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Vibrational and Conformational Studies of Cyclopropanecarboxaldehyde

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The infrared (3500 to 40 cm^{-1}) and Raman (3200 to 20 cm^{-1}) spectra have been recorded for gaseous and solid cyclopropanecarboxaldehyde, $c-C_3H_5CHO$. Additionally, the Raman spectrum of the liquid has been recorded and qualitative depolarization values have been obtained. It has been determined that the conformer with the oxygen atom *cis* to the three-membered ring is the more stable form at ambient temperature in the gaseous phase but in the liquid phase the *trans* is more stable and is the only conformer present in the spectra of the solid. From a temperature study of the Raman spectrum of the liquid an energy difference of 405 ± 20 cm^{-1} (1.16 kcal/mol) was obtained whereas the energy difference for the gaseous state was found to be approximately 60 cm^{-1}. The observed changes in ΔH in going from the gas to the liquid state indicate strong intermolecular association in the condensed phases which can account for the *trans* being more stable in the liquid and the stable conformer in the solid state. The asymmetric torsion of the *trans* conformer was observed in the far infrared spectrum as a type B band centered at 126 cm^{-1} and the corresponding torsion for the *cis* conformer was observed at 113 cm^{-1} as a type C band with six accompanying hot bands falling at lower frequencies. From these data the potential function for internal rotation of the asymmetric top has been determined and the following potential constants have been evaluated: $V_1 = 61 \pm 6$, $V_2 = 1494 \pm \pm 15$, $V_3 = -7 \pm 6$, and $V_4 = -39 \pm 6$ cm^{-1}. The calculated *trans* to *cis* and *cis* to *trans* barriers were determined to be equivalent with a value of 1521 cm^{-1}. A complete vibrational assignment is proposed for both conformers based on infrared band contours, depolarization values, and group frequencies. These results are compared to similar quantities in several related molecules.

INTRODUCTION

We have recently been investigating the vibrational spectra of carbonyl containing cyclopropane derivatives and the simplest of these derivatives is cyclopropanecarboxaldehyde, $c-C_3H_5CHO$, the conformational behavior of which has been the subject of several previous studies.[1-4] However, there do not appear to be any previous vibrational studies of this molecule and there is still a question concerning the more stable conformer. Bartell and coworkers[1] carried out an electron diffraction study of cyclopropanecarboxaldehyde at ambient temperature and concluded that in the gas phase there are two conformeric species of almost equal abundance. In their analysis of the radial distribution curve three basic types of conformers (*cis, trans* and *gauche*) were considered; however the mixture of conformers which best reproduced the observed radial distribution curve, regardless of the *gauche* dihedral angle, was the one consisting of 55% *cis* and 45% *trans*. The reported uncertainties in these quantities were 10%, but the data clearly indicates a nearly equal distribution of the two forms. Additionally, a lower limit to the barrier to internal rotation was estimated to be 2.5 kcal/mol.

From a microwave study of cyclopropanecarboxaldehyde, Volltrauer and Schwendeman[2] reported that the conformer with the oxygen atom *trans* to the three-membered ring is more stable by 10 ± 20 cm^{-1} (29 ± 52 cal/mol) than the species which has the oxygen atom *cis* to the three-membered ring. Additionally, the authors estimated the asymmetric torsional frequencies for the *trans* and *cis* conformers to be 123 ± 2 and 112.6 ± 4 cm^{-1}, respectively, and determined the values of the first three coefficients of a Fourier expansion of the torsional potential to be: $V_1 = -80 \pm 40$ cm^{-1}, $V_2 = 1535 \pm 140$ cm^{-1} and $V_3 = 96 \pm 35$ cm^{-1}. This potential function gave a *trans* to *cis* barrier of 4.43 ± 0.41 kcal/mol and a *cis* to *trans* barrier of 4.38 ± 0.41 kcal/mol, but the authors pointed out that the barrier uncertainties must be interpreted cautiously because the potential function was calculated assuming that the V_4 and higher terms in the Fourier expansion were zero.

More recently, an SCF-LCAO-MO calculation[3] was carried out on cyclopropanecarboxaldehyde from which it was determined that the *cis* conformation was energetically preferred over the *trans* species by 0.80 kcal/mol. Thus, different structural studies including electron diffraction, microwave and theoretical calculations have been carried out for the identification of the rotational isomers of cyclopropanecarboxaldehyde; however, when one considers the inherent experimental error in the aforementioned methods, considerable controversy still exists regarding the gas phase thermodynamically preferred conformation.

By direct observation of the torsional transitions with the associated »hot bands« in the far infrared spectrum of the gas phase, one can frequently determine the barriers to internal rotation for molecules with asymmetric tops.[5] Therefore, we have investigated the low frequency infrared spectrum of gaseous cyclopropanecarboxaldehyde at ambient temperature in order to determine the frequencies of the torsional transitions for the *trans* and *cis* conformers from which it was hoped that the torsional potential function could be more accurately determined and a definitive determination of the more stable conformer obtained. Additionally, since no previous vibrational studies have been reported, we are reporting a complete vibrational assignment for the gas, liquid and solid phases of cyclopropanecarboxaldehyde. The results of this infrared and Raman study are reported herein.

EXPERIMENTAL

The sample of cyclopropanecarboxaldehyde used in the present study was prepared by the oxidation of cyclopropylcarbinol (Aldrich Chemical Co.) using a method previously described in the literature.[6] Preparation and sample handling were carried out under vacuum. Purification was accomplished by using a low temperature vacuum fractionation column. The purity of the sample was checked by recording the mid-infrared spectrum of the gas phase and comparing it to the mid-infrared spectrum of the liquid which had been previously recorded.[7]

The Raman spectra were recorded on a Cary model 82 spectrophotometer equipped with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. Liquid samples were sealed in Pyrex capillaries. The variable temperature experiments were carried out in a cell similar to the one described by Miller and Harney,[8] while the spectrum of the solid phase was obtained by depositing the sample onto a blackened brass plate cooled by boiling nitrogen and contained in a cell fitted with quartz windows.

Mid-infrared spectra of the gas and solid from 3500 to 400 cm^{-1} were obtained using a Digilab model FTS-14C Fourier transform interferometer equipped with a Ge/KBr beamsplitter and a TGS detector. Far infrared spectra (450 to 80 cm^{-1}) of the gas, amorphous and annealed solids were obtained using a Digilab model FTS-15B Fourier transform interferometer equipped with a 6.25 μm Mylar beamsplitter and a TGS detector. The far infrared spectrum from which the frequencies of the asymmetric torsion were taken was recorded on a Nicolet 8000 interferometer equipped with a vacuum bench and a liquid helium cooled Ge bolometer containing a wedged sapphire filter and polyethylene windows. A 12.5 μm Mylar beamsplitter was employed and the sample was contained in a 1m cell.

