J. Am. Chem. Soc. **1991,** *113,* 9735-9742

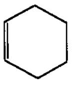
Far-Infrared Spectra, Two-Dimensional Vibrational Potential Energy Surface, and Conformation of Cyclohexene and Its Isotopomers

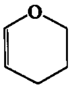
Vilma E. Rivera-Gaines, Sarah J. Leibowitz, and Jaan Laane*

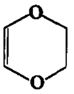
Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received May 29, 1991*

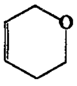
Abstract: The far-infrared spectra of cyclohexene and its *1-d*$_1$, *1,3,3-d*$_3$, *1,2,3,3-d*$_4$, *3,3,6,6-d*$_4$, and d_{10} isotopomers have been recorded and analyzed as a function of its ring-bending and ring-twisting vibrations. More than one-hundred transition frequencies corresponding to single and double quantum jumps of the bending, to the twisting, and to several twist-bend combinations were observed for the six isotopomers. From these data a two-dimensional vibrational potential energy surface was determined which defines the conformational energy of the molecule in terms of the two vibrational coordinates. Appropriate kinetic energy (reciprocal reduced mass) expansions were determined for these computations. The resulting potential energy surface is V (cm^{-1}) = $(3.25 \times 10^4)x^4 - (1.19 \times 10^4)x^2 + (2.18 \times 10^4)\tau^4 - (2.02 \times 10^4)\tau^2 + (1.53 \times 10^5)x^2\tau^2$, where x and τ represent the bending (Å) and twisting (radians) coordinates, respectively. Cyclohexene has an energy minimum at a twist angle of 39.0 ± 1.8°. This lies 4700 ± 500 cm^{-1} (13.4 ± 1.4 kcal/mol) below the planar conformation and approximately 3600 cm^{-1} (10.3 kcal/mol) below the bent form, which corresponds to a saddle point on the two-dimensional surface. The barrier to planarity for cyclohexene is 400–1200 cm^{-1} higher than in several analogues of oxygen and sulfur.

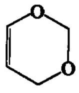
The molecular structure of cyclohexene (I) has been investigated by chemists for more than four decades. However, a quantitative understanding of the energies associated with the conformational changes has not been achieved. It is the intent of this paper to present an experimentally determined potential energy surface which elucidates this situation. The results will be compared to those of our recent work on four similar oxygen-containing analogues (II, III, IV, and V) of cyclohexene[1] as well as 5,6-dihydro-2*H*-thiopyran (VI).[2]

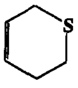

I


II

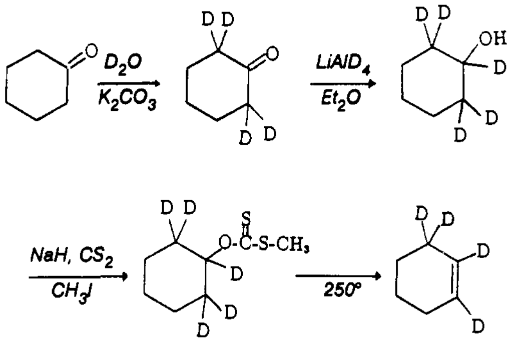

III


IV


V


VI

Scheme I



A planar conformation for the cyclohexene ring is energetically not favored both because of the eclipsing of the neighboring methylene groups and because the C–C–C ring angles in a planar ring must be close to 120° rather than the desired tetrahedral value. Another unfavorable conformation results if the ring twists about the double bond, perturbing the π system. The lowest energy conformations result from a ring-bending, which gives rise to a boat structure, and from a ring-twisting, which gives rise to a half-chair form. In 1948 Beckett, Freeman, and Pitzer[3] used conformational calculations to predict that the lowest energy structure of cyclohexene should have a twisted form. This C_2 conformation was estimated to be 2.7 kcal/mol more stable than the bent form. More than a decade later, Anet and Haq[4] concluded from nuclear magnetic resonance experiments that the bent structure of cyclohexene exists only as a transition state and not as a second conformer. These workers also estimated that the ΔH for the half-chair to boat interconversion is 5.3 kcal/mol. Liquid and solid infrared and liquid Raman spectra of cyclohexene and its d_{10} isotopomer were reported[5] in 1967; one year later the microwave spectrum[6] showed the molecule to be twisted. The twist angle was reported to be 30 ± 2°. The gas-phase Raman spectrum of the ring-twisting vibration was reported by Durig, Carter, and Carreira[7] (hereafter referred to as DCC). These authors used a one-dimensional approximation and calculated a potential energy barrier to planarity to be 8800 ± 1700 cm^{-1} (25 ± 5 kcal/mol) and the barrier to interconversion between bent and twisted forms to be 2630 ± 200 cm^{-1} (7.5 ± 0.6 kcal/mol). Smithson and Wieser[8] (hereafter referred to as SW) have recorded the far-infrared vapor-phase spectra of cyclohexene and reported many bands arising from the ring-puckering and ring-twisting vibrations along with several twist-bend sum and difference bands. They disagreed with the DCC analysis and used their own approximation to calculate a barrier to planarity of 6160 cm^{-1} (17.6 kcal/mol) and a barrier to interconversion of 2430 cm^{-1} (6.9 kcal/mol). Neither the DCC nor the SW study adopted a true two-dimensional model and therefore did not adequately consider the interaction between the ring-bending and ring-twisting vibrations.

In the present study, we have recorded improved far-infrared spectra of the ring-bending and ring-twisting vibrations of cyclohexene. In addition, we have also recorded the first far-infrared spectra of five deuterated derivatives of cyclohexene (*1-d*$_1$, *1,3,3-d*$_3$, *1,2,3,3-d*$_4$, *3,3,6,6-d*$_4$, and d_{10}). We have observed the vibrational transitions of the ring-bending (single and double quantum jumps), ring-twisting, and twist-bend combinations for many of the deuterated species as well as in the parent molecule. These data were analyzed using a two-dimensional potential energy function in terms of the ring-bending and ring-twisting coordinates, and kinetic

---

(1) Tecklenburg, M. M. J.; Laane, J. *J. Am. Chem. Soc.* **1989,** *111,* 6920–6926.

(2) Tecklenburg, M. M. J.; Villarreal, J. R.; Laane, J. *J. Chem. Phys.* **1989,** *91,* 2771–2775.

(3) Beckett, C. W.; Freeman, N. K.; Pitzer, K. S. *J. Am. Chem. Soc.* **1948,** *70,* 4227–4230.

(4) Anet, F. A. L.; Haq, M. Z. *J. Am. Chem. Soc.* **1965,** *87,* 3147–3150.

(5) Neto, N.; Di Lauro, C.; Castellucci, E.; Califano, S. *Spectrochim. Acta* **1967,** *23A,* 1763–1774.

(6) Scharpen, L. H.; Wollrab, J. E.; Ames, D. P. *J. Chem. Phys.* **1968,** *49,* 2368–2372.

(7) Durig, J. R.; Carter, R. O.; Carreira, L. A. *J. Chem. Phys.* **1974,** *60,* 3098–3103.

(8) Smithson, T. L.; Wieser, H. *J. Chem. Phys.* **1980,** *72,* 2340–2346.

