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Vibrational Potential Energy Surfaces of 3,4-Dihydro-2*H*-pyran, 3,6-Dihydro-2*H*-pyran, 2,3-Dihydro-1,4-dioxin, and 4*H*-1,3-Dioxin

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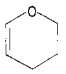
Abstract: The far-infrared and Raman spectra of several oxygen analogues of cyclohexene have been reported. The data have been reanalyzed for each molecule in terms of two-dimensional vibrational potential energy surfaces for the ring-bending and ring-twisting vibrations. Kinetic energy functions for each vibration were determined using vectorial methods. Coefficients for quartic–quadratic potential energy functions with fourth-order cross terms were calculated. In each case, the twisted (half-chair) conformation has the lowest energy. The bent (boat) conformations were determined to be saddle points in the surfaces with energies 3120 to 3830 cm^{-1} (37.2 to 45.6 kJ/mol) above the energy minima. The barriers to planarity range from 3500 to 4130 cm^{-1} (41.8 to 49.4 kJ/mol). The angles determined for the twisting of the ring are in satisfactory agreement with microwave results.

Infrared and Raman spectra have successfully been utilized to study the conformational energetics of many small ring molecules.[1-4] Most conformational analyses using far-infrared and Raman spectra have concentrated on four- and five-membered rings and have utilized one-dimensional potential energy functions to represent the ring-bending motions. However, the interaction of two[5,6] or three[7] vibrations has also been treated. Six-membered rings, which have three out-of-plane ring vibrations, have been investigated by these methods to a lesser degree because of their vibrational complexity. The conformational problem is simplified somewhat for cyclohexene and related molecules since a double bond in the ring restrains one of the vibrations (its frequency is increased) so that only the other two modes need to be considered for the potential energy surface studies. The highly coupled ring-bend and the single-bond ring-twist (SB twist) vibrations can therefore be utilized to represent the primary conformational changes. The third out-of-plane mode, the double-bond twist (sometimes called the torsion), is at a higher frequency and is not coupled as strongly.

The gas-phase far-infrared and Raman spectra of some oxygen analogues of cyclohexene have previously been reported.[8-11] Several series of bands for the ring-bending and ring-twisting vibrations and combination bands were observed for each molecule. The spectra of 3,4-dihydro-2*H*-pyran (I) (which in the past has been called 2,3-dihydropyran) and 2,3-dihydro-1,4-dioxin (II) (1,4-dioxene) were originally analyzed with a two-dimensional quartic–quadratic potential energy surface for the ring-twisting and ring-bending vibrations by Lord, Rounds, and Ueda[8] (LRU). The twisted (half-chair) conformation was found to have the lowest energy in each case. The twist angles at the energy minima, however, were calculated to be much larger than those determined by subsequent microwave[12,13] studies. The bent structures were calculated to have second minima on the potential surface only a few hundred cm^{-1} higher in energy than the twist forms. However, no evidence for the existence of the twist conformers has been found for any of these molecules from their microwave or infrared spectra.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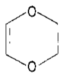
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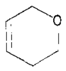
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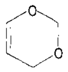
IV

Force-field (molecular mechanics) calculations on cyclohexene[14-16] predict that the bent structure is a transition state, rather than a stable structure, in the interconversion of the two equivalent twisted conformations. Using similar calculations, Dodziuk, von Voithenberg, and Allinger[17] did not find a bent structure for 3,4-dihydropyran or 1,4-dioxene and calculated a barrier to planarity about half of that determined from the far-infrared spectra by LRU.

One-dimensional potential energy functions for the twist vibrations of 3,6-dihydro-2*H*-pyran (III) and 4*H*-1,3-dioxin (IV) (1,3-dioxene) have been calculated by Dixon et al.[11] (DKSW) based on their far-infrared spectra and an assumed reduced mass. The calculated barriers to planarity in that work were similar in magnitude (3300 to 4820 cm^{-1}) to those reported for 3,4-dihydropyran and 1,4-dioxene. Because one-dimensional functions cannot be expected to give very meaningful results for molecules with two strongly coupled vibrations, these results cannot be considered reliable. In light of these discrepancies for all four of the molecules, we have reinvestigated these oxygen analogues of cyclohexene.

Experimental Section

3,4-Dihydro-2*H*-pyran was purchased from Aldrich and was dried over $LiAlH_4$. Gas-phase midinfrared spectra were recorded on a Digilab FTS-60 FT-IR in a 8-cm path-length heatable cell with KBr windows.

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Table I. Kinetic Energy Expressions[a] for the Bending and Twisting Vibrations

	I $\overline{CH_2CH_2CH{=}CHOCH_2}$	III $\overline{CH_2CH_2CH{=}CHCH_2O}$	II $\overline{CH_2OCH{=}CHOCH_2}$	IV $\overline{CH_2OCH{=}CHCH_2O}$
		Bending		
$g_{44}^{(0)}$	0.008 002	0.007 002	0.009 291	0.008 170
$g_{44}^{(2)}$	−0.029 313	−0.000 805	−0.065 038	−0.026 863
$g_{44}^{(4)}$	−0.083 323	−0.315 261	0.246 287	−0.156 861
$g_{44}^{(6)}$	0.640 954	1.364 097	−0.600 220	1.019 215
		Twisting		
$g_{55}^{(0)}$	0.033 716	0.045 422	0.035 712	0.045 869
$g_{55}^{(2)}$	0.000 094	−0.014 446	−0.001 324	−0.004 389
$g_{55}^{(4)}$	−0.024 269	−0.010 891	−0.028 876	−0.040 822
$g_{55}^{(6)}$	0.008 597	0.003 596	0.012 999	0.023 601
		Bend–Twist Interaction		
$g_{45}^{(0)}$	−0.001 221	−0.001 346	0.000 001	−0.000 041

[a] The form of the kinetic energy function is $g_{ij} = g_{ij}^{(0)} + g_{ij}^{(2)}x_k^2 + g_{ij}^{(4)}x_k^4 + g_{ij}^{(6)}x_k^6$.