THERMODYNAMIC STABILITY AND CONFORMATIONAL ENERGY DIFFERENCE

Because both the *cis* and *trans* rotamers of cyclopropanecarboxaldehyde are of C_s symmetry, two separate experiments must be carried out in order to determine the magnitude of the enthalpy difference separating the two conformations as well as which rotamer is thermodynamically preferred in the gas, liquid and solid phases. Although variable temperature experiments carried out in the gas and liquid phases allow us to determine the magnitude of ΔH ($\sim \Delta E$), they do not allow a conclusive decision as to which conformer is thermodynamically preferred unless an assignment of an individual fundamental to both the *cis* and *trans* conformers is possible. An assignment of the above nature can be made for cyclopropanecarboxaldehyde by employing experiments similar to those carried out by Mizushima and others.[9-11] They have shown that the rotamer which has the larger dipole moment will become progressively more stable as the dielectric constant of the medium increases. Thus, we have carried out variable temperature experiments in the gas and liquid phases in addition to variable solvent experiments for the liquid phase.

From the microwave investigation[2] of cyclopropanecarboxaldehyde the dipole moment of the *trans* rotamer was determined to have a value of $3.26 \pm \pm 0.01$ μ whereas that for the *cis* was 2.74 ± 0.01 μ. Two of the Raman lines which showed a significant change in relative intensity during our variable temperature experiments are located at 1363 and 1318 cm^{-1} in the Raman spectrum of the liquid, Figure 1A, and have been assigned to the α — CH in-plane bend for the two conformers. The assignment of the lower frequency line to the *trans* rotamer is based on the data reported in Table I, where we found its intensity to increase significantly with increasing dielectric constant of the solvent. In order to determine the magnitude of the enthalpy difference separating the *cis* and *trans* conformers we have employed variable temperature experiments. Five sets of low temperature spectral data were obtained and the intensities of the aforementioned Raman lines were measured as a function of temperature in the liquid phase (Table II). A plot of the natural logarithm of the intensity ratio versus the reciprocal of the absolute temperature for the temperature range 24° to —36 °C was prepared, Figure 2. From the slope of this plot, $\Delta H/R$, the magnitude of the enthalpy difference was determined to be 1.2 kcal/mol. This value is in excellent agreement with that determined during an NMR investigation[4], 1.5 kcal/mol, and allows us to conclusively state that the *trans* rotamer is thermodynamically preferred in the liquid phase.

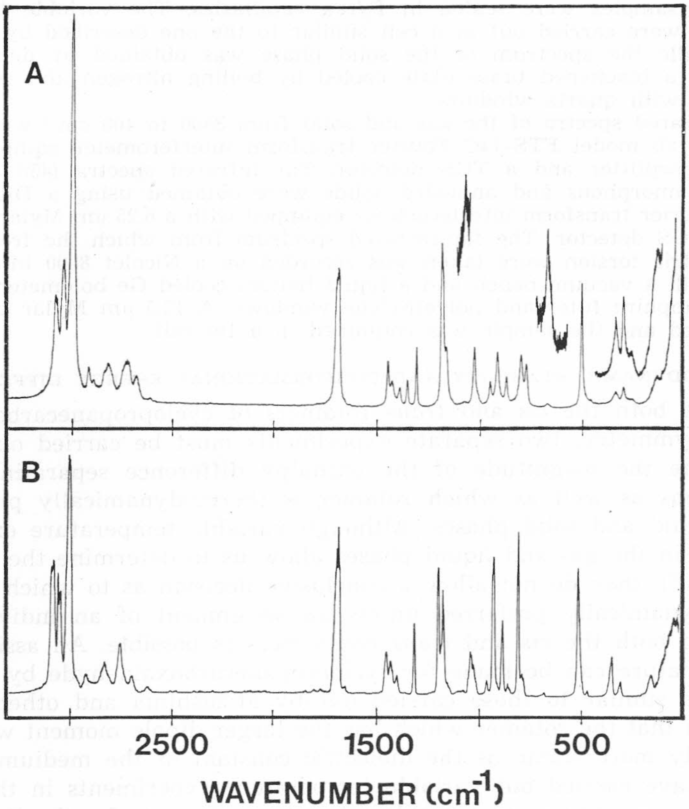

Figure 1. Raman spectra of liquid (A) and solid (B) cyclopropanecarboxaldehyde.

TABLE I

Conformation Equilibrium Dependence on Solvent Dielectric Constant for Cyclopropanecarboxaldehyde

Solvent	Dielectric constant	I_c/I_T	% cis	% trans
carbon disulfide	2.60	0.524	34	66
cyclopropanecarboxaldehyde	—	0.414	29	71
acetonitrile-d_3	37.5	0.304	23	77

TABLE II

Temperature and Intensity Ratios (1363/1318) for the Conformational Study of Liquid Cyclopropanecarboxaldehyde

T °C	1000 $(1/T)$ K^{-1}	$K = I_c/I_t$	$-\ln K$
24	3.347	0.338	1.089
14	3.48	0.325	1.12
—16	3.89	0.251	1.38
—27	4.06	0.225	1.49
—36	4.22	0.210	1.56

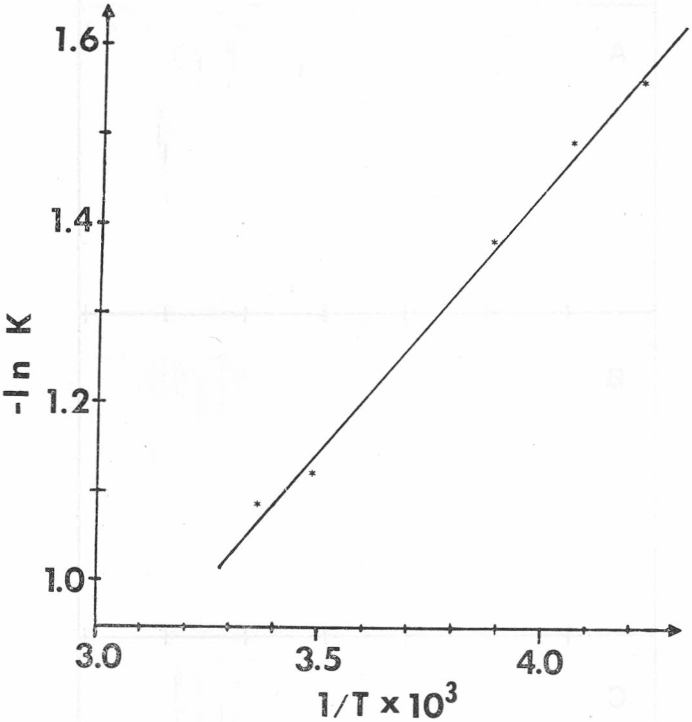

Figure 2. Temperature and intensity ratios (1362/1318 cm^{-1} lines) for the conformational study of cyclopropanecarboxaldehyde.

