hydrocarbon chain is involved in the phase transition.

Finally, further examination of the data reveals that the bands of the perpendicular polarized spectra of DMPC are more intense than those in the parallel spectra. Band intensity depends upon the magnitude of the interaction of the bond dipole with the electric field which is a function of the angle of incidence and the optical constants of the reflective substrate (in this case, water). Qualitatively the difference in polarized spectra for DMPC translates into a more random, liquid-like arrangement of the flexible hydrophobic chains. DMPC monolayer spectra contrast with those of DSPC where the methylene stretch intensities are stronger and independent of polarization. The similarity in polarized intensities of DSPC suggests that these molecules are standing nearly upright and are essentially close-packed and well-oriented at the A/W interface, which are established characteristics of condensed films.[23] The exact orientations may be calculated from the band intensities in each polarization. The angles of the hydrocarbon chains relative to the substrate are currently under investigation in this laboratory.[40]

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Microwave, Infrared, and Raman Spectra, Conformational Stability, Structure, Dipole Moment, and Vibrational Assignment for Cyclopropyl Isocyanate

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Abstract: The microwave spectrum of cyclopropyl isocyanate, c-C_3H_5NCO, has been recorded from 18.5 to 40.0 GHz. Two sets of *a*-type, R-branch transitions have been observed and assigned, on the basis of the rigid rotor model, to the trans and the cis conformers, which have the isocyanate moiety oriented in an s-trans or s-cis fashion, respectively, relative to the three-membered ring. In addition to the ground vibrational state transitions, lines due to two excited states of the CNC bend and four excited states of the asymmetric torsion for the trans conformer, as well as one torsional excited state for the cis form, have been assigned. The B and C rotational constants for the ground vibrational state of the trans and cis conformers are the following: $B = 1784.303 \pm 0.003$, $C = 1716.133 \pm 0.003$ and $B = 2186.797 \pm 0.010$, $C = 2106.242 \pm 0.010$ MHz, respectively. The values of the A rotational constants for both conformers were not well determined because the measured transitions are not very sensitive to these constants. From the relative intensity measurements in the microwave spectrum, the torsional frequency is estimated to be 24 cm^{-1} for the trans conformer and 14 cm^{-1} for the cis form. The dipole moment components determined from the Stark effect are $|\mu_a| = 2.56 \pm 0.02$, $|\mu_c| = 0.71 \pm 0.03$, and $|\mu_t| = 2.65 \pm 0.02$ D for the trans conformer and $|\mu_a| = 2.720 \pm 0.004$, $|\mu_b| = 0.17 \pm 0.01$, and $|\mu_t| = 2.726 \pm 0.001$ D for the cis conformer. With reasonably assumed structural parameters for the cyclopropyl moiety and bond distances for the isocyanate group, estimates of the differences between the cis and trans conformers of the title molecule for the following parameters were made: r(C–N), ∠CNC, and ∠CCN. The infrared (3300 to 30 cm^{-1}) and Raman (3300 to 10 cm^{-1}) spectra have been recorded for the gas and the solid states. Additionally, the Raman spectrum of the liquid has been recorded and qualitative depolarization values have been obtained. Based on the band contours, depolarization values, and group frequencies, the normal vibrational modes have been assigned. From a temperature study of the Raman lines of an assigned conformer pair in the liquid phase, the value of ΔH between conformers has been determined to be 39 ± 5 cm^{-1}, with the trans form being more stable. However, from the Raman spectrum of the solid the cis conformer has been determined to be the preferred form in the crystal. These results are compared with the corresponding quantities in some similar molecules.

The changes in the cyclopropane ring structure upon substitution have been investigated recently for compounds with various unsaturated and saturated substituents. From the microwave study[1] of cyanocyclopropane and cyclopropylacetylene, the ring C_1C_2 bond adjacent to the point of substitution was determined to be about 0.025 Å larger than the C_2C_3 bond opposite to the substituted carbon. In isocyanocyclopropane, however, the C_1C_2 distance determined from the microwave study[2] was found to be only 0.008 Å larger than the C_2C_3 distance. These differences in the ring CC distances were explained on the basis of π conjugative interactions of the substituents with the cyclopropane ring. The smaller difference between the two ring CC distances in isocyanocyclopropane is significant in view of the fact that the atom attached to the cyclopropane ring is N in isocyanocyclopropane and C in the former two compounds.

We have recently investigated the microwave spectrum of cyclopropyl isothiocyanate[3] and determined that the molecule exists as an equilibrium mixture of the trans and cis conformers at ambient temperature. Only one torsional excited state was observed and assigned for each of the two conformers in the microwave spectrum suggesting, perhaps, that a small energy barrier exists between the two conformers and that most of the molecules are freely rotating at room temperature. The structural parameters

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[†] Taken in part from the thesis of R. J. Berry which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

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obtained from the microwave study for the two conformers of cyclopropyl isothiocyanate were used as input for the ab initio optimizations of the geometry by using the STO-3G basis set.[4] These optimizations predicted the C_1C_2 bond to be 0.009 Å larger than the C_2C_3 bond for both the trans as well as the cis conformers of cyclopropyl isothiocyanate, which is in close agreement with the difference in the CC distances obtained for isocyanocyclopropane.[2] The rotational constants obtained from the microwave study[3] along with the difference in the two CC distances obtained from the ab initio predictions[4] were used as constraints to further refine the geometry of cyclopropyl isothiocyanate in order to fit the electron diffraction pattern[4] obtained for this molecule. From ab initio calculations the trans conformer was predicted to be more stable than the cis form by 121 cm^{-1}, whereas from the electron diffraction study this energy difference was determined to be approximately 200 cm^{-1}.

In the present study the analysis of the microwave spectrum of cyclopropyl isocyanate has been carried out in order to determine the stable conformations of this molecule and to obtain reasonable structural parameters from the rotational constants obtained for each conformer. The dipole moment components for the stable conformations assigned in the microwave spectrum have been determined from the Stark effect. The Raman and infrared spectra of cyclopropyl isocyanate in the fluid and solid phases have been recorded and frequencies assigned to the fundamental modes of the stable conformers. The results of these studies are reported herein.

Experimental Section

Cyclopropyl isocyanate was synthesized according to the method of Moffett and Rudzik[5] by reacting cyclopropylcarbonyl chloride (Aldrich) with sodium azide in trimethylene glycol dimethyl ether (triglyme) under a dry N_2 atmosphere. The solvent, triglyme (Aldrich), was treated with CaH_2 followed by NaOH pellets to remove traces of water and was distilled under vacuum in a dry N_2 atmosphere. The purity of the solvent and the chloride was checked by NMR prior to carrying out the reaction. The product cyclopropyl isocyanate was purified by a low-temperature fractionation column. Its purity was checked by recording its infrared spectrum and gas chromatogram and found to be greater than 99% pure. The sample was stored in a sample tube equipped with a greaseless stopcock, and kept cold in a 2-propanol–dry ice bath.

The microwave spectra were recorded on a Hewlett-Packard Model 8460A MRR spectrometer with a Stark modulation frequency of 33.3 kHz. The sample pressure was maintained between 3 and 20 μ, and the Stark cells were cooled by dry ice while recording the spectrum. The frequencies were measured in the range 18.5–40.0 GHz and the frequency accuracy is estimated to be 0.05 MHz.

