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Microwave Spectrum and Conformational Equilibrium of Propyl Isocyanate

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The microwave spectrum of $CH_3CH_2CH_2NCO$ has been studied in the frequency region from 15 to 31 GHz. The molecule has been found to exist in two rotameric forms both having *syn* conformation about the C–N bond; rotamer I (G_s), see Figs. 1 and 2, with the CH_3 group *gauche* to the C–N bond and conformer II (A_s) where the methyl group is *anti* to the isocyanato substituent. The rotational constants of rotamer I are $A=6236\pm1$ MHz, $B=2372.064\pm0029$ MHz and $C=1864.603\pm033$ MHz, and those of conformer II are $A=11\,116\pm6$ MHz, $B=1635.104\pm0.015$ MHz and $C=1466.649\pm0.016$ MHz. The $NC_bC_cC_d$ and $C_aNC_bC_c$ dihedral angles and the C_aNC_b angle (Fig. 2) are in form I 60(2), 0(2), and 148(1)°, and in form II 180(2), 0(2), and 143.5(1)°, respectively. From relative intensity measurements the two conformers are found to be of approximately the same energy with $\Delta G°=-0.23(15)$ kcal/mol at 195 °C and $\Delta H°=0(0.4)$ kcal/mol.

The three sets of vibrational satellites assigned for conformation I show that the molecule is very flexible. The excited states have tentatively been assigned as the C–N torsion (38(20) cm^{-1}), the CNC bend (74(30) cm^{-1}) and the central C–C torsion. Extensive coupling between these low-frequency modes seems to be present. No excited states were observed for conformation II possibly because of large-amplitude vibrations.

In recent years, several studies have been made on the rotational isomerism about single C–C bonds in n-propanes having only one substituent in the 1-position.[1-9] In all these cases, an equilibrium is found to exist between a conformation having the methyl group approximately *gauche* to the substituent and a conformation with the two groups in the *anti* position. Except for *n*-butane,[8] where the *anti* form is found to be energetically favoured, the *gauche* forms are generally found to be slightly the more stable,[1-7,9] as depicted in Table 1. Some studies have also paid attention to conformational relations in molecules where simultaneous rotation about single carbon–carbon and carbon–hetero-

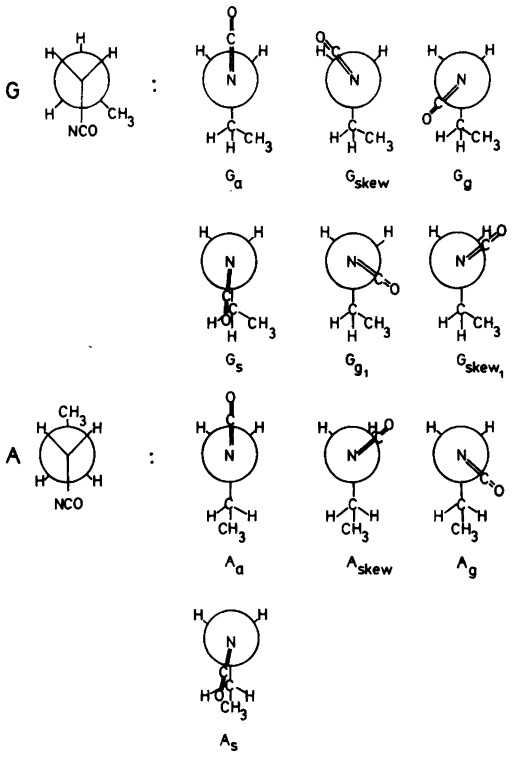

Fig. 1. Ten possible rotameric forms of $CH_3CH_2CH_2NCO$. Further conformations are also possible. The G_s and A_s conformations were found experimentally.

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Table 1. Energy differences between rotamers of mono-substituted propanes, $CH_3CH_2CH_2X$.