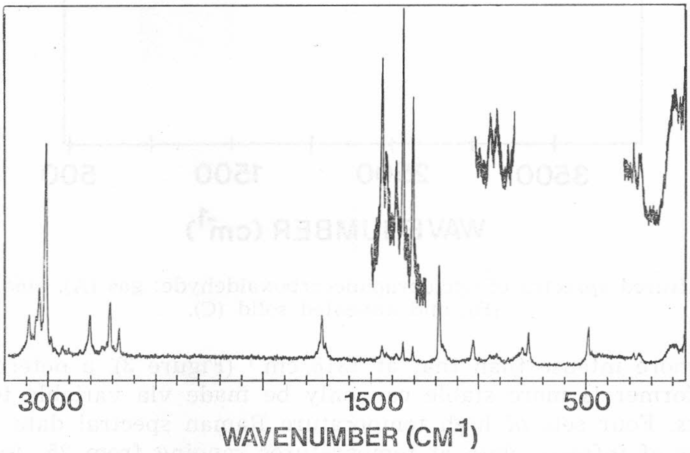

Figure 3. Raman spectrum of gaseous cyclopropanecarboxaldehyde.

As previously mentioned, considerable controversy currently exists regarding the thermodynamically preferred conformation in the gas phase of cyclopropanecarboxaldehyde. Although the gas phase Raman line at 1363 cm^{-1}

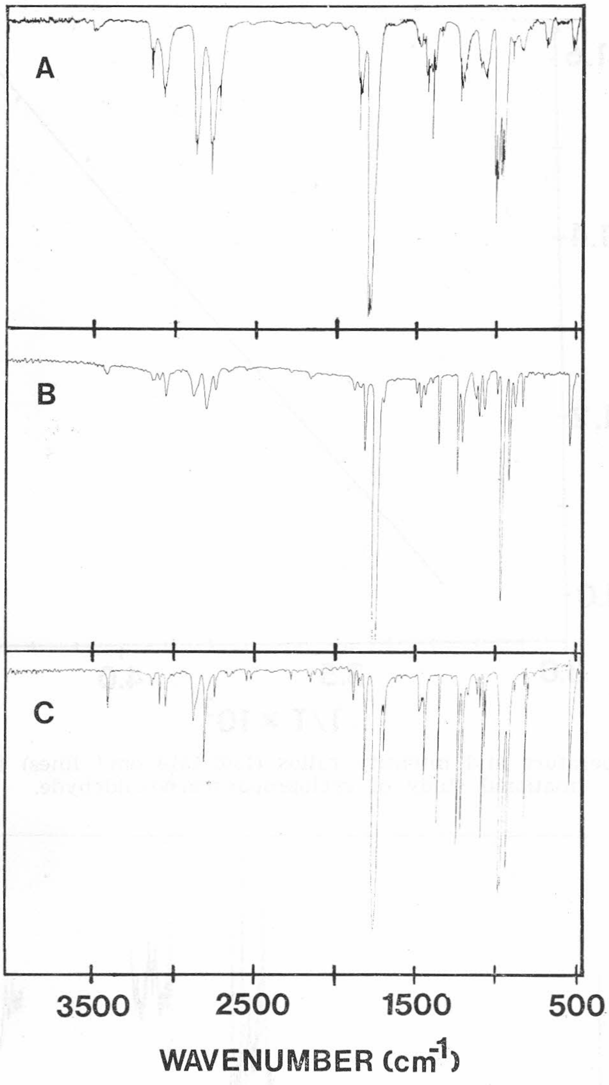

Figure 4. Infrared sprectra of cyclopropanecarboxaldehyde: gas (A), amorphous solid (B), and annealed solid (C).

is clearly more intense than that at 1318 cm^{-1} (Figure 3), a determination of which conformer is more stable can only be made via variable temperature experiments. Four sets of high temperature Raman spectral data in addition to nine sets of infrared data at temperatures ranging from 25° to 105 °C for the gas phase were obtained. From these data the changes in relative intensity and integrated absorbance were immeasurably small over ~ 10° increments; however, from the values obtained at room temperature and at 105°, the Raman line and infrared band (Figure 4) centered at 1318 cm^{-1} could be shown to increase in intensity relative to that at 1363 cm^{-1} with increasing temperature. It can, therefore, be concluded that the *cis* rotamer is thermodynamically preferred over the *trans* for the gas phase. From these two data points the value of ΔH ($\sim \Delta E$) was determined to be ~ 60 cm^{-1} which is much smaller than in the liquid phase. Our conclusion that the gas phase value of ΔH is small is consistent with our potential function, which is discussed herein, in addition to the value determined from variable temperature experiments carried out during the microwave investigation ($\Delta E = 10 \pm 20$ cm^{-1}).[2]

Since multiple conformers were found to be present in the fluid phases, the sample was cooled to approximately —130 °C in an attempt to isolate a single molecular form in the crystalline solid. It is clear from the Raman spectrum of the annealed solid, Figure 1B, that only the Raman line at 1318 cm^{-1} remains and thus only the *trans* rotamer is present in the solid phase of cyclopropanecarboxaldehyde.

ASYMMETRIC TORSION

In general, the most accurate torsional potential data for the gas phase have been obtained from the analysis of the low frequency vibrational spectra; therefore, we have undertaken a careful examination of the far infrared spectrum of gaseous cyclopropanecarboxaldehyde in the region of 450 to 50 cm^{-1}. The observed gas phase spectrum is shown in Figure 5A. From the microwave study it was shown that the c-principal axis is perpendicular to the symmetry plane in the *cis* conformer; however, for the *trans* rotamer the b-principal axis is perpendicular to the symmetry plane. Consequently, the asymmetric torsions which are out-of-plane modes should give rise to infrared bands having C- and B-type contours for the *cis* and *trans* rotamers, respectively. On the basis of the microwave study, the torsional modes are expected to have frequencies below 150 cm^{-1} and it appears that we have observed a B-type minimum at 126 cm^{-1} and a series of rather sharp C-type Q branches beginning at 113 cm^{-1} (Figure 6). The assignment of the $1 \leftarrow 0$ transition of the assymmetric torsion at 126 cm^{-1} for the high energy *trans* conformer is consistent with the value of 123.6 ± 2.0 cm^{-1} predicted from the microwave investigation, as is our assignment of the $1 \leftarrow 0$ transition for the low energy *cis* rotamer, where a frequency of 112.6 ± 4.0 cm^{-1} was previously predicted. Although it is somewhat unusual to assign the asymmetric torsion of the high energy conformer to a higher frequency than the corresponding fundamental for the low energy species, this is what we have previously observed for cyclopropylcarbonyl fluoride[12]. Additionally, if one assumes that the *cis* to *trans* and *trans* to *cis* barriers are approximately equal, then in order for the *trans* fundamental to occur at a higher frequency than the *cis*, the harmonic approximation indicates the F-number, a kinetic term in the Hamiltonian which is discussed herein, for the *trans* species should be larger than for the *cis* rotamer. This is what we have determined where the F-number for the *cis* conformer was calculated to be 2.4 cm^{-1} whereas for the *trans* species this parameter has a value of 3.1 cm^{-1}. Therefore, based on our variable temperature experiments in the gas phase and our variable solvent experiments carried out in the liquid phase we have assigned the higher frequency B-type minimum to the high energy *trans*

