

Low-Frequency Vibrational Spectra and Ring-Puckering Potential Energy Function of 1,3-Dioxole. A Convincing Demonstration of the Anomeric Effect

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Abstract: 1,3-Dioxole, $\text{OCH}_2\text{OCH}=\text{CH}$, has been synthesized and its far-infrared and low-frequency Raman spectra have been analyzed. The gas-phase far-infrared spectrum shows a series of eleven single-quantum-jump and three triple-quantum-jump transitions in the 40–330 cm^{-1} region. The low-frequency Raman spectrum exhibits eight ring-puckering transitions corresponding to $\Delta\nu = 2$ or 4 transitions in the 160–300- cm^{-1} region. The ring-puckering potential energy function was determined to be $V(\text{cm}^{-1}) = (1.59 \times 10^6)x^4 - (4.18 \times 10^4)x^2$, where x is the ring puckering coordinate in angstroms. This function indicates that the molecule is puckered with a barrier to planarity of 275 cm^{-1} and a bending angle of 24° . The unexpected nonplanarity of 1,3-dioxole is attributed to the anomeric effect which can be present in molecules with O–C–O linkages. Molecular mechanics calculations utilizing the MM3 parametrization predict a planar structure for this molecule. However, the anomeric effect dictates that each of the $=\text{C}-\text{O}-\text{C}-\text{O}$ torsional angles should have a strong desire to increase from 0° toward 90° in order to optimize $n-\sigma^*$ overlap. When the MM3 force field is modified to reflect this by increasing the magnitude of the 2-fold torsional potential energy term V_2 to -5.965 kcal/mol, a reasonably good agreement between the experimental and molecular mechanics potential functions can be obtained.

Introduction

The conformations of many small-ring molecules are determined primarily by ring-angle strain and torsional forces. For molecules such as cyclobutane and cyclopentene the angle strain tends to keep the rings planar whereas the CH_2-CH_2 torsional interactions favor puckered ring conformations. For six-membered-ring molecules (e.g. cyclohexene and cyclohexane) both the angle strain and torsional forces favor nonplanar conformations. A particularly suitable method for characterizing the energetics of the conformational changes in these types of molecules involves the use of far-infrared and low-frequency Raman spectroscopy to determine the one- or two-dimensional vibrational potential energy functions governing the conformational changes.¹⁻³ These potential functions provide the conformational energy minima, the bending and/or twisting angles, the barriers to planarity, and the barriers to various interconversion processes.

The conformations and barriers to planarity (if any) of cyclopentene and the analogous molecules shown in Figure 1 can readily be understood in terms of the torsional and angle strain forces. The average angle in a planar five-membered ring is 108° , and this value decreases as the ring is puckered. Thus, for molecules I through VIII, which prefer to have internal X=C=C angles (X = C, O, S, or Si) of approximately 120° and which prefer to have most of the other ring angles close to the tetrahedral value of 109.5° , the angle strain increases as the rings pucker. On the other hand, the two CH_2-CH_2 torsional interactions in cyclopentene (I) are of sufficient magnitude to twist the molecule into a puckered conformation with a dihedral angle of 26° and a barrier to planarity of 232 cm^{-1} .⁴ 2,3-Dihydrofuran (II) has similar angle strain and torsional forces, but since only one CH_2-CH_2 interaction is present, the barrier is only 83 cm^{-1} .⁵ The

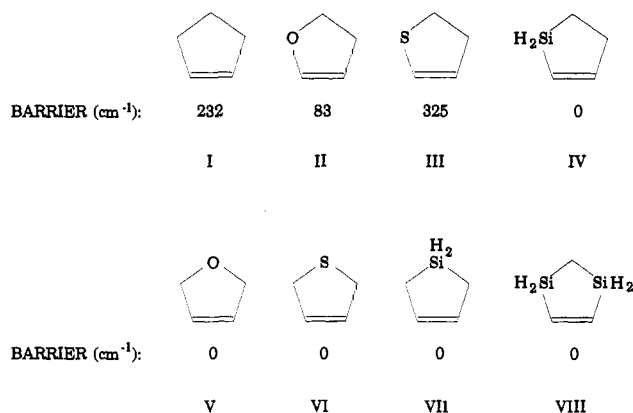


Figure 1. Barriers to inversion for five-membered rings.