X	Compound	Technique[a]	$E_{anti} - E_{gauche}$ (kcal/mol)	Ref.
F	Propyl fluoride	MW	0.47(31)	1
Cl	Propyl chloride	MW, IR	0.00(5) (MW), 0.05(15) (IR)	2, 3
Br	Propyl bromide	IR	0.1(2)	3
I	Propyl iodide	LRMW[b]		4
CN	Butyronitril	MW	<1	5
NC	Propyl isocyanid	MW	0.29(14)	6
CCH	1-Pentyne	MW	0.77(10)	7
CH_3	Butane	ED	−0.63(35)	8
OH	Propyl alcohol	MW, ED	0.29(15) (MW)	9
OCH_3	Methyl propyl ether	MW[c]		10
CHO	Butanal	MW[d]		11
NCO	Propyl isocyanate	MW	0(0.4)	This work

[a] Technique: MW-microwave spectroscopy, LRMW, low resolution micr.spectr.; IR, infrared spectroscopy; ED, electron diffraction. [b] *anti* and *gauche* rotamers observed. [c] Only one *anti-anti* form observed. [d] *anti-anti* and *gauche-anti* isomers assigned.

atom bonds can take place. Hayashi *et al.* have studied the microwave spectrum of $CH_3CH_2CH_2$-OCH_3, where rotational isomerism about the central C−C as well as C−O bonds is possible. Only one conformation, the *anti-anti* form was found to predominate.[10]

This paper discusses the microwave spectrum and structure of propyl isocyanate, a compound where internal rotation about C_b-C_c and C_b-N bonds (Fig. 2) may give rise to a relatively large number of conformations. Ten probable rotamers are shown in Fig. 1. They are interchangeable by appropriate rotations about the C_b-C_c and C_b-N bonds. Further forms are, of course possible, for example C_b-N *syn* to the C_c-C_d bond, but these are supposed to be of considerable higher energies due to steric strains.

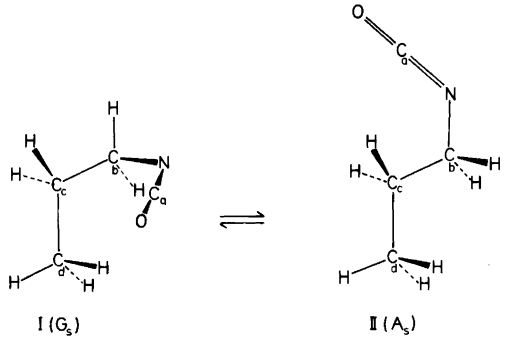

Fig. 2. The two assigned conformations of $CH_3CH_2CH_2NCO$. An equilibrium exists between these two forms.

It is far from easy to predict which of the several rotational isomers given in Fig. 1 that are the more stable ones. The rotamer named A_a would be analogous to the *anti-anti* form found in methyl propyl ether.[10] In ethyl isocyanate, the conformation having the C−C and N=C bonds *syn* to each other is found to predominate.[12] The same preference is found in ethyl isothiocyanate.[13] If propyl isocyanate is regarded as a methyl substituted ethyl isocyanate, the G_s and A_s isomers shown in Fig. 1, both having *syn* conformation about the C_b-N bond, would be expected as favoured forms of the molecule. These two forms were indeed assigned. However, the spectrum is so dense that further forms may coexist with the G_s and A_s rotamers.

EXPERIMENTAL

The sample of propyl isocyanate obtained from Fluka A.G. was used without further purification. The microwave spectrum was studied in the frequency region from 16.5 to 31.0 GHz, using a conventional Stark modulated spectrometer.[14] The measurements were all carried out at dry ice temperature to enhance the intensity of the absorption lines.

RESULTS

Microwave spectrum and assignment of the conformation I. Preliminary rotational constants were computed for the various *gauche* rotamers using

Table 2. Observed and predicted rotational constants for the gauche conformations of $CH_3CH_2CH_2NCO$.

	Obs.	Calc.[a]					
		G_s	G_{g1}	G_{skew1}	G_a	G_{skew}	G_g
A(MHz)	6263.1	6027.28	6367.66	8176.25	11302.57	10602.73	7325.48
B(MHz)	2372.06	2541.30	2436.93	1898.17	1603.65	1635.95	2010.10
C(MHz)	1864.60	1956.39	1868.64	1628.33	1470.76	1528.10	1769.03
κ	−0.7693	−0.7126	−0.7474	−0.9176	−0.9730	−0.9762	−0.9132
Δ(uÅ)	22.71	24.39	16.29	17.68	16.23	25.86	34.72
$\phi(°)$[b]		0	60	120	180	−120	−60

[a] These rotational constants were calculated using the same bond angles and distances as shown in Table 9 except for $\angle C_aNC_b$ and $\angle NC_bC_cC_d$ which were kept constant at 142.1 and 60°, respectively. [b] ϕ, Dihedral angle about the C_b-N bond; see Fig. 1.

