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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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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Table I. Observed[a] and Calculated Frequencies (MHz) for 2-Tetrahydropyranylcarbinol

transition[b] $J'_{K'_{-1}K'_{+1}} - J''_{K''_{-1}K''_{+1}}$	OH species ν_{obsd}	OH species $\Delta\nu^c$	OD species ν_{obsd}	OD species $\Delta\nu^c$
$13_8 - 12_8$	33 148.02	−0.08	32 630.91	0.01
$13_7 - 12_7$			32 670.73	−0.05
$13_{5,9} - 12_{5,8}$	33 348.04	−0.02	32 826.73	0.04
$13_{5,8} - 12_{5,7}$	33 382.92	−0.02	32 860.15	−0.06
$13_{4,10} - 12_{4,9}$	33 396.42	−0.02		
$13_{4,9} - 12_{4,8}$	33 792.43	−0.07	33 259.18	0.02

[a] Accurate to ±0.05 MHz. [b] Unresolved asymmetry doublets labeled by limiting prolate quantum number only. [c] Observed minus calculated frequency from rigid rotor fit.

Table II. Rotational Constants (MHz) and Principal Axis Coordinates (Å) of Hydroxyl Hydrogen for 2-Tetrahydropyranylcarbinol

	OH species	OD species
A	4064.0 (3)[a]	4017.8 (2)
B	1412.043 (5)	1390.046 (4)
C	1124.141 (3)	1106.652 (2)

r_s H coordinates (in OH principal axis system)

	obsd[b]	calcd +sc, 300	calcd ap, 60
a	2.377	−2.530	−2.578
b	1.214	1.274	−1.264
c	0[c]	−0.176	−0.139

[a] Numbers in parentheses are standard deviations from least-squares fit. [b] Sign undetermined. [c] Assumed value; the Kraitchman calculation gives an imaginary value for the c coordinate.

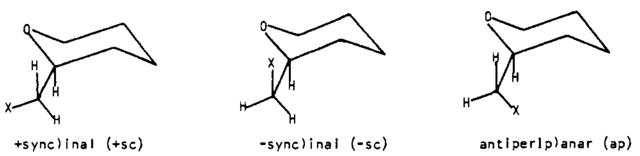

Figure 1. Designation of the hydroxymethyl or aminomethyl moiety in D-pyranoses (X = OH or NH_2).

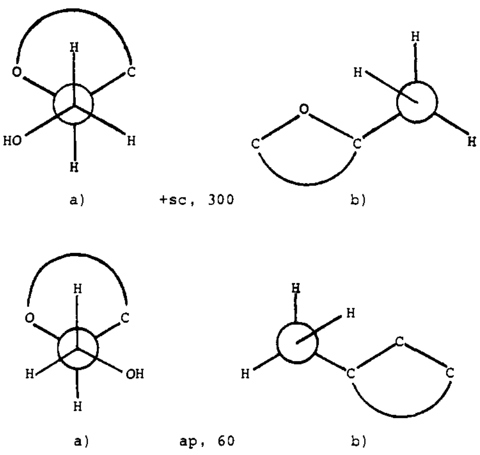

Figure 2. The +sc, 300 and ap, 60 conformations of 2-tetrahydropyranylcarbinol viewed along (a) C(2)-C bond and (b) C-O(H) bond. +sc, 300 is the favored structure in the gas phase; see text.

those calculated for +sc, 300 and ap, 60 model structures (see Table II and Figure 2). Unfortunately, a unique choice of conformation is still difficult to make owing to the similar magnitude of the two sets of calculated coordinates. But distinction can be made through the expected magnitudes of the dipole moment components along the principal axes. Similar arguments to establish molecular conformation have recently been proposed for glycine.[4] The dipole components were computed for the two possible conformations using the bond moments $\overrightarrow{\text{C-O}}$ = 0.74 D and $\overrightarrow{\text{H-O}}$ = 1.51 D[5] and the simple assumption that the total dipole moment is given by their vector sum. The results are (1) for +sc, 300, μ_a = 1.30, μ_b = 0.38, and μ_c = 0.23 D and (2) for ap, 60, μ_a = 1.03, μ_b = 1.48, and μ_c = 0.26 D, which predict a large difference in the (μ_b/μ_a) ratio between the two conformations.[6]

