Methyl Internal Rotation and ^{14}N Nuclear Quadrupole Coupling from the Rotational Spectra of Ethyl Isocyanide, *iso*-Propyl Isocyanide and *gauche*- and *trans-n*-Propyl Isocyanide

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The barrier heights (V_3) hindering methyl internal rotation were determined with microwave Fourier transform spectroscopy from the ground vibrational state for the title molecules and found to be $V_3 = 3.336(52)$ kcal/mol for ethyl isocyanide, $V_3 > 3.1$ kcal/mol for *iso*-propyl isocyanide, $V_3 = 2.894(23)$ kcal/mol for *gauche-n*-propyl isocyanide and $V_3 = 2.954(22)$ kcal/mol for *trans-n*-propyl isocyanide. The quadrupole coupling constants of *iso*-propyl isocyanide are $\chi_{aa} = 179.3(31)$ kHz, $\chi_{bb} = -140(15)$ kHz and $\chi_{cc} = -39(15)$ kHz; the constants of *trans-n*-propyl isocyanide were determined to be $\chi_{aa} = 268.1(71)$ kHz, $\chi_{bb} = -108(23)$ kHz and $\chi_{cc} = -160(23)$ kHz.

Introduction

The parameters of the methyl internal rotation have been determined for a number of lower alkyl compounds, especially in the ethyl, *iso*-propyl and *n*-propyl series, but relatively little is known of the corresponding alkyl isocyanides. The same is true for the ^{14}N nuclear quadrupole coupling in isocyanides, observable as a hyperfine structure in the pure rotational spectra.

The rotational constants of ethyl isocynide, CH_3CH_2NC, have first been determined by Job et al. [1]. In a subsequent study, Bolton et al. [2] derived the barrier to methyl internal rotation from a vibrational transition of *liquid* ethyl isocyanide at 203 cm^{-1} to be 2.5 kcal/mol. Independently, Anderson and

Table 1. Rotational and centrifugal distortion constants with standard errors of ethyl-, *iso*-propyl-, *gauche*- and *trans-n*-propyl isocyanide in the I^r representation according to Watson [17] in the reduction as specified (A or S, order of the analysis given in parantheses). $\varkappa$: Parameter of asymmetry; σ: standard deviation of the fit; n: number of transitions.

		ethyl-NC	*iso*-propyl-NC	*gauche-n*-propyl-NC			*trans-n*-propyl-NC
A	[MHz]	27 760.012(16)	7 963.0888(28)	10 209.0253(13)	A	[MHz]	23 693.7163(26)
B	[MHz]	5 117.3217(34)	4 316.7588(21)	3 479.24159(44)	B	[MHz]	2 407.65324(28)
C	[MHz]	4 561.8953(29)	3 088.8102(21)	2 859.95891(37)	C	[MHz]	2 278.84572(27)
Δ_J	[kHz]	3.7327(38)	1.238(73)	3.7474(17)	D_J	[kHz]	0.4326(12)
Δ_{JK}	[kHz]	−59.757(55)	10.611(11)	−22.380(10)	D_{JK}	[kHz]	−12.454(33)
Δ_K	[kHz]	644.02(11)	−3.91(30)	67.0597(48)	D_K	[kHz]	275.07(37)
δ_J	[kHz]	0.9158(4)	0.2921(60)	1.19831(26)	d_1	[kHz]	−55.804(56)
δ_K	[kHz]	14.294(27)	6.831(81)	7.579(11)	d_2	[kHz]	−0.7488(89)
Φ_J	[Hz]	0.063(13)	6.831(81)	−0.0023(49)			
Φ_{JK}	[Hz]	1.15(35)		0.44(15)			
Φ_{KJ}	[Hz]	−3.93(10)		−2.00(49)			
Φ_K	[Hz]	55.4(68)		3.01(35)			
φ_J	[Hz]	0.0118(11)		0.0096(21)			
φ_{JK}	[Hz]	0.35(12)		−0.43(16)			
φ_K	[Hz]	9.2(29)		6.3 (21)			
Reduction		A (6)	A (4)	A (6)			S (4)
$\varkappa$		−0.9521	−0.4962	−0.8315			−0.9880
σ	[kHz]	6	16	7			9
n		78	55	66			40