The far-infrared spectra of the gas (which was contained in a 10-cm cell) and of the solid were recorded on a Digilab Model 15B FT-IR spectrometer equipped with a mercury arc source, a TGS detector, and a 6.25-μ beam splitter. The spectral region (370–30 cm^{-1}) for the gaseous sample in a 1-m cell was also recorded on a Nicolet Model 8000 Fourier transform interferometer equipped with a vacuum bench, a liquid helium cooled Ge bolometer, and the 12.5- and 25-μ beam splitters. The mid-infrared spectra of the gas and the solid (using a standard low-temperature cell) were recorded on a Digilab Model 14C FT-IR spectrometer equipped with a Ge/KBr beam splitter and a TGS detector. The mid-infrared spectrum of the gas was recorded in a 10-cm path-length cell at a pressure of 2 torr as well as at ambient vapor pressure.

The Raman spectra were recorded on a Cary Model 82 Raman spectrometer equipped with an ITT FW-130 photomultiplier tube and a Spectra Physics Model 171 argon ion laser operating on the 5145-Å line. The spectra of the liquid, sealed in a glass capillary, and the solid were recorded using a laser power of approximately 100 mW at the sample. The spectrum of the solid was obtained by depositing the sample onto a blackened brass plate in a cell equipped with quartz windows. The spectrum of the liquid at 130 K was obtained by cooling the capillary containing the liquid in a Cryogenic Technology Spectrim cryostat equipped with quartz windows. A variable-temperature study in the range from 280 to 130 K for conformer bands in the Raman spectrum of the liquid was also carried out using the cryostat. The Raman spectrum of the gas at ambient vapor pressure was recorded by using the standard Cary multipass cell with 1-W laser power at the sample.

Table I. Predicted and Observed Rotational Constants (MHz) for Some Possible Conformers of Cyclopropyl Isocyanate

	trans	gauche	skew	cis	obsd 1	obsd 2
A	17293	15163	11782	10397	16991	10161
B	1770	1869	2084	2192	1784	2187
C	1703	1777	1975	2117	1716	2106
κ	−0.991	−0.986	−0.978	−0.982	−0.991	−0.980
B + *C*	3473	3646	4059	4309	3500	4293

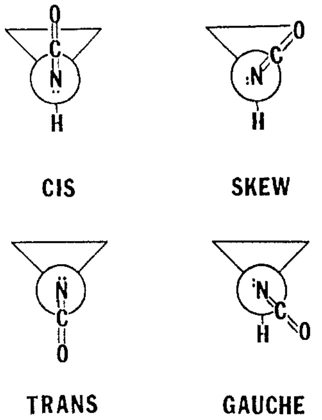

Figure 1. Possible conformations of cyclopropyl isocyanate.

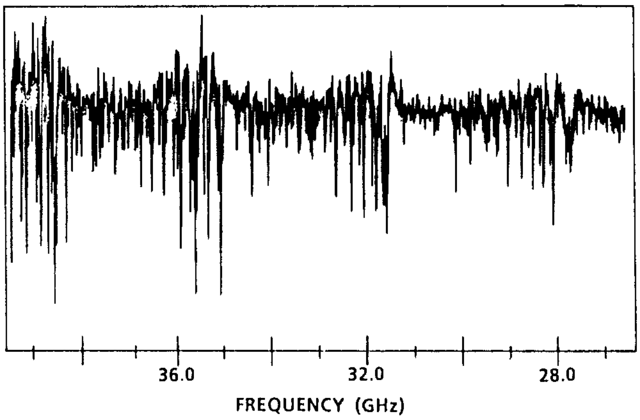

Figure 2. Microwave spectrum of cyclopropyl isocyanate from 26.5 to 39.5 GHz.

Microwave Spectrum

The initial structural parameters for cyclopropyl isocyanate were assumed from those reported for cyclopropyl chloride[6] and vinyl isocyanate[7,8] with a bent NCO group similar to that found[9] in HNCO. The parameters were used to calculate the rotational constants (Table I) for the four possible stable forms (Figure 1) of cyclopropyl isocyanate. The rotational constants thus obtained were used to predict the microwave spectrum for each conformer. The trans and the cis conformers belong to the C_s point group with the symmetry plane containing the NCO moiety and bisecting the cyclopropane ring. The symmetry plane contains the *a* and the *c* principal axes for the trans conformer and the *a* and the *b* principal axes for the cis conformer. Therefore, only *a*- and *c*-type transitions for the trans conformer and *a*- and *b*-type transitions for the cis conformer are expected in the microwave spectrum. The NCO moiety, which is the major contributor to the dipole moment, lies roughly along the *a* principal axis for both the trans and the cis conformers. Therefore, *a*-type transitions separated by approximately the sum of the *B* and *C* rotational constants are expected to be the most intense in the microwave spectrum of both

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Table II. Rotational Constants (MHz), Centrifugal Distortion Constants (kHz), and Moments of Inertia[a] (u Å^2) of *trans*-Cyclopropyl Isocyanate in the Ground State and the Excited States of the Torsion and the CNC Bend

	ground state	$v_{27} = 1$	$v_{27} = 2$	$v_{27} = 3$	$v_{27} = 4$	$v_{16} = 1$	$v_{16} = 2$
A	16991 ± 14	16553 ± 12	16152 ± 15	15749 ± 13	15326 ± 20	17304 ± 16	17518 ± 26
B	1784.303 ± 0.003	1801.781 ± 0.003	1819.609 ± 0.006	1838.584 ± 0.006	1860.173 ± 0.011	1786.870 ± 0.003	1789.644 ± 0.005
C	1716.133 ± 0.003	1724.775 ± 0.003	1734.329 ± 0.006	1745.335 ± 0.006	1758.939 ± 0.011	1719.281 ± 0.003	1722.505 ± 0.004
Δ_J	0.17 ± 0.01	0.27 ± 0.01	0.42 ± 0.02	0.63 ± 0.02	1.16 ± 0.05	0.15 ± 0.01	0.18 ± 0.02
Δ_{JK}	50.8 ± 0.6	39.3 ± 0.6	28.9 ± 1.1	17.8 ± 1.2	−24 ± 2.0	56.4 ± 0.7	66.8 ± 0.9
κ	−0.991	−0.990	−0.988	−0.987	−0.985	−0.991	−0.991
I_a	29.744	30.531	31.289	32.089	32.975	29.206	28.849
I_b	283.236	280.488	277.736	274.874	271.683	282.829	282.391
I_c	294.487	293.012	291.397	289.560	287.320	293.948	293.398
Δ_b	40.995	43.055	44.950	46.775	48.612	40.325	39.856

[a] Conversion factor: 505 379 MHz u Å^2.

these conformers. These conclusions are made on the basis that, for the similar structure of *cis*-ethyl isocyanate,[10] only *a*-type transitions were observed and the dipole moment components from Stark measurements were: $\mu_a = 2.81 \pm 0.02$, $\mu_b = 0.03$, and $\mu_c = 0.0$ D.

The microwave spectrum of cyclopropyl isocyanate recorded in the region 26.5 to 39.5 GHz at a Stark voltage of 1000 V and a gas pressure of 5 μ of Hg is shown in Figure 2. Four series of *a*-type transitions beginning at roughly 28.0, 31.5, 35.0, and 38.5 GHz can be clearly observed in this spectrum. These transitions (labeled "obsd 1" in Table I) have been assigned to the trans conformer since the observed separation of 3.5 GHz is closest to the separation predicted ($B + C = 3.473$ GHz) for the trans conformer. Each of these four series of *a*-type transitions contains several *a*-type main bands. The most intense main band series at approximately 27 997, 31 496, 34 994, and 38 492 MHz has been assigned to the ground state. The remaining main bands, all of which occur at higher frequencies relative to those for the ground state, have been assigned to excited states of the two lowest frequency vibrational modes. The vibrational frequency for the torsional mode is expected to lie below 50 cm^{-1}, and the CNC bending mode has been assigned a frequency of 126 cm^{-1}. Therefore, the main bands for successively higher excited states of the CNC bend are expected to decrease in intensity more rapidly than those for successive torsional excited states. Two series of *a*-type main bands lie relatively close to the main band for the ground state. The series closest to the ground state is observed at 28 040, 31 540, 35 051, and 38 555 MHz, whereas the next series is observed at 28 090, 31 600, 35 110 and 38 620 MHz. These two series have been assigned to the excited state of the CNC bending mode since the intensity of the two series diminishes rapidly from the first series to the second. A third and fourth excited-state series of *a*-type main bands for the CNC bend were also observed but they were quite weak. The separation between the main band for the ground state and the main bands for successively higher excited states of the CNC bend was observed to be fairly constant.