Calculations

The two-dimensional vibrational Hamiltonian used to analyze the spectroscopic data is given below

$$\mathcal{H}_{\text{vib}} = -\frac{\hbar^2}{2}\left[\frac{\partial}{\partial x_1}g_{44}\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_1}g_{45}\frac{\partial}{\partial x_2} + \frac{\partial}{\partial x_2}g_{45}\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2}g_{55}\frac{\partial}{\partial x_2}\right] + V \quad (1)$$

where x_1 is the ring-bending coordinate, x_2 is the ring-twisting coordinate, and g_{ij} are the kinetic energy functions (reciprocal reduced masses) for the bending ($i = j = 4$), twisting ($i = j = 5$), and the bend–twist interaction ($i = 4, j = 5$). The potential energy function is taken to have quadratic and quartic terms for each vibration and an interaction term. This is given by

$$V(x_1,x_2) = a_1x_1^4 + b_1x_1^2 + a_2x_2^4 + b_2x_2^2 + cx_1^2x_2^2 \quad (2)$$

The basis functions used for determining the energy levels and wave functions from the two-dimensional calculations were taken to be the products of one-dimensional wave-function solutions for each coordinate. For ring-twisting, the one-dimensional functions were obtained by solving a Hamiltonian with an appropriate double minimum quartic–quadratic potential function. For ring-bending, harmonic oscillator functions were used. These two one-dimensional wave functions were then multiplied together to give the basis set for the two-dimensional calculation. Typically, 15 basis functions in each coordinate were used yielding a 225 × 225 Hamiltonian matrix. After making an initial estimate for the coefficients of the two-dimensional potential energy function, the Hamiltonian was solved and the coefficients were adjusted with a least-squares procedure until the best agreement between the observed and calculated vibrational frequencies was found.

Vector methods for calculating the kinetic energy functions of four- and five-membered rings[18,19] have previously been described. Recently, we developed the vector models for representing the ring-bending and ring-twisting vibrations of six-membered rings[20] (Figure 1). The kinetic energy terms (reciprocal reduced masses) for ring-bending, g_{44}, and for ring-twisting, g_{55}, were calculated for 40 values of each coordinate. Sixth-order polynomial expressions for each as a function of coordinate were derived[21] using a Newton–Raphson technique. The bend–twist cross term, g_{45}, was also calculated. The kinetic energy functions for the molecules studied here are given in Table I.

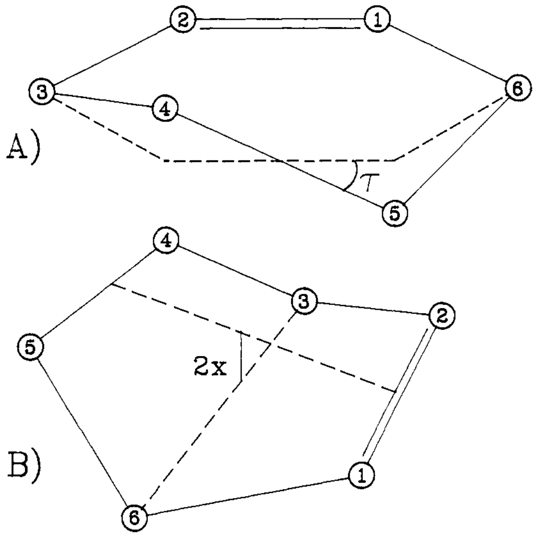

Figure 1. Vibrational coordinates for cyclohexene-like molecules: (A) twisted conformation, (B) bent conformation.

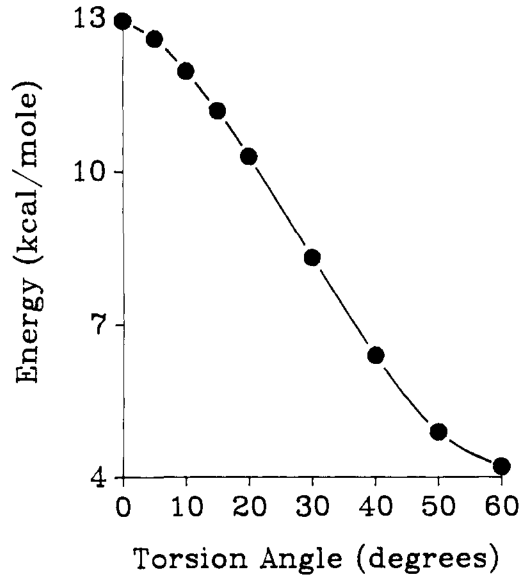

Figure 2. Potential energy as a function of the torsion angle (equals 2τ) calculated by molecular mechanics methods for 3,4-dihydro-2*H*-pyran (I) (60° = twisted conformation; 0° = bent conformation).

The relative energies of the various conformations of the molecules were also estimated using the molecular mechanics program, MM2.[22] We have found that molecular mechanics

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Table II. Two-Dimensional Potential Energy Functions[a] for Bending and Twisting of Oxygen Analogues of Cyclohexene

	I	III	II	IV
	$CH_2CH_2CH{=}CHOCH_2$	$CH_2CH_2CH{=}CHCH_2O$	$CH_2OCH{=}CHOCH_2$	$CH_2OCH{=}CHCH_2O$
a_1 (cm^{-1}/Å^4)	4.24×10^4	5.99×10^4	1.59×10^5	7.08×10^4
b_1 (cm^{-1}/Å^2)	-1.01×10^4	-1.19×10^4	-1.39×10^4	-1.04×10^4
a_2 (cm^{-1}/Å^4)	2.48×10^4	2.09×10^4	2.92×10^4	3.08×10^4
b_2 (cm^{-1}/Å^2)	-2.01×10^4	-1.86×10^4	-2.20×10^4	-2.08×10^4
c (cm^{-1}/Å^4)	1.70×10^5	1.74×10^5	1.96×10^5	2.27×10^5