Experimentally it was found impossible to obtain resolved Stark effects for such weak, high-J transitions. However, the small μ_c value predicted for both +sc, 300 and ap, 60 conformations is consistent with the observed slow Stark effects of the a-type $J + 1_{1,J+1} - J_{1,J}$ and $J + 1_{0,J+1} - J_{0,J}$ transitions despite a large μ_c Stark coefficient. This large coefficient is due to the c-type near degeneracy between the $J_{1,J}$ and $J_{0,J}$ levels for high J values.[7] More significantly, the nearby b-type $J + 1_{1,J+1} - J_{0,J}$ and $J + 1_{0,J+1} - J_{1,J}$ transitions are too weak to observe even with precise frequency predictions. The same b-type lines were readily assigned in the spectrum of cyclohexanecarboxaldehyde.[8] From observed intensities of the a-type lines it is estimated that $\mu_b \leq 0.3\ \mu_a$, which is strong evidence for the +sc, 300 conformation for 2-tetrahydropyranylcarbinol in the gas phase (see Figure 2).

2-Aminomethyltetrahydropyran. A sample of the high-resolution spectral assignments of the vibrational ground state of 2-aminomethyltetrahydropyran and three deuterated species is presented in Table III. Rotational constants derived from rigid rotor fits are shown in Table IV. Only B + C could be

Table III. Observed[a] and Calculated Frequencies (MHz) for 2-Aminomethyltetrahydropyran

transition[b] $J'_{K'_{-1}K'_{+1}} - J''_{K''_{-1}K''_{+1}}$	NH_2 species ν_{obsd}	NH_2 species $\Delta\nu^c$	NDH″ species ν_{obsd}	NDH″ species $\Delta\nu^c$	NH′D species ν_{obsd}	ND_2 species ν_{obsd}	ND_2 species $\Delta\nu^c$
$15_8 - 14_8$	37 819.82	−0.21	37 122.09	−0.05	36 858.59	36 209.03	0.05
$15_7 - 14_7$			37 178.96	0.06	36 910.52	36 259.48	0.09
$15_{6,10} - 14_{6,9}$			37 265.95	−0.10		36 337.31	0.17
$15_{6,9} - 14_{6,8}$			37 272.16	−0.10		36 341.67	0.08
$15_{5,11} - 14_{5,10}$			37 381.44	0.19		36 444.02	0.16
$15_{5,10} - 14_{5,9}$			37 479.22	−0.01		36 518.85	0.16
$15_{4,11} - 14_{4,10}$	38 860.81	−0.01	38 128.91	0.00			
$15_{3,13} - 14_{3,12}$						35 924.47	0.12
$15_{3,12} - 14_{3,11}$			38 812.19	−0.01		37 799.43	0.09
$15_{2,13} - 14_{2,12}$						36 992.99	−0.07
$15_{1,15} - 14_{1,14}$	34 332.46	0.06					
$15_{0,15} - 14_{0,14}$	34 341.90	0.05					

[a] Accurate to ±0.05 MHz. [b] Unresolved asymmetry doublets labeled by limiting prolate quantum number only. [c] Observed minus calculated frequency from rigid rotor fit.