analogous sulfur compound (III) has a barrier of 325 cm^{-1} ,⁶ with the increased barrier arising from the decreased angle strain. The larger sulfur atom in the ring has a smaller CSC angle bending force constant and opposes the puckering to a lesser extent. The planarity of silacyclopent-2-ene (IV) is somewhat surprising.⁷ Apparently, silicon d orbitals interact with the olefinic π system sufficiently to overcome CH_2-CH_2 and CH_2-SiH_2 torsional interactions which tend to pucker the molecule. 2,5-Dihydrofuran⁸ (V) and 2,5-dihydrothiophene⁹ (VI) each are planar, as expected, since there are no torsional forces tending to pucker the

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molecule. Silacyclopent-3-ene¹⁰ (VII) is also planar but the potential function has a very broad minimum. The SiH₂-CH₂ torsional forces favor a puckered ring but are not quite large enough to overcome the angle strain. 1,3-Disilacyclopent-4-ene (VIII) is similarly planar and nonrigid.¹¹

The experimentally determined ring-puckering potential function for each molecule has the form^{1,12}

$$V(x) = ax^4 + bx^2 \quad (1)$$

where a and b are potential energy parameters and x is the ring-puckering coordinate. This coordinate is defined as one-half the perpendicular distance between two ring diagonals. One diagonal connects the two atoms adjacent to the double bond; the other connects the atom across from the double bond to the center of the double bond. For a planar structure $x = 0$; for puckered structures it may be positive or negative. It has been shown^{13,14} that the potential energy parameters both have angle strain and torsional components:

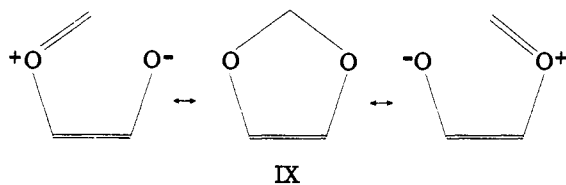
$$a = a_{str} + a_{tors} \quad (2)$$

and

$$b = b_{str} + b_{tors} \quad (3)$$

The value of b_{str} arises primarily from initial angle strain within the ring. If this is smaller in magnitude than b_{tors} , which for molecules I-III is negative, the ring becomes puckered. However, if $b_{str} \geq |b_{tors}|$, the ring remains planar, and this is the case for molecules IV-VIII.

From these above considerations it would be expected that 1,3-dioxole (IX), the molecule which we have investigated here, should be planar since it has no CH₂-CH₂ interactions. However, the conformations of molecules containing C-X-C-Y moieties, where X = N, O, or S and Y = Br, Cl, F, N, O, or S, can be affected by the *anomeric effect*. It is anticipated that the O-C-O linkage in 1,3-dioxole can result in significant anomeric interactions which can be represented by the resonance structures shown below.



IX

The anomeric effect, so named by Lemieux,¹⁵ was first identified in carbohydrate chemistry but has now been recognized as having importance for many molecules with the C-X-C-Y linkage.¹⁵⁻¹⁹ The initial observation for sugars was that, contrary to expectations from steric considerations, the axial methoxyl at the anomeric carbon was more stable than its equatorial counterpart. As shown by the resonance forms for 1,3-dioxole, the anomeric effect involves

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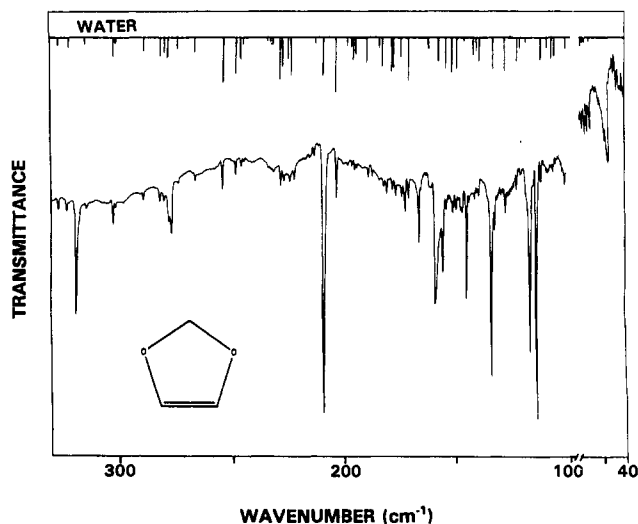


