

Nitrogen Quadrupole Coupling in the Rotational Spectrum of 1-Isocyanoprop-2-yne, $\text{HC}\equiv\text{CCH}_2\text{NC}$

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The rotational spectrum of 1-isocyanoprop-2-yne, $\text{HC}\equiv\text{CCH}_2\text{NC}$, has been measured in the vibrational ground state by microwave Fourier transform spectroscopy from 5 to 26.5 GHz. The nuclear quadrupole hyperfine splittings due to ^{14}N have been analysed to obtain the coupling constants $\chi_{aa} = 290.3(78)$ kHz, $\chi_{bb} = 10.6(80)$ kHz and $\chi_{cc} = -300.9(80)$ kHz.

I. Introduction

1-Isocyanoprop-2-yne, commonly and in the following called propargyl-isocyanide, has first been prepared by Zwikker and Stephany [1] according to the method of Schuster et al. [2]. The microwave spectrum of propargyl-isocyanide has recently been assigned by McNaughton et al. [3], who reported the rotational constants, four quartic centrifugal distortion parameters according to Watson's S-reduced asymmetric rotor hamiltonian [4], and the dipole moment components along the a and b principal axes of inertia. McNaughton et al. could not resolve any splittings due to ^{14}N nuclear quadrupole coupling.

The coupling constants of isocyanides are known to be small in comparison with other nitrogen-containing compounds such as the isomeric cyanides. We are interested in the resolution of the ^{14}N hyperfine structure in the spectra of isocyanides to provide a systematic experimental basis for a better understanding of the local electronic environment of the nitrogen nucleus (for a listing of quadrupole coupling data of isocyanides, see Table 4).

Recent studies on *ab-initio* calculations of nitrogen quadrupole coupling constants via the electric field gradient [5–8] have shown that a meaningful comparison of experimental and *ab-initio* values can be made by a) using large basis sets of high local quality [7–8] or by b) employing a scaling factor for a given hybridization of the nitrogen atom [6]. A method similar to the latter would introduce scaling factors not only for a given hybridization but also for a single func-

tional group X, in this case with X equal to NC. This method's main disadvantage would be its requirement of a larger number of experimental and *ab-initio* values for any such functional group.

Standard cw-microwave techniques [9] do not provide the resolution required to observe the hyperfine structure (hfs) in the rotational spectra of most isocyanides. With the waveguide microwave Fourier transform (MWFT) spectrometers in our laboratory [10] we were able to resolve the hfs of propargyl-isocyanide.

II. Experimental

Propargyl-isocyanide was prepared according to the method of McNaughton et al. [3]. The identity of the compound was confirmed by $^1\text{H-NMR}$ spectroscopy [1].

The microwave spectrum was recorded with waveguide MWFT spectrometers in the J- and K-band (5.0 to 8.0 GHz and 18.0 to 26.5 GHz, respectively) [11, 12]. The cell temperature was -45°C and the sample pressure was around 0.1 Pa (0.8 mTorr).

The splittings were refined by a line shape analysis [13] performed on the time domain signal to minimize line overlap effects on the transition frequencies obtained after Fourier transformation.

III. Results and Discussion

The experimental transition frequencies are given in Table 1, as well as the calculated values, deviations, and theoretical intensities of the hyperfine components. Where a splitting of components with compara-

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Table 1. Rotational transitions of propargyl-isocyanide, $\text{HC}\equiv\text{CCH}_2\text{NC}$. J , K_- , K_+ , F : Rotational transition and hyperfine component quantum numbers, v_{unsplit} : Hypothetical center frequency (MHz), calculated from observed components, Δv_{obs} , Δv_c : Observed and calculated difference from center frequency (kHz), δ : Observed minus calculated frequency (kHz), I_c : Theoretical relative intensities of the hyperfine components. Two unsplit transitions used for centrifugal distortion analysis are listed as well.