bond lengths and angles mainly taken from propyl isocyanide[6] and ethyl isocyanate.[3] As the N=C=O group with a large dipole moment lies close to the a-axis in all *gauche* conformations a large μ_a was expected in each case. Consequently, the *gauche* rotamers were all expected to exhibit strong a-type R-branch transitions. Table 2 lists the various rotational constants from which the ground-state spectra of the anticipated isomers were predicted. The observed spectrum of propyl isocyanate was dense and complicated, consisting of a large number of weak absorption lines throughout the examined spectral range. The search was first concentrated to the 22.0−26.5 GHz region where the Stark effect of the strongest lines was studied carefully. The assignment began with the tentative identification of the $4_{1,3}\rightarrow5_{1,4}$ transition, found near the frequency predicted for G_{g1} and slightly away from the frequency expected for the G_s rotamer. The subsequent observation of $5_{0,5}\rightarrow6_{0,6}$ and $4_{2,2}\rightarrow5_{2,3}$ led to a set of unrefined rotational constants. The frequencies of further a-type R-branch lines were then predicted and identified. Attempts were also made to find high J b-type Q-branch transitions, but no such lines could be assigned, probably owing to small intensities. This is in keeping with a CNDO/2[15] calculation which yielded $\mu_a=2.31$ D, $\mu_b=0.47$ D and $\mu_c=0.430$ for the G_{g1} conformer and $\mu_a=2.43$ D, $\mu_b=0.72$ D and $\mu_c=0.06$ D for the G_s rotamer. A total of 23 a-type R branch transitions were ultimately assigned as shown in Table 3.

The derived spectroscopic constants appear in Table 4. Due to the small dependence of the A rotational constant of the observed a-type R-branch transitions, only the B and C rotational constants could be very accurately determined. The affiliation of conformer I with G_s (Fig. 1) will be discussed in a following section.

Table 3. Microwave spectrum of the ground vibrational state of conformation I of $CH_3CH_2CH_2NCO$.

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion (MHz)
$3_{0,3}\rightarrow4_{0,4}$	16501.48	−0.25	−2.00
$3_{2,2}\rightarrow4_{2,3}$	16908.96	0.07	−1.57
$3_{2,1}\rightarrow4_{2,2}$	17351.80	0.12	−1.60
$3_{1,2}\rightarrow4_{1,3}$	17858.73	0.44	−1.91
$4_{1,4}\rightarrow5_{1,5}$	19732.93	−0.68	−3.81
$4_{0,4}\rightarrow5_{0,5}$	20348.07	−0.34	−3.88
$4_{2,3}\rightarrow5_{2,4}$	21076.92	0.14	−4.38
$4_{2,2}\rightarrow5_{2,3}$	21906.95	0.24	−3.47
$4_{1,3}\rightarrow5_{1,4}$	22216.16	0.40	−3.80
$5_{1,5}\rightarrow6_{1,6}$	23586.79	−0.16	−6.65
$5_{0,5}\rightarrow6_{0,6}$	24093.26	−0.16	−6.69
$5_{2,4}\rightarrow6_{2,5}$	25205.86	−0.14	−6.14
$5_{3,3}\rightarrow6_{3,4}$	25602.28	0.16	−5.32
$5_{3,2}\rightarrow6_{3,3}$	25746.20	0.21	−5.37
$5_{4,1}\rightarrow6_{4,2}$	25577.11	0.10	−4.10
$5_{2,3}\rightarrow6_{2,4}$	26521.01	−0.18	−6.32
$5_{1,4}\rightarrow6_{1,5}$	26487.67	−0.12	−6.60
$6_{1,6}\rightarrow7_{1,7}$	27407.33	0.55	−10.62
$6_{0,6}\rightarrow7_{0,7}$	27783.13	0.60	−10.61
$6_{2,5}\rightarrow7_{2,6}$	29290.18	−0.22	−10.01
$6_{3,4}\rightarrow7_{3,5}$	29886.14	−0.16	−9.11
$6_{3,3}\rightarrow7_{3,4}$	30197.73	−0.32	−9.25
$6_{1,5}\rightarrow7_{1,6}$	30646.71	−0.25	−10.48

[a] ±0.10 MHz.