0002-7863/91/1513-9735$02.50/0

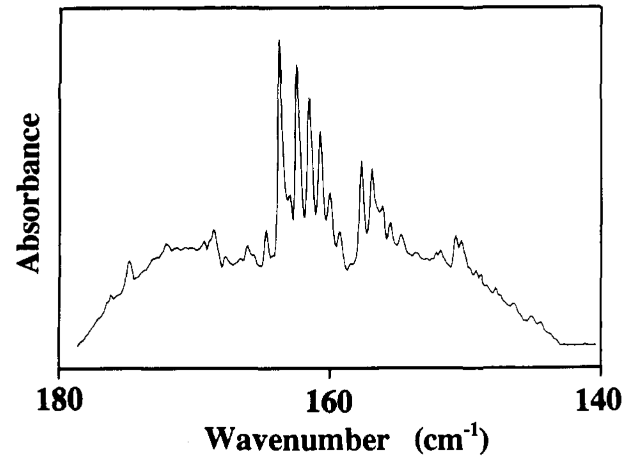


Figure 1. Ring-bending infrared spectrum of cyclohexene (50 Torr, 20-m path, 0.25-cm^{-1} res); the maximum absorbance is 1.4.

energy expansions were calculated for both the ring-twisting and ring-bending vibrations for each isotopic species. The results provide the first comprehensive and quantitative picture of the conformational processes of cyclohexene.

Experimental Section

Cyclohexene was purchased from MCB. The deuterated derivatives cyclohexene-*1*-d_1, cyclohexene-*1,3,3*-d_3, and cyclohexene-*1,2,3,3*-d_4 were synthesized following procedures similar to those used in the preparation of isotopically substituted cyclopentenes.[9] Two other deuterated species, cyclohexene-*3,3,6,6*-d_4 and cyclohexene-d_{10}, were purchased from MSD isotopes. Only the preparation of the d_4 species, shown in Scheme I, will be discussed in detail since the d_1 and d_3 isotopomers were prepared in a similar manner.

The first step involved the deuteration of the α-hydrogens of cyclohexanone (Aldrich) following the procedure of Ellis and Maciel.[10] (In the preparation of the d_1 derivative the α-hydrogen atoms were not exchanged.) Next, 36 g (0.35 mol) of cyclohexanone-*2,2,6,6*-d_4 were reduced with excess (5.0 g or 0.12 mol) $LiAlD_4$ (aldrich), or $LiAlH_4$ for the *1,3,3*-d_3 derivative, following the procedure of Lipnick.[11] A xanthate was then prepared[12] under a nitrogen atmosphere by mixing 5.0 g (0.21 mol) of NaH (Aldrich) in anhydrous ethyl ether with 25 g (0.24 mol) of cyclohexan-1-ol-*1,2,2,6,6*-d_5, 9.7 g (0.13 mol) of carbon disulfide (MCB), and 19.2 g (0.13 mol) of methyl iodine (Aldrich). The *O*-cyclohexyl-*1,2,2,6,6*-d_5-*S*-methyl xanthate was added dropwise to boiling biphenyl (Aldrich). The cyclohexene-*1,2,3,3*-d_4, 16 g (0.18 mol), was separated by vacuum distillation. The purities of the isotopomers were verified by nuclear magnetic resonance (NMR) spectroscopy, and the results are available elsewhere.[13]

Gas-phase far-infrared spectra were recorded on a Bomem DA3.002 fourier transform infrared spectrometer. The samples were contained in a variable path length (0.75–21 m) multireflectance Wilk's cell fitted with polyethylene windows which had been pounded to eliminate fringing patterns. Mylar beam splitters of appropriate thicknesses were used: 3 μm for the 300–800-cm^{-1} region, 6 μm for the 125–350-cm^{-1} region, 12 μm for the 40–200-cm^{-1} region, and 25 μm for the 10–125-cm^{-1} region. A Globar source was used in each spectral region. A liquid helium cooled bolometer with a germanium detector was used for the region below 350 cm^{-1}. For the 300–800-cm^{-1} range a liquid helium cooled bolometer with a silicon-boride detector was employed. Spectra typically were recorded with a resolution of 0.25 cm^{-1}.

Results and Discussion

Far-Infrared Spectra. A planar cyclohexene ring of C_{2v} symmetry would have an infrared active B_2 ring-bending vibration (with a type C gas-phase band contour) and an infrared inactive A_2 ring-twisting motion. For twisted (C_2) or bent (C_s) conformations both vibrations are infrared active, although the twisting vibration is expected to have weak intensity. Upon asymmetric deuteration (*1*-d_1, *1,3,3*-d_3, *1,2,3,3*-d_4) even the planar form is reduced to C_s symmetry for which both the twisting and bending are infrared active. The spectra of these deuterated species, which are discussed below, do in fact show enhanced intensity for the ring-twisting motion. However, substitution of the heavier deuterium atoms for the hydrogens has the effect of reducing the amplitudes of vibration and the infrared absorption intensities of the bands associated with the ring-bending motion.

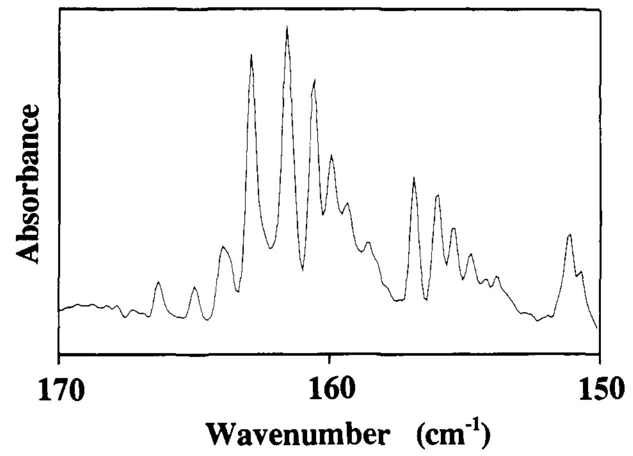


Figure 2. Ring-bending infrared spectrum of cyclohexene-*1*-d_1 (30 Torr, 20-m path, 0.25-cm^{-1} res); the maximum absorbance is 1.1.

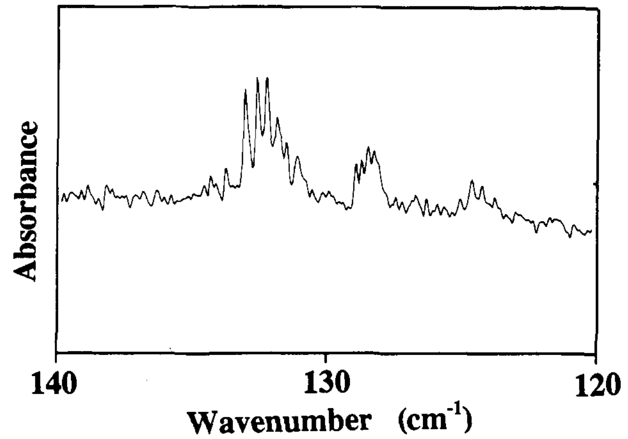


Figure 3. Ring-bending infrared spectrum of cyclohexene-d_{10} (30 Torr, 20 m path, 0.25-cm^{-1} res); the maximum absorbance is 0.2.