J'	K'_-	K'_+	$\leftarrow J$	K_-	K_+	$F' \leftarrow F$	v_{unsplit}	Δv_{obs}	Δv_c	δ	I_c
1	0	1	0	0	0	0	1	5789.081	-147	-145	-2 0.20
				1	1				72	73	-1 0.60
				2	1				-14	-15	1 1.00
1	1	1	2	0	2	0	1	5878.568	71	68	3 0.24
				1	1				71	76	-5 0.18
				1	2				-71	-71	0 0.54
				2	2				-71	-74	3 0.18
				2	3				20	20	0 1.00
2	1	1	2	0	2	1	1	18177.129	75	76	-1 0.36
				2	2				-75	-76	1 0.56
				2	3				21	18	3 0.13
				3	3				21	22	-1 1.00
3	1	2	3	0	3	2	2	18736.225	31	47	-16 0.53
				3	3				-68	-59	-9 0.72
				4	4				31	20	11 1.00
4	1	3	4	0	4	3	3	19500.713	26	38	-12 0.62
				4	4				-50	-53	3 0.78
				5	5				26	19	7 1.00
5	1	4	5	0	5	4	4	20486.559	25	34	-9 0.68
				5	5				-48	-51	3 0.82
				6	6				25	19	6 1.00
5	1	4	5	1	5	4	4	5398.719	38	52	-14 0.68
				5	5				-75	-78	3 0.82
				6	6				38	30	8 1.00
6	1	5	6	0	6	5	5	21713.077	25	32	-7 0.73
				6	6				-52	-50	-2 0.84
				7	7				25	20	5 1.00
6	1	5	6	1	6	5	5	7555.242	39	50	-11 0.73
				6	6				-76	-78	2 0.84
				7	7				39	31	8 1.00
7	1	6	7	0	7	6	6	23202.265	26	31	-5 0.76
				7	7				-54	-51	-3 0.87
				,	8	8			26	21	5 1.00
8	1	7	8	0	8	7	7	24977.781	26	31	-5 0.79
				8	8				-52	-52	0 0.88
				9	9				26	22	4 1.00
4	0	4	3	1	3			6524.831			
6	2	5	7	1	6			7434.773			

ble intensities could not be resolved, the experimental transition frequency was used for both hyperfine components. For the fit procedure, the contributions to the two unresolved hyperfine components were intensity weighted.

The ^{14}N hfs was analysed by a first order perturbation treatment [14] in the coupled basis constructed

Table 2. Quadrupole coupling constants of propargyl-isocyanide. Standard deviations in units of the last digit. σ : Standard deviation of the fit, Δv : Mean experimental splitting.

$\chi^+ = \chi_{bb} + \chi_{cc} = -290.3$ (78) kHz
$\chi^- = \chi_{bb} - \chi_{cc} = 311.5$ (83) kHz
$\chi_{aa} = 290.3$ (78) kHz
$\chi_{bb} = 10.6$ (80) kHz
$\chi_{cc} = -300.9$ (80) kHz
$\sigma = 6.5$ kHz
$\Delta v = 87$ kHz
Correlation coefficient $(\chi^+, \chi^-) = 0.08$

Table 3. Results of the fourth order centrifugal distortion analysis according to Watson's S-reduction in the I' representation, with the correlation coefficient matrix. A, B, C: Rotational constants (MHz), D_J , D_{JK} , D_K , d_J , d_K : Quartic centrifugal distortion parameters (kHz). Standard deviations in units of the last digit. σ : Standard deviation of the fit.

$A = 20527.875$ (33)	1.00
$B = 3074.6060$ (65)	.12 1.00
$C = 2714.5243$ (62)	.19 .85 1.00
$D_J = 2.26$ (9)	.18 .91 .91 1.00
$D_{JK} = -75.6$ (2)	-.01 .03 .00 -.18 1.00
$D_K = 2200.$ (10)	.78 .18 .14 .29 -.34 1.00
$d_J = -0.60$ (1)	-.15 .29 .18 -.07 .08 -.41 1.00
$d_K = -0.07$ (4)	-.23 -.24 .16 -.06 .08 -.49 .96
$\sigma < 1$ kHz	

with the symmetric rotor wavefunctions, to provide the quadrupole coupling constants χ^+ and χ^- by a least squares analysis [15].