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Table 2. Selected rotational transitions of ethylisocyanide, CH_3CH_2NC. Internal rotation splittings included. J, K_-, K_+ rotational quantum numbers. ν_A, ν_E: frequencies of the A- and E-species components of the internal rotation doublet [MHz]; Δ: measured doublet splitting $\nu_A - \nu_E$ [kHz]; $\delta\Delta$: difference of calculated and measured splittings [kHz]; ν_0: hypothetical frequency without internal rotation [MHz]; δ_6: difference of calculated 6th order centrifugal corrected and measured frequency [kHz]; *: center frequency of hfs multiplet. $\delta\Delta$ and δ_6 result from a fit of all measured transitions [18].

$J'K'_-K'_+ \leftarrow JK_-K_+$	ν_A / ν_E	Δ / $\delta\Delta$	ν_0	δ_6
1 0 1 ← 0 0 0	–	–	9 679.201 *	1
2 0 2 ← 1 0 1	–	–	19 348.221	4
3 0 3 ← 2 0 2	–	–	28 996.921	−4
3 0 3 ← 2 1 2	–	–	6 899.727 *	2
3 1 2 ← 2 1 1	–	–	29 864.202	−1
3 2 1 ← 2 2 0	–	–	29 079.001 *	13
4 0 4 ← 3 0 3	–	–	38 615.253	−7
8 3 6 ← 9 2 7	25 005.5462	54.6	25 005.510	5
	25 005.4916	−0.4		
10 1 10 ← 9 2 7	8 900.4397	−53.9	8 900.475	0
	8 900.4936	2.1		
10 3 7 ← 11 2 10	10 005.5304	53.2	10 005.494	1
	10 005.4772	3.8		
12 4 9 ← 13 3 10	33 029.0936	74.4	33 029.045	7
	33 029.0192	−4.6		
15 4 11 ← 16 3 14	4 744.8223	66.3	4 744.778	1
	4 744.7560	−0.7		
16 1 16 ← 15 2 13	25 857.8462	−88.0	25 857.905	4
	25 857.9342	1.4		
17 1 17 ← 16 2 14	25 682.6499	−97.9	25 682.715	8
	25 682.7478	3.0		
17 3 15 ← 16 4 12	4 887.9846	−64.8	4 888.028	1
	4 888.0494	1.0		
18 3 16 ← 17 4 13	14 433.7367	−59.3	14 433.777	−4
	14 433.7960	−2.7		
18 5 13 ← 19 4 16	20 581.0537	68.1	20 581.008	−4
	20 580.9856	4.7		
19 5 14 ← 20 4 17	10 631.2658	72.1	10 631.218	−3
	10 631.1937	−2.1		
20 1 20 ← 19 2 17	20 144.7532	−123.1	20 144.835	−11
	20 144.8763	0.0		
22 4 18 ← 21 5 17	10 905.7411	−67.2	10 905.785	−2
	10 905.8083	5.3		
23 4 19 ← 22 5 18	21 523.8828	−58.9	21 523.922	−1
	21 523.9417	1.0		
23 6 18 ← 24 5 19	17 079.8999	69.5	17 079.858	−1
	17 079.8304	7.4		
24 6 19 ← 25 5 20	6 970.2874	69.9	6 970.242	−2
	6 970.2175	−5.3		
27 7 21 ← 28 6 22	24 028.4002	85.1	24 028.362	−22
	24 028.3151	5.1		
28 5 23 ← 27 6 22	23 816.0781	−53.3	23 816.114	−6
	23 816.1314	0.5		

Gwinn [3] determined the barrier to internal rotation from the microwave (MW) spectrum of the first excited torsional mode. They assumed a plausible structure to calculate the moment of inertia (I_α) of the methyl top and the angle between the principal axis of inertia a of the molecule and the internal rotation axis

Table 3a. Selected rotational transitions of isopropyl isocyanide, $(CH_3)_2CHNC$. ν_0: measured frequency [MHz], δ_4: difference $\nu_c - \nu_0$ of calculated ν_c and measured frequency [kHz]. See also Table 2.

