occur. The deviation of the rotational constants A of the two isomers (Table 3, columns a and b) of the order of 350 kHz can be rationalized when consider-

Table 3. Comparison of the rigid rotor rotational constants of isocyano- and cyano-pentafluorobenzene. a, b: Results of this work, c results from transition frequencies as given by Sharma and Doraiswamy [15], analyzed with the same program as in column a and b; d results of Sharma and Doraiswamy. A, B, C: Rotational constants [GHz]; $\varkappa$: parameter of asymmetry; Δ: inertial defect [amu Å^2]; σ: standard deviation of the fit [MHz]; n: number of transitions.

	a C_6F_5–NC	b C_6F_5–CN	c C_6F_5–CN	d C_6F_5–CN
A	1.029 686 8(47)	1.029 351(44)	1.026 787(64)	1.026 82(30)
B	0.792 206 9(29)	0.764 603(21)	0.776 326(17)	0.776 34(10)
C	0.447 727 65(7)	0.438 721 5(33)	0.442 058(18)	0.442 06(10)
$\varkappa$	0.183 9	0.103 5	0.143 3	0.143 3
Δ	0.0177	–.0019	0.0587	0.0811
σ	0.004	0.011	1.5	–
n	31	10	42	42

Table 4. ^{14}N nuclear quadrupole coupling constants χ_{gg} ($g = a, b\, c$) in MHz of cyano- and isocyano-pentafluorobenzene, compared to the constants of cyano- and isocyanobenzene.

	χ_{aa}	χ_{bb}	χ_{cc}	Ref.
C_6F_5–CN	−4.51(41)	2.50(23)	2.01(23)	This work
C_6H_5–CN	−4.244(4)	2.280(5)	1.954(5)	[8]
C_6F_5–NC	0.96(11)	−0.79(6)	−0.17(6)	This work
C_6H_5–NC	0.4115(70)	−0.3858(79)	−0.0257(79)	[3]

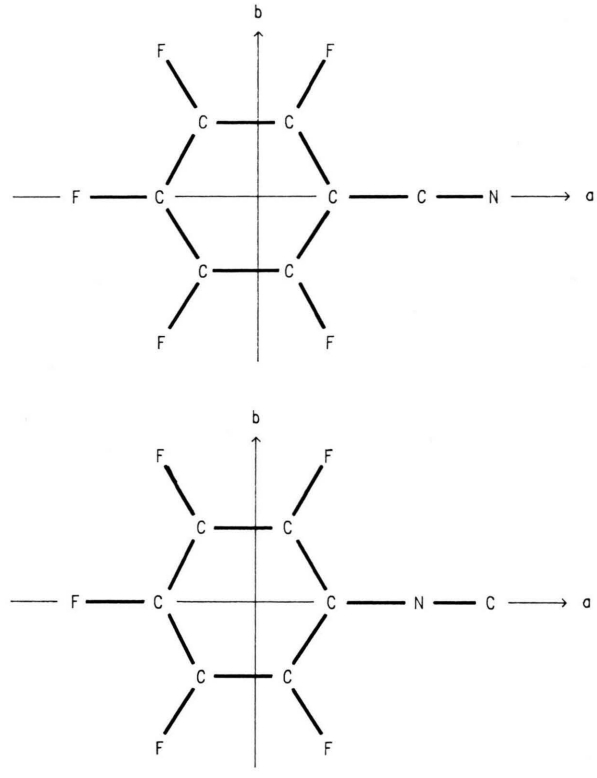

Fig. 1. Cyano- and isocyano-pentafluorobenzene in their principal axis systems. The bond lengths have been set to plausible values, all angles are 120°.

ing different effects of the functional groups on the structure of the C_6F_5-frame and possibly slightly different vibrational contributions. 3. The hyperfine splittings in the spectra of the title compounds (see also below) further corroborate our assignment. All observed splittings could be interpreted as originating from ^{14}N nuclear quadrupole coupling, and in no incident was a theoretically expected and experimentally resolvable splitting *not* observed.

Quadrupole Coupling

The ^{14}N nuclear quadrupole coupling constants χ_{gg} ($g = a, b, c$) of the title compounds are given in Table 4, together with literature data of cyano- and isocyanobenzene. The rather large uncertainties in the values presented in this work are due to the fact that splittings smaller than 50 kHz with a high relative uncertainty had to be analyzed.

The quadrupole coupling tensor for the molecules in Table 4 is diagonal when evaluated in the principal axis system of inertia, i.e. the principal axes of inertia and the principal axes of the coupling tensor coincide. For both cyanides, the quadrupole coupling constant χ_{aa} (and thus the efg in R–CN bond direction) is large and dominated by the nitrogen lone pair. The efg at the ^{14}N nucleus has almost cylindrical symmetry, as seen from the constants χ_{bb} (in plane) and χ_{cc} (perpendicular to the plane) of nearly equal magnitude. Effects of conjugation are small and relatively insensitive to ring substitution. The isocyanides exhibit coupling constants in the range typical for these compounds, i.e. generally smaller than 1 MHz with χ_{aa} positive. Fluorine substitution of the aromatic ring has a significant effect on the coupling constants (see Table 4): the constants increase by more than a factor of two. The conjugation of the isocyanide group with the aromatic ring is seen in the large asymmetry of the coupling tensor. The coupling constant and the efg at the ^{14}N nucleus perpendicular to the ring plane (χ_{cc}, see Fig. 1) is very much smaller than χ_{bb} in the ring plane and perpendicular to the R–NC bond direction, resulting

in a significant deviation of the coupling tensor from near-cylindrical symmetry expected in simple alkyl isocyanides such as ethyl isocyanide [18]. However, direct comparison is difficult since the quadrupole coupling tensors are normally determined in the principal axes system of the molecule and are thus not necessarily diagonal.

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