Table 4. Spectroscopic constants[a] for the ground vibrational state of conformation I of $CH_3CH_2CH_2NCO$.

$A_0 = 6263.1(10)$ MHz	$B_0 = 2372.064(30)$ MHz	$C_0 = 1864.604(33)$
$\Delta_J = 7.95(32)$ kHz	$\Delta_{JK} = -14.6(21)$ kHz	$\kappa = -0.769262$

[a] Uncertainties represent one standard deviation. Root-mean-square deviation $\sigma = 0.35$.

Table 5. Spectroscopic constants[a] for vibrationally excited states of conformation I of $CH_3CH_2CH_2NCO$.

Vibrational state	First ex. $C_b - N$ torsion	First ex. $C_a - N \equiv C_b$ bend	$C_b - C_c$ torsion
Number of transitions	21	16	15
σ^b (MHz)	0.56	0.67	0.52
A_v (MHz)	6530.9(18)	6550.9(27)	6622.6(36)
B_v (MHz)	2303.860(47)	2279.384(75)	2246.756(45)
C_v (MHz)	1803.665(56)	1820.107(72)	1814.926(68)
Δ_{JK} (kHz)	4.60(43)	3.23(60)	5.91(62)
Δ_{JK} (kHz)	−40.1(43)	−68(14)	30.3(94)
κ	−0.788377	−0.805834	−0.820357

[a] Uncertainties represent one standard deviation. [b] Root-mean-square deviation of the fit.

Vibrationally excited states. Several vibrationally excited satellite lines were associated with the ground state lines of conformation I. The satellites were all located towards lower frequencies as compared to their ground state counterparts with essentially the same Stark effect behavior as those of the ground state. Three of these were tentatively assigned to three different normal modes. The vibrationally excited states with the constants given in Table 5 were supposed to be large amplitude motions as the changes in the rotational constants upon excitation were considerable. Measurement of relative intensities[16] yielded 38 ± 20 cm^{-1} for the strongest series, which is assigned to the C_bN torsional mode. The corresponding frequency derived for CH_3CH_2NCO[12] is 150(50) cm^{-1}. The difference between these two torsional frequencies is large for unknown reasons. A total of 21 transitions were measured and used to determine the spectroscopic constants given in Table 5.

Attempts were made to see whether the changes in the rotational constants upon excitation could be reproduced by opening up the $C_aNC_bC_c$ dihedral angle of our molecular model (see below), keeping the other structural parameters fixed. A 13° opening of this angle reasonably well reproduces the observed changes in the B constant while poor agreement was found for the A and C rotational constants. The changes were calculated to be $\Delta A = 149.6$ MHz, $\Delta B = -62.3$ MHz and $\Delta C = -7.2$ MHz as compared to the observed values: $\Delta A = 267.8$ MHz, $\Delta B = -68.2$ MHz and $\Delta C = -60.9$ MHz. The reason for the discrepancy between the observed and calculated changes in the A and C rotational constants is probably that the torsional mode is more complicated than a simple rotation about the C−N bond. Coupling with the other low-frequency vibrations seems to be prominent.

The satellite lines belonging to the C−N torsion were about 75 % as intense as the corresponding ground state transitions. It was, therefore, expected that the second excited state should be quite easy to assign provided this normal mode behaved almost like a harmonic oscillator. However, despite considerable efforts no such lines were found. It is believed that this is caused by a non-harmonic behaviour of this motion. In fact, it is not improbable that the second excited C−N torsional state is near the barrier maximum and that this perhaps causes a rather anomalous pattern for the vibrational satellites.

Table 5 includes the spectroscopic constants derived from the sixteen lines of the second most intense vibrational state. These lines have about 60 % of the intensity of the corresponding ground state transitions at 195 K. Relative intensity measurements place this frequency at 74(30) cm^{-1}.

Referring to a microwave study of

Table 6. Observed and predicted rotational constants for the *anti* conformations of $CH_3CH_2CH_2NCO$.

	Obs.	Calc.[a]			
		A_s	A_g	A_{skew}	A_a
A(MHz)	11116.3	10848.99	12561.58	19072.71	26285.76
B(MHz)	1635.10	1653.74	1528.86	1331.61	1274.07
C(MHz)	1466.65	1475.30	1420.38	1315.12	1243.94
κ	−0.9651	−0.9619	−0.9805	−0.9981	−0.9975
Δ(uÅ)[a]	9.96	9.62	14.98	21.74	9.62
ϕ(°)[b]		0	60	120	180

[a] See text and comments to Table 2. The $NC_bC_cC_d$ angle of the *anti* isomers were kept constant at 180°. [b] ϕ, dihedral angle about the C_b-N bond; see Fig. 1.

