Nitrogen Quadrupole Coupling in the Microwave Ground State Spectra of Tertiary Butyl Isocyanide and Phenyl Isocyanide

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The microwave ground state spectra of tert.-butyl isocyanide, $(CH_3)_3CNC$, and phenyl isocyanide, C_6H_5NC, have been measured by microwave Fourier transform spectroscopy in the region 5.0 to 8.0 GHz and analysed for nuclear quadrupole hyperfine splitting due to ^{14}N. The nuclear quadrupole coupling constants are shown to be in accordance with structural predictions of the p-electron population at the nitrogen atom. The dipole moment of phenyl isocyanide was derived from the Stark effect of the $J_{K_-K_+} = 2_{02} - 1_{01}$ transition.

I. Introduction

Some years ago the microwave ground state spectra of tert.-butyl isocyanide, $(CH_3)_3CNC$, and phenyl isocyanide, C_6H_5NC, were measured and assigned by Bak et al. [1, 2], whose measurements form the starting point of the present study. They reported the rotational constants, but did not resolve nuclear quadrupole hyperfine splittings (hfs) for these molecules. The dipole moment of tert.-butyl isocyanide was determined in our laboratory a short time ago [3].

In this paper we present an investigation of the rotational spectra in the region 5.0 to 8.0 GHz with the high resolution of microwave Fourier transform (MWFT) spectroscopy to resolve the nitrogen hfs.

Additionally we determined the dipole moment of phenyl isocyanide by measurements of the Stark effect of the $J_{K_-K_+} = 2_{02} - 1_{01}$ transition.

II. Experimental

Tert.-butyl isocyanide was prepared according to [4] by the reaction of tert.-butyl bromide, $(CH_3)_3CBr$, purchased from Aldrich Chemie, Steinheim, with silver cyanide, AgCN, and used after vacuum destillation.

Phenyl isocyanide was prepared according to [5] by the reaction of formanilide, C_6H_5NHCHO, purchased from Aldrich Chemie, Steinheim, with potassium tert.-butoxide $(CH_3)_3COK$, and phosphorous oxychloride, $POCl_3$, and also used after vacuum destillation.

The spectra were recorded in the range 5.0 to 8.0 GHz by use of a microwave Fourier transform spectrometer which was modified in comparison to that described in [6]. Details of this schema will be published [7]. By a fault of the TWT amplifier, see part 17 in Fig. 1 of [6], we were forced to work with the signal source alone, which delivers approximately 100 mW in some ranges. This resulted in a remarkable decrease of sensitivity and of the range of polarization.

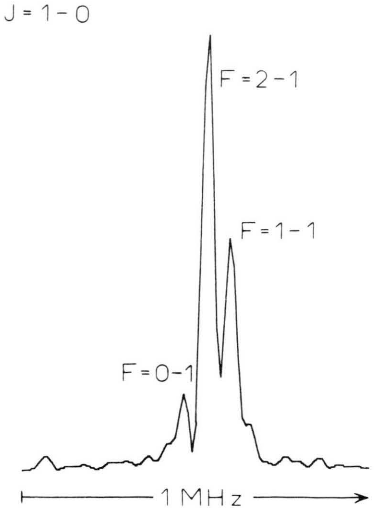

Fig. 1. $J = 1 - 0$ transition of tert.-butyl isocyanide. A section of 1 MHz out of a 25 MHz range of the power spectrum is given. Sample interval 20 ns, 19 200 k cycles, 1024 data points, supplemented by 3072 zeros, pressure 0.02 Pa (0.15 mTorr), temperature – 50 °C.

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The measurements of the Stark effect of phenyl isocyanide were made with a J-band waveguide cell with 34.85 × 15.80 mm inner dimension and 3 m length. To have a sufficiently homogeneous Stark field we inserted a septum about 8 mm thick tapered on both ends and ending 5 mm before the waveguide windows. By this reflections at the septum ends are quickly damped with the aid of neighbouring waveguide isolators (compare Fig. 1 of [6]). For calibration the $M = 1$ Stark lobe of the $J_{K_- K_+} = 1_{10} - 1_{11}$ transition of formaldehyde, H_2CO, with $\mu = 2.33148$ D [8] and rotational constants given in [9] was used. Because the two sections of the Stark cell were inequal, the Stark satellite splitted at field strengths higher then 200 V/cm. By this we estimated, that the precision of the position of the septum is better than 0.02 mm.