[a] $V(x_1,x_2) = a_1x_1^4 + b_1x_1^2 + a_2x_2^4 + b_2x_2^2 + cx_1^2x_2^2$, where x_1 and x_2 are the bend and twist coordinates, respectively.

calculations can provide useful approximations of conformational barriers of small ring molecules.[23] Previous molecular mechanics calculations[17] on 3,4-dihydropyran and 1,4-dioxene included the effect of the lone pairs on the oxygen atoms. We chose not to include these in our calculations since they mainly affect the total energy and not the energy difference between the conformers. The energy for the SB twist (half-chair) conformation was calculated by allowing unrestricted motion of all of the atoms. The energy of the planar conformation was calculated by fixing the z coordinates of the six ring atoms and allowing all of the other coordinates to relax. The energy of the bent conformation was calculated by fixing the z coordinates of atoms 3, 4, 5, and 6 (Figure 1). This procedure, however, allowed for some slight twisting of the double bond as well.

In order to determine whether the MM2 program predicts the bent conformation to be a maximum or minimum along the path connecting the two twisting minima on the potential energy surface, we employed the "torsion angle driving option" of the MM2 program. The calculation was initiated with coordinates at the conformational minimum (i.e., the twisted conformation). The torsion angle (2τ) formed by the bonds between atoms 3, 4, 5, and 6 was then incrementally decreased to 0°, and the energy and structure were calculated at each point. Figure 2 is a plot of the energy as a function of torsion angle for 3,4-dihydropyran. The energy smoothly increases from the twisted (60°) to the bent (0°) conformation without crossing any barrier. Burkert and Allinger have noted some problems with the "torsion angle driving option",[24] but these have mainly been with the prediction of false barriers. In this case, no barrier was found between the two conformations, and the molecular mechanics program clearly predicts that the bent conformation is an energy maximum on the potential energy pathway between the two minima.

Results and Discussion

For each of the molecules we have used the data previously reported.[8-10] However, the data have been, in part, reassigned and reanalyzed. In addition, the kinetic energy expressions calculated for these molecules (Table I) were not previously available. The potential energy parameters determined here are given in Table II. For 3,4-dihydropyran (I) and 1,4-dioxene (II) the twisted conformations have the lowest energies and the bent conformations have only slightly lower energies than the planar structures. This is contrary to the previous analyses of I and II by LRU[8] who predicted that the bent conformations are only a few hundred cm^{-1} higher in energy than the twist conformations. The twist angles, τ, calculated by LRU to be 48.5° and 51.0° for I and II, respectively, were determined to be 36.5° and 35.1° in the present study (Table III). The new values correspond more closely to the microwave results[12,13] (30.5° for I and 29.9° for II) and to the predictions from the MM2 program (30.6° for I and 29.3° for II). The barrier to planarity, the energy difference between the twisted and planar conformations, is much lower for each molecule with our calculation, 4080 cm^{-1} (I) and 4130 cm^{-1} (II), than with the LRU calculation, 6160 cm^{-1} (I) and 6840 cm^{-1} (II). MM2 predicts the barriers to be even lower, 3080 cm^{-1} for I and 2300 cm^{-1} for II. However, the MM2 calculations are only estimates based on an empirically determined force field.

Table III. Twist Angle τ (deg)[a] of Oxygen Analogues of Cyclohexene

molecule	infrared		micro-wave	MM2
	this work	LRU[b]		
$CH_2CH_2CH{=}CHOCH_2$ (I)	36.5	51.0	30.5[c]	30.6
$CH_2CH_2CH{=}CHCH_2O$ (III)	38.2		31.5[d]	33.6
$CH_2OCH{=}CHOCH_2$ (II)	35.1	48.5	29.9[e]	29.3
$CH_2OCH{=}CHCH_2O$ (IV)	33.2			30.9

[a] The angle formed by the bond between atoms 4 and 5 and the plane containing atoms 6, 1, 2, and 3 (see Figure 1). [b] Reference 8. [c] Reference 12. [d] Reference 29. [e] Reference 13.

The barrier to interconversion in each of these molecules is the lowest energy pathway between the two equivalent twisted conformations. The top of the barrier may occur at the bent, planar, or some other conformation. However, for these molecules the barrier to interconversion is also the energy difference between the bent and twisted structures. The barriers we have determined (Table IV) are somewhat higher than those calculated by LRU or by use of the MM2 program. For 1,4-dioxene (II), MM2 predicts that the barrier to interconversion also is the barrier to planarity (i.e., all bent structures are higher in energy than the planar conformation), but we found the bent structure to be 300 cm^{-1} lower than the planar structure and the barrier to interconversion to be 3830 cm^{-1}. LRU, however, calculated the bent structure to be much lower, just 521 cm^{-1} above the twist minimum. The LRU barrier to interconversion of 2890 cm^{-1} corresponds to a transitional conformation between the bent and twisted conformations. For 3,4-dihydropyran (I), LRU calculated a barrier to interconversion of 2430 cm^{-1} and predicted that a bent structure lies only 352 cm^{-1} above the twisted conformation. Our results correspond to a barrier to interconversion for I of 3480 cm^{-1}, and this is also the energy difference between the bent and twisted conformations. The bent conformation lies 600 cm^{-1} below the planar conformation. MM2 estimates the bent conformation to be 120 cm^{-1} below the planar form.

Barriers to interconversion have also been determined by variable-temperature NMR studies.[25,26] These are lower than our vibrationally determined barriers (Table IV), but the NMR studies were carried out in a vinyl chloride solvent while the infrared and microwave spectra were recorded in the gas phase. In comparing barriers it should be noted that adding the zero-point energy that is incorporated in the vibrational barriers would increase the NMR barriers by about 200 cm^{-1}. In an infrared laser irradiation study[27] of 3,4-dihydropyran (I), an energy difference of 1270 cm^{-1} was found between I and a transient species which was attributed to the bent conformation. A variety of possible species were considered and the assignment of the transient to the bent conformation was made based on a process of elimination, but no clear proof was presented. This value appears to be much too low to be assigned in this fashion.

