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(31) For example, the Cy-C-Cy angle of 115° found for **1** in the present work (Figure 2) is significantly larger than the Cy-Si-Cy angle of 112.4 (EFF calculation) or 112.0° (X-ray structure) found for **2**.[19]

Conformational Study of Cyclohexanecarboxaldehyde by Microwave Spectroscopy

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Abstract: The gas-phase microwave spectrum of cyclohexanecarboxaldehyde shows the presence of two stable conformational isomers. Both conformers have a chair cyclohexane ring with an equatorial aldehyde substituent, but differ in the value of the torsional angle about the C_1-CHO bond. Relative intensity measurements show that the gauche conformer (C=O eclipsing ring C_1—C_2) is more stable than the cis form (C=O eclipsing axial C_1—H) by 720 ± 200 cal/mol. A lower bound on the barrier height separating the two equivalent gauche forms has also been obtained.

Introduction

The stable conformations for CH_2XCOY compounds usually occur with the C=O bond eclipsing a C—H or a C—X bond,[1] although there are several known exceptions to this rule.[2] All these latter molecules exist in two conformations which both possess a plane of symmetry. Cyclopropanecarboxaldehyde[3] and cyclopropanecarbonyl fluoride[4] are also unusual since in each case two conformations exist with the carbonyl group cis or trans to the cyclopropane ring. The present investigation was undertaken to determine the conformations adopted by the six-membered cyclic ring compound, cyclohexanecarboxaldehyde (Figure 1). There is also some interest in comparing the results obtained here with a liquid-phase NMR study,[5] and with a previous molecular mechanics calculation on this system.[6]

Experimental Section

The sample was obtained from the Aldrich Chemical Co. and was used without further purification. All spectra were taken on a Hewlett-Packard 8460 A microwave spectrometer. Useful intensities could only be obtained in R-band (26.5-40.0 GHz), with the sample cell cooled to ~−20 °C.

Results

Spectral Assignments. The low-resolution microwave spectrum revealed two distinct band series, arising from a-type, R-branch transitions of two separate conformers of cyclohexanecarboxaldehyde.[7] The measured band spacing yielded two values for B + C which were both consistent with a chair cyclohexane ring with an equatorial aldehyde substituent. As expected, no band series corresponding to axial conformations were observed. To determine the C_1-CHO torsional angles corresponding to the observed conformations, a high-resolution microwave study was undertaken.

A sample of the high-resolution assignment for cyclohexanecarboxaldehyde presented in Tables I and II confirms that the observed conformations are cis (C=O eclipsing axial C_1—H) and gauche (C=O eclipsing ring C_1—C_2). The near prolate nature ($\kappa = -0.8$) for both species led to characteristic bunching of lines in the a-type, R-branch spectrum of the high K_{-1} transitions. Recognition of these patterns at low Stark modulation voltages considerably simplified the assignment process. Radio frequency-microwave double resonance was also used to confirm initial assignments made under Stark modulation.[8] The spectrum of the gauche conformer fit a simple rigid rotor model exceedingly well; the cis conformer, however, required the introduction of small centrifugal distortion constants to obtain a good fit (Table III).[9] The spectrum of the gauche conformer also revealed the existence of two vibrational satellites, assumed to arise from successively excited states of the torsional mode about C_1-CHO. Relative intensity measurements give a fundamental vibrational spacing of 100 ± 40 cm^{-1}.

Structural Calculations. In the cis conformer, the aldehyde group lies in the plane of symmetry (a,c), and the quantity $P_{bb} = \frac{1}{2}(I_a + I_c - I_b) = \Sigma m_i b_i^2$ is independent of the aldehyde parameters. Following the procedure described for cyclohexyl fluoride by Pierce and Nelson,[10] the ring angle C-C-C was adjusted to fit the observed value of P_{bb}. Good agreement with the cis rotational constants was then obtained by introducing the aldehyde substituent in the equatorial position with structural parameters assumed from acetaldehyde[1a] (Table IV). Only small adjustments of the angles HC_1C and C_1CO (increase each by ~0.5°) were necessary to achieve an essentially exact fit.