The sample pressure was around 0.02 Pa (0.15 mTorr) and the cell temperature was around − 50 °C for tert.-butyl isocyanide and 0.04 Pa (0.3 mTorr) and − 28 °C for phenyl isocyanide, respectively.

III. The Spectra and Analysis

The measured frequencies and their assignments are listed in Table 1a and 1b for tert.-butyl isocyanide and phenyl isocyanide, respectively. Figures 1 and 2 give examples of the recordings. The measurements are refined by line contour analysis [10]. For tert.-butyl isocyanide the observed triplet pattern of the $J = 1 - 0$ transition was analysed with the rigid symmetric top Hamiltonian

$$H = BP^2 + (A - B)\, P_z^2, \tag{1}$$

supplemented by the interaction of one coupled nucleus [11]. The rotational constant B and the quadrupole coupling constants of ^{14}N eQq could be fitted (program SYM2Q). The results are given in Table 2a. The standard error of the fit is 0.6 kHz and the mean experimental splitting 60 kHz.

Table 1a. Measured frequencies ν_{obs} of tert.-butyl isocyanide, $(CH_3)_3CNC$, refined by line contour analysis of overlying hfs components. The given frequencies are mean values of four measurements with different polarizing frequencies. ν_{calc}: calculated with constants of Table 2a. $\nu_{unsplit}$: hypothetical frequency without hfs-splitting. Frequencies in MHz.

$J'-J$	$F'-F$	ν_{obs}	ν_{calc}	$\nu_{unsplit}$
1−0	0−1	5864.2666	5864.2668	5864.3463
	2−1	5864.3388	5864.3384	
	1−1	5864.3858	5864.3861	

Table 1b. Measured frequencies ν_{obs} of phenyl isocyanide, C_6H_5NC, refined by line contour analysis of overlying hfs components. See also Table 1a.

$J'\,K'_-\,K'_+ - J\,K_-\,K_+$	$F'-F$	ν_{obs}	ν_{calc}
2 0 2 − 1 0 1	3−	5797.639	5797.645
	2−		
2 1 1 − 1 1 0	1−	6190.356	6190.464
	3− 2	6190.437	
	2− 1	6190.564	
2 1 2 − 1 1 1	1− 0	5453.028	5453.231
	3− 2	5453.213	
	2− 1	5453.334	
5 1 4 − 5 1 5	6− 6	5501.466	5501.508
	4− 4		
	5− 5	5501.594	
9 2 7 − 9 2 8	10−10	6035.072	6035.101
	8− 8		
	9− 9	6035.157	
13 3 10−13 3 11	14−14	5650.694	5650.714
	12−12		
	13−13	5650.754	
18 4 14−18 4 15	19−19	6829.898	6829.915
	17−17		
	18−18	6829.949	

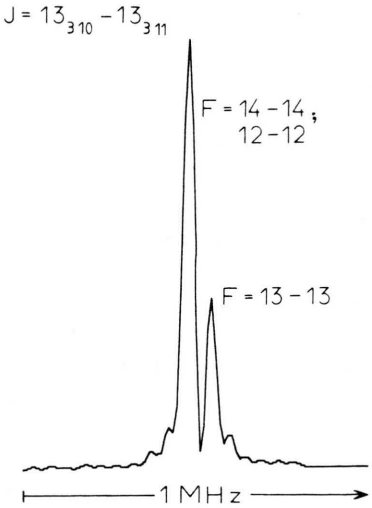


Fig. 2. $J = 13_{3\,10} - 13_{3\,11}$ transition of phenyl isocyanide. A section of 1 MHz out of a 25 MHz range of the power spectrum is given. Sample interval 20 ns, 6400 k cycles, 1024 data points, supplemented by 3072 zeros, pressure 0.04 Pa (0.3 mTorr), temperature − 28 °C.

Table 2a. Rotational and quadrupole coupling constants of tert.-butyl isocyanide $(CH_3)_3CNC$. Standard deviations in brackets in units of the last digit. σ: standard deviation of the fit, $\overline{\Delta\nu}$: mean experimental splitting.