Figure 2. Far-infrared spectrum of vapor-phase 1,3-dioxole (20 Torr in a 20-cm cell). The frequencies and relative intensities of the water peaks, which also contribute weakly to the spectrum, are indicated.

donation of electron density from a lone pair on one oxygen atom into the adjacent carbon-oxygen bond. The interaction is believed to be the result of $n-\sigma^*$ overlap¹⁶⁻¹⁸ and is at a maximum when the -C-O-C-O torsional angle is at 90° . A planar 1,3-dioxole ring cannot have any anomeric interaction, but puckering the ring progressively increases the magnitude of this effect and can provide conformational stabilization.

We undertook this investigation of 1,3-dioxole to determine whether the anomeric effect would be great enough to pucker this ring molecule, and if so, to what extent. All other simple five-membered-ring molecules which have been found in earlier studies to be nonplanar are so because of the presence of CH₂-CH₂ interactions. Since 1,3-dioxole does not possess these, any barrier to planarity would have to arise from the anomeric effect.

Experimental Section

1,3-Dioxole (bp $51-52^\circ\text{C}$) was synthesized at the University of Texas-Pan American following the procedure of Field.²⁰ The proton NMR and gas-phase mid-infrared spectra confirmed the identity and purity of the sample.

The gas-phase far-infrared spectra were recorded at Texas A&M University on a Bomem DA3.002 interferometer using 20 Torr of sample in an 18-cm cell with polyethylene windows which had been deformed by pounding to eliminate fringing patterns. A liquid-helium-cooled germanium bolometer served as the detector. Typically, 2000 scans at 0.25 or 0.50 cm^{-1} resolution were recorded. A globar or mercury source and mylar beam splitters were employed to record the far-infrared spectra in the different spectral regions: 12 μm for the 75-350- cm^{-1} region and 25 μm for the 20-125- cm^{-1} region.

The low-frequency gas-phase Raman spectrum was recorded using an Instruments SA Jobin Yvon U-1000 monochromator equipped with a Coherent Radiation Innova 20 argon ion laser source. The laser power was adjusted to be approximately 1 W at the sample for the 5145 Å excitation line. A 5 cm gas cell was used to contain 200 Torr of 1,3-dioxole, and the ISA multipassing optics were used to increase the total laser intensity at the instrument focus.

Results and Discussion

Figures 2 and 3 show the vapor-phase far-infrared spectrum (40-60 and 100-330 cm^{-1}) and Raman spectrum (90-350 cm^{-1}) of 1,3-dioxole (IX), respectively. The far-infrared spectrum, expected to arise primarily from $\Delta v = 1$ and 3 transitions, which produce type C bands with sharp Q branches, consists of a number of regularly spaced bands in the 110-180 cm^{-1} region and a very

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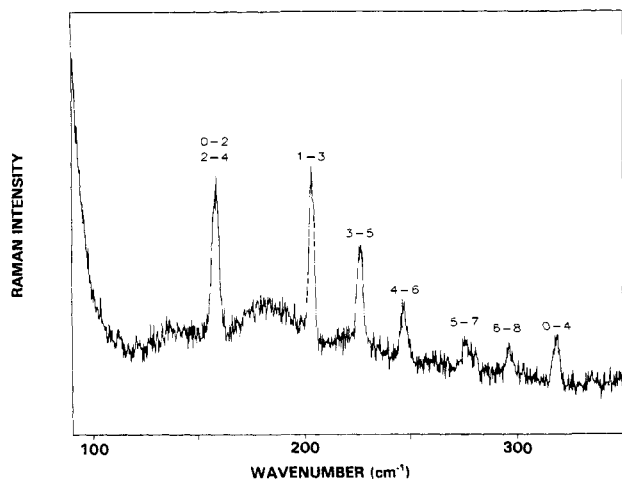


Figure 3. Vapor-phase Raman spectrum of 200 Torr of 1,3-dioxole.