A similarly constant but much larger separation between the ground-state main band and main bands for successively higher excited states of the torsional mode of the trans conformer was observed. The main band series for the first excited torsional state lie at 28 206, 31 730, 35 254, 38 777 MHz. These main bands show a small decrease in intensity relative to the ground-state main bands, and second, third, and fourth excited states of the torsional mode were identified subsequently, by their relatively constant separation and slight decrease in intensity with increasing excited state. It is interesting to note that the intensity of the main bands for the first excited state of the CNC bend was found to be approximately equal to the intensity of the main band for the fourth torsional excited state. The excited-state series for the torsional mode came to an end abruptly after the fourth excited state presumably because the fifth torsional excited state lies above the barrier to internal rotation.

After having identified the *a*-type main bands for the trans conformer in the ground state and the various excited states, the remaining regions were searched carefully for *a*-type main bands due to the cis conformer. Three series of *a*-type transitions were located in the region predicted by using the assumed structure for the cis conformer. Two sets of *a*-type main bands were observed in each of these three series. The first set was observed at 30 042, 34 331, and 38 618 MHz with a separation of approximately 4288 MHz, whereas the second set was observed at 29 746, 33 993, and 38 241 MHz with a separation of approximately 4247 MHz (labeled "obsd 2" in Table I). The separation of these two sets of main bands is closest to the predicted separation ($B + C = 4309$ MHz, Table I) for *a*-type main bands of the cis conformer. Therefore, these two sets of *a*-type main bands have been assigned to the cis conformer. The intensities of these two sets of main bands were found to be almost identical and no additional main bands were located for the cis conformer. Therefore, the ground state and the excited state for the cis conformer have been assigned on the basis of careful intensity measurements and will be discussed later. Undoubtedly, the similar intensities of the two observed states for the cis conformer permit the assignment of the excited state to the low-frequency torsional mode.

Initially, the rotational lines for the three R-branch series $J{+}1_{1,J+1} \leftarrow J_{1,J}$, $J{+}1_{1,J} \leftarrow J_{1,J-1}$, and $J{+}1_{0,J+1} \leftarrow J_{0,J}$ were measured for the ground states and the various excited states of the two conformers. The frequencies of the lines with J values ranging from 7 to 10 for the trans conformer and J values from 6 to 8 for the cis conformer in the various vibrational states for both conformers were fit to the rigid rotor model separately for each state. The good frequency fit obtained in this manner permitted the estimation of the rotational constants for each state from which the entire microwave spectrum of *a*-type R-branch transitions in the region from 18.0 to 40.0 GHz was predicted for each state of the two conformers. With the help of the predicted frequencies, additional lines in the K-band region were located and measured in order to improve on the uncertainty of the rotational constants determined from the fit. Additionally, several $K_{-1} = 2$ lines were identified, measured, and included in the frequency fit. Having included all the measured $K_{-1} = 0$, 1, and 2 lines for the various states of the trans conformer the frequency fit was improved by including the centrifugal distortion terms Δ_J and Δ_{JK} (Table II). The uncertainties in the calculated B and C rotational constants were found to be less than 0.01 MHz (Table II) except for the fourth excited state of the torsion. The statistical uncertainty in the A constant was found to be 12 to 26 MHz (Table II) because of the poor dependence of the *a*-type transitions on the A rotational constant. Similarly, the B and C rotational constants were calculated to within an uncertainty of 0.02 MHz for the two states of the cis conformer by including all of the measured $K_{-1} = 0$, 1, 2 lines in the fit and using the distortion constants Δ_J and Δ_{JK}. The uncertainty in the A constant was found to be rather large (13 and 54 MHz, Table III) for the same reason as stated above. The inclusion of additional centrifugal distortion constants Δ_K, δ_J, and δ_K resulted in an increase in the uncertainty for B and C. Therefore, these constants were excluded from the fits of the various states for the two conformers. Tables of the observed and calculated microwave frequencies for trans and cis c-C_3H_5NCO may be found in the supplementary material.

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Table III. Rotational Contants (MHz), Centrifugal Distortion Constants (kHz), and Moments of Inertia[a] (u Å^2) of *cis*-Cyclopropyl Isocyanate in the Ground State and the First Torsional Excited State

	ground state	$v_{27} = 1$
A	10161 ± 13	10376 ± 54
B	2186.797 ± 0.010	2156.154 ± 0.019
C	2106.242 ± 0.010	2094.606 ± 0.019
Δ_J	1.91 ± 0.06	2.60 ± 0.11
Δ_{JK}	35 ± 2	51 ± 4
κ	−0.980	−0.985
I_a	49.737	48.707
I_b	231.105	234.390
I_c	239.944	241.277
Δ_c	40.898	41.820

[a] Conversion factor: 505 379 MHz u Å^2.

Intensity measurements at room temperature (298 K) and near dry-ice temperature (taken as 213 K) were carried out for the transitions $8_{1,8} \leftarrow 7_{1,7}$, $9_{1,9} \leftarrow 8_{1,8}$, and $9_{0,9} \leftarrow 8_{0,8}$ for the ground state and the first torsional excited state of the trans conformer and for the two states of the cis conformer. This study was made in order to confirm the assignment of the torsional excited state and also to predict the vibrational frequencies for the torsional mode of the two conformers. The following equation was used to calculate the torsional frequency:

$$\nu = -kT \ln (I_1/I_0)$$

where k is the Boltzmann constant, T is the temperature, and I_1 and I_0 are the measured intensities for the same transition of the first excited state and the ground state. The values of ν calculated for the trans conformer were found to be 37, 13, and 22 cm^{-1} at room temperature and 26, 17, and 29 cm^{-1} near dry-ice temperature. Assuming the higher frequency main bands to be due to the ground state of the cis conformer, ν was calculated to be 10, 16, and 13 cm^{-1} at room temperature and 5, 28, and 12 cm^{-1} at 213 K. Therefore, the average torsional frequency determined from these measurements is 24 ± 9 cm^{-1} for the trans conformer and 14 ± 8 cm^{-1} for the cis conformer. Additionally, these measurements indicate that the torsional excited states for the trans conformer lie on the higher frequency side of the ground state, whereas the torsional excited state for the cis conformer lies on the lower frequency side of the ground state. Further evidence for this assignment of the torsional excited state was obtained by computing the rotational constants at internal rotation angles corresponding to the trans and the cis conformer and 5° away from these two forms. These calculations predict the torsional excited state of the two conformers to lie on the correct side relative to the ground state as shown in the microwave data.