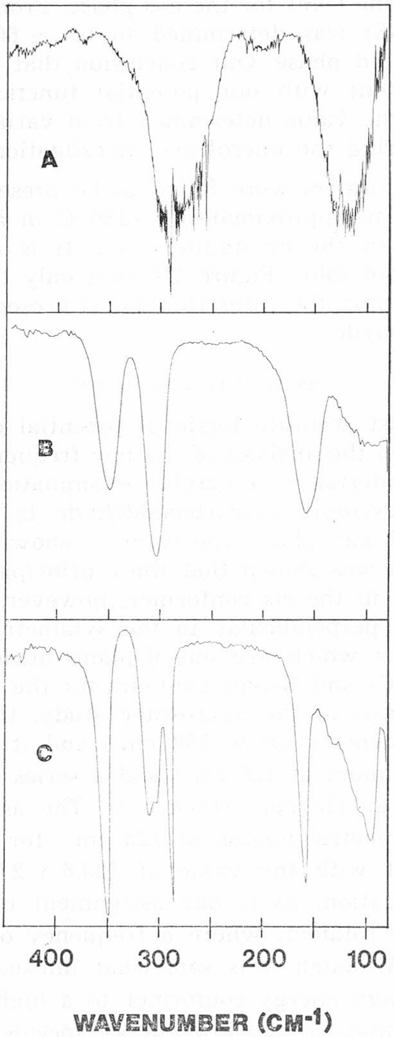

Figure 5. Far infrared spectrum of cyclopropanecarboxaldehyde: gas (A), amorphous solid (B), and annealed solid (C).

conformer, and the series of Q branches beginning at 113 cm^{-1} to be the torsional transitions of the low energy *cis* conformer. The observed torsional transitions along with their assignments are listed in Table III.

Using these frequencies for the torsional transitions of the *cis* and *trans* conformers, the asymmetric torsional potential function of cyclopropanecarboxaldehyde was calculated. To determine the barriers to internal rotation of the CHO moiety, we used a computer program similar to the one described

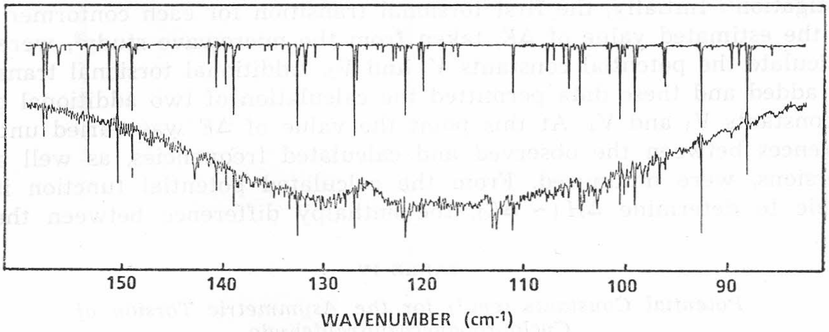

Figure 6. Asymmetric torsional transitions of gaseous cyclopropanecarboxaldehyde, 12.5 µm beamsplitter and 0.125 cm^{-1} resolution. The upper spectrum is that of water collected at the same instrumental conditions.

TABLE III

Observed and Calculated (cm^{-1}) Asymmetric Torsional Transitions for Cyclopropanecarboxaldehyde

	Transition	Obs.	Calc.[a]	Δ
trans	1←0	126.0	126.0	0.0
cis	1←0	113.2	112.5	0.7
	2←1	110.9	110.9	0.0
	3←2	—	109.2	—
	4←3	—	107.2	—
	5←4	104.3	105.3	—1.0
	6←5	102.8	103.1	—0.3
	7←6	100.1	100.8	—0.7
	8←7	98.2	98.2	—0.6
	9←8	96.6	95.3	1.3

[a] Calculated by using potential constants from Table IV and $F_0 = 2.7203$, $F_1 = -0.3213$, $F_2 = 0.0359$, $F_3 = -0.0033$, $F_4 = 0.0004$, $F_5 = -0.00009$, and $F_6 = 0.00006$.

by Lewis *et al.*[13], in which the torsional potential can be represented as a Fourier cosine series in the internal rotation angle:

$$V(\Theta) = \sum_{i=1}^{6} (V_i/2)(1 - \cos i\,\Theta)$$

where Θ is the torsional angle and i is the foldness of the barrier. The program determines the coefficients V_i ($i \leq 6$) from the input of the observed torsional transitions and the internal rotational constant $F(\Theta)$ which is varied as a function of the dihedral angle. The angle dependence of $F(\Theta)$ can also be expressed as a Fourier series:

$$F(\Theta) = F_0 + \sum_{i=1}^{6} F_i \cos i\,\Theta.$$

The series coefficients for the rigid rotation of the CHO moiety listed in Table IV were obtained by utilizing reasonable geometric parameters which yielded principal moments of inertia similar to those found in the microwave investigation[2]. Initially, the first torsional transition for each conformer along with the estimated value of ΔE, taken from the microwave study[2], were used to calculate the potential constants V_1 and V_2. Additional torsional transitions were added and these data permitted the calculation of two additional potential constants V_3 and V_4. At this point the value of ΔE was varied until the differences between the observed and calculated frequencies, as well as the dispersions, were minimized. From the calculated potential function it was possible to determine ΔH ($\sim \Delta E$), the enthalpy difference between the two conformers in the vapor state, to be 60 cm^{-1} (172 cal/mol), with the *cis* rotamer being more stable. The calculated potential function yielded equivalent *cis* to *trans* and *trans* to *cis* barriers of 1521 cm^{-1} (4.34 kcal/mol).

TABLE IV

Potential Constants (cm^{-1}) for the Asymmetric Torsion of Cyclopropanecarboxaldehyde

Coefficient	Value	Dispersion	Microwave[a]
V_1	61	6	—80±40
V_2	1494	15	1535±140
V_3	—7	6	96±35
V_4	—39	6	
ΔE	60		10±20

[a] Reference 2.

VIBRATIONAL ASSIGNMENT

Although vibrational assignments for cyclopropylcarbonyl chloride,[14] bromide[15] and fluoride[12] have been published, there are no previous vibrational studies on the aldehyde. Additionally, a considerable amount of ambiguity exists in the literature with regard to the fundamental vibrations of the CXO moiety, as well as for some of the carbon-hydrogen bending motions for the three-membered ring. Therefore, the present study was also carried out in order to provide a complete vibrational assignment for c-C_3H_5CHO. The observed frequencies and vibrational assignment for cyclopropanecarboxaldehyde are presented in Tables V and VI, respectively.