Table I. Observed and Calculated Far-Infrared and Raman Frequencies (cm^{-1}) of 1,3-Dioxole

transition	frequency			relative intensity	
	obs	calc ^a	Δ	obs	calc ^a
far-infrared					
1 \rightarrow 2	158.6	158.4	0.2	0.5	1.1
2 \rightarrow 3	47.9	48.8	-0.9	0.2	0.3
3 \rightarrow 4	113.1	113.9	-0.8	1.0	1.0
4 \rightarrow 5	115.9	115.8	-0.1	0.6	0.8
5 \rightarrow 6	133.3	132.9	-0.4	0.7	0.7
6 \rightarrow 7	144.4	143.8	0.6	0.4	0.4
7 \rightarrow 8	155.0	153.8	1.2	0.3	0.2
8 \rightarrow 9	165.9	162.5	3.4	0.2	0.1
9 \rightarrow 10	172.0	170.7	1.6	0.2	0.1
10 \rightarrow 11	180.0	177.7	2.3	0.1	0.03
11 \rightarrow 12	185.8	185.7	0.1	0.08	0.02
0 \rightarrow 3	208.6	209.9	-1.3	(1.0)	(1.0)
1 \rightarrow 4	319.7	321.1	-1.4	0.5	0.2
2 \rightarrow 5	277.0	278.6	-1.6	0.2	0.2
Raman					
0 \rightarrow 2	161.3	161.0	0.3	0.9 ^b	0.6
1 \rightarrow 3	206.3	207.2	-0.9	(1.0)	(1.0)
2 \rightarrow 4	161.3	162.7	-1.4	0.9 ^b	0.4
3 \rightarrow 5	229.0	229.8	-0.8	0.6	0.7
4 \rightarrow 6	249.0	248.8	0.2	0.4	0.5
5 \rightarrow 7	278.0	276.8	1.2	0.3	0.4
6 \rightarrow 8	299.0	297.6	1.3	0.2	0.3
0 \rightarrow 4	321.8	323.8	-2.0	0.3	0.5

^a $V(\text{cm}^{-1}) = (1.59 \times 10^6)x^4 - (4.18 \times 10^4)x^2$ for x in Å. $g_{44}(x) = 0.0104575 - 0.0848264x^2 + 0.246789x^4 - 0.782108x^6$. ^b The observed relative intensity is the sum of the 0 \rightarrow 2 and 2 \rightarrow 4 transitions; total intensity: obs = 0.9, calc = 1.0.

intense band at 208.6 cm^{-1} . In addition, bands at 47.9 and 158.6 cm^{-1} and the doublet at 113.1 and 115.9 cm^{-1} add to the complexity of the spectrum. Planar molecules such as IV–VIII each show regular series of bands arising from the type of potential function given in eq 1 with $b > 0$. The irregularities in the far-infrared spectrum of 1,3-dioxole are characteristic of a nonplanar molecule. The 1,3-dioxole Raman spectrum, expected to arise from polarized $\Delta\nu = 2$ transitions, appears to have a more regular pattern, but as will be seen, it confirms that this molecule has a double-minimum potential energy function. The Raman spectrum was especially helpful in making the assignments of the transitions since the Raman frequencies (with double quantum jumps) should be sums of adjacent infrared transition frequencies. For example, the Raman band at 229.0 cm^{-1} is the sum of the infrared frequencies at 113.1 and 115.9 cm^{-1} . The former corresponds to the $\nu = 3 \rightarrow 5$ transition while the infrared bands represent the 3 \rightarrow 4 and 4 \rightarrow 5 transitions.