A plot of the calculated rotational constants as a function of torsional angle about C_1-CHO, using the cis structural parameters, is shown in Figure 2. Comparison with the observed gauche rotational constants gives a dihedral angle of 117 ± 10°. The dispersion indicates that some other structural changes are occurring upon internal rotation.

Table I. Observed[a] and Calculated Frequencies (MHz) for *cis*-Cyclohexanecarboxaldehyde

transition[b] $J'_{K'_{-1}K'_{+1}} - J''_{K''_{-1}K''_{+1}}$	ν_{obsd}	$\Delta\nu$[c]
$14_{0,14} - 13_{0,13}$	31 392.50	0.00
$14_{1,14} - 13_{1,13}$	31 364.00	0.01
$14_{3,11} - 13_{3,10}$	35 251.19	0.06
$14_8 - 13_8$	33 982.84	−0.01
$14_9 - 13_9$	33 958.87	−0.02

[a] Accurate to ±0.05 MHz. [b] Unresolved asymmetry doublets labeled by limiting prolate quantum number only. [c] Observed minus calculated frequencies from constants of Table III.

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Table II. Observed[a] and Calculated Frequencies (MHz) for Gauche Cyclohexanecarboxaldehyde

transition[b] $J'_{K'_{-1}K'_{+1}} - J''_{K''_{-1}K''_{+1}}$	$v = 0$ ν_{obsd}	$v = 0$ $\Delta\nu^c$	$v = 1$ ν_{obsd}	$v = 1$ $\Delta\nu^c$	$v = 2$ ν_{obsd}	$v = 2$ $\Delta\nu^c$
			a Type			
$14_{0,14} - 13_{0,13}$	32 752.77	0.00	32 787.00	0.04	32 819.77	0.01
$14_{1,14} - 13_{1,13}$	32 741.10	0.03	32 775.32	0.05	32 808.17	0.07
$14_{1,13} - 13_{1,12}$	34 708.89	−0.04	34 736.77	−0.08	34 764.41	−0.04
$14_{2,13} - 13_{2,12}$	34 467.55	0.03	34 495.88	0.00		
$14_{2,12} - 13_{2,11}$	36 896.31	−0.04				
$14_{3,12} - 13_{3,11}$	35 784.00	0.04	35 807.54	0.07	35 832.05	0.04
$14_{3,11} - 13_{3,10}$	37 756.22	0.09				
$14_7 - 13_7$	36 139.62	−0.12	36 161.40	−0.02	36 184.86	−0.03
			b Type			
$14_{0,14} - 13_{1,13}$	32 724.90	−0.02	32 759.05	−0.08		
$14_{1,14} - 13_{0,13}$	32 768.91	−0.01	32 803.02	−0.08		

[a] Accurate to ±0.05 MHz. [b] Unresolved asymmetry doublets labeled by limiting prolate quantum number only. [c] Observed minus calculated frequencies from constants of Table III.

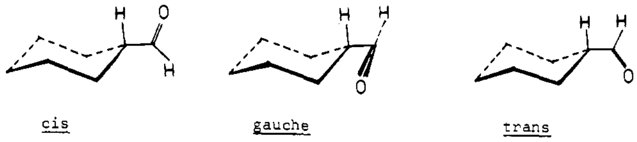

Figure 1. Possible rotameric forms for cyclohexanecarboxaldehyde.