$J'K'_-K'_+ \leftarrow JK_-K_+$	ν_0	δ_4
1 0 1 ← 0 0 0	7 405.563 *	1
2 0 2 ← 1 0 1	14 549.683 *	0
2 1 1 ← 1 1 0	16 038.970 *	−2
2 1 2 ← 1 1 1	13 583.142 *	2
3 2 1 ← 2 2 0	23 192.192 *	5
3 2 2 ← 3 1 2	9 281.737	−24
4 0 4 ← 3 0 3	27 507.940	−11
4 1 3 ← 3 1 2	31 437.156	−13
4 2 3 ← 3 2 2	29 416.088	−10
4 3 2 ← 3 3 1	30 053.966	19
5 2 4 ← 5 1 4	5 128.752	−2
6 2 4 ← 6 2 5	11 406.750	−7
7 3 4 ← 7 3 5	5 358.762	−1
7 3 5 ← 7 2 5	10 513.784	−8
8 3 6 ← 8 2 6	7 408.436	5
9 3 7 ← 9 2 7	4 724.386	5
10 4 6 ← 10 4 7	7 322.203	−2
11 4 8 ← 11 3 8	9 577.887	8
12 5 7 ← 12 5 8	5 060.386	7
13 5 8 ← 13 5 9	9 257.987	−1
14 5 10 ← 14 4 10	11 664.330	19
16 6 10 ← 16 6 11	11 176.794	−4
18 7 11 ← 18 7 12	7 661.494	11
19 7 12 ← 19 7 13	13 085.385	−4
20 8 12 ← 20 8 13	4 905.840	23
21 8 13 ← 21 8 14	8 976.581	13
23 9 14 ← 23 9 15	5 769.507	24
24 9 15 ← 24 9 16	10 302.065	6
26 10 16 ← 26 10 17	6 649.787	21
29 11 18 ← 29 11 19	7 546.192	8
34 13 21 ← 34 13 22	5 245.562	−20

Table 3b. Rotational transitions of $(CH_3)_2CHNC$ split by ^{14}N-hfs. F: quantum number of hfs levels; ν: measured frequency [MHz]; δ: difference of measured and calculated frequency of hfs components. Hypothetical center frequencies see Table 3a.

$J'K'_-K'_+ \leftarrow JK_-K_+$	$F' \leftarrow F$	ν	δ
1 0 1 ← 0 0 0	0 ← 1	7 405.471	−1
	1 ← 1	7 405.607	−1
	2 ← 1	7 405.554	0
2 0 2 ← 1 0 1	1 ← 0	14 549.732	−1
	1 ← 1	14 549.588	−10
	2 ← 1	14 549.680	2
	2 ← 2	14 549.732	0
	3 ← 2	14 549.680	−1
2 1 1 ← 1 1 0	2 ← 1	16 039.014	0
	3 ← 2	16 038.958	0
2 1 2 ← 1 1 1	1 ← 0	13 583.054	1
	2 ← 1	13 583.174	−4
	3 ← 2	13 583.125	1
3 2 1 ← 2 2 0	3 ← 2	23 192.244	1
	4 ← 3	23 192.177	−1