$B = 2\,932.17315(17)$ MHz; $\overline{\Delta\nu} = 60$ kHz
$eQq = 159.1(10)$ kHz; $\sigma = 0.6$ kHz
Correlation coefficient: $|(B, eQq)| = 0.3$.

Table 2b. Quadrupole coupling constants of phenyl isocyanide C_6H_5NC. See also Table 2a. For the hfs analysis rotational constants of [2] were taken.

$\chi_+ = \chi_{bb} + \chi_{cc} = -411.5(70)$ kHz
$\chi_- = \chi_{bb} - \chi_{cc} = -360.1(87)$ kHz
$\chi_{aa} = 411.5(70)$ kHz
$\chi_{bb} = -385.8(79)$ kHz $\overline{\Delta\nu} = 105$ kHz
$\chi_{cc} = -25.7(79)$ kHz $\sigma = 4$ kHz
Correlation coefficient: $|(\chi_+, \chi_-)| = 0.016$.
$A = 5659.5190$ MHz,
$B = 1639.7757$ MHz,
$C = 1271.1538$ MHz.

Table 3. Quadrupole coupling constants [kHz] of some isonitriles.

	χ_{aa}	χ_{bb}	χ_{cc}	Ref.
CH_3-NC	489.4(4)	−244.7(2)	−244.7(2)	[13]
C_2H_5-NC	253.2(59)	−106(11)	−148(11)	[17]
$CH_2=CH-NC$	258(5)	−258(6)	0(6)	[18]
C_3H_5-NC	331(3)	−128(9)	−204(9)	[19]
$(CH_3)_3C-NC$	159.1(10)	−79.6(5)	−79.6(5)	this work
C_6H_5-NC	411.5(70)	−385.8(79)	−25.7(79)	this work

Table 4. Measurements of the dipole moment μ_a of phenyl isocyanide for $J_{K_-K_+} = 2_{02} - 1_{01}$.
ν_1: $F = 2-1$; $M_F = 1$;
ν_2: $F = 3-2$; $M_F = 1$;
ν_3: $F = 2-2$; $M_F = 2$.
E [V/cm] field strengths; field free frequency, see Table 1b. For the analysis rotational constants and quadrupole coupling constants of Table 2b were taken. Conversion factor: $1\,D = 3.3356 \cdot 10^{-30}$ Asm.

E	ν_1	ν_2	ν_3
13.03	–	5797.653	–
26.06	5797.531	5797.710	5797.875
39.09	5797.349	5797.830	5797.963
52.10	5797.085	5798.018	5798.185
65.15	5796.759	5798.290	5798.395
78.18	5796.331	5798.641	4798.726
91.22	5795.854	5799.007	5799.116
104.23	–	5799.481	5799.580
117.76	–	5800.003	5800.088
129.75	–	5800.503	5800.590
142.73	–	–	5801.222
155.69	–	5801.817	5801.902
168.67	–	5802.530	5802.622

$\mu_a = 4.018(3)$ D refered to $\mu = 2.33148$ D of H_2CO [8].
$\mu_a = 13.402(98) \cdot 10^{-30}$ Asm.

For phenyl isocyanide the ^{14}N hfs was analysed by first order perturbation theory to provide the quadrupole coupling constants (program HT1NQ and DH14KS). The deviations from the hypothetical rigid rotor lines were added to the observed frequencies ν_{obs} of the hfs components. The hypothetical hfs unsplit line was then calculated as a mean value. The results are given in Table 2b. The standard error of the fit is 4 kHz and the mean experimental splitting 105 kHz.

As only few measurements of the hfs in isonitriles have been reported we give in Table 3 a comparison of the coupling constants.

The measurements of the Stark effect of the $2_{02} - 1_{01}$ transition of phenyl isocyanide are given in Table 4. The Stark splittings were evaluated with the inclusion of ^{14}N quadrupole coupling. It was necessary to diagonalise the Hamiltonian matrix in the coupled symmetric top basis $|FM_FJKI\rangle$ [12] for the $M_F \geqq 1$ with inclusion of elements from $F_{min} = M_F - 1$ to $F_{max} = J + I + 1$ for a given J (program EQ).

For the fitting procedure the values for the rotational constants A, B, C and for the quadrupole coupling constants χ_+ and χ_- were taken from Table 2b. The result is given in Table 4.