CH_3CH_2NCS[13] where the C−N torsion and CNC bending motion are located at 58(30) cm^{-1} and 107(30) cm^{-1}, the vibrational satellite corresponding to 74(34) cm^{-1} can be ascribed to the first excited state of the C_aNC_b bending mode. By opening up the $C_a=N-C_b$ angle of our model 4°, keeping the other structural parameters fixed, we found that the changes in the rotational constants upon excitation were reasonably well reproduced. These changes were calculated to be $\Delta A=209.8$ MHz, $\Delta B=-93.8$ MHz and $\Delta C=-39.9$ MHz as compared to the observed values: $\Delta A=287.8$ MHz, $\Delta B=-92.7$ MHz and $\Delta C=-44.5$ MHz.

Fifteen *a*-type *R*-branch lines of the third excited state were assigned. The derived spectroscopic constants are given in Table 5. The origin of this mode is uncertain; we believe it is the central C−C torsion, but it could possibly be the methyl torsion or another low bending mode. By opening up the $NC_bC_cC_d$ dihedral angle approximately 11° the changes in the rotational constants were calculated to be $\Delta A=179.8$ MHz, $\Delta B=-133.6$ MHz and $\Delta C=-47.2$ MHz. The observed values are; $\Delta A=359.5$ MHz, $\Delta B=-125.3$ MHz and $\Delta C=-49.7$ MHz. The *B* and *C* rotational constants were thus acceptably well reproduced, while discrepancies were found for the *A* constant, probably indicating a motion more complicated than a simple rotation about the C_b-C_c bond.

Assignment of conformation II. Preliminary rotational constants were computed for the various *anti* rotamers using the same parameters as for the *gauche* structure, except for the $C_bC_cC_d$ angle and the NC_bC_c angle. The latter two angles were decreased by 1° in the *anti* form, in accordance with findings in other related molecules.[6,7,17-19] As can be seen from Table 6, the *anti* conformers were all predicted to be near-prolate asymmetric rotors, probably displaying dominant series of *a*-type *R*-branch transitions.

Tentative identification of the $6_{1,5}\rightarrow7_{1,6}$ transition from its typical Stark effect led to the prediction and observation of the $7_{1,6}\rightarrow8_{1,7}$ and $7_{1,7}\rightarrow8_{1,8}$ transitions, all three candidates located at frequencies near those predicted from rotational constants corresponding to the A_s rotamer. A set of unrefined rotational constants was computed was computed from these lines. A total of 23 lines of this conformation were assigned, allowing an accurate determination of the *B* and *C* rotational constants. No *b*-type *Q*-branch lines could be identified. This is consistent with the results from a CNDO/2 calculation[15] on the A_s conformer giving $\mu_a=2.37$ D, $\mu_b=0.43$ D and $\mu_c=0.0$ D.

The measured ground state frequencies are tabulated in Table 7, showing that the frequencies of conformer II deviate little from a rigid rotor spectrum. As shown in Table 3, the conformer I frequencies deviate more from a rigid rotor spectrum than those of conformer II. This might be caused by the large dependence of the rotational constants of I on changes in the torsional angle around the central C−C bond, while in the A_s form the rotational constants would be quite insensitive to changes in this angle. Table 8 lists the derived spectroscopic constants, the *A* constant being rather uncertain due to the small dependence of the *A* rotational constant of the assigned lines.

No excited states belonging to the A_s conformer could be identified from the microwave spectrum. This is probably due to low intensities of the satellite lines. In fact, the ground-state lines of the

Table 7. Microwave spectrum of the ground vibrational state of conformation II of $CH_3CH_2CH_2NCO$.