$J'K'_-K'_+ \leftarrow JK_-K_+$	ν	Γ	Δ	$\delta\Delta$	ν_0	δ_6
2 0 2 ← 1 0 1	–	–	–	–	12 637.488	3
4 1 3 ← 4 1 4	–	–	–	–	6 179.825	−11
6 1 6 ← 5 1 5	–	–	–	–	35 893.574	4
6 4 3 ← 7 3 4	–	–	–	–	4 196.578	−12
14 8 6 ← 15 7 9	9 446.9282	A	–	–	9 446.933	23
	9 446.6114	E*	316.8	−7.1		
14 8 7 ← 15 7 8	9 446.4988	A	–	–	9 446.504	9
	9 446.8305	E*	−331.7	9.1		
15 6 10 ← 14 7 7	4 970.4497	A	–	–	4 970.444	9
	4 970.3891	E	60.6	−14.7	–	
19 7 13 ← 18 8 10	16 970.7621	A	–	–	16 970.754	0
	16 970.6866	E	75.5	−3.7	–	
20 5 15 ← 20 5 16	4 232.6384	A	–	–	4 232.629	5
	4 232.6242	E	14.2	−0.3	–	
23 9 14 ← 22 10 13	14 309.4145	A	–	–	14 309.406	10
	14 309.0904	E*	324.1	−6.8	–	
23 9 15 ← 22 10 12	14 308.9914	A	–	–	14 308.982	1
	14 309.2889	E*	−297.5	4.2	–	
24 5 19 ← 24 5 20	17 351.4540	A	–	–	17 351.424	−5
	17 351.4084	E	45.6	−0.7	–	
25 6 19 ← 25 6 20	4 772.2337	A	–	–	4 772.222	5
	4 772.2163	E	17.4	−1.3	–	
26 9 17 ← 25 10 16	34 380.3861	A	–	–	34 380.375	−11
	34 380.4710	E	−84.9	4.8	–	
	34 376.5659	E*	3820.2	5.1	–	
26 9 18 ← 25 10 15	34 376.3972	A	–	–	34 376.386	1
	34 376.2706	E	126.6	0.2	–	
27 5 22 ← 27 5 23	35 279.4064	A	–	–	35 279.360	4
	35 279.3372	E	69.2	−3.2	–	
27 6 21 ← 27 6 22	10 042.6164	A	–	–	10 042.592	−3
	10 042.5797	E	36.7	1.3	–	
28 10 18 ← 27 11 17	32 962.2131	A	–	–	32 962.201	10
	32 961.5870	E*	626.1	−8.2	–	
28 10 19 ← 27 11 16	32 961.4771	A	–	–	32 961.465	−1
	32 962.0669	E*	−589.8	6.9	–	
30 7 23 ← 30 7 24	5 126.8840	A	–	–	5 126.870	−1
	5 126.8634	E	20.6	−1.7	–	
31 6 25 ← 31 6 26	30 539.4577	A	–	–	30 539.402	1
	30 539.3742	E	83.5	5.3	–	
32 7 25 ← 32 7 26	10 537.9423	A	–	–	10 537.917	−2
	10 537.9037	E	38.6	−2.7	–	
35 8 27 ← 35 8 28	5 309.5134	A	–	–	5 309.497	2
	5 309.4882	E	25.2	0.2	–	
37 8 29 ← 37 8 30	10 733.2988	A	–	–	10 733.270	−1
	10 733.2556	E	43.2	−2.3	–	
40 9 31 ← 40 9 32	5 334.2531	A	–	–	5 334.236	3
	5 334.2268	E	26.3	−0.3	–	

Table 4. Selected rotational transitions of *gauchge-n*-propylisocyanide, $H_3CCH_2CH_2NC$. Internal rotation splittings included. ν: measured frequency [MHz]; Γ: symmetry species A, E, E*, E* designates "forbidden" transition; Δ: splitting $\nu_A - \nu_\Gamma$; $\delta\Delta$: difference between calculated and observed splitting [kHz]; ν_0: hypothetical frequency [MHz] without internal rotation; δ_6: difference of calculated frequency and ν_0 [kHz]. See also Table 2.

of the internal rotor. The authors obtained a value of $V_3 = 3.650(75)$ kcal/mol. One aim of this study was to resolve the discrepancy between the two older values and to determine the barrier height from the ground vibrational state, possibly without assumptions on the molecular structure. The quadrupole coupling constants of ethyl isocyanide have been given by Fliege and Dreizler [4]. A redetermination in the course of the analysis of the spectrum did not significantly improve the quality of the coupling constants.