For both conformers in which the double bond is either *cis* or *trans* to the cyclopropane ring, the symmetry is C_s and the normal vibrations span the irreducible representations $16A' + 11A''$. The A′ vibrations should give rise to polarized lines in the Raman spectra of the fluid phases, whereas the A″ vibrations will be depolarized. For the *cis* conformer the *c*-principal axis is perpendicular to the symmetry plane; consequently, the out-of-plane (A″) modes should give rise to C-type infrared band contours, and the in-plane (A′) modes should exhibit A, B, or A/B hybrid-type contours. In the case of the *trans* rotamer the *b*-principal axis is perpendicular to the symmetry plane; consequently, the out-of-plane (A″) modes should give rise to B-type infrared band contours, and the in-plane (A′) modes should exhibit A, C or A/C hybrid-type contours. As it would be expected, when one uses the moments of inertia determined from the microwave investigation,[2] the calculated separations for the P—R maxima and relative intensities of the Q-branches on the A and C type bands are quite different in the two conformations; nevertheless, it was frequently difficult to distinguish between the A- and C-type bands because of the overlap of the fundamentals from the two conformers. Therefore, considerable reliance had to be placed on the depolarization data to distinguish between the in- and out-of-plane modes. In many cases the same fundamentals for both conformations are nearly degenerate and, for simplicity, they have not been separated in Table V.

Carbon-Hydrogen Modes

Assignment of the CH stretching region of the spectrum was facilitated by the Raman spectrum of the gas (Figure 3) where pronounced Q-branches were observed at 3102, 3055 and 3026 cm^{-1} which must be the A′ modes associated with the CH stretches of the ring. The corresponding A″ modes appear to be nearly degenerate with the in-phase motions but are apparent in the spectrum of the solid (Figure 1B). It is clear from both the infrared and Raman spectra that at least two and as many as seven bands or lines are observed between 2900 and 2600 cm^{-1} where only one fundamental is expected, *i. e.*, the aldehydic CH stretch. The numerous bands in this region are most satisfactorily explained as an interaction of the aldehydic CH stretch fundamental with the overtone of the aldehydic CH bending vibration near 1400 cm^{-1}. Since aldehydes with a large variety of side groups give rise to a similar doublet[16] (see the infrared spectrum of the gas (Figure 4A)), it is unconvincing to assign this to any interactions with overtones or combinations of the ring. Since the intensities of both bands in the stretching region are of greater intensity than the 1395 cm^{-1} band, in addition to having inappropriate frequencies, it would not make sense to assign either band as a simple overtone. This must involve Fermi resonance of the overtone with the fundamental which means that both bands involve aldehydic CH stretch and both bands involve the overtone of the aldehydic CH bend at 1395 cm^{-1}.

The assignments proposed for the CH_2 bending modes are consistent with those previously given for several similar molecules where the best correlation is with the normal modes of cyclopropylcarbonyl fluoride.[12] The CH_2 deformations occur at characteristic frequencies (1464 and 1426 cm^{-1}), as do the A′ CH_2 twist (1151 cm^{-1}) and the two CH_2 wagging motions (1082 and 1034 cm^{-1}). However, the assignment for the A″ CH_2 twist and the two CH_2 rocking modes are not straightforward. The CH_2 twist (A″), obscured by the ring breathing mode in cyclopropylcarbonyl fluoride,[12] is readily observable at 1175 cm^{-1} in the Raman spectrum of the solid; however, its depolarization ratio is perturbed by the strongly polarized ring breathing mode in the Raman spectrum of the liquid. We have assigned the A″ CH_2 rock to a weak Raman line at 855 cm^{-1} in the spectrum of the solid. Although this frequency is consistent with the cyclopropyl halides[17-20] and cyclopropylcarbonyl chloride[14], it has been assigned to the A′ CH_2 rock in cyclopropylcarbonyl fluoride.[12] Similarly, the A′ CH_2 rock for the *trans* rotamer is assigned to the weak infrared band at 774 cm^{-1} in the spectrum of the solid and the corresponding motion for the *cis* rotamer has been assigned to the weak infrared band at 670 cm^{-1} which disappears in going to the solid.

The only remaining carbon-hydrogen modes are the out-of-plane aldehydic CH bend and the in- and out-of-plane α CH bend. The former fundamental

TABLE V

Observed[a] Infrared and Raman Frequencies (cm^{-1}) *for Cyclopropanecarboxaldehyde*

INFRARED				RAMAN						ASSIGNMENT[b]	
Gas	Rel. Int.	Solid	Rel. Int.	Gas	Rel. Int.	Liquid	Rel. Int. & Depol.	Solid	Rel. Int.	ν_i	Approximate Description
3470	vw										
3116 R											
3108 Q	m	3102	vw			3095	s, dp	3095	sh	ν_{17}	CH_2 antisymmetric stretch
3102 Q	m	3090	sh	3102	m	3085	sh, p	3085	s	ν_1	CH_2 antisymmetric stretch
3096 P											
				3070	sh			3063	s	ν_2	CH stretch
3058 Q	m	3052	vw	3055	m	3055	s	3053	sh		
3034 R											
3027 Q				3026	s					ν_3	CH_2 symmetric stretch
3020 P											
								3030	sh	ν_{18}	CH_2 symmetric stretch
3008 Q	sh	3017	m			3015	vs, p	3010	vs	ν'_3	CH_2 symmetric stretch
						2925	w, p	2930	m		
2828 R		2905	vw								
2823 Q	s	2840	m	2822	m	2830	m, p	2840	m	ν_4	aldehydic CH stretch
2820 P		2828	sh					2815	sh		in Fermi resonance with ν_7
2736 R											
2728 Q		2768	m	2728	m	2747	m, p	2760	m		
2720 P											
								2745	sh		
2688 Q											
2683 Q	sh	2713	m	2685	m	2697	w, p	2707	m		
2681 Q											
						2630	vw, p	2632	w		
1824 R		1856	w								
1816 Q	m	1826									
1810 P		1812	w								
1747 R											
1740 Q	vs	1776	s	1740	m					ν_5	CO stretch
1732 P											

Table V continued.

INFRARED				RAMAN						ASSIGNMENT^b	
Gas	Rel. Int.	Solid	Rel. Int.	Gas	Rel. Int.	Liquid	Rel. Int. & Depol.	Solid	Rel. Int.	ν_i	Approximate Description
1724 Q						1707	sh, p	1710	sh		
1720 Q	vs	1698	vs	1722	sh	1700	s, p	1695	s	ν'_5	CO stretch
1716 P								1687	s		
		1668	w								
1468 R											
1464 Q	w	1446	w	1462	w	1457	m, p	1454	m	ν'_6	CH_2 symmetric deformation
1450 P											
				1443	w					ν_6	CH_2 symmetric deformation
1426 Q	sh	1426	m			1438	sh, dp	1434	m	ν_{19}	CH_2 antisymmetric deformation
1406 R											
1396 Q	m	1408	w	1396	w	1400	w, p	1398	m	ν_7	aldehydic CH bend
1394 Q											
1388 P											
1372 R											
1363 Q	m			1363	w	1363	m, p			ν_8	CH bend
1361 Q	m										
1354 P											
1326											
1317	w	1322	s	1317	w	1318	m, p	1318	s	ν'_8	CH bend
1308											
1202 R											
1197 Q	m	1200	s	1195	s	1195	vs, p	1197	s	ν_9	ring breathing
1193 Q											
1183 P	m										
1172 R	sh	1174	s	1175	sh	1175	sh, p	1175	s	ν_{20}	CH_2 twist
1164 Q	sh										
1159 Q	sh										
1151 Q	sh	1146	sh					1150	sh	ν_{10}	CH_2 twist
1147 Q	sh										
								1100	vvw		

Table V continued.