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion (MHz)
$5_{1,5}\rightarrow 6_{1,6}$	18087.26	−0.10	−0.51
$5_{0,5}\rightarrow 6_{0,6}$	18532.21	−0.09	−0.79
$5_{2,4}\rightarrow 6_{2,5}$	18601.27	0.41	0.34
$5_{2,3}\rightarrow 6_{2,4}$	18678.18	−0.11	0.33
$5_{1,4}\rightarrow 6_{1,5}$	19097.30	0.24	−0.51
$6_{1,6}\rightarrow 7_{1,7}$	21093.33	−0.37	−0.93
$6_{2,5}\rightarrow 7_{2,6}$	21695.25	0.20	0.07
$6_{2,4}\rightarrow 7_{2,5}$	21818.58	0.24	0.04
$6_{1,5}\rightarrow 7_{1,6}$	22270.67	0.10	−0.93
$7_{1,7}\rightarrow 8_{1,8}$	24096.40	−0.09	−1.50
$7_{0,7}\rightarrow 8_{0,8}$	24628.42	−0.06	−1.85
$7_{2,6}\rightarrow 8_{2,7}$	24786.54	0.05	−0.37
$7_{3,5}\rightarrow 8_{3,6}$	24839.47	−0.51	1.52
$7_{2,5}\rightarrow 8_{2,6}$	24970.10	−0.02	−0.41
$7_{1,6}\rightarrow 8_{1,7}$	25439.46	−0.06	−1.50
$8_{1,8}\rightarrow 9_{1,9}$	27095.46	0.06	−2.24
$8_{0,8}\rightarrow 9_{0,9}$	27653.39	0.04	−2.61
$8_{2,7}\rightarrow 9_{2,8}$	27874.90	0.09	−0.97
$8_{3,6}\rightarrow 9_{3,7}$	27950.13	0.22	1.14
$8_{2,6}\rightarrow 9_{2,7}$	28134.37	−0.09	−1.05
$8_{1,7}\rightarrow 9_{1,8}$	28602.72	−0.33	−2.24
$9_{1,9}\rightarrow 10_{1,10}$	30090.36	0.21	−3.18
$9_{2,8}\rightarrow 10_{2,9}$	30959.63	0.01	−1.77

[a] ±0.10 MHz.

A_s form generally were of lower intensities compared to those of the G_s isomer. This makes it, of course, more difficult to assign excited states of this conformation. Large-amplitude motions which are presumed to be present in this form as well would also complicate the assignment of excited states.

The remaining unassigned transitions of the spectrum. Having completed the assignments of the two rotational isomers, which included all the strongest transitions, there remained approximately 100 unassigned lines of intermediate intensities and several hundred weak ones in the spectrum. Despite careful Stark-effekt studies of most of these intermediate intensity lines, none of them could be reliably identified, though some of them behaved in a way similar to that of unresolved high J a-type R-branch lines with $K_{-1}=1$ or $K_{-1}=0$. It is highly probable that some of these lines belong to further vibrationally excited states of conformations I and II. If it is assumed that the lowest normal mode of conformer II is approximately the same as for rotamer I, this mode should appear with observable intensity. In addition, such a mode having a ground state κ value of −0.96 was expected to display a near prolate symmetric rotor pattern thus allowing a relatively precise prediction of lines from one single correct identification. Despite considerable efforts, no such assignment could be made.

The existence of several further conformers in addition to the two assigned in this work was also considered as a possible explanation of the remaining lines. An extensive search was made for all the *gauche* and *anti* rotamers shown in Fig. 1. Unfortunately, no set of lines could be assigned to any of these isomers.

Structure of the two conformers. Only three rotational constants were determined for both conformations shown in Fig. 2. The lack of isotopically substituted species thus prevents a rigorous determination of rotameric structures. However, by transferring structural parameters of propyl isocyanide[6] and ethyl isocyanate[3] to the respective parts of the molecule, it was possible to reproduce fairly well the observed rotational constants of the two rotamers. The $C_aNC_bC_c$, $NC_bC_cC_d$ and C_aNC_b angles were fitted, while the remaining bond lengths and angles of our model were kept constant at the values shown in Table 9 during the calculations.

It was necessary to open up the C_aNC_b angle of the C_s form by 6° as compared to the corresponding angle of *syn* CH_3CH_2NCO. A value of 148(1)° was thus determined. The dihedral angles $C_aNC_bC_c$ and $NC_bC_cC_d$ were both found to have the normal values of 0(2) and 60(2)°, respectively.

From Table 2 it can be seen that the G_{g1} conformation of propyl isocyanate cannot be completely ruled out on the basis of the observed rotational constants because of the similarities in the structures. In fact, it was first believed that the

Table 8. Ground-state rotational constants[a] and centrifugal distortion constants[a] for conformation II of $CH_3CH_2CH_2NCO$.