The MW spectrum and dipole moment of *iso*-propyl isocyanide, $(CH_3)_2CHNC$, has been published previously [5]. In the present study, the quadrupole coupling constants are reported, together with a lower limit of V_3 and refined rotational and centrifugal distortion constants.

n-Propyl isocyanide, $CH_3CH_2CH_2NC$, exists in an equilibrium of a *gauche* and *trans* conformation with respect to the central carbon-carbon bond. The MW spectra of both conformers were assigned by Fuller and Wilson [6]. In the case of the *trans* conformer, however, a large uncertainty in the rotational constant A remained. The ^{14}N nuclear quadrupole coupling constants of the *gauche* isomer were determined by Vor-

Table 5a. Selected rotational transitions of *trans-n*-propyl isocyanide, $H_3CCH_2CH_2NC$. Internal rotation splittings included. See Table 2.

$J'K'_-K'_+ \leftarrow JK_-K_+$	ν_A / ν_E	Δ / $\delta\Delta$	ν_0	δ_4
2 0 2 ← 1 0 1	–	–	9 372.405*	−3
2 1 1 ← 1 1 0	–	–	9 501.844*	−4
3 0 3 ← 2 0 2	–	–	14 057.126*	−6
4 1 3 ← 3 1 2	–	–	19 002.422	−7
5 0 5 ← 4 0 4	–	–	23 420.640	−10
5 2 3 ← 4 2 2	–	–	23 443.128	2
5 1 4 ← 5 0 5	–	–	22 337.856	2
7 2 6 ← 8 1 7	–	–	24 274.321	14
9 2 7 ← 10 1 10	20 975.9290	278.0	20 975.741	−9
	20 975.6510	−15.1		
13 2 11 ← 14 1 14	6 137.2485	296.0	6 137.051	−9
	6 136.9525	4.0		
16 3 14 ← 17 2 15	25 479.2740	493.0	25 478.962	6
	25 478.7810	9.4		
17 3 15 ← 18 2 16	20 403.8470	496.0	20 403.530	5
	20 403.3510	18.0		
18 3 15 ← 19 2 18	18 718.4570	446.0	18 718.153	6
	18 718.0110	4.7		
19 3 17 ← 20 2 18	10 060.9809	477.2	10 060.669	0
	10 060.5037	4.3		
20 3 17 ← 21 2 20	9 848.7756	449.5	9 848.473	6
	9 848.3261	5.8		
21 3 18 ← 22 2 21	5 477.3288	451.3	5 477.028	3
	5 476.8775	3.5		
23 2 21 ← 22 3 20	5 996.6139	468.7	5 996.926	30
	5 997.0826	0.3		
24 1 24 ← 23 2 21	21 471.7000	273.0	21 471.884	−10
	21 471.9730	4.7		
25 2 24 ← 24 3 21	7 324.3596	445.5	7 324.661	0
	7 324.8051	3.9		
26 4 22 ← 27 3 25	22 525.7880	517.0	22 525.406	−9
	22 525.2710	−7.2		
28 2 27 ← 27 3 24	19 538.1440	422.0	19 538.427	−2
	19 538.5660	10.7		
29 4 26 ← 30 3 27	6 631.6350	622.2	6 631.238	−1
	6 631.0128	12.1		

Table 5b. Rotational transitions of *trans-n*-propylisocyanide, $H_3CCH_2CH_2NC$, split by ^{14}N-hfs. See also Table 3b. Hypothetical center frequencies see Table 5a.