INFRARED				RAMAN						ASSIGNMENT[b]	
Gas	Rel. Int.	Solid	Rel. Int.	Gas	Rel. Int.	Liquid	Rel. Int. & Depol.	Solid	Rel. Int.	ν_i	Approximate Description
1082 Q	sh	1088	m			1084	vw, p	1080	vvw	ν_{21}	CH_2 wag
1074 Q		1069	m								
1040 R		1048	s					1050	sh		
1034 Q	m	1036	s	1030	w	1035	m, p	1040	m	ν_{11}	CH_2 wag
1028 P											
		1026	sh			1018	sh, dp			ν_{22}	CH bend
972 R											
965 Q	s			960	vw	960	m, p	960	w	ν_{12}	C—C stretch
963 Q											
956 P											
934 R											
926 Q	s	927	s	930	vw	925	m, dp	925	s	ν_{23}	ring deformation
923 Q											
919 P											
882 R											
875 Q	w	890	s	877	vw	880	m, p	880	s	ν_{13}	ring deformation
868 P											
		857	m					855	w	ν'_{24}	CH_2 rock
820 bd	w			808	vw	820	sh, dp	—	—	ν_{24}	CH_2 rock
		799	w			808	m, dp	804	s	ν'_{25}	aldehydic CH bend
770 bd	vw	784	s	783	m	780	m, dp	786	sh	ν_{25}	aldehydic CH bend
		774	w							ν'_{14}	CH_2 rock
674 R											
670 Q	w					678	vw, p	673	vvw	ν_{14}	CH_2 rock
666 Q											
664 Q											
660 P											
506 Q											
504 Q		510	s	504	m	508	vs, p	516	s		
502 Q	w	490	sh					500	sh	ν_{15}	C=O bend
494 P											
								460	vw		$\nu_{16} + \nu_{27}$

Table V continued.

INFRARED				RAMAN						ASSIGNMENT[b]	
Gas	Rel. Int.	Solid	Rel. Int.	Gas	Rel. Int.	Liquid	Rel. Int. & Depol.	Solid	Rel. Int.	ν_i	Approximate Description
340	sh	355	m			340	m, dp	346	m	ν'_{26}	ring-CHO bend
300 R											
291 Q	w			295	vw					ν_{16}	ring-CHO bend
280 P											
		310	m			303	m, p	305	m	ν'_{16}	ring-CHO bend
		304	m								
		289	m								
256 Q				270	vw	265	sh			ν_{26}	ring-CHO bend
130 R											
126 ctr	w	164	m			142	m, dp	155	m	ν'_{27}	asymmetric torsion
116 P											
113 Q	w			110	bd						asymmetric torsion
		133	m								
		110	m								
		145	m								
		80	m								lattice modes
								45	s		
								27	s		

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[a] Abbreviations used: s, strong; m, moderate; w, weak; v, very; sh, shoulder; p, polarized; dp, depolarized; P, Q and R refer to vibrational rotational branches and ctr refers to a band center.

[b] The fundamentals denoted ν'_n refer to the *trans* conformation.

for the *trans* rotamer is assigned to the strong line observed at 304 cm^{-1} in the Raman spectrum of the solid based on this line's absence in the spectra of cyclopropylcarbonyl fluoride[12] and chloride.[14] It is clear that the corresponding fundamental for the *cis* rotamer is nearly degenerate with the A′ CH_2 rock. Although the CH in-plane bend, whose frequency is well established, can be confidently assigned to the polarized line at 1362 cm^{-1} in the Raman spectrum of the liquid, as well as to the distinct Q-branch at 1363 cm^{-1} in the Raman spectrum of the gas, the out-of-plane mode presents a problem. We have chosen to assign it to the depolarized shoulder observed at 1018 cm^{-1} in the Raman spectrum of the liquid and, although this frequency is relatively consistent with the corresponding mode in cyclopropylcarbonyl fluoride[12] (964 cm^{-1}) and chloride[14] (982 cm^{-1}), an assignment to a higher frequency would be more consistent with the cyclopropyl halides[17-20] (1136 cm^{-1} in cyclopropyl bromide).[20] Alternatively, it could be assigned to the strong infrared band observed at 1048 cm^{-1} in the spectrum of the solid and provided this line does not arise as a result of crystal field effects, this would appear to be a more reasonable assignment.

Skeletal Modes

As with cyclopropylcarbonyl fluoride[12] and chloride,[14] the assignments for the three vibrations associated with the ring are consistent with those previously proposed for the corresponding vibrations in the cyclopropyl halides[17-20] The ring breathing fundamental is observed at 1195 cm^{-1}, and the two ring deformations are observed at 930 and 877 cm^{-1}, with the latter being polarized and thus assigned to the A′ mode. It is interesting to note that, typically, the A″ modes will be much weaker than the A′ modes in the Raman spectrum of the gas; however, this does not appear to be the case for cyclopropanecarboxaldehyde. As expected, the Q-branch is sharper for the A′ mode though it is weaker in intensity than the corresponding A″ fundamental. The remaining skeletal stretches are the CO and CC modes. The assignment of the former fundamental is straightforward and has been observed as a strong Q-branch observed at 1740 cm^{-1} in the Raman spectrum of the gas. The assignment of the CC stretch to the weak Raman line observed at 960 cm^{-1} in the spectrum of the solid is consistent with the assignment of the corresponding fundamental in cyclopropylcarbonyl fluoride[12] and chloride;[14] however, its variance in intensity with phase change clearly indicates its association with a conformer peak, and indeed two nearly degenerate Q--branches (965 and 963 cm^{-1}) have been observed in the infrared spectrum of the gas.

The assignment for the fundamental vibrations of cyclopropanecarboxaldehyde below 600 cm^{-1} is somewhat complicated due to the sample's sensitivity to the annealing process. We have observed a similar sensitivity in the case of cyclopropylcarbonyl fluoride,[12] and cyclopropylcarbonyl chloride.[14]

It is clear that the strong line observed at 516 cm^{-1} in the Raman spectrum of the solid arises from the A′ CO bend; however, the assignment of the two ring-CHO bends is not straighforward. For the *trans* rotamer the A″ and A′ ring-CHO bends can be confidently assigned to the two solid phase Raman lines occurring at 346 and 305 cm^{1-}, respectively. Based on the change in relative intensity as one proceeds to the solid of the two liquid phase

TABLE VI

Fundamental Vibrations[a] *(cm^{-1}) for* cis *and* trans *Cyclopropylcarboxaldehyde*