The overall fit between the observed spectroscopic data and the calculated values is generally only slightly better than in the previous calculations for I and II by LRU (Tables V and VI).

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Table IV. Barriers (cm^{-1}) to Interconversion (B_{int}) and Energy Differences (cm^{-1}) between the Twisted and Planar Conformations ($\Delta E_{p,t}$) and between the Bent and Twisted Conformations ($\Delta E_{b,t}$)

	infrared									
	this work			literature			molecular mechanics			NMR
molecule	$\Delta E_{p,t}$	$\Delta E_{b,t}$	B_{int}	$\Delta E_{p,t}$	$\Delta E_{b,t}$	B_{int}	$\Delta E_{p,t}$	$\Delta E_{b,t}$	B_{int}	B_{int}
$CH_2CH_2CH{=}CHOCH_2$ (I)	4080	3480	3480	6160[a]	352[a]	2430[a]	3080	2960	2960	2310[c]
$CH_2CH_2CH{=}CHCH_2O$ (III)	4130	3540	3540	4820[b]		4820[b]	3570	2080	2080	
$CH_2OCH{=}CHOCH_2$ (II)	4130	3830	3830	6840[a]	521[a]	2890[a]	2300	2300	2300	2670[d]
$CH_2OCH{=}CHCH_2O$ (IV)	3500	3120	3120	3300[b]		3300[b]	2270	2270	2270	2520[e]

[a] Reference 8. [b] Reference 11. [c] Reference 25. [d] Reference 26. [e] Reference 28.

Table V. Infrared Transition Frequencies for 3,4-Dihydro-2*H*-pyran (I)

	frequency (cm^{-1})		
$(\nu_{35},\nu_{36}) - (\nu_{35}',\nu_{36}')$	obsd	calcd	Δ
	Ring-Twisting Bands[a]		
(0,0)–(2,0)	280.1	281.1	-1.0
(2,0)–(4,0)	277.6	276.8	0.8
(4,0)–(6,0)	274.8	272.4	2.4
(6,0)–(8,0)	271.3	267.9	3.4
(0,1)–(2,1)	274.8	276.5	-1.7
(2,1)–(4,1)	271.3	271.9	-0.6
(4,1)–(6,1)	266.5	267.1	-0.6
(0,2)–(2,2)	269.5	271.9	-2.4
(2,2)–(4,2)	266.5	267.2	-0.7
(0,3)–(2,3)	265.0	267.6	-2.6
	Ring-Bending Bands[b]		
(0,0)–(0,1)	177.2	175.1	2.1
(0,1)–(0,2)	175.8	174.7	1.1
(0,2)–(0,3)	174.5	174.2	0.3
(0,3)–(0,4)	173.4	173.7	-0.3
(0,4)–(0,5)	172.5	173.1	-0.6
(0,5)–(0,6)	172.0[c]	172.5	-0.5
(2,0)–(2,1)	171.7	170.4	1.3
(2,1)–(2,2)	170.3	170.2	0.1
(2,2)–(2,3)	170.3	169.8	0.5
(2,3)–(2,4)	170.3	169.4	0.9
(2,4)–(2,5)	168.8[c]	168.8	-0.8
(4,0)–(4,1)	163.8	165.5	-1.7
(4,1)–(4,2)	165.7	165.5	0.2
(4,2)–(4,3)	165.7	165.2	0.5
(6,0)–(6,1)	157.4	160.1	-2.7
(6,1)–(6,2)	159.3	160.5	-1.2
	Twist-Bend Difference Bands[b]		
(2,0)–(0,1)	102.9	106.0	-3.1
(2,1)–(0,2)	98.8	101.7	-2.9
(2,2)–(0,3)	94.8	97.7	-2.9
(2,3)–(0,4)	91.6	93.8	-2.2
(2,4)–(0,5)	88.9	90.1	-1.2
(2,5)–(0,6)	86.8	86.4	0.4
(4,0)–(2,1)	106.0	106.4	-0.4
(4,1)–(2,2)	100.7	101.7	-1.0
(4,2)–(2,3)	96.9	97.3	-0.4
(6,0)–(4,1)	109.5	106.9	2.6
(8,0)–(6,1)	113.9	107.7	6.2

[a] From ref 9. [b] From ref 8 except as noted. [c] From ref 10.

Table VI. Infrared Transition Frequencies for 2,3-Dihydro-1,4-dioxin (II)

	frequency (cm^{-1})		
$(\nu_{35},\nu_{36})-(\nu_{35}',\nu_{36}')$	obsd	calcd	Δ
	Ring-Twisting Bands[a]		
(0,0)–(2,0)	297.4	299.9	-2.5
(2,0)–(4,0)	294.9	295.2	-0.3
(4,0)–(6,0)	291.4	290.2	1.2
(6,0)–(8,0)	289.0	285.0	4.0
(0,1)–(2,1)	291.4	291.4	-3.0
(2,1)–(4,1)	288.1	289.3	-1.2
(4,1)–(6,1)	285.1	283.9	1.2
(0,2)–(2,2)	285.1	289.2	-4.1
(2,2)–(4,2)	281.7	283.9	-2.2
(0,3)–(2,3)	281.7	284.3	-2.6
(0,4)–(2,4)	277.6	279.5	-1.9
	Ring-Bending Bands[b]		
(0,0)–(0,1)	191.3	190.6	0.7
(0,1)–(0,2)	190.7	190.5	0.2
(0,2)–(0,3)	189.9	190.2	-0.3
(0,3)–(0,4)	189.3	189.9	-0.6
(0,4)–(0,5)	188.8	189.5	-0.7
(0,5)–(0,6)	188.1	189.0	-0.9
(0,6)–(0,7)	187.4	188.4	-1.0
(2,0)–(2,1)	185.4	185.2	0.2
(2,1)–(2,2)	185.4	185.4	0.0
(2,2)–(2,3)	185.4	185.3	0.1
(2,3)–(2,4)	185.4	185.1	0.3
(2,4)–(2,5)	185.4	184.7	0.6
(4,0)–(4,1)	178.6	179.3	-0.7
(4,1)–(4,2)	179.9	180.0	-0.1
(4,2)–(4,3)	179.9	180.2	-0.3
(6,0)–(6,1)	171.1	173.0	-1.9
(6,1)–(6,2)	174.1	174.4	-0.3
(8,0)–(8,1)	163.0	166.1	-3.1
	Twist-Bend Difference Bands[b]		
(2,0)–(0,1)	106.2	109.2	-3.0
(2,1)–(0,2)	100.9	103.9	-3.0
(2,2)–(0,3)	96.6	99.0	-2.4
(2,3)–(0,4)	92.5	94.4	-1.9
(2,4)–(0,5)	88.8	90.0	-1.2
(4,0)–(2,1)	109.8	110.0	-0.2
(4,1)–(2,2)	103.1	104.0	-0.9
(4,2)–(2,3)	97.8	98.6	-0.8
(6,0)–(4,1)	113.9	111.0	2.9
(6,1)–(4,2)	105.0	103.9	1.1
(6,2)–(4,3)	98.0	98.1	-0.1