In addition to the main bands due to the trans and the cis conformers, a third set of main bands at approximately 19 718, 23 662, 27 605, 31 548, and 35 491 MHz, separated by about 3943 MHz, was observed in the microwave spectrum. These main bands were rather complex and found to be composed of several bands lying relatively close together. Attempts to fit these bands to the rigid rotor model were not successful. These bands may possibly be due to c-C_3H_5NCO molecules in torsional states above the cis–trans barrier or, possibly, an impurity. Since the torsional frequencies are so low and since the torsional excited states cease rather abruptly, the former explanation seems quite reasonable, especially considering that the torsion–rotation coupling would lead to strong deviations from the rigid rotor model. The observed separation of 3943 MHz for this third set of unassigned main bands for cyclopropyl isocyanate lies in between the predicted separation (Table I) for the gauche and the skew conformers, although it is somewhat closer to the skew form. It is even closer to the average separation for the trans and the cis conformers of 3897 MHz which lends confidence to the possibility of c-C_3H_5NCO molecules above the cis-trans barrier.

Dipole Moment

The dipole moment and its components along the principal axes were determined for both conformers of cyclopropyl isocyanate from the quadratic Stark effect. Most of the M components of the $9_{1,9} \leftarrow 8_{1,8}$ transition for the trans conformer and the $7_{1,6} \leftarrow 6_{1,5}$ transition of the cis conformer were measured at Stark voltages in the range from 0 to 1200 V and were input into a program developed by Groner et al.[11] The components μ_b for the trans conformer and μ_c for the cis conformer were assumed to be 0 since they do not lie in the symmetry plane. The Stark coefficients and the dipole moment components calculated from the measured frequencies of the Stark lobes are listed in Table IV.

Table IV. Stark Coefficients (MHz cm^2 V^{-2}) and Dipole Moment Components (Debye) of *trans*- and *cis*-Cyclopropyl Isocyanate

trans			cis		
transition	$\|M\|$	$(\Delta\nu/E^2) \times 10^6$	transition	$\|M\|$	$(\Delta\nu/E^2) \times 10^6$
$9_{1,9} \leftarrow 8_{1,8}$	0	−0.37	$7_{1,6} \leftarrow 6_{1,5}$	0	−0.64
	3	0.32		1	−0.92
	4	0.87		2	−1.78
	5	1.58		3	−3.21
	6	2.43		4	−5.21
	7	3.45		5	−7.77
	8	4.62		6	−10.91
$\|\mu_a\|$	2.56 ± 0.02			2.720 ± 0.004	
$\|\mu_b\|$	0.0 (by symmetry)			0.17 ± 0.01	
$\|\mu_c\|$	0.71 ± 0.03			0.0 (by symmetry)	
$\|\mu_t\|$	2.65 ± 0.02			2.726 ± 0.001	
σ/MHz[a]	0.1			0.08	

[a] Standard deviation in the fit of the Stark lobe frequencies.

Molecular Structure

The rotational constants calculated from the microwave spectra of *cis*- and *trans*-cyclopropyl isocyanate were used to refine the structural parameters. Since the B and the C constants are well determined for both conformers, in principle, only two independent parameters can be determined. The A constant, although not as well determined, was introduced as a constraint on the structural parameters, with a large uncertainty, thereby allowing for estimated values for three structural parameters for both conformers.

The parameters associated with the methylene hydrogen atoms and the secondary hydrogen atom were kept fixed at the values reported for cyclopropyl chloride.[6] The structures reported for isocyanic acid[9] and vinyl isocyanate[7,8] were used to make reasonable assumptions for the structure of the NCO moiety, with a bent NCO group similar to that found in isocyanic acid. The CC distance adjacent to the substituted carbon atom, $r(C_1-C_2)$, can be estimated from the planar moment,[12] and the values calculated were 1.522 Å for the trans conformer and 1.520 Å for the cis form. Since these values are essentially the same as the value (1.520 ± 0.003 Å) obtained for this parameter for cyclopropyl isothiocyanate from an electron diffraction study[4] of this molecule, we fixed the C_1-C_2 bond distance at 1.520 Å and the C_2-C_3 bond distance at 1.515 Å, again the value obtained for this parameter for the corresponding isothiocyanate molecule. It should be noted that these parameters are nearly the same as the corresponding parameters in isocyanocyclopropane.[2]

Finally, it was assumed that the r(C–N) distance should not vary more than 0.01 Å between the two conformers. With these parameters fixed, the r(C–N), ∠CNC, and ∠CCN were initially calculated for both conformers by diagnostic least-squares adjustment as described by Groner et al.[11] The values for the A rotational constants were given an uncertainty 10 times the statistical uncertainties listed in Tables III and V. The initial parameter values were chosen so they would span the known values for these parameters from other similar compounds with the C–N distance taken from the value for this distance in vinyl isocyanate[7] with a sufficient uncertainty to give the value of this parameter found in the corresponding sulfur compound. The results of these calculations are listed in Table V where the indicated uncertainties are the statistical variations. If the difference in the r(C–N)

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Table V. Diagnostic Least-Squares Adjustment of the Structural Parameters of Cyclopropyl Isocyanate and Calculated Rotational Constants (MHz)

parameter	initial value	estimated uncertainty	adjusted value *trans*-C_3H_5NCO	adjusted value *cis*-C_3H_5NCO
$r(C_1-C_2)$, Å	1.520	fixed		
$r(C_2-C_3)$, Å	1.515	fixed		
r(C-H, trans), Å	1.082	fixed		
r(C-H, cis), Å	1.086	fixed		
$r(C_1$-H, sec), Å	1.079	fixed		
∠HCH, deg[a]	116.2	fixed		
r(N=C), Å	1.210	fixed		
r(C=O), Å	1.170	fixed		
∠NCO, deg	172.6	fixed		
$r(C_1-N)$, Å	1.382	±0.030	1.417 ± 0.010	1.407 ± 0.014
$\angle C_1NC$, deg	135.0	±5.0	136.9 ± 3.8	138.6 ± 1.3
$\angle C_2C_1N$, deg	118.7	±3.0	117.9 ± 1.1	120.3 ± 2.4
$\angle C_2C_1H$, deg	116.1	fixed		

molecule	rotational constant	exptl value	calcd value	Δ
trans-C_3H_5NCO	*A*	16991	17390	-399
	B	1784.303	1784.301	0.002
	C	1716.133	1716.135	-0.002
cis-C_3H_5NCO	*A*	10161	10282	-121
	B	2186.797	2186.798	-0.001
	C	2106.242	2106.241	0.001

[a] The HCC angles utilized were the same as those from ref 6.

between the two conformers were permitted to be 0.020 Å then the difference in the C_2C_1N angle between the two conformers became larger, but the C_1NC angle remained essentially the same. It is interesting to note that for the cis conformer the major uncertainty is for the ∠CCN, whereas for the trans conformer the major uncertainty is for ∠CNC. If the assumed heavy atom structural parameters for the ring are near to the actual values, then the determined parameters should be good estimates of the actual values for cyclopropyl isothiocyanate. In fact, because of the relationship between the $C_1C_2(C_3)$ and C_2C_3 distances where an elongation of the $C_1C_2(C_3)$ bond results in a contraction of the C_2C_3 bond, the determined parameters do not change appreciably with changes in the assumed heavy atom structural parameters of the ring.

