Quadrupole Hyperfine Structure in the Rotational Spectrum of n-Propyl Isocyanide

K. Vormann, R. Schwarz, and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

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An investigation of the ^{14}N quadrupole hyperfine structure in the rotational spectrum of n-propyl isocyanide is presented. It was possible to resolve the multiplets by using microwave Fourier transform spectroscopy.

In this work we analyse the quadrupole coupling of synclinal (gauche) n-propyl isocyanide, $CH_3CH_2CH_2NC$. Thereby we continue our efforts to investigate isocyanides [1–4] by microwave Fourier transform (MWFT) spectroscopy [5–7]. Because the hyperfine structure (hfs) splittings of isocyanides are quite narrow, MWFT spectroscopy is superior to Stark spectroscopy.

The two rotational isomers of n-propyl isocyanide, the antiperiplanar (trans) and the synclinal form were first measured and assigned by Fuller and Wilson [8]. Their publication was the basis of our investigation. We failed to resolve the less present antiperiplanar form. Probably the product of our preparation of n-propyl isocyanide was not pure enough.

We made two attempts to prepare the substance. The first attempt was made using the prescription given in [8], but without further purification by preparative – scale vapour phase chromatography because it was not available. The reaction mixture contained only a little of n-propyl isocyanide; most of the mixture consisted of the educt n-propyl iodide. In the second preparation we tried to dehydrate N-n-propylformamide. First we prepared the N-n-

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40–60, D-2300 Kiel.

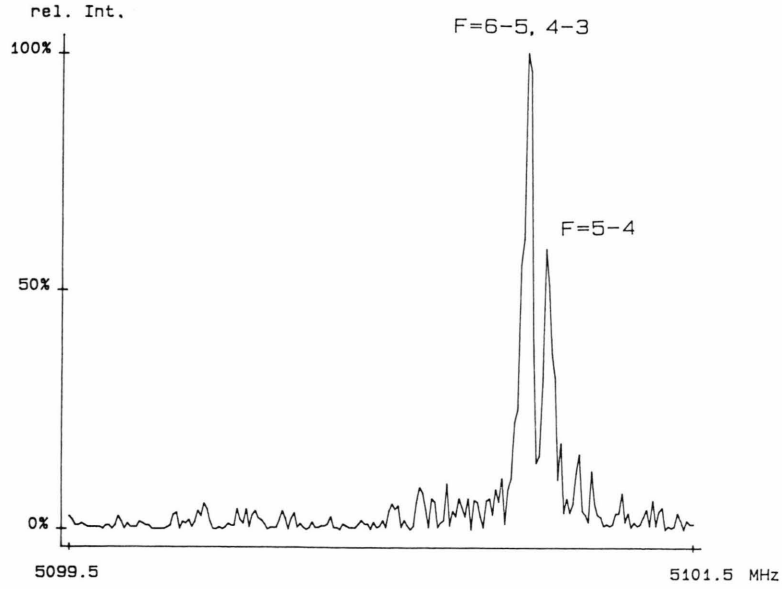

Fig. 1. Nitrogen-hfs of the transition $JK_-K_+ - J'K'_-K'_+ = 5_{15} - 4_{22}$; power spectrum, sample interval: 50 ns, $1.6 \cdot 10^8$ cycles, 1024 data points supplemented with 1024 zeros, microwave polarizing frequency: 5101.5 MHz, pressure: 0.1 mTorr, temperature: − 50 °C.

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Table 1. Measured line frequencies [MHz] of n-propyl isocyanide with hfs-splittings. ν: measured frequency, $\Delta\nu_{hfs}$: hfs-splitting referred to the strongest component, δ_{hfs}: deviation of the experimental and the calculated splitting, ν_0: hypothetical unsplit line frequency calculated with the hfs-splittings added to the frequencies of the components, δ_0 [kHz]: deviation from the centrifugal distortion calculation.