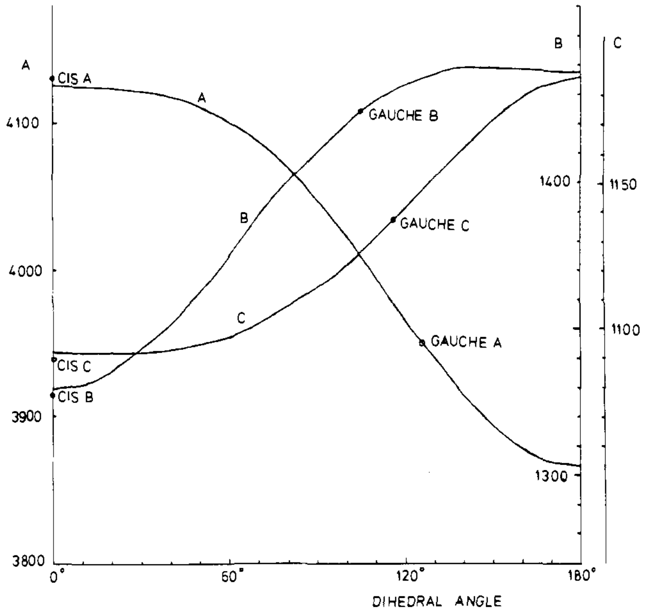

Figure 2. Variation of rotational constants (MHz) with dihedral angle about C_1-CHO for cyclohexanecarboxaldehyde.

Table III. Rotational Constants (MHz) and Centrifugal Distortion Constants (kHz) for Cyclohexanecarboxaldehyde

	cis $v = 0$	gauche $v = 0$	gauche $v = 1$	gauche $v = 2$
A	4131.52 (9)[a]	3951.70 (9)	3944.5 (2)	3938.4 (2)
B	1327.701 (5)	1424.402 (2)	1424.705 (6)	1425.178 (6)
C	1090.131 (6)	1137.299 (1)	1138.627 (2)	1139.885 (3)
Δ_J	0.03 (1)			
Δ_{JK}	3.16 (2)			

[a] Errors represent one standard deviation from least-squares fit.

Table IV. Moments of Inertia (amu Å^2) and the Structure of *cis*-Cyclohexanecarboxaldehyde

ring geometry	aldehyde geometry
∠CCC[a] = 112.3°	∠HC$_1$C[e] = 106.7°
β[b] = 52.4°	C$_1$-C[f] = 1.501 Å
C-C[c] = 1.526 Å	C=O[f] = 1.216 Å
C-H[c] = 1.096 Å	C-H[f] = 1.114 Å
∠HCH[d] = 106.7°	∠C$_1$CO[f] = 123.9°
	∠C$_1$CH[f] = 117.5°

	obsd	calcd
I_a	122.322	122.495
I_b	380.640	380.113
I_c	463.592	462.885
$\frac{1}{2}(I_a + I_c - I_b)$	102.637	102.634

[a] Determined from P_{bb}. [b] Dihedral angle between alternate C-C bonds, derived from ∠CCC. [c] Assumed from propane; see ref 10. [d] Derived from relation ∠CCC + ∠HCH = twice the tetrahedral angle; see ref 10. [e] Assumed equal to ∠HCH at ring methylene group. [f] Assumed from acetaldehyde; see ref 1a.

Conformational Energy Difference. The cis-gauche energy difference was determined by relative intensity measurements for several different pairs of a-type transitions. The ratio of cis to gauche a-dipole moment components is necessary for the analysis of this data. A Stark effect dipole moment determination was not feasible for this molecule; therefore a simple dipole moment calculation was undertaken, using a value of 2.3 D as the moment along the C=O bond.[11] This gave a value of 1.33 for the a-dipole moment ratio. The gauche conformer is then more stable than the cis by 720 ± 200 cal/mol.

Internal Barrier. R-Branch, b-type transitions were assigned for the $v = 0$ and $v = 1$ torsional states of gauche cyclohexanecarboxaldehyde (b-type transitions for $v = 2$ were too weak to observe). Since the b-dipole moment is an odd function of the torsional angle about C_1-CHO, it connects torsional states of opposite parity. b-Type microwave transitions will therefore show splittings equal to twice the torsional tunnelling frequency.[12] A careful examination was made of the b-type transitions in the $v = 0$ and $v = 1$ states: no splittings were observed. This gives a lower bound of 1.7 kcal/mol for the potential barrier at the trans conformation as measured from the two equivalent gauche minima.[13]

Discussion

The observed conformations of cyclohexanecarboxaldehyde follow the usual trend for the simpler CH_2XCOY compounds.[1] Our result that the gauche conformer is more stable than the cis by 720 ± 200 cal/mol is in reasonable agreement with the liquid-phase NMR ΔH value of 400 cal/mol measured by

Karabatsos and Hsi.[5] It is in excellent agreement with the prior molecular mechanics prediction by Allinger et al.[6] of 760 cal/mol; no other details of the potential function for internal rotation about C_1-CHO were given in their calculation.