Approximate Description	*cis*	*trans*
A′		
ν_1 CH$_2$ antisymmetric stretch	3102	3085 (3108)[b]
ν_2 CH stretch	3055	3063 (3070)[b]
ν_3 CH$_2$ symmetric stretch	3026	3010 (3008)
ν_4 aldehydic CH stretch	2822	2840
ν_5 CO stretch	1740	1695 (1722)
ν_6 CH$_2$ symmetric deformation	1443	1454 (1462)
ν_7 aldehydic CH bend	1396	1398
ν_8 CH bend	1363	1318 (1317)
ν_9 ring breathing	1195	1197
ν_{10} CH$_2$ twist	1151	1150
ν_{11} CH$_2$ wag	1030	1040
ν_{12} C—C stretch	960	960
ν_{13} ring deformation	877	880
ν_{14} CH$_2$ rock	808	855
ν_{15} CCO bend	504	516
ν_{16} ring-CHO in plane	295	305
A″		
ν_{17} CH$_2$ antisymmetric stretch	—	3095
ν_{18} CH$_2$ symmetric stretch	—	3030
ν_{19} CH$_2$ antisymmetric deformation	1426	1434
ν_{20} CH$_2$ twist	1175	1175
ν_{21} CH$_2$ wag	1082	1080 (1074)
ν_{22} CH bend	—	1025
ν_{23} ring deformation	930	925
ν_{24} CH$_2$ rock	808	786
ν_{25} aldehydic CH bend	—	804
ν_{26} ring-CHO	270	346 (340)
ν_{27} asymmetric torsion	113	155 (126)

[a] The frequencies for the *cis* conformer are from the spectra of the vapor whereas those for the *trans* rotamer have been taken from the spectra of the solid phase.

[b] The parentheses denote the gas phase frequencies for the *trans* conformer.

Raman lines occurring at 340 and 303 cm^{-1}, it is clear that they are associated with the corresponding *cis* fundamentals. The shoulder observed at 265 cm^{-1} in the Raman spectrum of the liquid is absent in the spectrum of the solid and can thus be assigned to the A″ ring-CHO bend for the *cis* rotamer. This fundamental also gives rise to a weak Q-branch at 270 cm^{-1} in the Raman spectrum of the gas. The A′ ring-CHO bend has been assigned to the weak Raman line observed at 295 cm^{-1} in the spectrum of the gas. From Table V, it is clear that the far infrared spectrum of the solid does not correspond to the low frequency Raman spectrum. Reasons proposed for this apparent anomaly are presented in the section that follows.

The only remaining fundamental is the asymmetric torsion and this vibration has been assigned, for reasons previously discussed, to the B-type minimum occurring at 126 cm^{-1} and the C-type Q-branch observed at 113 cm^{-1} for the *trans* and *cis* rotamers, respectively.

SOLID PHASE

The differences observed as one proceeds from the far infrared spectrum of the gas to that of the annealed solid in cyclopropanecarboxaldehyde can not be accounted for when based solely on a change in conformation from the more stable *cis* rotamer in the gas phase to the preferred *trans* conformation in the solid. Although the far infrared spectrum of the amorphous solid coincides quite well with the corresponding Raman spectrum of the solid, the far infrared spectrum of the annealed solid is unique. The splitting observed on the 305 cm^{-1} band and the presence of the sharp band at 289 cm^{-1}, in addition to the number of observed lattice modes, indicates a complex solid phase structure with at least two molecules per unit cell. Such drastic changes in the spectrum could possibly be attributed to the formation of a dimer in the solid phase; however, this seems unlikely in consideration of the fact that the C=O and aldehydic C—H stretching frequencies are not significantly perturbed in the spectra of the solid. The formation of a dimer would result in both in- and out-of-phase motions for each fundamental and would account for the observed splittings in addition to the anomalous band at 289 cm^{-1}. The Raman spectrum of the solid may not coincide with that of the annealed far infrared spectrum for a number of reasons. If the dimer possesses a center of symmetry, mutual exclusion between the infrared and Raman spectra would be observed; alternatively, the spectrum of the Raman solid may not be completely annealed and thus the dimer may not have formed. As previously mentioned, we have observed a similar sensitivity to the annealing process of cyclopropylcarbonyl fluoride[12] and chloride[14]. In the case of the fluoride[12], we have reported that both the *cis* and *trans* rotamers are present in the annealed solid; furthermore, we have attributed our inability to isolate a single conformation to the similar sizes and electronegativities of the oxygen and fluorine atoms. In the case of the corresponding chloride[14], it was clear that the *cis* rotamer was present in at least 70% abundance in both the vapor and liquid phases; however, in the spectrum of the annealed solid only the *trans* rotamer was present. Thus, in the case of cyclopropanecarboxaldehyde, we believe the annealed solid phase spectrum results from a complex unit cell structure and is not due to a second crystalline phase. This conclusion is supported by the fact that two different spectra of the solid phase were only obtained after annealing and not by simply cycling the temperature as one would expect if the changes in the observed spectra were due to a phase transition.

DISCUSSION

The spectrum shown in Figure 6 was recorded at 0.12 cm^{-1} resolution and shows that the asymmetric torsional mode occurs as a predominant B-type band with a series of Q-branches occuring on the low frequency side. The choice of 126 cm^{-1} for the *trans* $1 \leftarrow 0$ transition, occurring as a B-type minimum, must be taken with caution. The minimum observed at 126 cm^{-1} may be a minimum resulting from overlap of the $1 \leftarrow 0$ transition with the higher excited torsional transitions of the *trans* rotamer. Additonally, the R-band envelope from the $1 \leftarrow 0$ transition for the *cis* rotamer could also be obscuring the actual B-type minimum. Thus, the frequency which we have taken could be in error as much as 5 cm^{-1}; however, this amount of error would not cause an appreciable change in the barriers which we have calculated. Similar to that observed in the far infrared investigation of propanal[21], the observed Q-branches, assigned as the 1 ← 0 transition and associated »hot bands« of the *cis* rotamer, do not follow the normal trend for the relative intensities expected from normal Boltzmann statistics, and a very careful analysis was necessary in order to assign these bands to the correct torsional transitions. Furthermore, as it can be seen in Figure 7, each torsional transition appears to have an excited state series associated with it. These excited state transitions most probably arise from the torsional fundamental being in an excited state of the ring-CHO bend. If indeed this is the case, then to handle the energetics of the asymmetric torsion of cyclopropanecarboxaldehyde as being solely dependent on the torsional dihedral angle would be an oversimplification, and the calculations should most probably include the bend angle as well. The reader should also note that the 3 ← 2 and 4 ← 3 torsional transitions for the *cis* rotamer have not been observed. This was also the case for propanal[21] where these transitions were observed as weak and very sharp Q-branches, and consequently were not observed in the 0.5 cm^{-1} resolution spectrum.