Vibrational Assignment

The presence of the cis and the trans conformers of cyclopropyl isocyanate in the gas phase was confirmed by the microwave study. Both of these forms have C_s molecular symmetry, wherein the NCO moiety bisects the plane of the cyclopropane ring. The 27 normal vibrations for these two conformers span the irreducible representations: $16A' + 11A''$. The A' vibrations for both these conformers must give rise to polarized bands in the Raman spectra of the fluid phases, whereas A'' vibrations must be depolarized. The plane of symmetry for the trans form contains the *a* and *c* principal axes, and therefore A' vibrations for this conformer will give rise to A, C, or A/C hybrid infrared band contours in the gas phase, whereas A'' vibrations must have B-type contours. However, for the cis conformer, the symmetry plane contains the *a* and *b* axes so infrared bands arising from A' vibrations must have A, B, or A/B hybrid band contours, whereas A'' vibrations are expected to have C-type contours. Thus, the infrared band contours, Raman depolarization data, and group frequencies provided the basis for the assignment of the fundamental modes. For the cyclopropyl moiety, the fundamental frequencies reported for cyclopropylcarbonyl halides (X = F, Cl),[13,14] cyclopropyl halides (X = Cl, Br, I),[15-17] cyclopropylamine,[18] and cyclopropyl isothiocyanate[19] have provided a useful comparison for the present assignments. In several instances, a revised vibrational assignment for these molecules has been utilized.[20] For the isocyanate moiety the frequencies reported for the methyl,[21] ethyl,[21] isopropyl,[21,22] allyl,[23] germyl,[24] and silyl[25] derivatives of isocyanic acid were used for comparison. (A complete listing of observed vibrational

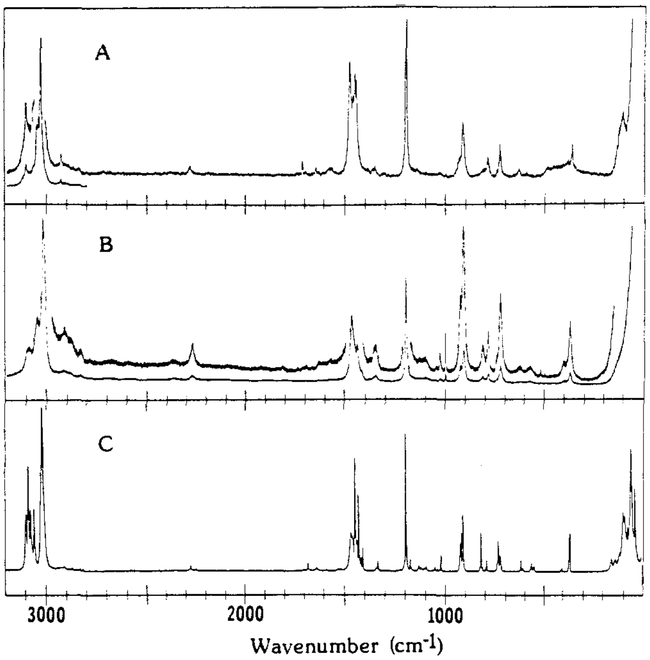

Figure 3. Raman spectra of gaseous (A), liquid (B), and solid (C) cyclopropyl isocyanate.

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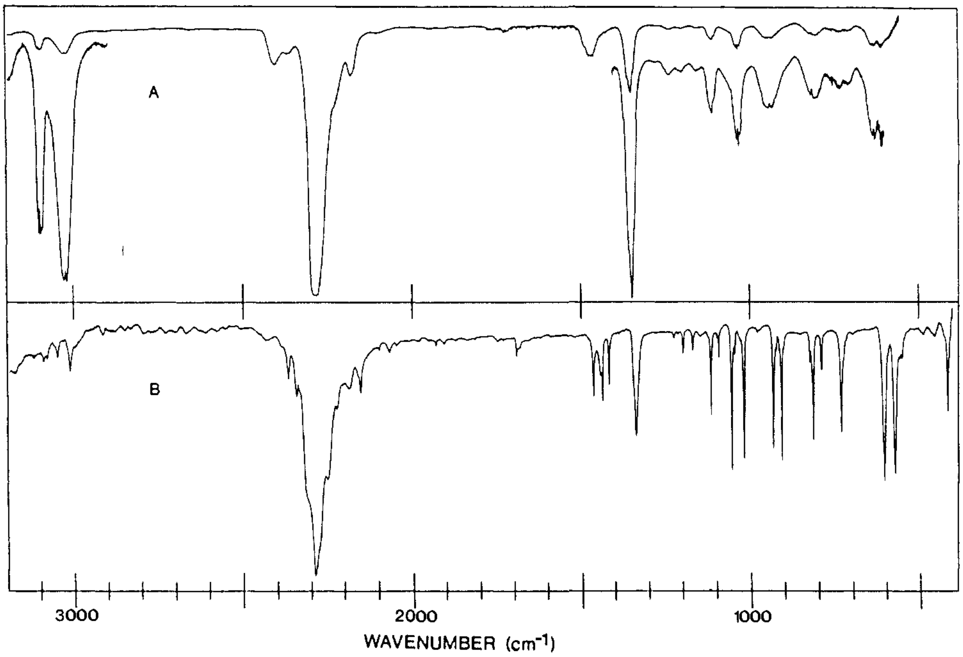

Figure 4. Mid-infrared spectra of gaseous (A) and solid (B) cyclopropyl isocyanate. The gas spectrum was taken at a pressure of 2 torr.

frequencies is available in the supplementary material for this article.)

Carbon–Hydrogen Modes. The Raman spectrum of the gas (Figure 3) contains four bands in the CH stretching region at 3107, 3054, 3044, and 3034 cm^{-1}. The bands at 3054 and 3044 cm^{-1} have been assigned as conformer bands for the CH(X) stretch. They appear at 3060 and 3055 cm^{-1} in the Raman spectrum of the unannealed solid (not shown). The solid was annealed by warming it to successively higher temperatures followed each time by cooling to liquid N_2 temperature, and the intensities of these two bands in the Raman spectrum were monitored. On repeatedly annealing the solid, the 3060-cm^{-1} band was observed to grow gradually weaker relative to the 3055 cm^{-1} band. However, after the sample was warmed to the temperature where it was completely annealed, the 3055-cm^{-1} band disappeared and only the 3060-cm^{-1} band remained. The Raman spectrum of the annealed solid contained sharp bands due to the lattice modes in the low-frequency region in contrast to the broad and ill-defined bands observed in this region for the unannealed solid. Therefore, it was concluded that despite the fact that the spectral evidence for the fluid phases and the unannealed solid phase indicated that the trans conformer is the more stable form, the Raman spectrum of the annealed solid suggests that the cis conformer is the preferred form in the crystalline state. That the cis conformer of this molecule is the conformer remaining in the annealed solid phase is further documented by "tracking" the bands associated with the CH_2 out-of-phase twist and the NCO out-of-plane bend (see Discussion) from the gas phase through the liquid phase, unannealed solid, and annealed solid phases. By virtue of the different principal axes lying in the symmetry plane of the cis and trans conformer, these two modes give rise to B-type bands for the trans conformer and C-type bands for the cis conformer, respectively. Only the peaks associated with the C-type bands for these modes are the ones which remain in the annealed, polycrystalline solid. In addition, the energy difference between these two conformers in the various phases appears to be quite small as indicated by the intensity measurements in the microwave spectrum, the ΔH study in the liquid, and the difficulty encountered in annealing the solid. The remaining two bands in the Raman spectrum of the gas at 3107 and 3034 cm^{-1} have been assigned to the antisymmetric CH_2 stretches and the symmetric CH_2 stretches, respectively. The 3107-cm^{-1} band splits into two bands in the Raman spectrum of the liquid (not shown) at 130 K. The 3102-cm^{-1} band in the liquid which appears as a shoulder at 130 K has been assigned to the trans conformer, but the corresponding band in the Raman spectrum of the unannealed solid could not be distinguished from the bands due to the cis conformer. Among the three bands that appear in the symmetric CH_2 stretching region in the Raman spectrum of the unannealed solid, the lowest frequency band at 3013 cm^{-1} disappears as the solid is annealed and therefore it has been assigned to the trans conformer.