[a] From ref 9. [b] From ref 8.

However, our potential energy function succeeds in calculating the correct trend (decreasing frequencies) in the pure bending series for 3,4-dihydropyran and 1,4-dioxene while that of LRU does not. DKSW[11] used a one-dimensional Hamiltonian to calculate the pure twisting frequencies of 3,4-dihydropyran (I) and 1,4-dioxene (II). While these workers found a good fit to their data with a simple model which ignored vibrational coupling, their barriers to planarity of 5906 and 6691 cm^{-1} for the two molecules, respectively, cannot be considered very meaningful. The LRU two-dimensional functions also predicted high barriers, 6160 and 6840 cm^{-1}, respectively. The two-dimensional function which we have determined does slightly worse in fitting the pure twisting frequencies but fits the rest of the data much better. In addition, the barriers and twist angles determined from our function agree much more closely with the MM2, NMR, and microwave results. The twisting data alone (as used for the one-dimensional calculations by DKSW) suggest higher barriers to planarity than are reasonable. The problem arises from the fact that the barriers must be extrapolated from data that extends to less than half of the barrier height. In such cases the barrier is generally estimated to be too high. The fit to the twisting frequencies can be improved by adding higher order force constants to the potential energy function. A negative sixth-order term for the twisting coordinate, for example, does improve the fit to the four fundamental twisting frequencies. However, at high values

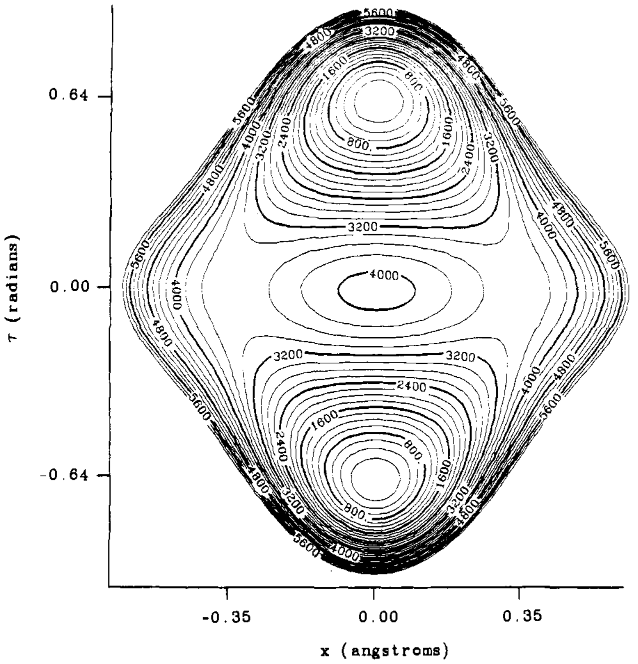

Figure 3. Potential energy surface for ring-bending (x) and ring-twisting (τ) of 3,4-dihydro-2H-pyran (I). Contour lines are drawn every 200 cm^{-1}.

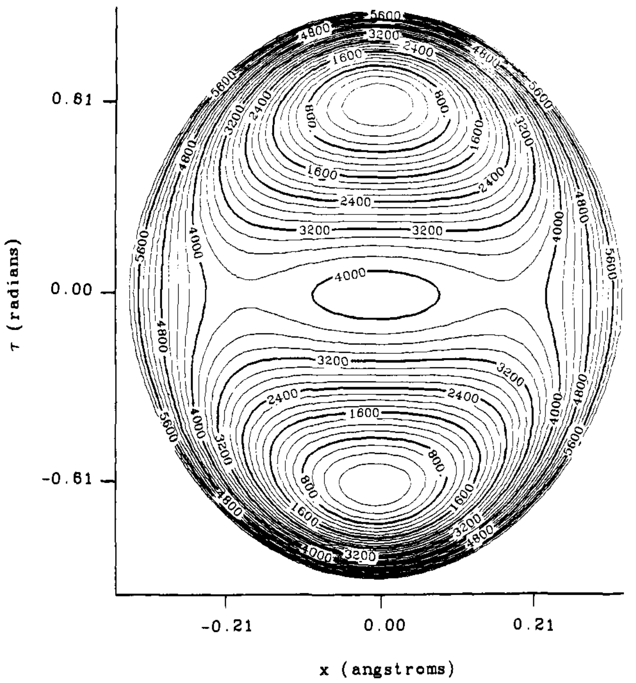

Figure 4. Potential energy surface for ring-bending (x) and ring-twisting (τ) of 2,3-dihydro-1,4-dioxin (II). Contour lines are drawn every 200 cm^{-1}.