$A_0=11116.3(65)$ MHz	$\Delta_J=0.922(83)$ kHz
$B_0=1635.104(15)$ MHz	$\Delta_{JK}=-23.7(15)$ kHz
$C_0=1466.650(16)$ MHz	
$\Delta=I_a+I_b-I_c=9.963$ uÅ^2	$\kappa=-0.965086$

[a] Uncertainties represent one standard deviation. Root-mean-square deviation $\sigma=0.24$.

assigned lines belonged to G_{g1}. We also managed to get a satisfactory fitting of observed and calculated rotational constants for this rotamer. To obtain this, however, we had to accept rather drastic structural changes as compared to those necessary for fitting the G_s model to the spectrum. The $C_aNC_bC_c$, $NC_bC_cC_d$ and C_aNC_b angles were determined to be 57, 72 and 140°, respectively. In addition, the refined G_g^1 structure could not reproduce the experimentally determined eqn. (1).

$$\Delta = I_a + I_b - I_c \quad (1)$$

Moreover, it showed poorer agreement between calculated and experimental I values than the *gauche-syn* form I. It is, therefore, concluded that the G_s form has undoubtedly been found and that this rotamer posesses a rather large C_aNC_b-angle of 148(1)°.

For the ground vibrational state of the *anti* form the experimentally determined value of $I_a + I_b - I_c$ is found to be 9.96 uÅ^2. This is in accordance with a model of the molecule that has a plane of symmetry where six hydrogen atoms will be located out of the plane. From Fig. 1 it can be seen that there are two possible *anti* isomers with a plane of symmetry; the A_a and the A_s forms. Comparison of the experimentally determined rotational constants with those calculated for the various *anti* isomers given in Table 6, shows that the A_s form clearly must be the favoured rotamer. The results from the fit of the selected angles are displayed in Table 9. The error limits in this table are believed to encompass reasonable differences between the assumed structural parameters and the real ones.

From Table 9 it can be seen that the methyl group is nearly exactly *gauche* in conformation I, and almost exactly *anti* in rotamer II. However, the conformation about the $C_b - N$ bond is identical in the two forms. A significant difference in the C_aNC_b valence angle of the two conformers is found. This angle is seen to be 4.5° larger in rotamer I than in II. A model of the two assigned conformations is shown in Fig. 2.

Energy difference between the two rotamers. Relative intensity measurements[20] were made to determine the energy difference between the two conformations. All relative intensities were

Table 9. Plausible structural parameters and observed and calculated rotational constants of the two rotamers of $CH_3CH_2CH_2NCO$.

Assumed structural parameters[a]

C=O (Å)	1.171	∠NCO (°)	0.0		∠NCH (°)	109.5
C=N (Å)	1.207	∠NC_bC_c (°)	110.5	*anti*	∠C_bC_cH (°)	109.5
C−N (Å)	1.426		111.5	*gauche*	∠C_cC_dH (°)	110.14
C−H (Å)	1.094					
		∠$C_bC_cD_d$ (°)	110.5	*anti*		
C_d-C_c (Å)	1.544		111.5	*gauche*		
C_c-C_d (Å)	1.536					

Fitted structural parameters

	Conformation I (G_s)	Conformation II (A_s)
∠$NC_bC_cC_d$ (°)	60.0(20)	180.0(20)
∠$C_aNC_bC_c$ (°)	0.0(20)	0.0(20)
∠C_aNC_b (°)	148.0(10)	143.5(10)

Rotational constants

	Conformation I			Conformation II		
	Obs.	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
A_o (MHz)	6263.10	6283.58	0.33	11116.30	11076.03	0.36
B_o (MHz)	2372.06	2376.48	0.19	1635.10	1633.47	0.10
C_o (MHz)	1864.60	1874.79	0.55	1466.65	1463.17	0.24

[a] See Fig. 2 for definitions of C_a, C_b, C_c and C_d.

Table 10. Intensity measurements,[a] equilibrium constants and Gibb's free energy difference of the ground vibrational states of conformations I and II of $CH_3CH_2CH_2NCO$.