J	K_-	$K_+ - J'$	K'_-	K'_+	$F - F'$	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [MHz]	ν_0 [MHz]	δ_0 [kHz]
1	0	1 – 0	0	0	2 – 1	6339.175			6339.183	2
					1 – 1	6339.223	−0.048	0.003		
					0 – 1	6339.112	0.063	0.005		
2	1	1 – 1	1	0	3 – 2	13297.576			13297.584	−4
					2 – 1	13297.619	−0.043	−0.003		
					1 – 0	13297.510	0.066	0.000		
2	0	2 – 1	1	1	3 – 2	5907.696			5907.708	30
					2 – 1	5907.757	−0.061	0.008		
					1 – 0	5907.667	0.029	0.003		
4	1	3 – 4	1	4	5 – 5	6197.829			6179.817	−60
					4 – 4	6179.778	0.051	−0.006		
					3 – 3	6179.847	−0.017	0.005		
5	1	4 – 5	0	5	6 – 6	12740.738			12740.729	−91
					4 – 4					
					5 – 5	12740.701	0.037	0.005		
5	1	5 – 4	2	2	6 – 5	5100.963			5100.984	82
					4 – 3					
					5 – 4	5101.026	−0.064	−0.001		
8	2	6 – 8	2	7	9 – 9	6989.018			6989.010	−28
					7 – 7					
					8 – 8	6988.995	0.023	0.003		

A	10208.988	(11)
B	3479.2378	(32)
C	2859.9623	(30)
χ^+	−152	(5)
χ^-	135	(8)
$\lvert(\chi^+, \chi^-)\rvert$	−0.09	
χ_{aa}	152	(5)
χ_{bb}	−9	(7)
χ_{cc}	−143	(7)

Table 2. Rotational [MHz] and quadrupole coupling constants [kHz] of synclinal n-propyl isocyanide. $\lvert(\chi^+, \chi^-)\rvert$ correlation coefficient. The standard deviation of the hfs analysis of 11 splittings is 5 kHz, the mean splitting is 46 kHz.

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

Compound	χ_{aa}	χ_{bb}	χ_{cc}	Ref.
CH_3NC	489.4 (4)	−244.7 (2)	−244.7 (2)	[15]
C_2H_5NC	253.2 (59)	−106 (11)	−148.0 (11)	[3]
CH_2CHNC	258 (5)	−258 (6)	0 (6)	[1]
$(CH_3)_3CNC$	159.1 (10)	−79.6 (5)	−79.6 (5)	[4]
C_6H_5NC	411.5 (70)	−385.8 (79)	−25.7 (79)	[4]
$CH_3CH_2CH_2NC$ synclinal	152 (5)	−9 (7)	−143 (7)	this work
C_3H_5NC	331 (3)	−128 (9)	−204 (9)	[2]

propylformamide by the reaction of $HCOOC_2H_5$ with $CH_3CH_2CH_2NH_2$. The N-n-propylformamide was dehydrated with p-toluenesulfonyl chloride in quinoline. We followed the discription of the preparation of methyl isocyanide [9].

The spectra were recorded at − 50 °C and pressures between 0.1 and 0.3 mTorr (0.013 and 0.04 Pa). The results are given in Table 1. The frequencies were obtained by a least squares fit of the signal in the time domain to eliminate effects of overlapping in the frequency domain (power spectra) [10, 11]. The assignment of the lines was checked by a centrifugal distortion analysis with Watson's A reduction of 4th order [12, 13] including the transitions of Table II of [8]. We give only the rotational constants in Table 2.

The hfs splittings were analysed by first order approximation [14] using the rotational costants of Table 2. The results are given in this table.

In Table 3 we compare the quadrupole coupling constants of isocyanides. Unfortunately there exist no structure determinations for these molecules with the exception of CH_3NC. Therefore a discussion is difficult. All molecules with exception of synclinal $CH_3CH_2CH_2NC$ have a plane of symmetry. Even for the aliphatic isonitriles there is a large variation of χ_{cc} in dependence on the substituent of the isonitrile group.

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