IV. Interpretation of the Nuclear Quadrupole Coupling Constants

The nuclear quadrupole coupling constants χ_{aa}, χ_{bb} and χ_{cc} listed in Table 3 may be identified with the diagonal elements χ_{gg}, $g = x, y, z$, of the principal nuclear quadrupole coupling tensor only in the cases when the symmetry permits this.

This is the case for tert.-butyl isocyanide, phenyl isocyanide, and also for methyl isocyanide previous investigated by Kukolich [13].

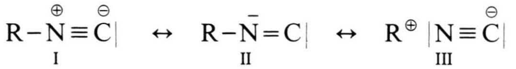
We interpret the measured quadrupole coupling constants in terms of contributions of various meso-

Table 5. Interpretation of ^{14}N hfs quadrupole coupling constants of tert.-butyl isocyanide, phenyl isocyanide and methyl isocyanide, see text. N_g: mean number of p-electrons ($g = x, y, z$); χ^m_{gg}: quadrupole coupling constants of mesomeric forms in MHz.

Mesomeric forms	Type	N_x	N_y	N_z	χ^m_{xx}	χ^m_{yy}	χ^m_{zz}
$\mathrm{R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}\vert}$	I	1	1	1	0.0	0.0	0.0
$\mathrm{R{-}\bar{N}{=}C\vert}$	II$_x$	2	1	1	−9.4	4.7	4.7
	II$_y$	1	2	1	4.7	−9.4	4.7
$\mathrm{R^{\oplus}\ \vert N{\equiv}\overset{\ominus}{C}\vert}$	III	1	1	3/2	2.35	2.35	−4.7

meric structures according to the approach of Townes and Dailey [14, 15].

We use the following mesomeric forms:



$$\underset{\mathrm{I}}{\mathrm{R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}\vert}} \leftrightarrow \underset{\mathrm{II}}{\mathrm{R{-}\bar{N}{=}C\vert}} \leftrightarrow \underset{\mathrm{III}}{\mathrm{R^{\oplus}\ \vert N{\equiv}\overset{\ominus}{C}\vert}}$$

and calculate the quadrupole coupling constants χ^m_{gg} $(g = x, y, z)$ for each structure using the equation

$$\chi^m_{gg} = \left(N_g - \frac{N_{g'} + N_{g''}}{2}\right) \cdot eQq_{210}; \quad g \neq g' \neq g'' \qquad g = x, y, z, \text{ cyclic} \quad (2)$$

with $eQq_{210} = -9.4$ MHz from [16] and x, y, z the principal axes of the quadrupole coupling tensor coinciding with the principal axes of the intertia tensor b, c, a.

The results are given in Table 5.

With the common assumption of sp orbitals on the nitrogen for the σ bonds the electronic charge distribution shows a spherical symmetry in the mesomeric form I. In fact the measured quadrupole coupling constants are small and therefore type I should be the main mesomeric structure.

In the mesomeric form II the constant χ^m_{zz} is positive and in type III negative, respectively. As for all three molecules the measured values $\chi_{zz} = \chi_{aa}$ are positive the form II should contribute to the electronic structure more than type III.

Because the measured constants χ_{zz} increase in the sequence tert.-butyl, phenyl, and methyl isocyanide the contribution of type III appears to decrease. This is in accordance with expectations on general chemical grounds, as the positive inductive effect of the tert.-butyl group is greater than that for the phenyl or methyl group.

In contrast to tert.-butyl and methyl isocyanide, the quadrupole coupling constants in x and y direction are not equal for phenyl isocyanide because of the symmetry. Therefore in the mesomeric structure II there are two possibilities for the orientation of the lone pair on nitrogen. In type II$_x$ of Table 5 the lone pair is orientated in x and in type II$_y$ in y direction, respectively. As $\chi_{xx} = \chi_{bb}$ of phenyl isocyanide is more negative than $\chi_{yy} = \chi_{cc}$ form II$_x$ should contribute to the electronic structure more than type II$_y$.

This is in agreement with the expectation that a lone pair in x direction nearby the positive nuclei of hydrogen in ortho positions is favoured with respect to a lone pair in y direction nearby the electron clouds above and below the phenyl group.

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