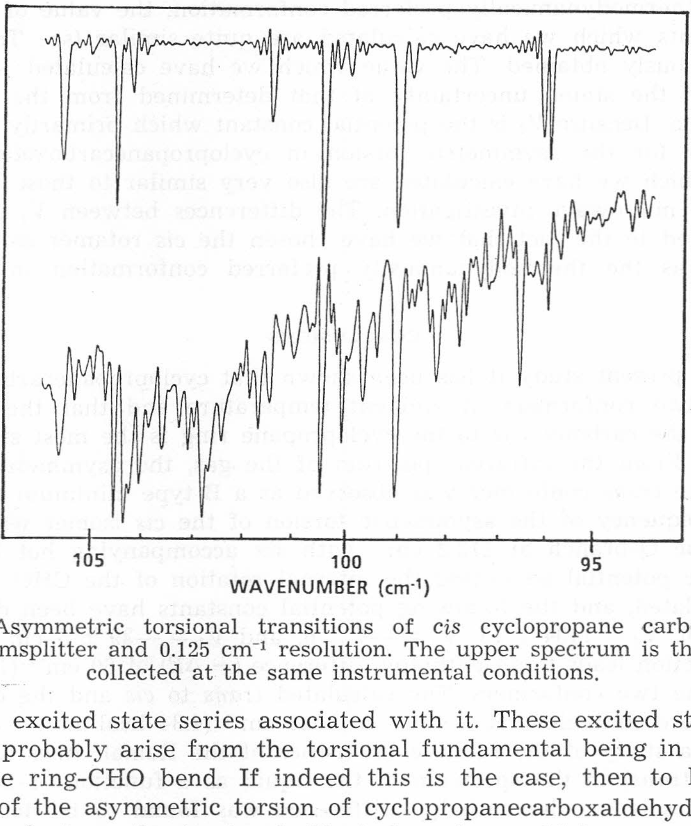

Figure 7. Asymmetric torsional transitions of *cis* cyclopropane carboxaldehyde, 12.5 μm beamsplitter and 0.125 cm^{-1} resolution. The upper spectrum is that of water collected at the same instrumental conditions.

The rather broad Q-branch observed at 142.8 cm^{-1} can most probably be attributed to a difference band between ν_{25} and ν_{23} ($\nu_{25} - \nu_{23} = 143$ cm^{-1}). It has not been chosen as a *cis* torsional transition because it is too far displaced from the maximum of 110 cm^{-1} observed for the asymmetric torsion in the Raman spectrum of the gas.

Of additional interest is a comparison of the potential constants which we have obtained to those which were determined from the investigation of the microwave spectrum of cyclopropanecarboxaldehyde.[2]

The calculated intensity of the *trans* species transition was determined to be 1.66 times greater than that of the *cis* and therefore these authors[2] concluded that the ground state of the *trans* configuration lay 10 ± 20 cm^{-1} below that of the *cis* species. Furthermore, they reported that the large uncertainty in this reported value of ΔE was due to difficulties with overlapping transitions. Although our assignment is in accordance with the *cis* rotamer being the thermodynamically preferred conformation, the value of the potential constants which we have calculated are quite similar (see Table IV) to those previously obtained. The value which we have calculated for V_2 is in fact within the stated uncertainty of that determined from the microwave investigation. Because V_2 is the potential constant which primarily determines the barrier for the asymmetric torsion in cyclopropanecarboxaldehyde, the barriers which we have calculated are also very similar to those determined during the microwave investigation. The differences between V_1 and V_3 can be attributed to the fact that we have chosen the *cis* rotamer as opposed to the *trans* as the thermodynamically preferred conformation in the vapor phase.

CONCLUSIONS

In the present study it has been shown that cyclopropanecarboxaldehyde exists as two conformers at ambient temperature and that the conformer which has the carbonyl *cis* to the cyclopropane ring is the most stable in the gas phase. From the infrared spectrum of the gas, the asymmetric torsional mode of the *trans* conformer was observed as a B-type minimum at 126 cm^{-1} and the frequency of the asymmetric torsion of the *cis* isomer was observed as a C-type Q-branch at 113.2 cm^{-1} with six accompanying hot bands. The asymmetric potential governing the internal rotation of the CHO moiety has been calculated, and the following potential constants have been determined: $V_1 = 61 \pm 6$, $V_2 = 1494 \pm 15$, $V_3 = -7 \pm 6$, and $V_4 = -39 \pm 6$ cm^{-1}. This potential function leads to an enthalpy difference ($\sim \Delta E$) of 60 cm^{-1} (172 cal/mol) between the two conformers. The calculated *trans* to *cis* and the *cis* to *trans* barriers were equivalent at a value of 1521 cm^{-1} (4.34 kcal/mol).

From a study of the relative intensities of the Raman lines at 1362 (*cis*) and 1318 (*trans*) in the spectrum of the liquid as a function of both temperature and solvent, the enthalpy difference was found to be 405 ± 20 cm^{-1} (1.16 kcal/mol) but in the liquid state the *trans* conformer is more stable than the *cis* rotamer. A complete vibrational assignment is presented for both the *cis* and *trans* conformers of cyclopropanecarboxaldehyde.

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SAŽETAK

Vibracijski i konformacijski studij ciklopropankarboksaldehida

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Snimljeni su infracrveni (3500—40 cm^{-1}) i Ramanovi (3200—20 cm^{-1}) spektri plinovitog i čvrstog ciklopropankarboksaldehida, $c\text{-}C_3H_5CHO$. Osim toga, snimljen je Ramanov spektar tekućine i dobivene kvalitativne depolarizacijske vrijednosti. Utvrđeno je, da je konformer s kisikom *cis* prema tročlanom prstenu stabilniji oblik pri sobnoj temperaturi u plinskoj fazi, ali je u tekućoj fazi *trans* stabilniji i jedini je konformer vidljiv u spektrima čvrstog stanja. Iz temperaturnog studija Ramanova spektra tekućine dobivena je energijska razlika od 405 ± 20 cm^{-1} (1,16 kcal/mol), dok je energijska razlika za plinsko stanje približno 60 cm^{-1}. Opažena razlika za ΔH prelaskom iz plinskog u tekuće stanje ukazuje na jaku intermolekulsku asocijaciju u kondenziranim fazama, što može objasniti da je *trans* stabilniji u tekućini i stabilni konformer u čvrstom stanju. Nesimetrična torzija *trans* konformera opaža se u dalekomu infracrvenom spektru kao vrpca tipa B centrirana pri 126 cm^{-1}, a odgovarajuća torzija za *cis* konformer opažena je pri 113 cm^{-1} kao vrpca tipa C sa šest pratećih vrućih vrpci koje padaju prema nižim frekvencijama. Iz tih podataka određena je potencijalna funkcija za unutarnju rotaciju nesimetričnog zvrka te su izvedene slijedeće potencijalne konstante: $V_1 = 61 \pm 6$, $V_2 = 1494 \pm 15$, $V_3 = -7 \pm 6$, and $V_4 = -39 \pm 6$ cm^{-1}. Proračunane su barijere za pretvorbe *trans* → *cis* i *cis* → *trans* te je utvrđeno da su ekvivalentne i iznose 1521 cm^{-1}. Predložena je potpuna vibracijska asignacija za oba konformera, temeljena na konturama infracrvenih vrpci, depolarizacijskim vrijednostima i skupinskim frekvencijama. Ti su rezultati uspoređeni sa sličnim veličinama nekoliko srodnih molekula.