The bands at 1456 and 1449 cm^{-1} in the Raman spectrum of the gas have been assigned as conformer bands for the in-phase CH_2 deformation. They appear at 1443 cm^{-1} as a polarized band in the liquid and at 1450, 1442, 1437, and 1433 cm^{-1} in the Raman spectrum of the unannealed solid. The 1449-cm^{-1} band in the gas phase has been assigned to the trans conformer based on the fact that the 1437-cm^{-1} band in the unannealed solid disappears as it is annealed (Figure 3). The weak, depolarized shoulder at 1423 cm^{-1} in the Raman spectrum of the liquid has been assigned to the out-of-phase CH_2 deformation. The weak Q-branch at 1422 cm^{-1}, corresponding to this shoulder, in the mid-infrared spectrum of the gas (Figure 4) has been assigned to the cis conformer. For the trans form, this mode is expected to give rise to a B-type band which is presumably too weak to be observed. However, a frequency of 1391 cm^{-1}, corresponding to a very weak band in the Raman spectrum of the gas (Figure 3) has been assigned to the trans conformer. The band at 1417 cm^{-1} in the Raman spectrum of the unannealed solid disappears as the solid is annealed, and therefore it has been associated with the 1391-cm^{-1} band in the gas.

Conformer bands for the in-plane CH bending mode have been observed in several monosubstituted cyclopropane derivatives since this motion is quite sensitive to the orientation of the substituent. The Raman spectrum of cyclopropyl isocyanate in the gaseous phase contains conformer bands for this mode at 1368 and 1355 cm^{-1}. The Raman spectrum of the liquid at room temperature contains only one broad, polarized band at 1355 cm^{-1}. However, upon cooling the liquid to 130 K, this band clearly resolves into two bands at 1362 and 1342 cm^{-1}. The Raman spectrum of the unannealed solid contains five bands in this region. The two higher frequency bands disappear as the solid is annealed, and therefore they have been assigned to the trans conformer. Based on this evidence the higher frequency bands at 1368 cm^{-1} in the gas and at 1362 cm^{-1} in the liquid have been assigned to the trans conformer. The very weak, depolarized band at 1101 cm^{-1} in the Raman spectrum of the liquid has been assigned to the out-of-plane CH bend. The mid-infrared spectrum of the gas contains two shoulders on the 1106-cm^{-1} band at 1115 and 1101 cm^{-1}. Assuming these two shoulders to be due to the R and P branches of a B-type band, the band center for this band is expected to appear as a minimum at 1108 cm^{-1}. The 1106-cm^{-1} band has been assigned as a C-type band, although the band contour evidence for the gas obtained in the present study is not very conclusive.

The out-of-phase CH_2 twist has been assigned to a very weak, depolarized shoulder at 1174 cm^{-1} in the Raman spectrum of the liquid. The mid-infrared spectrum of the gas contains weak features in this region. The band at 1175 cm^{-1} appears to be an R branch due to a B-type band centered at ~1171 cm^{-1} with a Q branch nearby at 1172 cm^{-1}, presumably due to a C-type band. The lower frequency band of the two bands at 1176 and 1170 cm^{-1} in the Raman spectrum of the unannealed solid disappears as the solid is annealed, and therefore it has been assigned to the trans conformer along with the type-B band. The in-phase CH_2 twist gives rise to a polarized Raman band at 1134 cm^{-1} in the liquid. Among the three Raman bands at 1134, 1123, and 1118 cm^{-1}, the lowest frequency band disappears as the solid is annealed and it has been assigned to the trans conformer. The infrared spectrum of the gas contains a distinct weak band at 1152 cm^{-1}, assigned as the R branch of a B-type band centered at 1147 cm^{-1} and a sharp Q branch at 1141 cm^{-1} assigned as a C-type band. The 1141-cm^{-1} band has been assigned to the trans conformer and therefore must shift down to a considerably lower frequency of 1118 cm^{-1} in the unannealed spectrum of the solid (Figure 3).

The out-of-phase CH_2 wag has been assigned to a very weak depolarized band at 1052 cm^{-1} in the Raman spectrum of the liquid. Among the four bands observed in this region in the Raman spectrum of the unannealed solid, only the 1050-cm^{-1} band disappears as the solid is annealed, and it has therefore been assigned to the trans conformer. Bands at 1034 and 1006 cm^{-1} in the Raman spectrum of the gas appear as polarized bands at 1032 and 1005 cm^{-1} in the liquid and have been assigned as conformer bands for the in-phase CH_2 wag. These two bands appear at 1035 and 1020 cm^{-1} in the Raman spectrum of the unannealed solid. The higher frequency band of the two disappears as the solid is annealed; therefore it has been assigned to the trans conformer.

The Raman spectrum of the liquid contains a depolarized band at 819 cm^{-1} and a polarized band at 728 cm^{-1} which have been assigned to the out-of-phase and the in-phase CH_2 rocks, respectively. The mid-infrared spectrum of the gas contains a distinct minimum at 812 cm^{-1} corresponding to the center of a B-type band which has been assigned to the trans conformer. The band contour in this region does not reveal any distinct features on top of the broad band at 801 cm^{-1} in order to locate the C-type Q branch for the cis conformer. Conformer bands for the CH_2 in-phase rock have been assigned to the 797- and 792-cm^{-1} bands in the Raman spectrum of the gas. They appear at 791 cm^{-1} in the liquid as a polarized band and at 798 and 794 cm^{-1} in the Raman spectrum of the unannealed solid. The 798-cm^{-1} band has been assigned to the trans conformer since it disappears as the solid is annealed (Figure 3).

Skeletal Modes. The antisymmetric NCO stretch gives rise to very strong bands in the mid-infrared spectra and appears as a weak, polarized band at 2278 cm^{-1} in the Raman spectrum of the liquid. The Raman spectrum of the unannealed solid contains three bands in this region at 2282, 2269, and 2255 cm^{-1}. The 2269-cm^{-1} band disappears as the solid is annealed; therefore it has been assigned to the trans conformer. Bands at 1482 and 1465 cm^{-1} in the Raman spectrum of the gas appear at 1471 cm^{-1} as a polarized band in the liquid and have been assigned to the symmetric NCO stretch. The bands at 1471 and 1463 cm^{-1} in the Raman spectrum of the annealed solid have been associated with the 1465-cm^{-1} band in the gas and assigned to the cis form. Consequently, the 1482-cm^{-1} band in the gas has been assigned to the trans conformer despite the fact that the corresponding band in the Raman spectrum of the unannealed solid could not be distinguished from the bands assigned to the cis form.

The ring breathing mode gives rise to a single strong band in the Raman spectra of all three phases. A weak, B-type band centered at 1202 cm^{-1} in the mid-infrared spectrum of the gas has been assigned to the cis conformer, whereas a weak Q branch at 1194 cm^{-1} has been assigned as a C-type band for the trans form. The depolarized band at 932 cm^{-1} in the Raman spectrum of the liquid has been assigned to the antisymmetric ring deformation. The B-type band centered at 936 cm^{-1} and the C-type Q branch at 930 cm^{-1} in the mid-infrared spectrum of the gas have been assigned to the trans and the cis conformers, respectively. The mid-infrared spectrum of the gas contains a broad band at 923 cm^{-1} in between the 927- and 918-cm^{-1} bands. This band has been assigned to the symmetric ring deformation for both conformers since the spectral evidence did not reveal the presence of two identifiable conformer bands. The B-type band centered at 717 cm^{-1} appears to have a rather sharp and strong R branch at 729 cm^{-1} suggesting, perhaps, that it contains a Q branch at 729 cm^{-1} as well. The Raman spectrum of the unannealed solid contains bands at 736, 730, and 725 cm^{-1}. The band at 730 cm^{-1} disappears as the solid is annealed; therefore it has been assigned to the CN stretch for the trans conformer.