Table VII. Infrared Transition Frequencies for 3,6-Dihydro-2H-pyran (III)

$(\nu_{35},\nu_{36})-(\nu_{35}',\nu_{36}')$	frequency (cm^{-1}) obsd[a]	calcd	Δ
	Ring-Twisting Bands		
(0,0)-(2,0)	299.7	298.4	1.3
(2,0)-(4,0)	296.4	293.7	2.7
(4,0)-(6,0)	292.2	288.6	3.6
(0,1)-(2,1)	292.2	292.7	-0.5
(2,1)-(4,1)	288.8	287.4	1.4
(4,1)-(6,1)	285.0[b]	281.7	3.3
(0,2)-(2,2)	286.8	287.8	-1.0
(2,2)-(4,2)	282.8	282.5	0.3
(4,2)-(6,2)	279.0[b]	277.1	1.9
(0,3)-(2,3)	281.2	283.2	-2.0
(2,3)-(4,3)	279.0	277.8	1.2
(0,4)-(2,4)	275.9	278.8	-2.9
	Ring-Bending Bands		
(0,0)-(0,1)	177.3	172.9	4.4
(0,1)-(0,2)	175.5	173.8	1.7
(0,2)-(0,3)	174.4	174.3	0.1
(0,3)-(0,4)	173.4	174.5	-1.1
(0,4)-(0,5)	172.7	174.6	-1.9
(0,5)-(0,6)	172.0	174.6	-2.6
(2,0)-(2,1)	170.2	167.2	3.0
(2,1)-(2,2)	169.5	168.9	0.6
(2,2)-(2,3)	168.8	169.7	-0.9
(2,3)-(2,4)	168.1	170.1	-2.0
(2,4)-(2,5)	167.3	170.2	-2.9
(4,0)-(4,1)	162.4	160.9	1.5
(4,1)-(4,2)	163.5	164.0	-0.5
(4,2)-(4,3)	165.1	164.9	0.2
(6,0)-(6,1)	151.9[b]	153.9	-2.0
(6,1)-(6,2)	159.2[b]	159.5	-0.3
(6,2)-(6,3)	160.3[b]	160.0	0.3
	Twist-Bend Difference Bands		
(2,0)-(0,1)	122.6	125.5	-2.9
(2,1)-(0,2)	117.3	118.9	-1.6
(2,2)-(0,3)	112.3	113.5	-1.2
(2,3)-(0,4)	107.7	108.7	-1.0
(2,5)-(0,6)	99.0	99.8	-0.8
(4,0)-(2,1)	126.6	126.6	0.0
(4,1)-(2,2)	119.3	118.5	0.8
(4,2)-(2,3)	113.9	112.9	1.0
(4,3)-(2,4)	110.6	107.7	2.9
(4,4)-(2,5)	100.6	103.0	-2.4
(6,0)-(4,1)	130.0	127.7	2.3

[a] From ref 11. [b] Reassigned.

of the coordinate the function turns around and goes to negative infinity. Since the frequency fit is already quite satisfactory considering that there are a number of approximations in this calculation (e.g., the neglect of interactions of the twist and bend with other vibrations), the use of additional potential constants is not warranted.

The potential energy surfaces for 3,4-dihydropyran (I) and 1,4-dioxene (II) are plotted in Figures 3 and 4. The central maximum occurs at the planar conformation, and there are two minima on the twisting coordinate axis corresponding to the two equivalent twisted conformations. To the right and left of the central maximum are saddle points along the bending coordinate. These demonstrate that the two equivalent bent structures are transition states in the interconversion of the two twisted conformations as predicted by MM2 (Figure 2). In LRU's surfaces, the bent conformations have minima lying 352 cm^{-1} (I) and 521 cm^{-1} (II) higher in energy than the twisted conformation. Their surfaces suggest that the bent conformations are stable structures and 10 to 20% of the molecules would be bent at room temperature. There is no evidence, however, of a bent structure in the microwave spectra of either molecule.[12,13] We have studied the vapor-phase midinfrared spectra of 3,4-dihydropyran at several temperatures (20 to 80 °C), but no bands attributable to a second conformation were found. Although lack of spectral evidence does not prove that a second conformation does not exist, it does mean that the energy difference between the bent and twisted structures in each of these molecules must be greater than 1000 cm^{-1} (rather than 352 or 521 cm^{-1} as predicted by LRU's potential energy surfaces).

The far-infrared spectra of 3,6-dihydropyran (III) and 1,3-dioxene (IV) were reported by DKSW[11] and three series of bending, twisting, and combination bands were assigned. Bands due to the third out-of-plane ring vibration, the twisting about the double bond, were also recorded and assigned. DKSW analyzed the data one-dimensionally, and only the four primary twisting transitions of each molecule were fit to a quartic–quadratic potential energy function. In our study, we have used more than 30 observed frequencies to determine the two-dimensional potential energy surfaces for both the bending and twisting vibrations for

Table VIII. Infrared Transition Frequencies for 4*H*-1,3-Dioxin (IV)