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Supplementary Material Available: Complete versions of Tables I and II (2 pages). Ordering information is given on any current masthead page.

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(13) A three-term potential function of the form $\Sigma_n(V_n 2)(1 - \cos n\theta)$ with $V_1 = -222$, $V_2 = -111$, and $V_3 = 550$ cm^{-1} has the right qualitative features to describe internal rotation about the C_1–CHO bond in cyclohexanecarboxaldehyde. It has three minima at $\theta = 0$ (cis) and ±120° (gauche), three maxima at $\theta \sim \pm 60$ and 180° (trans), $V_{(cis)} - V_{(gauche)} = 250$ cm^{-1}, and a gauche torsional fundamental spacing of 90 cm^{-1}. Furthermore, this potential function gives splittings of 0.12 MHz for b-type microwave transitions in the $v = 1$ state of the gauche conformer which is approximately the limiting resolution of the experiment. The minimum trans barrier, $V_{(trans)} - V_{(gauche)}$, is therefore 580 cm^{-1}.

High-Resolution Microwave Spectra and Conformations of 2-Tetrahydropyranylcarbinol and 2-Aminomethyltetrahydropyran

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Abstract: High-resolution microwave spectral assignments for single conformational isomers of both 2-tetrahydropyranylcarbinol and 2-aminomethyltetrahydropyran are reported. Spectra for various deuterated species have also been analyzed enabling the principal axis coordinates of the hydroxyl and amino hydrogen atoms to be determined. Two structures for both the carbinol (+sc, 300 or ap, 60) and for the amine (+sc, 300 or ap, 300) are consistent with this data, confirming the conclusions of a recent low-resolution study. Qualitative dipole moment arguments indicate that the observed conformation for both molecules is +sc, 300, which allows OH···O or NH···O internal hydrogen bonding.

Introduction

Low-resolution microwave spectroscopy has shown that 2-tetrahydropyranylcarbinol and 2-aminomethyltetrahydropyran exist predominantly as single conformational species in the gas phase.[1] However, the low-resolution results were unable to distinguish between two staggered conformations of both the hydroxymethyl and aminomethyl groups (+synclinal or antiperiplanar) attached in the equatorial position to the chair form of the tetrahydropyran ring (see Figure 1). This raises the question of whether internal hydrogen bonding between the 2-substituent and ring oxygen is important in determining the conformation of these molecules which are simple model compounds for the pyranose sugars. The present paper reports a high-resolution investigation and on the basis of this data preferred conformations for both molecules are proposed.

Experimental Section

Samples of 2-tetrahydropyranylcarbinol and 2-aminomethyltetrahydropyran were purchased from Aldrich Chemical Co. and used without further purification. Microwave spectra were recorded on a Hewlett-Packard 8460 A MRR spectrometer. The spectrum of the amine was weak and so high gain (−70 dBm) and a 3-s time constant in the detection system were necessary to obtain useful intensities. Spectra for deuterated species were obtained by D_2O exchange in the waveguide cell.

Results

2-Tetrahydropyranylcarbinol. A sample of the measured transitions for the vibrational ground state of 2-tetrahydropyranylcarbinol (OH and OD species) is shown in Table I together with rigid rotor fits. The asymmetry of the molecule ($\kappa = -0.80$) enabled an accurate determination of all three rotational constants from the a-type spectrum alone and these are shown in Table II. The substitution coordinates (r_s) of the hydroxyl hydrogen were then calculated by application of Kraitchman's equations[2,3] using the observed moments of inertia for the OH and OD species (see Table II). The c coordinate is too small to be located by this method which ignores vibrational effects.

The low-resolution results could safely rule out all conformations except +sc, 300 and ap, 60 (where the numbers refer to the dihedral angle between the O-H and C(2)-C bonds). This conclusion is confirmed in the present high-resolution work by comparison of the observed hydrogen coordinates with

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