Conformation I		Conformation II		$\frac{\alpha_1}{\alpha_2}$	K	$\Delta G°$ (kcal mol^{-1})
Transition	Frequency (MHz)	Transition	Frequency (MHz)			
$4_{2,2}\rightarrow5_{2,3}$	21906.95	$6_{2,4}\rightarrow7_{2,5}$	21818.58	1.24	1.79	−0.23
$4_{1,3}\rightarrow5_{1,4}$	22216.16	$6_{1,5}\rightarrow7_{1,6}$	22270.67	1.49	2.08	−0.28
$5_{0,5}\rightarrow6_{0,6}$	24093.26	$7_{1,7}\rightarrow8_{1,8}$	24096.40	1.05	1.38	−0.12
$6_{1,6}\rightarrow7_{1,7}$	27407.33	$8_{1,8}\rightarrow9_{1,9}$	27095.46	0.96	1.20	−0.07
$6_{0,6}\rightarrow7_{0,7}$	27783.18	$8_{0,8}\rightarrow9_{0,4}$	27653.39	2.41	3.01	−0.43
				Av. -0.23 ± 0.15		

[a] Dry-ice temperature (195 K).

measured at dry-ice temperature, and several sweeps were made over each pair of lines. Transitions not too widely spaced in the spectrum were selected and care was taken to ensure that they were all completely modulated. Moreover, these transitions did not seem to be perturbed by Stark components or other weaker unassigned transitions.

Table 10 lists the results of the relative intensity measurements of forms I and II. The ratios given in this table represent average values of the scans taken for each pair of transitions. The uncertainties given in Table 10 arise from several sources: Baseline inaccuracies, effects from wave guide reflections, variations in the half-widths of the absorption lines as well as uncertainties in the assumptions made during the theoretical development of the equilibrium constant for the equilibrium between forms I and II. This constant, K, was determined from the expression[21]

$$K = \frac{Fv^{I}=0}{Fv^{II}=0} = \frac{\alpha_1}{\alpha_2}\left(\frac{\nu_{II}}{\nu_{I}}\right)^2\left(\frac{A_{II}B_{II}C_{II}}{A_{I}B_{I}C_{I}}\right)^2$$

$$\frac{\lambda_{II}\mu_{gII}\exp(-E^{J}_{\tau,II}/kT)}{\lambda_{I}\mu_{gI}\exp(-E^{J}_{\tau,I}/kT)} \qquad (2)$$

where the symbols have similar meanings as in Ref. 21. Due to the weakness and the crowded nature of the spectrum, no dipole moment could be determined. In calculating the numerical value of K we thus assumed that $\mu_{aI}=\mu_{aII}$ ($\mu_{aI}=2.31$D and $\mu_{aII}=2.37$D from CNDO/2 calculations[15]). As can be seen from Table 10 a value of $\Delta G°=-0.23(15)$ kcal mol^{-1} at dry ice temperature was derived from our measurements.

As nothing is known about the frequencies of the normal modes of conformation II, the entropy difference of forms I and II is simply assumed to be $R\ln 2$. The number 2 is the statistical weight of rotamer 1. From eqn. 3

$$\Delta G° = \Delta H° - T\Delta S° \qquad (3)$$

the enthalpy difference is calculated to be 0(0.4) kcal mol^{-1}. Thus, the ground state of the two conformations has approximately the same energy, although the equilibrium constant favours rotamer I (Table 10).

DISCUSSION

It is interesting to note that the G_s and A_s forms have identical conformations about the C_b-N bond. A rotation about the central C−C bond thus does not seem to alter the conformational preference in the isocyanato part of the molecule. However, a significant change of the C_aNC_b angle is observed upon going from form I (148°) to form II (143.5°).

The steric conditions are probably worse in rotamer I than in II, as illustrated in Fig. 2. Calculations indicate that there is a critical non-bonded contact between one of the methyl hydrogens and the carbon atom of the isocyanato group. This carbon-hydrogen distance is found to be 2.5 Å, slightly less than the sum of their van der Waals radii which is 2.7 Å.[23] The same distance was found to be even shorter assuming a C_aNC_b angle

equal to the value found for rotamer II. It is, therefore, possible that the observed 4.5° C_aNC_b angle opening in conformation I results from steric repulsion between the NCO and the CH_3 groups. Despite the more crowded steric situation in form I, the two rotamers are found to have roughly the same energy. This contrasts a CNDO/2 calculation[15] on the energy difference between the two forms which yielded a value of 1.3 kcal mol^{-1}, conformation II being the more stable.

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