$(\nu_{35},\nu_{36})-(\nu_{35}',\nu_{36}')$	frequency (cm^{-1}) obsd[a]	calcd	Δ
	Ring-Twisting Bands		
(0,0)-(2,0)	325.8	326.7	-0.9
(2,0)-(4,0)	321.1	319.3	1.8
(4,0)-(6,0)	313.1	310.8	2.3
(6,0)-(8,0)	303.6	300.0	3.6
(0,1)-(2,1)	316.1	318.2	-2.1
(2,1)-(4,1)	309.0	309.8	-0.8
(4,1)-(6,1)	298.5	300.2	-1.7
(0,2)-(2,2)	309.0	311.4	-2.4
(2,2)-(4,2)	303.6[b]	303.5	0.1
(4,2)-(6,2)	294.5[b]	296.0	-1.5
(0,3)-(2,3)	303.6	304.9	-1.3
(2,3)-(4,3)	294.5[b]	296.6	-2.1
(0,4)-(2,4)	298.5	298.5	0.0
(0,5)-(2,5)	293.2	292.2	1.0
(0,6)-(2,6)	285.3[b]	286.0	-0.7
	Ring-Bending Bands		
(0,0)-(0,1)	189.6	187.5	2.1
(0,1)-(0,2)	188.5	188.7	-0.2
(0,2)-(0,3)	187.0	189.0	-2.0
(0,3)-(0,4)	187.0	189.0	-2.0
(2,0)-(2,1)	179.8	178.9	0.9
(2,1)-(2,2)	181.4	181.9	-0.5
(2,2)-(2,3)	181.4	182.5	-1.1
(4,0)-(4,1)	168.8	169.4	-0.6
(6,0)-(6,1)	153.7	158.8	-5.1
(6,1)-(6,2)	168.8[b]	171.5	-2.7
	Twist-Bend Difference Bands		
(2,0)-(0,1)	136.4	139.3	2.1
(2,1)-(0,2)	127.7	129.5	-1.8
(2,2)-(0,3)	122.1	122.4	-0.3
(2,3)-(0,4)	116.7	115.8	0.9
(4,0)-(2,1)	141.4	140.4	1.0
(4,1)-(2,2)	127.7	127.9	-0.2
(6,0)-(4,1)	145.2	141.4	3.8
(6,1)-(4,2)	122.1[b]	124.5	-2.4

[a] From ref 11. [b] Reassigned.

each molecule (Table II). The observed and calculated energy levels are given in Table VII for 3,6-dihydropyran and Table VIII for 1,3-dioxene. Several modifications of the assignments were made and these are indicated in the tables.

The barriers to planarity (4130 cm^{-1}) and interconversion (3540 cm^{-1}) for III (Table IV) are similar to those obtained for I. The barrier to planarity for III is lower than that calculated by DKSW (4816 cm^{-1}). MM2 calculations predict that the energy of the bent conformation for this molecule is 1490 cm^{-1} below that of the planar conformation, whereas we determine this value to be 590 cm^{-1}. The barrier to planarity for IV (3500 cm^{-1}) is about 600 cm^{-1} lower in energy than the barrier to planarity in the other three molecules. It is similar in value to that determined by DKSW with their one-dimensional calculation. The barrier to interconversion (3120 cm^{-1}) of IV is almost as high as the barrier to planarity which is quite compatible with the MM2 prediction that the barrier to planarity is the barrier to interconversion (i.e., the planar conformation is lower in energy than any bent form). A low-temperature NMR study of 1,3-dioxene[28] reported that the barrier to interconversion is much lower than that determined here; however, the NMR work was a liquid-phase study using Freon-21 as solvent, so some difference is anticipated. The twist angle of 38.2° at the minimum energy conformation for 3,6-dihydropyran (III) (Table III) is somewhat higher than the angles determined from microwave[29] and molecular mechanics calculations, 29.9° and 29.3°, respectively. Microwave data are not available for 1,3-dioxene (IV), but the twist angle of 33.2° determined here is close to the angle of 30.9° predicted by MM2. The potential

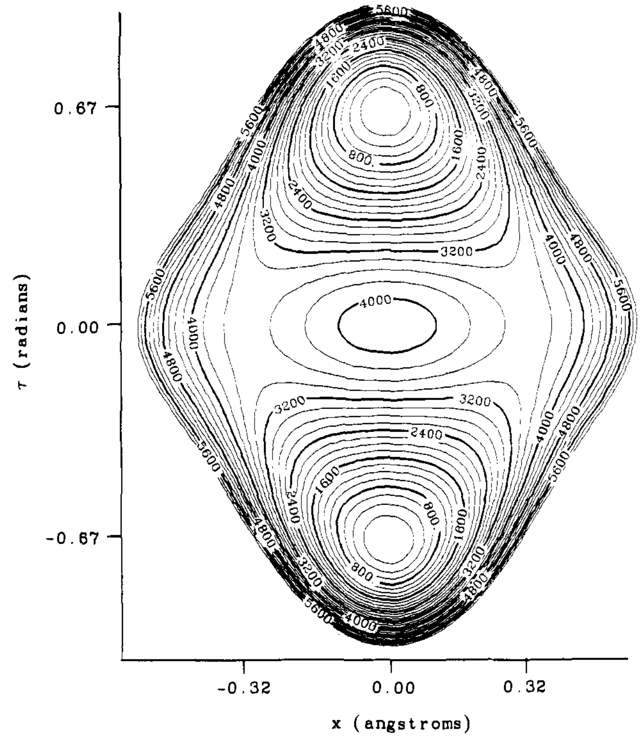

Figure 5. Potential energy surface for ring-bending (x) and ring-twisting (τ) of 3,6-dihydro-2*H*-pyran (III). Contour lines are drawn every 200 cm^{-1}.

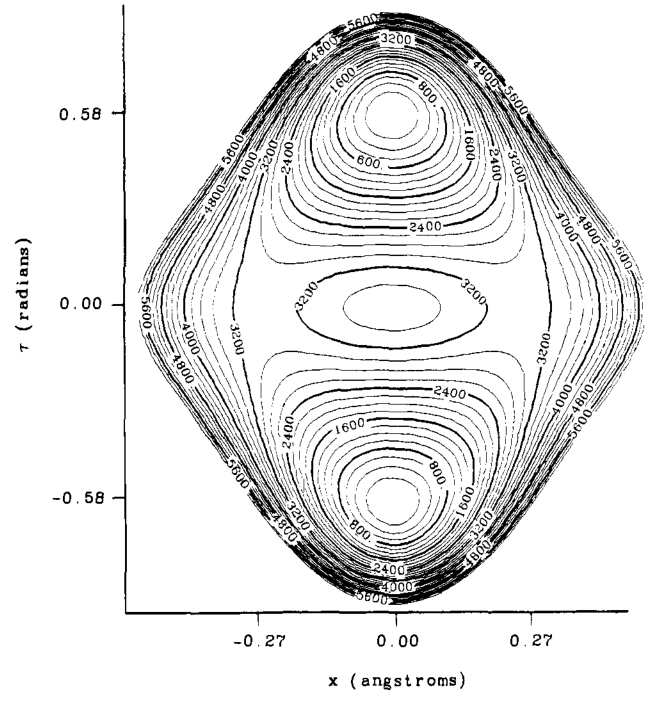

Figure 6. Potential energy surface for ring-bending (x) and ring-twisting (τ) of 4*H*-1,3-dioxin (IV). Contour lines are drawn every 200 cm^{-1}.

surface plots for III and IV (Figures 5 and 6) have minima at the twisted conformations and saddle points at the bent conformations. For each molecule the bent conformation is a transition state in the interconversion of the twisted conformations.