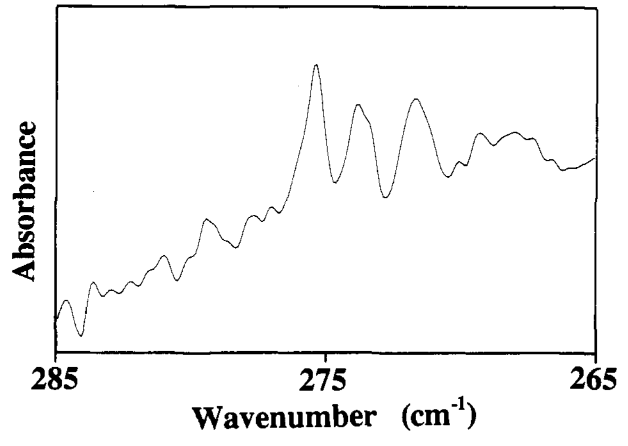


Figure 4. Ring-twisting infrared spectrum of cyclohexene (50 Torr, 20-m path, 0.25-cm^{-1} res); the maximum absorbance is 0.1.

Figures 1–3 show the far-infrared spectra of the ring-bending vibration of cyclohexene and its d_1 and d_{10} isotopomers. Figures 4 and 5 show the ring-twisting region for the d_0 and d_1 species, and Figure 6 shows the twist-bend sum band region for the d_1

---

(9) Villarreal, J. R.; Bauman, L. E.; Laane, J. *J. Phys. Chem.* **1976**, *80*, 1172–1177.

(10) Ellis, P. D.; Maciel, G. E. *J. Am. Chem. Soc.* **1970**, *92*, 5829–5833.

(11) Lipnick, R. L. *J. Mol. Struct.* **1974**, *21*, 411–421.

(12) Roberts, J. D.; Sauer, C. W. *J. Am. Chem. Soc.* **1949**, *71*, 3925–3929.

(13) Rivera-Gaines, V. G., Ph.D. Dissertation, Texas A&M University, 1989.

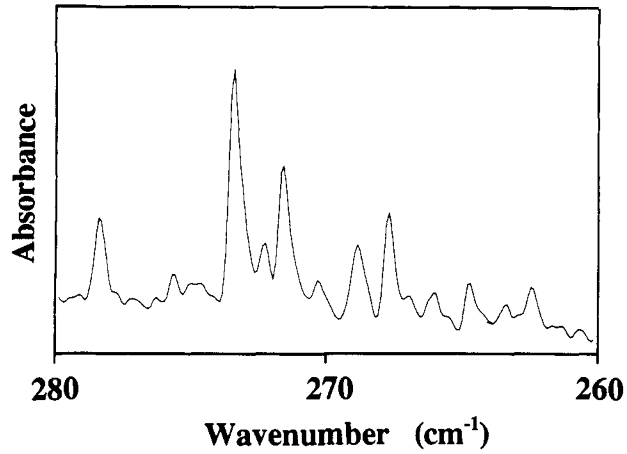


Figure 5. Ring-twisting infrared spectrum of cyclohexene-*1*-d_1 (30 Torr, 20-m path, 0.25-cm^{-1} res); the maximum absorbance is 0.5.

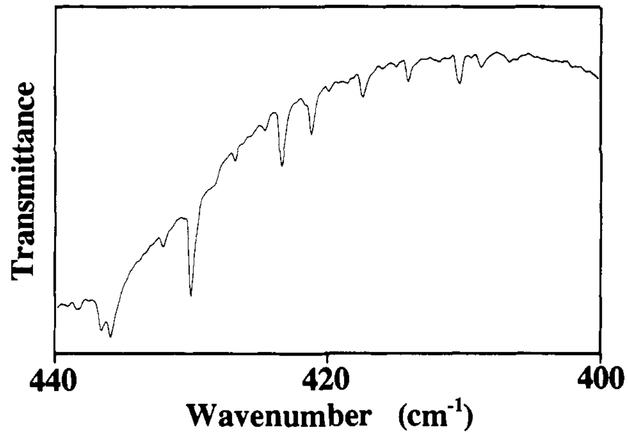


Figure 6. Twist-bend sum band infrared spectrum of cyclohexene-*1*-d_1 (30 Torr, 20-m path, 0.25-cm^{-1} res).

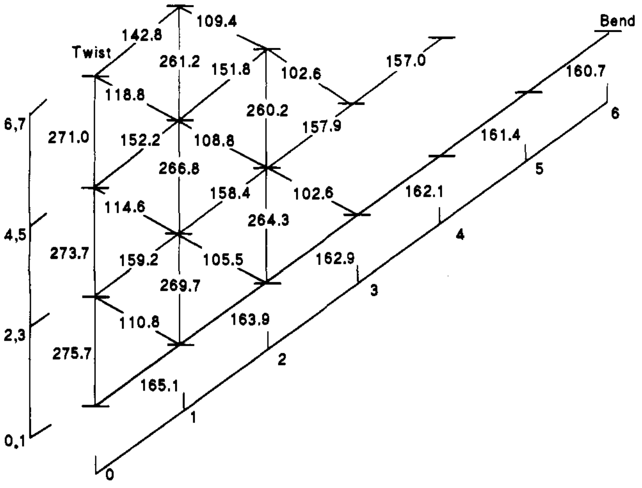


Figure 7. Energy level diagram and transitions for cyclohexene.

isotopomer. More detailed spectra for these and the other deuterated molecules can be found elsewhere.[13,14] Table I presents a listing of the observed frequencies and assignments for cyclohexene and compares these results to those of SW and DCC. Table II presents our data for the deuterated isotopomers. Both tables also list the frequencies calculated for our potential energy surface, which will be discussed below. The spectra can most easily be understood with reference to Figures 7 and 8 which show the energy level diagrams for the d_0 and d_1 isotopomers, respectively.

Table I. Observed and Calculated Frequencies (cm^{-1}) for Ring-Twisting and Ring-Bending of Cyclohexene-d_0

transitions	obsd	calcd	literature value SW[a]	literature value DCC[b]
(0,0)–(2,0)	275.7	276.3	276.2	275.5
(2,0)–(4,0)	273.7	272.8	273.7	274.0
(4,0)–(6,0)	[271.0][c]	269.1		
(0,1)–(2,1)	269.7	271.8	270.4	270.3
(2,1)–(4,1)	[266.8]	268.0		
(4,1)–(6,1)	[261.2]	263.8		
(0,2)–(2,2)	[264.3]	267.8		266.0
(2,2)–(4,2)	[260.2]	263.8		
(0,3)–(2,3)		263.9		260.8
(0,0)–(0,1)	165.1	162.9	165.1	
(0,1)–(0,2)	163.9	163.3	163.7	
(0,2)–(0,3)	163.0	163.6	162.5	
(0,3)–(0,4)	162.2	163.7		
(0,4)–(0,5)	161.4	163.7		
(0,5)–(0,6)	160.7	163.5		
(2,0)–(2,1)	159.2	158.4	159.3	
(2,1)–(2,2)	158.4	159.3	158.2	
(2,2)–(2,3)	156.8	159.7	158.2	
(2,3)–(2,4)	156.3	160.0	156.8	
(4,0)–(4,1)	152.2	153.6	152.1	
(4,1)–(4,2)	151.8	155.1	152.1	
(4,2)–(4,3)	151.6	155.8	153.8	
(6,0)–(6,1)	142.2	148.3		
(2,0)–(0,1)	110.6	113.4	111.0	
(2,1)–(0,2)	105.5	108.5	106.2	
(2,2)–(0,3)	102.6	104.2		
(4,0)–(2,1)	114.6	114.4	114.9	
(4,1)–(2,2)	108.8	108.7		
(4,2)–(2,3)	102.6	104.1		
(6,0)–(4,1)	118.8	115.5		
(6,1)–(4,2)	109.4	108.7		

[a] Reference 8. [b] Reference 7. [c] Values in square brackets are derived from observed frequencies.