Table I summarizes both the far-infrared and Raman assignments for 1,3-dioxole. The intense infrared band at 208.6 cm^{-1}

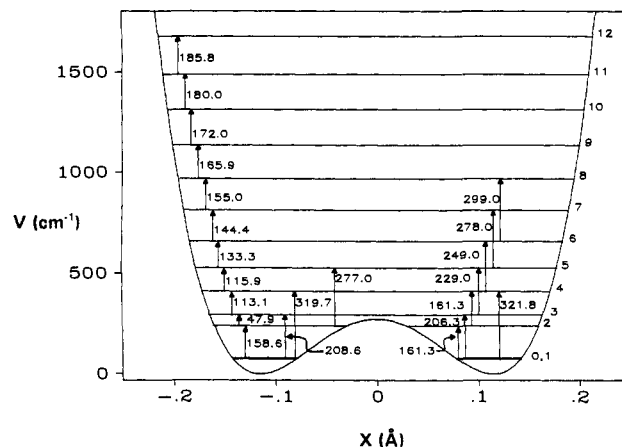


Figure 4. Ring-puckering potential energy function and observed infrared (left) and Raman (right) transitions of 1,3-dioxole.

can be seen to be the 0 \rightarrow 3 transition while 158.6 cm^{-1} corresponds to 1 \rightarrow 2. By utilizing the 47.9- cm^{-1} value for the 2 \rightarrow 3 frequency separation, the inversion doublet can be determined to be 2.1 cm^{-1} . Excellent correspondence can be found between the observed infrared and Raman frequencies. It should be noted that in the Raman spectrum, the band at 161.3 cm^{-1} is actually an unresolved doublet. On the basis of the observed infrared frequencies, the 0 \rightarrow 2 and 2 \rightarrow 4 Raman bands should occur at 160.7 and 161.0 cm^{-1} . Because the spectral slit width used to record the Raman spectrum was 3 cm^{-1} , these bands could not be resolved.

Determination of Potential Energy Function. The quantum mechanical Schrödinger equation

$$\mathcal{H}(x)\psi(x) = E\psi(x) \quad (4)$$

with

$$\mathcal{H}(x) = (-\hbar^2/2) \partial/\partial x g_{44}(x) \partial/\partial x + V(x) \quad (5)$$

must be solved in order to determine the quantum states for a ring-puckering potential energy function given in eq 1. Here, $g_{44}(x)$ represents the reciprocal reduced mass function for the ring-puckering coordinate x . The vector methods and computer programs necessary for calculating $g_{44}(x)$ have previously been presented.^{21,22} The MM3 molecular mechanics program of Allinger²³ was used to estimate the bond distances and bond angles for planar 1,3-dioxole. These were then utilized to calculate the $g_{44}(x)$ expansion

$$g_{44}(x) = 0.0104575 - 0.0848264x^2 + 0.246789x^4 - 0.782108x^6 \quad (6)$$

The availability of this kinetic energy expansion allows us to determine the potential energy parameters a and b of eq 1 utilizing the methods and computer programs we have previously described.^{1,12} The double-minimum potential function for the ring pucker of 1,3-dioxole is thus calculated to be

$$V(\text{cm}^{-1}) = (1.59 \times 10^6)x^4 - (4.18 \times 10^4)x^2 \quad (7)$$

where the puckering coordinate is given in angstroms. The barrier to planarity is found to be 275 cm^{-1} and the energy minima occur at $x = \pm 0.11$ Å or dihedral angles of $\pm 24^\circ$. Figure 4 shows this potential energy function along with the observed infrared and Raman transition frequencies. Table I compares the observed

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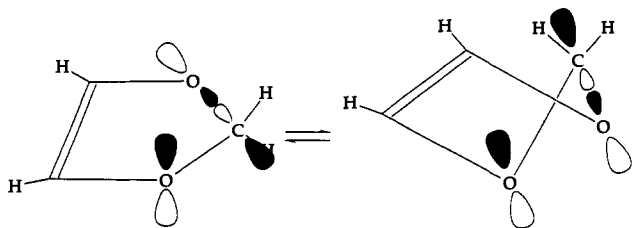


Figure 5. Orientation of the n and σ^* orbitals involved in the anomeric effect for planar and puckered conformations of 1,3-dioxole.