The A-type band at 630 cm^{-1} and the B-type band centered at 619 cm^{-1} (Figure 4) have been assigned to the trans and the cis conformers, respectively. They appear at 635 and 623 cm^{-1} in the Raman spectrum of the gas and at 617, 611, and 606 cm^{-1} in the Raman spectrum of the unannealed solid. The 611-cm^{-1} band disappears from the spectrum upon annealing, and therefore it has been associated with the trans conformer. The out-of-plane NCO bend has been assigned to the B-type band centered at 591 cm^{-1} and a C-type Q branch at 572 cm^{-1} for the trans and the cis conformers, respectively. Among the four bands in this region in the Raman spectrum of the unannealed solid, the two higher frequency bands disappear as the solid is annealed and have therefore been associated with the trans conformer.

The out-of-plane CCN bend has been assigned to the depolarized band at 416 cm^{-1} in the Raman spectrum of the liquid. The C-type Q branch at 418 cm^{-1} and the B-type band centered at 410 cm^{-1} have been assigned as conformer bands for this mode. Conformer bands for the in-plane CCN bend have been assigned to the 388- and 367-cm^{-1} bands in the Raman spectrum of the gas. The A-type band in the far-infrared spectrum (Figure 5) with R and P branches at 370 and 360 cm^{-1}, respectively, contains two sets of Q branches. The ones at 367 and 366 cm^{-1} are sharp and more akin to C-type Q branches and have been assigned to the cis form, whereas the Q branches at 364 and 363 cm^{-1} are broader and have been assigned to the trans form.

The CNC in-plane bend has been assigned to a B-type band centered at 126 cm^{-1}. The fundamental frequency of the out-of-plane CNC bend estimated from the intensity measurements in the microwave spectrum is too low to be observed in the vibrational spectra. However, this band is expected to move up to a higher frequency upon solidification and has therefore been assigned to the 61-cm^{-1} band in the Raman spectrum of the solid.

A comparison of the assigned vibrational frequencies of cyclopropyl isocyanate with those of cyclopropyl isothiocyanate is provided in Table VI. With the exception of the CN stretch and the obvious modes associated with the oxygen for sulfur substitution in the NCX moiety, the frequencies clearly match up very well. In fact, since the CN bond length in cyclopropyl isocyanate is shorter than that in cyclopropyl isothiocyanate, it should not be unexpected that the CN stretch for this molecule is substantially (~100 cm^{-1}) higher in frequency than that for the sulfur compound. Both of these factors argue for stronger conjugation between the NCO and cyclopropyl moieties than for the NCS and ring fragments.

ΔH in the Liquid

In order to determine the enthalpy difference between the trans and the cis conformers of cyclopropyl isocyanate, a Raman temperature study was carried out for the liquid. The bands assigned to the in-phase CH_2 wag for each conformer are the only well-separated conformer band pair in the Raman spectrum of the liquid at room temperature and, therefore, they were chosen for this study. Assuming the areas of the conformer bands to be temperature dependent, the enthalpy difference (ΔH) was obtained

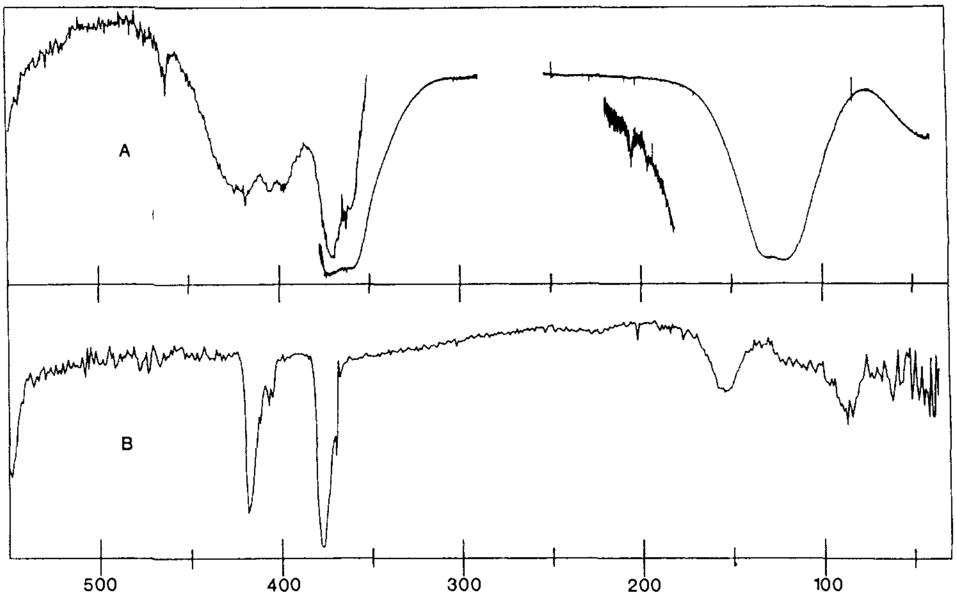

Figure 5. Far infrared spectra of gaseous (A) and solid (B) cyclopropyl isocyanate.

Table VI. Comparison of Vibrational Frequencies (cm^{-1}) for the Cyclopropyl Psuedohalides

	mode	c-C_3H_5NCS[a]	c-C_3H_5NCO[b]
A′	CH_2 antisymmetric stretch	3100	3102 (3090)
	CH(X) stretch	3041	3044 (3052)
	CH_2 symmetric stretch	3016	3013 (3024)
	NCX antisymmetric stretch	2121	2269 (2278)
	NCX symmetric stretch	1008	1482 (1471)
	CH_2 deformation	1448	1449 (1443)
	CH bend	1351	1362 (1342)
	ring breathing	1209	1194 (1200)
	CH_2 twist	?	1118 (1134)
	CH_2 wag	1031	1032 (1005)
	ring deformation	851	915
	CH_2 rock	770	797 (792)
	CX stretch	620	728 (717)
	NCX bend	454	627 (623)
	CCX bend	351	376 (378)
	CNC bend	96	107
A″	CH_2 antisymmetric stretch	3086	3102 (3090)
	CH_2 symmetric stretch	3016	3013 (3024)
	CH_2 deformation	1416	1391 (1423)
	CH_2 twist	1170	1174
	CH bend	1090	1101
	CH_2 wag	1046	1050 (1052)
	ring deformation	913	936 (932)
	CH_2 rock	814	819 (823)
	NCX bend	525	591 (573)
	CCX bend	391	410 (416)
	CNC bend	?	61

[a] These frequencies were taken from ref 3 and 19. [b] This work. The frequencies quoted in brackets are for the cis conformer.

from the slope of the plot of $-\ln K$ vs. T^{-1} by using the equation:

$$-\ln K = (\Delta H/RT) - (\Delta S/R)$$

where K is the ratio of the areas of the conformer bands (A cis/A trans) at temperature T, R is the gas constant, and ΔS is the entropy difference. The area ratio was used instead of an intensity ratio because the band due to the cis form was considerably narrower than the one due to the trans conformer. The spectrum of these two bands was recorded five times for each temperature, at 16 temperatures (ranging from 7 to −143 °C) at intervals of 10 °C. The average area ratio was used in the calculations. From the slope of the plot, ΔH was determined to be 111 cal/mol (39 ± 5 cm^{-1}), with the trans form being more stable, and ΔS has a value of 0.042 ± 0.017 eu for the liquid.