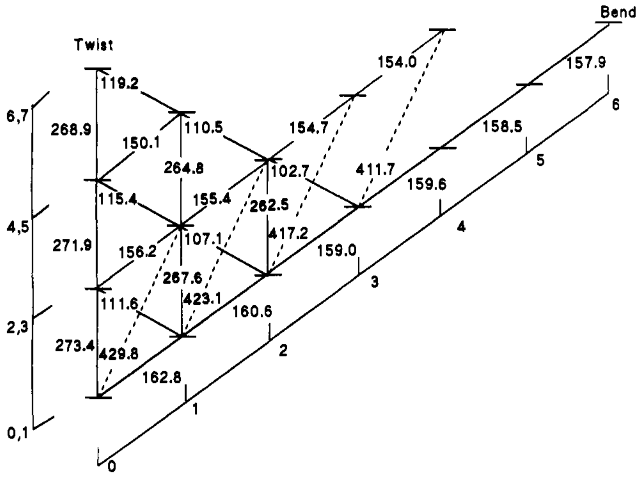


Figure 8. Energy level diagram and transitions for cyclohexene-*1*-d_1.

As will be shown, the cyclohexene molecule is twisted (C_2) with a substantial barrier to planarity. The twisting vibration is weakly infrared active, occurs deep within a double-minimum potential well, and results in a vibrational series of 275.7, 273.7, and 271.0 cm^{-1} for the d_0 species. The bending vibration at the energy minimum (orthogonal to the twisting) is governed by a potential function which is close to harmonic and gives rise to a series of closely spaced bands near 165 cm^{-1}. The spectra are complicated by the fact that many of the excited states are substantially populated, and bands can be seen originating from both twisting and bending excited states. Thus, while the fundamental bending frequency occurs at 165.1 cm^{-1} for the doubly degenerate ground

---

(14) Leibowitz, S. J., Ph.D. Dissertation, Texas A&M University, 1991.

Table II. Observed and Calculated Frequencies (cm^{-1}) for Ring-Twisting and Ring-Bending Vibrations of Cyclohexene Deuterated Derivatives

	1-d$_1$		*1,3,3-d$_3$*		*1,2,3,3-d$_4$*		*3,3,6,6-d$_4$*		d_{10}	
transitions	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
				Ring-Twisting						
(0,0)-(2,0)	273.4	274.1	269.1	269.9	267.5	268.0		263.5		228.0
(2,0)-(4,0)	271.9	270.7	267.5	266.0	264.9	264.2		259.6		225.5
(4,0)-(6,0)	268.9	267.1		261.5		259.6		254.3		222.7
(0,1)-(2,1)	267.6	269.6	264.5	264.7		262.8		258.3		224.8
(2,1)-(4,1)	264.8	265.8	267.5	260.4		258.5		253.8		222.0
(0,2)-(2,2)	262.5	265.6	259.0	261.1		259.3		255.2		222.0
				Ring-Bending						
(0,0)-(0,1)	161.8	159.7	150.7	149.1	149.5	147.6	145.1	143.2	133.1	131.2
(0,1)-(0,2)	160.6	160.3	149.5	150.5	148.2	148.9	144.7	144.9	132.6	131.8
(0,2)-(0,3)	159.6	160.6	148.2	151.2	146.7	149.5	143.5	145.6	132.3	132.3
(0,3)-(0,4)	159.0	160.7			146.1	149.9	143.1	146.0	132.0	132.5
(0,4)-(0,5)	158.5	160.7					142.5	146.4	131.8	132.7
(0,5)-(0,6)	157.9	160.6							131.6	132.6
(2,0)-(2,1)	156.2	155.2	146.6	144.0	143.6	142.4			129.1	128.0
(2,1)-(2,2)	155.4	156.3	145.9	146.9	142.6	145.6			128.9	129.0
(2,2)-(2,3)	154.7	156.8	145.6	147.7	141.7	146.0			128.7	129.6
(2,3)-(2,4)	154.0	157.1							128.4	130.0
(4,0)-(4,1)	150.1	150.3			138.3	136.7			125.3	124.6
(4,1)-(4,2)									124.8	126.1
(4,2)-(4,3)									124.5	127.0
				Ring-Bending (Double Quantum Transitions)						
(0,0)-(0,2)	322.2	320.0	301.1	301.6						
(0,1)-(0,3)	320.4	320.9								
(0,2)-(0,4)	318.8	321.3								
(0,3)-(0,5)	317.6	321.4								
				Twist-Bend Differences						
(2,0)-(0,1)	111.6	114.4	118.4	120.8	118.8	120.4				
(2,1)-(0,2)	107.1	109.3	114.8	114.2	116.4	113.9				
(2,2)-(0,3)	102.7	105.0	111.9	109.9						
(4,0)-(2,1)	115.4	115.5	123.5	122.0	122.8	121.8				
(4,1)-(2,2)	110.5	109.5	116.7	113.5						
(6,0)-(4,1)	119.2	116.8								
				Twist-Bend Sums						
(0,0)-(2,1)	429.8	429.3								
(0,1)-(2,2)	423.1	425.9								
(0,2)-(2,3)	417.2	422.4								
(0,3)-(2,4)	411.7	418.9								

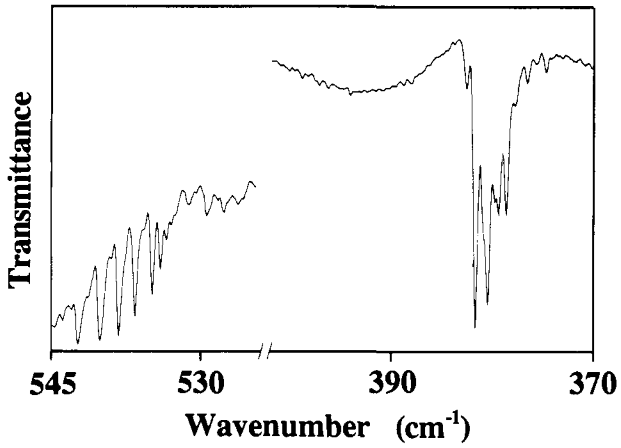


Figure 9. Infrared spectra of the double-bond (DB) ring-twisting (370–400 cm^{-1}) and the DB twist-bend sum bands (525–545 cm^{-1}) of 1-cyclohexene-d_1 (30 Torr, 20-m path, 0.25-cm^{-1} res).

state (with twisting quantum numbers of 0 and 1), it drops to 159.2 cm^{-1} in the $v_t = 2$ state, to 152.2 cm^{-1} in the $v_t = 4$ state, and to 142.2 cm^{-1} in the $v_t = 6$ state (for simplicity we utilize only the even twisting quantum numbers for the doubly degenerate states). Similarly, the twisting frequencies in the lowest three (non-degenerate) bending states occur at 275.7, 269.7, and 264.3 cm^{-1}. As shown in Figures 7 and 8 the assignment of the bands is generally confirmed by the observation of several combinations and overtones. In particular, twist-bend sum and difference bands help to confirm many of the assignments. For cyclohexene our observations are similar to those of SW except that we have observed several additional bands. The data of DCC are lower resolution Raman values but also agree fairly well. For the five deuterated isotopomers no previous data have been reported. As noted above, the asymmetric deuteration of the d_1, d_3, and d_4 species enhances the intensity of the twisting bands in the infrared spectra.