and calculated frequencies and intensities based on the function in eq 7. The agreement for the 22 observed transitions is quite remarkable since only two potential energy parameters (a and b) were utilized. This kind of result is typical, however, for many of the ring-puckering systems which we have studied over the years.¹

The ring-twisting vibration about the double bond for 1,3-dioxole gives rise to a Raman band centered around 502 cm^{-1} . This is at quite a high frequency as compared to values of 392 and 390 cm^{-1} for cyclopentene⁴ and 2,5-dihydrofuran,⁸ respectively. The band resembles a type B band (no Q branch) of an infrared spectrum. Because of its relatively high frequency, this mode is not expected to significantly interact with the ring-puckering motion or to affect the one-dimensional approximation used for the puckering mode.

Origin of the Double-Minimum Potential Energy Function.

Since the nonplanarity of 1,3-dioxole cannot arise from angle strain or $\text{CH}_2\text{-CH}_2$ torsional forces, it clearly results from the anomeric effect. Figure 5 shows that for a planar ring molecule the effective oxygen nonbonded orbital, which is perpendicular to the ring, cannot interact with the C-O σ^* orbital which lies in the plane of the ring. However, some orbital overlap can occur when the ring puckers, thus stabilizing the puckered conformation. This anomeric effect would reach a maximum when the ring dihedral angle is 90° . Since the ring-angle strain increases with puckering, however, the equilibrium molecular conformation (determined experimentally to be at a dihedral angle of 24°) represents a balance between these opposing forces.

In order to better assess the forces contributing to the ring-puckering potential energy function, we carried out MM3 molecular mechanics calculations as a function of the ring-puckering coordinate. At selected values of x , we allowed the computer program to calculate the minimum steric energy. When this was done utilizing the MM3 parametrization, the planar structure was calculated to have the lowest steric energy. Lauritsen and Allinger¹⁹ have recognized the importance of the anomeric effect for $\text{C-O-CH}_2\text{-O}$ linkages and have provided a prescription for incorporating it into the calculations. Nonetheless, MM3 predicts 1,3-dioxole to be planar. Figure 6 compares our experimentally determined ring-puckering potential energy function to that calculated from the MM3 program. The molecular mechanics calculation predicts a broad minimum at the planar structure and fails to produce a double minimum in the potential function.

The torsional parameters for rotation about the O-C bond in each $\text{-C-O-CH}_2\text{-O-}$ linkage have been given by Lauritsen and Allinger¹⁹ for the anomeric effect to be $V_1 = 0.25\text{ kcal/mol}$, $V_2 = -2.00\text{ kcal/mol}$, and $V_3 = 1.72\text{ kcal/mol}$. Utilization of these parameters produces the broad single minimum potential energy function shown in Figure 6. For 1,3-dioxole it should be the 2-fold potential term V_2 which primarily reflects the magnitude of the anomeric effect. Therefore, in our MM3 calculations, we increased the magnitude of this term until the calculated barrier matched that determined experimentally. This was achieved for $V_2 = -5.965\text{ kcal/mol}$. The modified MM3 potential energy curve resulting from the adjusted V_2 value is also shown in Figure 6 as MM3 (adj).

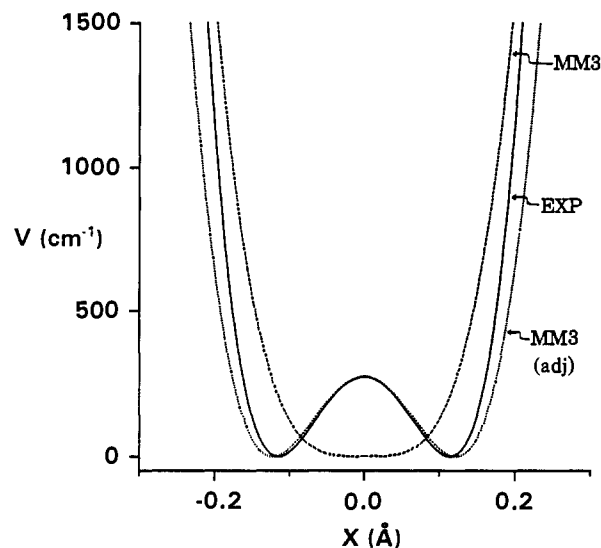


Figure 6. Comparison of experimental ring-puckering potential energy function with functions calculated from the MM3 molecular mechanics program. The MM3 (adj) curve was obtained by adjusting the V_2 torsional constant to obtain agreement with the experimental ring-puckering barrier value.