The results of the analysis are given in Table 2. The standard deviation of the fit is 6.5 kHz and the mean experimental splitting is 87 kHz.

The hypothetical center frequencies of the multiplets given in Table 1 and the transition frequencies reported in [3] were used for a centrifugal distortion analysis. McNaughton et al. [3] have noted a high correlation between the rotational constant A and the distortion parameter D_K , but with the combined data a simultaneous fit of all constants was possible. The constants presented in Table 3 are in good agreement with the previously reported ones.

Table 4 gives a listing of ^{14}N quadrupole coupling constants of isocyanides known to the authors. There is a discrepancy between the two reported values for tertiary butyl-isocyanide [20, 21]. Kasten et al. [21] determined $\chi_{aa} = \chi_{zz}$ (z : symmetry axis) from the $J = 1 \leftarrow 0$ transition alone, while Howard et al. [20] recorded all transitions up to $J = 3 \leftarrow 2$, $K = 2$.

The values of the coupling constants are generally small, with the exception of trifluoromethyl-is-

Table 4. Comparison of ^{14}N quadrupole coupling constants (kHz) of isocyanides. Standard deviation in units of the last digit.

Molecule	χ_{aa}	χ_{bb}	χ_{cc}	Ref.
1 $\text{CF}_3\text{—NC}$	1060. (30)	—530. (30)	—530. (30)	[16]
2 $\text{CH}_3\text{—NC}$	489.4 (4)	—244.7 (4)	—244.7 (4)	[17]
3 $\text{CH}_3\text{CH}_2\text{—NC}$	253.2 (59)	—106. (11)	—148. (11)	[18]
4 $(\text{CH}_3)_2\text{CH—NC}$	179. (3)	—133. (22)	46. (22)	[19]
5 $(\text{CH}_3)_3\text{C—NC}$	165. (2)	—82.5 (20)	—82.5 (20)	[20]
	159.1 (10)	—79.5 (10)	—79.5 (10)	[21]
6 <i>gauche</i> - $\text{CH}_3\text{CH}_2\text{CH}_2\text{—NC}$	152. (5)	—9. (7)	—143. (7)	[22]
7 $\text{H}_2\text{C=CH—NC}$	258. (5)	—258. (6)	0. (6)	[23]
8 $\text{HC}\equiv\text{C—CH}_2\text{—NC}$	290.3 (78)	10.6 (80)	—300.9 (80)	This work
9 <i>cyclo</i> - $\text{C}_3\text{H}_5\text{—NC}$	331. (3)	—128. (9)	—204. (9)	[24]
10 $\text{C}_6\text{H}_5\text{—NC}$	411.5 (70)	—385.8 (79)	—25.7 (79)	[21]

cyanide **1** which exhibits a surprisingly large constant $\chi_{aa} = \chi_{zz}$. The molecules **2** to **5** have been arranged in an order of increasing methyl substitution on the α carbon atom. As the structures of the asymmetric rotors are not known to sufficient accuracy, a comparison of the elements of the quadrupole coupling tensor with one axis coinciding with the $\text{C—N}\equiv\text{C}$ bond direction is difficult at present, if not impossible.

To provide a minimum of comparison, the coupling constants invariant to a rotation of the quadrupole coupling tensor into the $\text{C—N}\equiv\text{C}$ bond direction have been printed in bold type. From molecule **1** to **5**, a continuous decrease of χ_{cc} (χ_{bb}) is obvious, with the c (or b) axis perpendicular to a symmetry plane of the molecule. χ_{cc} (or χ_{bb}) are very sensitive to substitution at the α carbon atom. The values for molecules **6** to **10**

do not show any systematic pattern. This is expected because of the structural and chemical diversity of the latter group.

An interpretation of the quadrupole coupling data with respect to the electronic environment of the nitrogen nucleus thus awaits further structural results or an extended *ab-initio* study.

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