$J'K'_-K'_+ \leftarrow JK_-K_+$	$F' \leftarrow F$	ν	δ
2 0 2 ← 1 0 1	1 ← 0	9 372.472	0
	2 ← 1	9 372.401	4
	2 ← 2	9 372.485	1
	3 ← 2	9 372.401	−2
2 1 1 ← 1 1 0	1 ← 0	9 501.737	0
	2 ← 1	9 501.911	0
	3 ← 2	9 501.828	0
3 0 3 ← 2 0 2	2 ← 1	14 057.138	1
	3 ← 2	14 057.124	2
	4 ← 3	14 057.124	−1

Table 6. Methyl internal rotation parameters of ethyl-, *gauche*- and *trans-n*- propyl isocyanide with standard errors. Numbers in square brackets have been held constant during the analysis, see also text. I_z: moment of inertia of the methyl internal rotor; $\omega_1(s)$: first Fourier coefficient; $\measuredangle(g, i)$: angle between the principal axis g ($g = a, b, c$) and the internal rotation axis; F: reduced rotational constant of the internal rotation; s: reduced barrier height; V_3: barrier height of the internal rotation; σ: standard deviation of the fit; n: number of transitions used for the analysis.

		ethyl-NC	*gauche-n*-propyl-NC	*trans-n*-propyl-NC
I_z	[amu · Å^2]	3.255 (39)	[3.168]	[3.157]
$\omega_1(s)$	[10^{-6}]	−0.7291 (122)	−1.528 (80)	−3.609 (107)
$\measuredangle(a, i)$	[°]	46.31 (36)	73.0 (28)	15.1 (26)
$\measuredangle(b, i)$	[°]	43.69 (36)	30.8 (18)	74.9 (26)
$\measuredangle(c, i)$	[°]	[90.0]	65.1 (26)	[90.0]
F	[GHz]	173.0 (23)	163.62 (23)	185.94 (67)
s		89.91 (17)	82.42 (53)	74.08 (29)
V_3	[kJ/mol]	13.96 (22)	12.11 (10)	12.367 (92)
	[kcal/mol]	3.336 (52)	2.894 (23)	2.954 (22)
σ	[kHz]	3.6	5.4	10.8
n		38	26	21

mann et al. [7]. The internal rotation parameters of both isomers were determined in this study, as well as the quadrupole coupling constants of the *trans* conformer, for which improved rotational and centrifugal distortion constants could also be obtained.

Experimental

All isocyanides were prepared from the corresponding N-alkyl formamides by dehydration with *p*-tosyl chloride in quinoline [8, 9] and purified by destillation. The microwave Fourier transform (MWFT) spectra were obtained as described previously for waveguide [10–13] and pulsed molecular beam [14, 15] spectrometers. To minimize effects of overlapping lines on transition frequencies obtained after Fourier transformation, the transient molecular emission signal was fitted to the transition frequencies [16].

Results

a) Rotational Spectra

The refined rotational and centrifugal distortion constants of the title molecules are presented in Table 1. The analysis was performed according to the procedure set out by Watson [17], using the I^r representation and either the S- or A-reduction as specified in Table 1. Whereas in the case of *iso*-propyl and *trans-n*-propyl isocyanide inclusion of fourth order centrifugal distortion constants sufficed for an ade-

Table 7. Comparison of barrier heights (V_3) hindering methyl internal rotation (kcal/mol) of alkyl compounds R–X, determined by microwave spectroscopy.

X \ R	ethyl-	*iso*-propyl-	*gauche-n*-propyl-	*trans-n*-propyl-
–H	2.893 (3) [23] [a]	3.166 (27) [25]		
–CN	3.007 (90) [26]	?	3.090 (25) [27]	3.115 (48) [27]
–NC	3.336 (52) [b]	> 3.1 [b]	2.894 (23) [b]	2.954 (22) [b]
–F	3.349 (4) [28]	3.323 (2) [29]	2.758 (35) [21]	2.710 (8) [21]
$-^{35}$Cl	3.602 (10) [30]	3.929 (3) [31]	?	?
$-^{79}$Br	3.665 (117) [32]	4.109 (7) [33]	?	?