Table II. Ring-Puckering Potential Energy Parameters for Five-Membered-Ring Compounds

molecule	μ (u) ^a	a ($10^5\text{ cm}^{-1}/\text{\AA}^4$)	b ($10^4\text{ cm}^{-1}/\text{\AA}^4$)	ref
$\text{CH=CHCH}_2\text{CH}_2\text{CH}_2$ (I)	117.9	7.06	-2.56	4
$\text{CH}_2\text{CH=CHOCH}_2$ (II)	109.6	9.68	-1.87	5
$\text{CH}_2\text{CH=CHSCH}_2$ (III)	126.8	8.39	-3.30	6
$\text{CH}_2\text{CH=CHSiH}_2\text{CH}_2$ (IV)	129.6	18.28	1.84	7
$\text{CH}_2\text{CH=CHCH}_2\text{O}$ (V)	86.2	4.80	0.80	8
$\text{CH}_2\text{CH=CHCH}_2\text{S}$ (VI)	104.3	2.48	0.97	9
$\text{CH}_2\text{CH=CHCH}_2\text{SiH}_2$ (VII)	128.6	2.13	-0.05	10
$\text{CH=CHSiH}_2\text{CH}_2\text{SiH}_2$ (VIII)	138.7	1.48	0.30	11
$\text{CH=CHOCH}_2\text{O}$ (IX)	95.6	15.9	-4.18	this work

^a μ is the reduced mass.

While our value for V_2 is nearly three times greater than that recommended for the MM3 calculations, it is not inconsistent with calculations carried out for dimethoxymethane²⁴ and related molecules¹⁶⁻¹⁸ where barriers in the 4-8 kcal/mol range are common.

Table II compares the potential energy parameters of 1,3-dioxole (IX) to those of cyclopentene (I), 2,5-dihydrofuran (V), 2,3-dihydrofuran (II), and the other olefinic five-membered rings shown in Figure 1. For 2,5-dihydrofuran, the torsional forces are small and cannot overcome the angle strain. Thus, the parameter b is positive and the molecule has a planar equilibrium configuration. For cyclopentene, 2,3-dihydrofuran, and 1,3-dioxole, however, the torsional forces are clearly strong enough to overcome the angle strain resulting in a negative value of b . The magnitude of b for cyclopentene is larger than that of 2,3-dihydrofuran, as expected due to the presence of two $\text{CH}_2\text{-CH}_2$ torsional interactions vs only one for 2,3-dihydrofuran. However, the magnitude of b for 1,3-dioxole is greater than the value for cyclopentene even though 1,3-dioxole has no adjacent methylene groups. Clearly, the anomeric effect here is even more significant for 1,3-dioxole than the methylene-methylene torsional interactions are for cyclopentene.

The relatively large magnitude ($15.9 \times 10^5\text{ cm}^{-1}/\text{\AA}^4$) of the quartic parameter a for 1,3-dioxole in Table II also reflects the presence of unusual bonding interactions. This term arises

primarily from angle strain effects and increases when conjugation or π bonding is present. Only 2-silacyclopentene (IV), which is believed to have $p_{\pi}-d_{\pi}$ interactions, has a value of a greater than that of 1,3-dioxole.

Conclusion

We believe that the experimentally determined ring-puckering potential energy function for 1,3-dioxole presented here represents the best and most reliable demonstration of the anomeric effect. 1,3-Dioxole is puckered with a dihedral angle of 24° and a barrier to planarity of 275 cm^{-1} (0.79 kcal/mol). Without the anomeric effect this molecule would clearly be planar.

We thought 'twas strain or forces steric, but here we found 'twas anomeric.

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