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

Z. Naturforsch. 43a, 277–279 (1988); received December 2, 1987

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$_3$CH$_2$CH$_2$NC. 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-

![Fig. 1. Nitrogen-hfs of the transition $JK + K = JK' + K'$, $F = 5 - 4$; power spectrum, sample interval: 50 ns, 1.6 - 10$^5$ cycles, 1024 data points supplemented with 1024 zeros, microwave polarizing frequency: 5101.5 MHz, pressure: 0.1 mTorr, temperature: $-50^\circ$C.](image-url)
propylformamide by the reaction of HCOOC₂H₅ with CH₃CH₂CH₂NH₂. The N-n-propylformamide was dehydrated with p-toluenesulfonyl chloride in quinoline. We followed the discription of the prepara-
tion 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$_3$NC. Therefore a discussion is difficult. All molecules with exception of synclinal CH$_3$CH$_2$CH$_2$NC have a plane of symmetry. Even for the aliphatic isonitriles there is a large variation of $\chi_{ee}$ in dependence on the substituent of the isonitrile group.

We thank the members of our group for help, Prof. Dr. D. Hoppe for advice, the Deutsche Forschungsgemeinschaft, the Land Schleswig-Holstein and the Fonds der Chemie for funds. The calculations were made at the computer center of the University of Kiel.