The two forces which primarily determine the conformations of these ring molecules are the angle strain and the torsional strain resulting from adjacent CH_2 groups. A planar six-membered ring molecule of the type examined here would have one or more adjacent CH_2 groups which are eclipsed and inner ring angles which are forced to be near 120°. Bending or twisting of the ring decreases both the angle strain and torsional strain by reducing

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(28) Camerlynek, R.; Anteunis, M. A. *Tetrahedron* **1975**, *31*, 1837–1840.
(29) Wells, J. A.; Malloy, T. B. *J. Chem. Phys.* **1974**, *60*, 3987–3993.

the inner ring angles and staggering the methylene groups. All four of the molecules studied in this work have similar angle strain, but the higher values for a_1, for II and IV (Table II), which have two oxygen atoms in their rings, do reflect the higher angle strain at oxygen atoms as compared to carbon. These molecules also have different numbers of eclipsing CH_2 groups. 3,4-Dihydropyran (I) has two pairs of adjacent CH_2 groups; 3,6-dihydropyran (III) and 1,4-dioxene (II) each have one pair; and 1,3-dioxene (IV) has no adjacent CH_2 groups. As a result, IV has a barrier to planarity that is 600 cm^{-1} lower in energy than the other three molecules. Somewhat surprisingly, the extra pair of adjacent CH_2 groups does not increase the barrier to planarity for I relative to II or III. In fact, all three molecules have similar barriers to planarity.

Although these potential energy surfaces fit the data well, small improvements could be realized by including other interacting vibrations. In particular, the out-of-plane double-bond twist (DB twist), which was neglected, no doubt couples somewhat with the single-bond ring-twisting mode. Weaker series of bending and twisting bands originating in the excited states of the DB twist have been assigned for 3,6-dihydropyran and 1,3-dioxene by DKSW, and these demonstrate a small amount of interaction with this mode. Inclusion of the DB twist in the calculations could improve the potential energy surface and slightly lower the calculated barriers to interconversion between the two twisted conformations. However, a three-dimensional potential surface calculation would be required if the DB twist were included, and the magnitude of the problem would become unmanageable. Only in one highly symmetric case[7] (1,3-disilacyclobutane) has a three-dimensional potential surface been successfully determined.

Conclusions

Although LRU's published potential energy surfaces give reasonable values for barriers to interconversion for I and II, their central barriers are too high and they predict the presence of stable bent conformations which have not been observed in the infrared and microwave spectra. In this work we have determined improved potential energy surfaces for the oxygen analogues of cyclohexene. Each of these has energy minima corresponding to the twisted conformations. The bent conformations are at saddle points on the surfaces and are not energetically stable. The barriers to planarity and the twist angles of the lowest energy structures determined here are somewhat higher than those determined from MM2 and microwave studies but are in much better agreement than the previous vibrational investigations. The potential energy surfaces are well defined by vibrational data at lower energies but are more poorly determined in the region of the central barrier. Thus, while we are confident that the barriers reported here are considerably better than those of LRU or DKSW, they are not determined with the same confidence as barriers for four- and five-membered ring molecules.[1-4] Nonetheless, the results of this work, when viewed together with the NMR and microwave results, help provide a coherent picture of the conformational energy differences for these four molecules.

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Chemical Deformation Densities.[†] 1. Principles and Formulation of Quantitative Determination

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Abstract: Molecular electron densities are often examined in the form of difference densities (DDs). Conventionally they are defined with respect to the superimposed densities of the *spherically averaged* atoms. These DDs are denoted here as *total difference densities* (TDDs). They are particularly useful for the discussion of the electrostatic fields created by molecules in the space around them. However, only atoms with spatially nondegenerate ground states are of necessity spherically symmetric. Most atoms with open p and d shells are not, and consequently their TDDs are often dominated by *quadrupolar* density distributions which are the result of the *orientation of the undeformed atomic ground states.* These orientational effects can be quite large and hide the genuine *atomic deformations* that are associated with molecule formation. Because of the superposition of the atomic orientation and chemical deformation effects, it is intrinsically difficult to compare TDDs of different systems, and the term "deformation densities" for them seems unfortunate. As a more appropriate quantity for the elucidation of the nature of chemical binding, *chemical deformation densities* (CDDs) are defined here with respect to the reference density of a promolecule whose *unperturbed* atoms, in addition to being *positioned* at their correct places in the molecule, have their ground-state multipoles uniquely *oriented.* This procedure is also a natural one from an information theoretical point of view. An unambiguous algorithm is formulated for the determination of the atomic orientation parameters and for the construction of CDDs from given molecular electron densities. An algorithm for the evaluation of orientation parameters from X-ray scattering data is presented elsewhere.

1. Introduction and Concepts

It has become customary to discuss electron density distributions in molecules and crystals in terms of difference densities defined with respect to reference densities of "promolecules". Conventionally these are chosen as superpositions of *spherically averaged* (and thermally smeared) densities of free atoms placed at optimal positions. We shall call such difference densities *total difference densities* (TDDs). By contrast, we propose here that not only the positions but also the *orientations of the nonspherical multipolar electron densities of the atoms in their ground states* be optimized when forming reference densities. The resulting difference densities are denoted as *chemical deformation densities* (CDDs).

In this first section the fundamental considerations are outlined. In the second section the mathematical definition of CDDs and an algorithm for their numerical determination are presented. In

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