Discussion

In the present study, the rotational constants of the trans and the cis forms of cyclopropyl isocyanate have been obtained from the microwave spectrum. The structures determined from the rotational constants allow for a longer C–N distance and a smaller CCN angle in the trans form as compared to the cis form, with similar CNC and NCO angles in both forms. An improved structure could probably be obtained if the rotational constants together with the difference in the ring C–C distances predicted by ab initio calculations were used as constraints in a structure determination by electron diffraction similar to the procedure used for cyclopropyl isothiocyanate.[4] When these three techniques are combined, the resulting geometry is perhaps the best accessible without extensive isotopic studies.

In comparing the calculated structural parameters for c-C_3H_5NCO to those of c-C_3H_5NCS it is found that the CN distance is longer for both conformers of the NCO compound than for the corresponding conformers of the NCS compound. This no doubt arises from different effective conjugation of the NCX moiety with the cyclopropane ring with the sterically smaller oxygen atom. This conclusion is also corroborated by smaller CNC angles in the isocyanate molecule than in the isothiocyanate compound.

From intensity measurements in the microwave spectrum, the separation between the ground and the first torsional excited state has been calculated to be 24 ± 9 and 14 ± 8 cm^{-1} for the trans and the cis conformers, respectively. Assuming an equidistant separation between subsequent torsional excited states, a torsional potential function can be proposed to accommodate the four torsional excited states for the trans conformer and one excited state for the cis. The values of ΔH and the barriers to internal rotation of the trans and the cis conformers estimated from this potential function are 92, 120, and 28 cm^{-1}, respectively, but there is a considerable margin of error in these values. The region where torsional bands are expected to appear in the far-infrared spectrum of the gas contains a broad and weak band centered at approximately 35 cm^{-1}. However, this band does not have any identifiable B- or C-type contour due to the trans or the cis conformers, respectively. From the variable-temperature Raman study, the trans conformer has been determined to be more stable in the liquid phase also, but only by 39 ± 5 cm^{-1}. In the solid phase, however, the Raman data indicate that the energy of the cis conformer is lower than that of the trans. A plausible explanation for this may be that the somewhat spherical structure of the cis conformer as opposed to the more linear trans form is preferred in the crystal. The splittings of the Raman bands for the solid indicate that the cis conformer contains more than one molecule per unit cell.

The infrared and Raman spectra of cyclopropyl isocyanate have been investigated in detail. The band contours for the two conformers calculated from the experimental rotational constants do not differ significantly. Furthermore, since most structural parameters in the trans and the cis forms are found to be similar, their vibrational spectra of the fluid phases are also expected to be similar, resulting in a severe overlap of bands. Therefore, it is very difficult to find convincing evidence for the presence of more than one conformer in the vibrational spectra without the help of high-resolution infrared spectra of the gas. A similar situation was found for cyclopropyl isothiocyanate where the vibrational analysis[19] preceded the microwave study,[3] and it could justify the presence of only the cis conformer, whereas the microwave data clearly proved that both the cis and trans forms exist in the gas phase. Subsequently, from the electron diffraction results[4] it was found that the trans form is 72% abundant at 35 °C temperature in the gas phase. In the present study a complete vibrational assignment has been proposed for the normal modes of cyclopropyl isocyanate, and conformer bands have been assigned for several of these modes.

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Supplementary Material Available: Tables of rotational and vibrational frequencies and their assignments (7 pages). Ordering information is given on any current masthead page.

The Continuously Rotated Cellular Reactor

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Abstract: Cells are created in liquids in the annular gap between concentric cylinders when the inner cylinder is rotated—the Taylor vortex. The continuously rotated cellular reactor, CRCR, is the development of this phenomenon into a practical reactor with reaction localized in individual cells. The reaction locus is selectable by reactant concentration and stoichiometry. Reaction time is inversely proportional to the cylinder rotation frequency. A column of cells with discrete pH values is developed by the neutralization of HCl with NaOH in 2 h. A robust pH column is prepared with phosphate buffer solutions. Molecular transport in the CRCR is given by the Gaussian equation $\langle \bar{n} - {}^1/_2 \rangle = 4\pi DFt/d^2F_c$, where $\bar{n}$ is the mean cell number, d (cm) the gap radius, F (Hz) the inner cylinder and F_c the critical Taylor frequency, t (s) the time, and D (cm^2/s) the molecular diffusion constant. Potential applications are mentioned.

A simple apparatus is introduced which provides spatial and temporal control of solution reactions and the potential for molecular selectivity. The continuously rotated cellular reactor (CRCR) is the equivalent of the continuously stirred tank reactor[1] but is generated in a *single* vessel. The CRCR depends on the phenomenon of the Taylor vortex.[2,3]

The Taylor vortex is generated in a liquid in the annular gap ($d = b - a$ cm) between a rotating (F Hz) inner cylinder (o.d. $= 2a$ cm) and a stationary outer cylinder (i.d. $= 2b$ cm). The vortex motion creates cells of uniform height ($\sim d$ cm),[3,4] in which the fluid spirals helically as it rotates about the inner cylinder. The vortices are counterrotating in adjacent cells, and the angular momentum in the vertical plane changes sign at the cell boundaries (Figure 1).[5] The boundaries are sharp and horizontal provided $F_c < F < \sim 10F_c$, where F_c is the critical frequency for onset of the Taylor vortex.[3,6] Uniform rotation maintains the basic cellular form and motion indefinitely. Each cell contains a central core whose rotation is unperturbed by the surrounding liquid.[5,7] The phenomena of stable liquid cells containing unmixed cores led us to explore the practical potential of a reactor based on vortex motion.

A CRCR was constructed from a 100-mL graduated cylinder, a 1-cm Truebore stirrer centrally located with ground glass joints, and an overhead stirrer operating at 0.5–3 Hz. For water in the CRCR, F_c was calculated (see Experimental Section) to be 0.247 Hz. Samples were added and removed by syringe through a sidearm. The operation of the CRCR is illustrated by the generation of a column of pH cells from HCl, NaOH, and indicator (Figure 2). A more robust pH column can be generated rapidly by combining solutions of H_3PO_4, Na_3PO_4, and pH 7 phosphate buffer at 1 Hz for 10 min and the pH profile maintained for 5–10 h at 0.5 Hz (Figure 3).

Key qualitative features are the following: (1) Sharp cell boundaries can be maintained for hours between reactive solutions differing in concentration by 10 orders of magnitude. (2) Reaction is localized to the cells immediately adjacent to the reaction interface. (3) The location of the reaction interface is established rapidly (<5 min) and is selected by concentration, stoichiometry, and diffusion constant. For equimolar acid/base solutions, the interface occurs at the column center. (4) Reaction time is inversely proportional to F and so may be selected. (5) Reagents can be added to or removed from any point in the column by syringe while maintaining the cellular structure. (6) Density differentials can be tolerated as shown in Figure 2 where the denser base solution is located between the less dense acid layers. When the stirrer is stopped, the base layer flows to the bottom of the

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(6) (a) Walowit, J.; Tsao, S.; DiPrima, R. C. *Appl. Mech.* **1964**, *31*, 585–93. (b) DiPrima, R. C.; Eagles, P. M.; Ng, B. S. *Phys. Fluids* **1984**, *27*, 2403–2411. (c) Dominguez-Lerma, M. A.; Ahlers, G.; Cannell, D. S. *Phys. Fluids* **1984**, *27*, 856–860. The critical values of ref 6a–c and the equation in ref 5 agree within 0.5%.

(7) Marcus, P. S. *J. Fluid Mech.* **1984**, *146*, 65–113.