In addition to the spectra resulting from the ring-bending and ring-twisting (about the single bond) vibrations, the spectra of the d_1 isotopic species also shows strong features due to the ring-twisting about the double bond (DB twist), which has become "more" infrared active (A$''$ symmetry for a planar C_s point group as opposed to A_2 in C_{2v} for the d_0 species) for this isotopomer. Figure 9 shows two segments of the infrared spectrum for this species. The fundamental and hot bands occur near 380 cm^{-1} while the DB twist-bend sum bands are present near 540 cm^{-1}. Figure 10 shows the energy levels and transitions for both of these series. Both the hot bands ($\Delta v_b = 0$) and the sum bands ($\Delta v_b = 1$) establish the energies (±0.1 cm^{-1}) of the bending states in the excited state of the DB twist. The energy spacings for the excited state determined from these data are also shown in Figure 10. As can be seen, the corresponding energy spacings in the excited state are 1.1 ± 0.3 cm^{-1} lower than those in the ground state, indicating that only a small amount of interaction occurs between the DB twisting and the ring-bending. In comparison, the sin-

Table III. Calculated Kinetic Energy Expansions[a] for the Ring-Bending and Ring-Twisting of Cyclohexene and Its Deuterated Derivatives

	d_0	*1*-d_1	*1,3,3*-d_3	*1,2,3,3*-d_4	*3,3,6,6*-d_4	d_{10}
			Bending			
$g_{44}^{(0)}$	0.00681	0.00655	0.00568	0.00558	0.00525	0.00439
$g_{44}^{(2)}$	−0.00346	−0.00458	0.00475	−0.00355	0.00116	0.00643
$g_{44}^{(4)}$	−0.25292	−0.23447	−0.25045	−0.23877	−0.24910	−0.20515
$g_{44}^{(6)}$	0.10800	0.10204	0.92596	0.90200	0.77166	0.70424
			Twisting			
$g_{55}^{(0)}$	0.03152	0.03110	0.02987	0.02953	0.02828	0.01932
$g_{55}^{(2)}$	0.00545	0.00540	0.00616	0.00607	0.00672	0.00867
$g_{55}^{(4)}$	−0.03193	−0.03188	−0.03037	−0.03034	−0.02904	−0.01972
$g_{55}^{(6)}$	0.01898	0.01917	0.01673	0.01682	0.01492	0.00634

[a] The form of the kinetic energy function is $g_{ii} = g_{ii}^{(0)} + g_{ii}^{(2)}x_k^2 + g_{ii}^{(4)}x_k^4 + g_{ii}^{(6)}x_k^6$, where $k = 1$ and $i = 4$ correspond to the ring-bending and where $k = 2$ and $i = 5$ correspond to the ring-twisting. The units of $g_{ii}^{(n)}$ are au^{-1} Å^{-n} for $i = 4$ and au^{-1} rad^{-n} for $i = 5$.

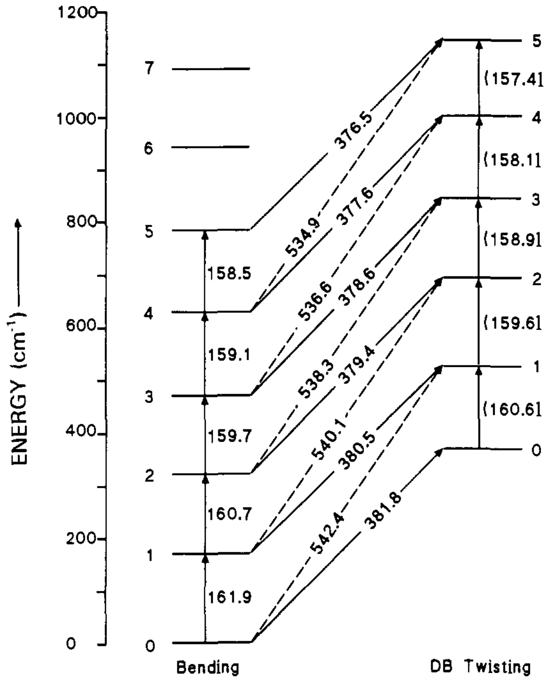


Figure 10. Energy levels and transitions for the DB ring-twisting hot bands and DB twist-bend sum bands for cyclohexene-d_1.

gle-bond ring-twisting excited state has spacings for the bending levels which are about 6 cm^{-1} lower than in the ground state. This reflects the higher degree of interaction between the single-bond twisting and the bending. The two-dimensional potential surface derived below only considers the bending and twisting vibrations (excluding the DB twist). Thus, the validity of the determination requires that interaction with the DB twist be small, and indeed it is.

Kinetic Energy Expansions. We have previously presented the definition of the ring-bending and ring-twisting coordinates[1,15] (Figure 11) and described the calculation of the kinetic energy (reciprocal reduced mass) expansions for the two modes.[15] Table III presents the results for the six isotopic species. Previous work on cyclohexene has not had the availability of this type of data. It should be noted here that the principal kinetic energy cross term g_{45} for cyclohexene-d_0, -*3,3,6,6*-d_4, and -d_{10} is zero since the bending and twisting motions of a planar (C_{2v}) ring have different symmetry species. For the asymmetrically deuterated species g_{45} is very small and thus has not been included in the calculations.

Vibrational Potential Energy Surface. The calculation of the two-dimensional vibrational potential energy surface was carried out in a manner very similar to that described for the oxygen analogues of cyclohexene.[1] Insight into the selection of initial potential energy parameters is provided in that study and also in our investigation of silacyclopentane.[16] The vibrational Hamiltonian used to analyze the spectroscopic data is given by

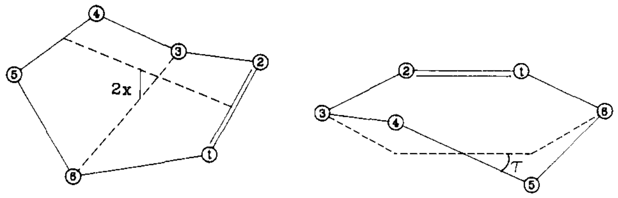


Figure 11. Definition of the ring-bending (x) and ring-twisting (τ) vibrations of cyclohexene.

$$\mathcal{H}(x,\tau) = -\tfrac{1}{2}\hbar^2(\partial/\partial x\; g_{44}(x)\; \partial/\partial x + \partial/\partial\tau\; g_{55}(\tau)\; \partial/\partial\tau) + V(x,\tau) \qquad (1)$$

where x and τ are the ring-bending and ring-twisting coordinates (Figure 1) in Å and radians, respectively, as previously defined.[1,15] The g_{ii} terms are the kinetic energy expansions for the bending ($i = 4$) and the twisting ($i = 5$). [The first three subscripts ($i = 1$–3) are generally reserved for the molecular rotations.] The potential energy function has the form

$$V(x,\tau) = a_1x^4 + b_1x^2 + a_2\tau^4 + b_2\tau^2 + cx^2\tau^2 \qquad (2)$$

where the a_i, b_i, and c are the potential energy coefficients. The basis sets used for the two-dimensional energy level calculations were taken to be products of one-dimensional wave-function solutions for each coordinate.[1] Symmetry-factored Hamiltonian matrices with typical dimensions of 400 were diagonalized to obtain the results.