Table IV. Rotational Constants (MHz) and Principal Axis Coordinates (Å) of Amino Hydrogens for 2-Aminomethyltetrahydropyran

	NH_2 species	ND_2 species	NDH″ species	NH′D species
A	4041.0 (2)[a]	3947.1 (3)	3989.6 (4)	
B	1391.137 (4)	1327.79 (1)	1365.384 (9)	$B + C =$
C	1114.462 (3)	1072.55 (2)	1094.15 (1)	2443.3

r_s H′ coordinates (in NH_2 principal axis system)

		calcd	
	obsd[b]	+sc, 300	ap, 300
a	2.608	−2.569	−2.618
b	1.280	1.284	−1.275
c	0.153	−0.220	−0.182

r_s H″ coordinates (in ND_2 principal axis system)

		calcd	
	obsd	+sc, 300	ap, 300
a	3.018	−2.819	−2.839
b	0.299	0.408	−0.357
c	1.103	1.144	1.159

[a] Numbers in parentheses are standard deviations from least-squares fit. [b] Sign undetermined.

determined for the NH′D species owing to weak intensities and interference from lines of the NDH″ species. Therefore r_s coordinates of the amino hydrogens H′ and H″ had to be calculated in the NH_2 and ND_2 principal axes systems, respectively (see Table IV).

The low-resolution results for 2-aminomethyltetrahydropyran were consistent with only the +sc, 300 and ap, 300 conformations (where the numbers refer to the dihedral angle between the N-H and C(2)-C bonds). These conformations are shown in Figure 3. The present high-resolution assignments confirm this conclusion but the ambiguous choice of conformation still remains, as is evident from the observed and calculated amino hydrogen coordinates shown in Table IV. However, there is a difference in predicted (μ_b/μ_a) ratios for the +sc, 300 and ap, 300 conformations. The results of a bond moment calculation with $\overrightarrow{H\text{-}N} = 1.31$ D and $\overrightarrow{C\text{-}N} = 0.22$ D are (1) for + sc, 300, $\mu_a = 0.96$, $\mu_b = 0.65$, and $\mu_c = 1.29$ D and (2) for ap, 300, $\mu_a = 0.68$, $\mu_b = 1.69$, and $\mu_c = 1.26$ D. In contrast to 2-tetrahydropyranylcarbinol, the a-type $J + 1_{1,J+1} - J_{1,J}$ and $J + 1_{0,J+1} - J_{0,J}$ transitions for 2-aminomethyltetrahydropyran modulate at very low Stark voltages consistent with the predicted larger μ_c dipole moment for both +sc, 300 and ap, 300 conformations. Furthermore, the accurately predicted b-type spectrum is too weak to be detected, giving an estimated $\mu_b \leq 0.7\ \mu_a$ for this molecule. This would favor the +sc, 300 conformation for 2-aminomethyltetrahydropyran in the vapor state (see Figure 3).

Discussion

Further support for the above-proposed conformations for 2-tetrahydropyranylcarbinol and 2-aminomethyltetrahydropyran is provided by high-resolution microwave studies in the vapor phase of the simpler model compounds 2-methoxyethanol[9] and 2-methoxyethylamine.[10] Both molecules were found to exist predominantly as single conformations with structures analogous to the + synclinal ones shown in Figures 2 and 3, allowing OH···O and NH···O internal hydrogen bonds.

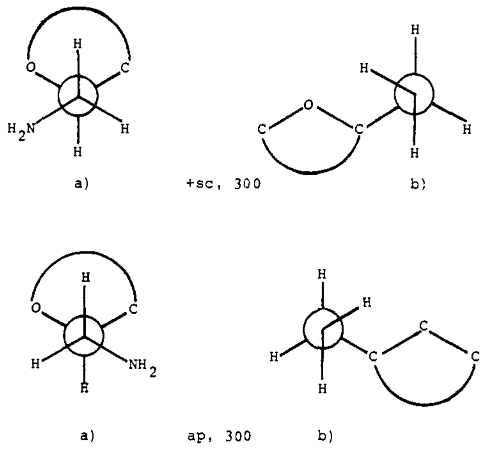

Figure 3. +sc, 300 and ap, 300 conformations of 2-aminomethyltetrahydropyran viewed along (a) C(2)–C bond and (b) C–N bond. +sc, 300 is the favored structure in the gas phase; see text.

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

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