[a] Determined from the perturbation-allowed torsional spectrum. – [b] This work.

Table 8. ^{14}N Nuclear quadrupole coupling constants of *iso*-propyl and *trans-n*-propyl isocyanide, standard error in parentheses.

	iso-propyl-NC	*trans-n*-propyl-NC
χ_{aa} [kHz]	179.2 (31)	268.1 (71)
χ_{bb} [kHz]	–140.0 (15)	–108.0 (23)
χ_{cc} [kHz]	–39.0 (15)	–160.0 (23)

quate description of the observed spectra, the analysis had to be extended to sixth order for the remaining two molecules.

A selection of the transition frequencies used for the analysis are listed in Tables 2–5, including the frequencies for individual components of split rotational lines. The complete list of line frequencies is given in [18] and deposited under TNA 27 at the library of the University of Kiel [19]. For ethyl isocyanide, only center frequencies are listed for lines showing hyperfine structure due to nuclear quadrupole coupling.

b) Methyl Internal Rotation

The observed splittings of rotational lines due to methyl internal rotation (Tables 2, 4, and 5a) were analyzed according to the internal axis method (IAM) of Woods [20], the results are listed in Table 6. In the case of the two conformers of *n*-propyl isocyanide, the moments of inertia of the internal rotor could not be fitted to the experimental data and were fixed to the values of the respective conformers of *n*-propyl fluoride [21]. The angle between the axis of the internal rotor and the principal axis of inertia *c* (perpendicular to the mirror plane) was fixed to 90° for ethyl and *trans-n*-propyl isocyanide.

No internal rotation splittings could be observed in the MW spectrum of *iso*-propyl isocyanide. From the moment of inertia of the methyl groups in *iso*-propyl fluoride [22] and values of the angles between the axes of the internal rotors and the three principal axes *a*, *b*, and *c* of the molecule derived from a plausible molecular structure, we estimated the lower limit of the barrier height V_3 to be 3.1 kcal/mol. For a barrier lower than the value given, some splittings due to internal rotation would have been resolved with the spectrometers used.

The barrier heights hindering methyl internal rotation in various alkyl compounds, as determined by MW spectroscopy, have been compiled in Table 7. Ethane, which is not directly accessible to MW spectroscopy due to the lack of a dipole moment, has been included for comparison. The barrier height for this molecule has been determined from an analysis of the perturbation-allowed torsional spectrum [23].

c) Quadrupole Coupling

The data in Tables 3b and 5b have been used to determine the ^{14}N nuclear quadrupole coupling constants of *iso*-propyl and *trans-n*-propyl isocyanide with the usual first order treatment [24]. The results are listed in Table 8.

Discussion

Comparison of the ^{14}N nuclear quadrupole coupling data of *iso*-propyl and *trans-n*-propyl isocyanide with the constants of other isocyanides is difficult because the principal axes of the coupling tensor do not coincide with principal axes of inertia of the molecule. However, the constants are in the range typical for alkyl isocyanides, i.e. smaller than 1 MHz with χ_{aa} positive.

The internal rotation parameters determined for the title molecules are in accord with those of other alkyl compounds, see Table 7. The barrier to internal rotation in ethyl isocyanide is very similar to that in ethyl fluoride and differs significantly from the value of the cyanide.

Thus the stereoelectronic effects of a fluoro- and isocyano-substituent on the barrier height are comparable. The two conformers of the different *n*-propyl compounds have almost the same barrier to internal rotation, which is thus insensitive to the relative orientation of the substituent *X* to the methyl group. However, the substituent effect is not negligible, as can be seen from the difference in V_3 in *trans-n*-propyl cyanide and fluoride. Since there is very little dependence of V_3 on the conformation, one can certainly not argue with steric effects of the substituents to account for the different barrier heights in different *n*-propyl compounds. At this point, we cannot offer an explanation for the observed effects.

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