Although our computer programs have least-squares fitting routines for adjusting the potential energy parameters, we did not feel, for reasons described below, that the best "mathematical fit" actually gave the best representation of the potential energy surface. In order to understand this, one must consider the trends in the various observed spectral series. The bending series near 165 cm^{-1} is nearly harmonic with a small amount of "negative anharmonicity". As we showed previously,[16] eq 2 gives rise to a local one-dimensional potential function for the bending motion at the minimum energy of the ring-twisting coordinate ($\tau_0 = b_2/2a_2$) of the form

$$V(x,\tau_0) = a_1x^4 + (b_1 + c\tau_0^2)x^2 + K_T \qquad (3)$$

where K_T is a constant. This means that, as a first approximation, the bending motion according to eq 3 will be harmonic with some quartic character, which gives rise to some "positive anharmonicity". Consequently, in these calculations it is difficult to reproduce the slowly decreasing frequency trend for the bending series without adding additional potential energy parameters. Nevertheless, we chose to limit the number of variable parameters to five since this set results in only a minor error in the calculation of the bending series. Equation 3 allows us to obtain a reliable

---

(15) Tecklenburg, M. M. J.; Laane, J. *J. Mol. Spectrosc.* **1989**, *137*, 65–81.

(16) Colegrove, L. F.; Wells, J. C.; Laane, J. *J. Chem. Phys.* **1990**, *93*, 6291–6302.

Table IV. Differences in Twisting and Bending Frequencies (cm^{-1}) in Various Excited Quantum States of Cyclohexene as a Function of Ring-Twisting Barrier[a]

difference ($\nu_A - \nu_B$)			calculated for different B_{pt} (cm^{-1})							
ν_A	ν_B	obsd	3000	3500	4000	4500	5000	5500	6000	6500
			Bending in Excited States of Twisting							
(0,0)-(0,1)	(2,0)-(2,1)	5.9	9.2	6.1	5.3	4.5	4.0	3.6	3.2	2.9
(2,0)-(2,1)	(4,0)-(4,1)	7.0	10.8	6.9	5.9	5.0	4.4	3.9	3.5	3.2
(4,0)-(4,1)	(6,0)-(6,1)	9.4	12.9	7.6	6.7	5.5	4.8	4.2	3.8	3.5
			Pure Twisting							
(0,0)-(2,0)	(2,0)-(4,0)	2.0	7.0	5.1	4.3	3.7	3.2	2.7	2.4	2.1
(2,0)-(4,0)	(4,0)-(6,0)	2.7	8.3	5.5	4.6	3.8	3.5	2.9	2.5	2.2
			Twisting in Excited States of Bending							
(0,0)-(2,0)	(0,1)-(2,1)	6.0	9.2	6.2	5.3	4.6	4.1	3.6	3.2	3.0
(0,1)-(2,1)	(0,2)-(2,2)	5.4	8.4	5.4	4.8	4.2	3.6	3.4	3.2	2.9

[a] B_{pb} is taken to be 1100 cm^{-1}.

Table V. Two-Dimensional Potential Energy Functions[a] for the Ring-Bending and Ring-Twisting of Cyclohexene and Analogues

	a_1 (cm^{-1}/Å^4)	b_1 (cm^{-1}/Å^2)	a_2 (cm^{-1}/rad^4)	b_2 (cm^{-1}/rad^2)	c (cm^{-1}/(Å^2·rad^2))
$CH_2CH_2CH{=}CHCH_2CH_2$ (I)	3.25×10^4	-1.19×10^4	2.18×10^4	-2.02×10^4	1.53×10^5
$CH_2CH_2CH{=}CHOCH_2$ (II)	4.24×10^4	-1.01×10^4	2.46×10^4	-2.00×10^4	1.70×10^5
$CH_2OCH{=}CHOCH_2$ (III)	15.9×10^4	-1.39×10^4	2.92×10^4	-2.20×10^4	1.96×10^5
$CH_2CH_2CH{=}CHCH_2O$ (IV)	5.99×10^4	-1.19×10^4	2.29×10^4	-2.04×10^4	1.91×10^5
$CH_2OCH{=}CHCH_2O$ (V)	7.08×10^4	-1.04×10^4	3.31×10^4	-2.23×10^4	2.44×10^5
$CH_2CH_2CH{=}CHCH_2S$ (VI)	2.43×10^4	-0.38×10^4	2.26×10^4	-1.97×10^4	1.03×10^5

[a] $V(x,\tau) = a_1x^4 + b_1x^2 + a_2\tau^4 + b_2\tau^2 + cx^2\tau^2$, where x and τ are the ring-bending and ring-twisting coordinates, respectively. The parameters for the oxygen analogues are from ref 1; those for the sulfur molecule are from ref 2.

estimate for ($b_1 + c\tau_0^2$), the coefficient of the harmonic term, since this is primarily responsible for the nearly harmonic bending frequency at 165.1 cm^{-1}.

The substantial frequency drops of the bending frequencies in the twisting excited states were judged to be highly significant in the determination of the potential energy surface since these are a reflection of the interaction between the bending and twisting vibrations. Similarly, the frequency decreases of the twisting transitions in the bending excited states are reflective of this interaction. Consequently, in the selection of the potential energy parameters we made a strong effort to reproduce these trends.

The pure twisting transitions (with no associated bending) have been used previously, without consideration of the other data, by DCC and SW to estimate the barrier to planarity from essentially one-dimensional models. However, as we have shown,[1,16] such one-dimensional estimates generally overstate the height of this barrier. Nonetheless, the observed frequency decreases in the twisting series, occurring deep within the potential wells, represent important data which we considered in evaluating the nature of the surface.

For our potential energy surface it is essential that the pure bending and pure twisting frequencies be accurately calculated, and this requirement gives rise to several relationships between the different potential energy parameters a_i, b_i, and c. These relationships have previously been described.[16] Using these constraints, we chose to carry out the energy level calculations for a variety of different magnitudes of the barrier to planarity (i.e. the energy difference between the twisted and planar forms B_{pt}) and the barrier to interconversion between bent and twisted forms B_{bt}. We carefully examined the characteristics of the functions with B_{pt} ranging from 3000 to 6500 cm^{-1}, and for each of these we considered B_{bt} values from 0 to 3000 cm^{-1}. Table IV shows how several calculated frequency trends compare to observed values for different B_{pt} values when B_{pb} is fixed at 1100 cm^{-1}. The calculations carried out at other B_{pb} values show similar trends. This table shows that the optimal value of B_{pt} is different for the different types of series. For the bending frequencies in the excited states of the twisting, the best fit is obtained with a barrier to planarity of about 3400 cm^{-1}. For the pure twisting, the best fit occurs at about B_{pt} = 6000 cm^{-1} (this explains the high values reported by DCC and SW), while for the twisting in the excited states of the bending, B_{pt} = 3600 cm^{-1} gives the best agreement. As a whole, we have selected 4700 cm^{-1} as the barrier that gives the best overall fit, and we estimate the uncertainty to be about 500 cm^{-1} since the extreme values do not *simultaneously* give rise to reasonable values for each of the calculated spectral series. Our final parameters also have taken into consideration all of the data for all of the isotopomers and are therefore quite well defined. For Table IV the barrier to interconversion was fixed at 1100 cm^{-1} which we selected as the optimal value. A very slight improvement in frequency fit can be obtained by increasing this value by a few hundred cm^{-1}. However, when this is done, the potential function then has shallow energy minima corresponding to the bent conformations. Since we nor anyone else have experimentally detected the presence of this form as a stable conformer, we believe these minima do not exist or, at most, are very shallow.

As should be evident, the simple mathematical form of the potential surface given in eq 2 is somewhat limited in exactly representing both the shape (curvature) of the surface and the barrier heights. Consequently, there will be some frequency deviations between the observed and calculated values. These are shown in Tables I and II. Nonetheless, the frequency fit for all isotopic models can be seen to be excellent, especially in view of the simple model.

The potential energy surface determined for all of the isotopic forms of cyclohexane is

$$V(\text{cm}^{-1}) = (3.25 \times 10^4)x^4 - (1.19 \times 10^4)x^2 + (2.18 \times 10^4)\tau^4 - (2.02 \times 10^4)\tau^2 + (1.53 \times 10^5)x^2\tau^2 \quad (4)$$

and the contour diagram for this function is shown in Figure 12. Figure 13 shows this surface more graphically. The twisting coordinate for the energy minimum corresponds to an angle of 39.0 ± 1.8°.

Comparison to Related Molecules. Table V compares the potential energy constants determined for cyclohexene to those previously found for four oxygen containing analogues[1] and 5,6-dihydro-2*H*-thiopyran.[2] Table VI compares the twist angles and various energy barriers for these molecules. We have previously discussed[1,2] in some detail some of the factors contributing to the magnitudes of the potential energy constants and the energy barriers of the oxygen- and sulfur-containing compounds. Namely, a_1 and a_2 (especially the former) reflect angle strain effects while

Table VI. Twist Angle and Energy Barriers of Cyclohexene and Analogues[a]

	twist angle τ (deg)			energy barrier (cm^{-1})				
molecule	infrared	microwave	MM2	B_{pt}(IR)[b]	B_{pt}(MM2)	B_{int}(IR)[c]	B_{int}(MM2)	B_{int}(NMR)[d]
$CH_2CH_2CH{=}CHCH_2CH_2$ (I)								
this work	39.0	30.1[e]	30.4	4700	3790	3600	1670	1820[f]
DCC[g]				8800 (or 9591[h])		2630 (or 2841[h])		
SW[h]				5826		2571		
$CH_2CH_2CH{=}CHOCH_2$ (II)	36.5	30.5[i]	30.6	4080	3080	3480	2960	2310[j]
$CH_2OCH{=}CHOCH_2$ (III)	35.1	29.9[k]	29.3	4130	2300	3830	2300	2670[l]
$CH_2CH_2CH{=}CHCH_2O$ (IV)	38.2	31.5[m]	33.6	4130	3570	3540	2080	
$CH_2OCH{=}CHCH_2O$ (V)	33.2		30.9	3500	2270	3120	2270	2520[n]
$CH_2CH_2CH{=}CHCH_2S$[o] (VI)	37.8		30.5	4280	3560	4130	1370	

[a] Reference 1 unless otherwise indicated. [b] The barrier between planar and twisted structures. [c] The barrier to interconversion, $B_{int}(IR) = B_{pt} - B_{pb}$. [d] Nuclear magnetic resonance value for solution sample. [e] Reference 6. [f] Reference 3. [g] Reference 7 [h] Reference 8. [i] Wells, J. A.; Malloy, T. B. *J. Chem. Phys.* **1974**, *60*, 2132–2138. [j] Reference 18. [k] Lopez, J. C.; Alonso, J. L. Z. *Z. Naturforsch.* **1985**, *40a*, 913–919. [l] Reference 19. [m] Wells, J. A.; Malloy, T. B. *J. Chem. Phys.* **1974**, *60*, 3987–3993. [n] Reference 20. [o] Reference 2.

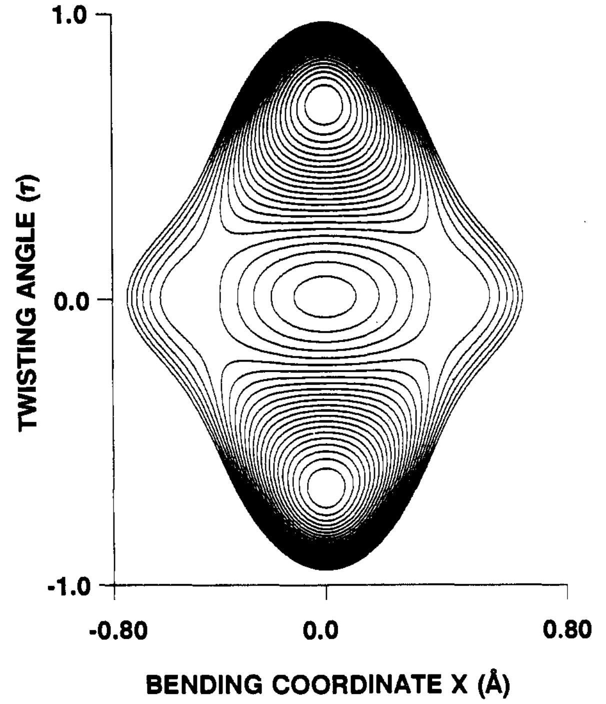


Figure 12. Two-dimensional vibrational potential energy surface for cyclohexene in terms of the ring-bending and ring-twisting coordinates. The contour lines are 200 cm^{-1} apart.

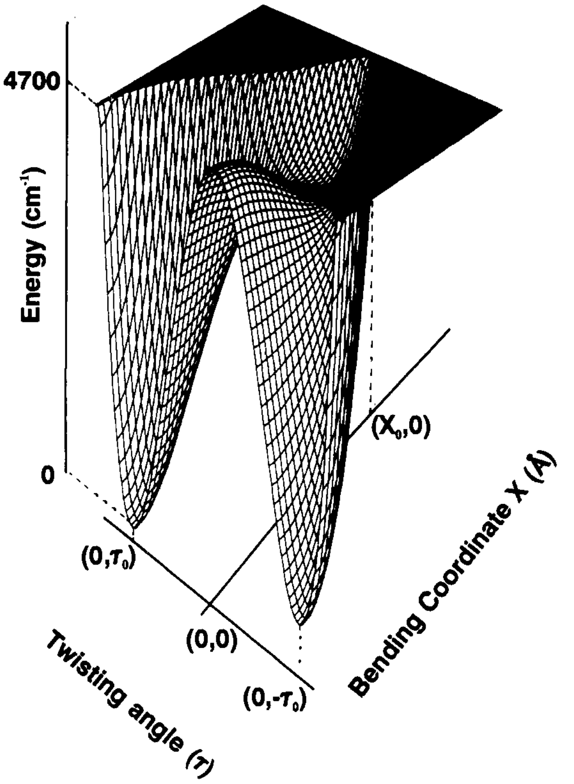


Figure 13. Three-dimensional representation of half of the cyclohexene potential energy surface.

torsional forces primarily result in negative contributions to b_1 and b_2. The overall angle strain for cyclohexene is expected to be less than in the oxygen-containing compounds, and this is reflected by the fact that a_1 and a_2 for cyclohexene are less than for the pyrans and the dioxins. The a_1 quartic constants ($\times 10^4$ $cm^{-1}/Å^4$) for the bending motion for the rings containing two oxygen atoms are 7.0 and 15.9 (for both oxygens next to the double bond) whereas they are 6.0 and 4.2 for the rings with one oxygen atom. The cyclohexene value, for the ring containing none of the more highly strained oxygen atoms, is 3.3. Similarly, the a_2 ($\times 10^4$ cm^{-1}/rad^4) constant for the twisting, which is less sensitive to the angle strain, changes from 3.3 and 2.9 for the rings with two oxygen atoms to 2.3 and 2.5 for the rings containing one oxygen atom. The cyclohexene value is 2.2, again reflecting decreased angle strain. For the thiopyran, the decreased angle strain at the sulfur atom results in relatively low a_1 and a_2 values although the latter is very similar to that for cyclohexene. The relative b_1 and b_2 values for these six molecules are more difficult to compare since angle strain effects along with the torsional forces contribute to these values. On the whole, these values are similar for all the molecules except that the b_1 value of the thiopyran is lower. It should be noted that both b_1 and b_2 are negative for all of these molecules, including $CH_2OCH{=}CHCH_2O$ which has no CH_2–CH_2 torsional interactions, indicative of the fact that the C–O–C angles, in particular, have a strong desire to become considerably smaller than the average ring angle of 120° for a planar ring. Twisting or bending of the six-membered ring, as effected by a negative b_1 or b_2 constant, reduces the interior angles of the ring. The cross term c is a measure of the interaction between the bending and twisting motions and is remarkably constant at $2.0 \pm 0.5 \times 10^5$ $cm^{-1}/(Å^2{\cdot}rad^2)$ for cyclohexene and its oxygen analogues. Only for the ring containing the heavy sulfur atom is this value appreciably smaller. The self-consistency of these data and the observation of the expected trends in the magnitudes of the potential constants provide additional confidence in the reliability of our results.

Table VI shows that, as expected from its four CH_2–CH_2 torsional interactions, the energy difference between the planar and twisted forms (B_{pt}) of cyclohexene (4700 cm^{-1} or 13.4 kcal/mol) is greater than that for any of its analogues. This difference would be even greater if it were not for the fact that the angles at the oxygen and sulfur atoms in the heterocyclic rings have a strong tendency to become smaller than the values required for the planar structures. The lowest value (3500 cm^{-1} or 10.0 kcal/mol) of B_{pt} occurs, however, for the dioxin molecule with no CH_2–CH_2 torsional interactions. Among these molecules the barrier to interconversion (B_{int}), which is the energy between the twisted and bent forms, was calcualted to be between 3120 and 3600 cm^{-1}, and these values correspond to energy differences between planar and bent forms of 150 to 1100 cm^{-1}. The lowest of these B_{pb} values is for thiopyran, the highest for cyclohexene.

Comparison to Previous Studies. As discussed above, the previous infrared and Raman studies of DCC and SW did not utilize two-dimensional potential energy functions to simultaneously analyze their ring-twisting and ring-bending data. Thus, their approximations, which resulted in much larger energy differences between the planar and twisted energy structures (B_{pt}) and between planar and bent forms ($B_{pb} = B_{pt} - B_{int}$), cannot be considered to be reliable.

On the other hand, the twist angle of 30.1° reported from microwave work[4] is in reasonably good agreement with our value of 39.0°. Since both the ring-twisting and ring-bending are large-amplitude vibrations, the molecule distorts considerably even in the vibrational ground state during the course of its out-of-plane vibrations.

The nuclear magnetic resonance studies of cyclohexene[3] and its analogues[17-19] in solution have resulted in calculated barriers to interconversion which are 600–1800 cm^{-1} less than those calculated from our infrared data. Differences are expected in as much as the NMR work was carried out in vinyl chloride or Freon-21 as solvents rather than in the gas phase. Nonetheless, the 1780-cm^{-1} difference in B_{int} for cyclohexene is surprising. Our data could still be fit reasonably well using a B_{int} value as low as 3200 cm^{-1} (instead of 3600 cm^{-1}), but in this case a new pair of minima occur in the potential energy surface corresponding to bent forms (i.e. one form is bent "up" and one bent "down"). We do not believe such minima exist. Our data clearly do show that B_{int} for the gas phase is much larger than the reported NMR value of 1820 cm^{-1} for the solution.

In Table VI we have also compared our results to predictions from molecular mechanics programs (MM2).[20] The MM2 parameters have been derived from existing empirical data in the literature and are intended primarily to predict structure rather than energy differences. In all cases, the molecular mechanics calculations predict both B_{pt} and B_{int} values to be less than those we have determined. Qualitatively, the relative magnitudes for B_{pt} among the six molecules are in agreement. However, B_{int} values agree less well.

In summary, the potential energy surface derived from our infrared data show the cyclohexene molecule to be twisted by 39.0°, a value considerably smaller than previously predicted from vibrational data by DCC and SW. This twist angle, however, is larger than reported in a microwave study.[6] The twist form was found to be 13.4 ± 1.4 kcal/mol lower in energy than the planar form while the bent form, which represents a saddle point on the energy surface, lies approximately 3.1 kcal/mol below the planar form and 10.3 kcal/mol above the twisting minimum. NMR studies of cyclohexene in solution[4] had reported the latter value to be 5.2 kcal/mol.

Acknowledgment. The authors thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

---

(17) Bushweller, C. H.; O'Neil, J. W. *Tetrahedron Lett.* **1969**, 4713–4716.

(18) Larken, R. H.; Lord, R. C. *J. Am. Chem. Soc.* **1972**, *95*, 5129–5132.

(19) Camerlynek, R.; Anteunis, M. A. *Tetrahedron* **1975**, *31*, 1837–1840.

(20) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982; ACS Monograph 177.

Ab Initio Vibrational Analysis of Hydrogen-Bonded *trans*- and *cis*-*N*-Methylacetamide

Noemi G. Mirkin and Samuel Krimm*

Contribution from the Biophysics Research Division and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109. *Received April 15, 1991*

Abstract: In order to characterize the vibrational dynamics of the hydrogen-bonded *N*-methylacetamide (NMA) molecule, we have calculated the energies, geometries, and force constants (at the 4-31G* level) of *trans*-NMA and *cis*-NMA to which are hydrogen bonded two H_2O molecules, one at the NH group and one at the CO group. The force constants for *trans*-NMA were scaled to experimental frequencies for NMA in aqueous solution and resulted in predicted frequencies within 5 cm^{-1} of observed bands. Experimental data for *cis*-NMA are more limited, but transfer of scale factors from the isolated molecule permitted verification of the assignments of two resonance Raman bands proposed to be characteristic of this isomer.

The development of a reliable vibrational force field for the polypeptide chain is a prerequisite to the effective use of normal-mode analysis in rigorously correlating infrared and Raman spectra with structure of peptides and proteins. An extensive empirically refined force field has broken new ground in furthering this goal,[1] but such force fields are by their nature restricted and not unique. It is, therefore, natural to turn to ab initio methods to obtain the most comprehensive force fields for such analyses.

In the absence of ab initio calculations at the highest levels of basis set and electron correlation, which may not be feasible for large systems, it is necessary to scale the force constants in order to obtain agreement with experimental frequencies.[2] While generalized scale factors can give useful results, as we showed in the case of a study of conformers of dipeptides of glycine[3] and alanine,[4,5] a reliable set of force constants requires scaling to a relatively complete set of observed and assigned frequencies. The simplest protein-model peptide system for which this is possible

---

(1) Krimm, S.; Bandekar, J. *Adv. Protein Chem.* **1986**, *38*, 181–364.

(2) Fogarasi, G.; Pulay, P. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York, 1985; Vol. 14, pp. 125–219.

(3) Cheam, T. C.; Krimm, S. *J. Mol. Struct.* **1989**, *193*, 1–34.

(4) Cheam, T. C.; Krimm, S. *J. Mol. Struct.* (*Theochem*) **1989**, *188*, 15–43.

(5) Cheam, T. C.; Krimm, S. *J. Mol. Struct* (*Theochem*) **1990**, *206*, 173–203.

0002-7863/91/1513-9742$02.50/0