function and this in turn leads to more precise conclusions about the properties of the various conformations of the seven-membered rings, as discussed in the following paper.

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References and Notes

(1) Supported in part by the National Science Foundation.
(2) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).
(3) J. B. Hendrickson, *J. Am. Chem. Soc.*, **89**, 7036 (1967).
(4) J. B. Hendrickson, *J. Am. Chem. Soc.*, **89**, 7047 (1967).
(5) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tymimski, and F. A. van-Catledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968).
(6) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967).
(7) D. F. Bocian, H. M. Pickett, T. C. Rounds, and H. L. Strauss, *J. Am. Chem. Soc.*, **97**, 687 (1975).
(8) D. F. Bocian and H. L. Strauss, *J. Am. Chem. Soc.*, following paper in this issue.
(9) E. B. Wilson Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1965.
(10) R. B. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965). This force field cannot be directly applied, since our molecules do not allow a simple trans–gauche classification and, therefore, we have chosen the trans or gauche constants to apply to those atoms most nearly in the appropriate relationship to one another. We have set the bend–bend force constants which are <0.02 mdyn Å^{-1} equal to zero.
(11) R. G. Snyder and G. Zerbi, *Spectrochim. Acta, Part A*, **23**, 391 (1967). See note in ref 10 concerning the force fields.
(12) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **53**, 376 (1970).
(13) (a) H. M. Pickett, Ph.D. Dissertation, University of California, Berkeley, 1969; (b) T. R. Borgers, Ph.D. Dissertation, University of California, Berkeley, 1965; (c) J. A. Greenhouse, Ph.D. Dissertation, University of California, Berkeley, 1968.
(14) H. M. Pickett, G. M. Bradley, and H. L. Strauss, *Appl. Opt.*, **9**, 2397 (1970).
(15) O. H. Wheeler and J. L. Mateos, *Bol. Inst. Quim. Univ. Nac. Auton. Mex.*, **9**, 29 (1959). *Chem. Abstr.* **54**, 13 861b (1960).
(16) P. A. Bazhulin, Kh. E. Sterin, T. F. Balanova, O. P. Solovova, N. B. Turova-Pollak, and B. A. Kanzanski, *Otel. Khim. Nauk.*, **No. 1**, 7 (1946). *Chem. Abstr.*, **42**, 62 481 (1948).
(17) R. C. Lord, private communication. *Chem. Abstr.* **56**, 9590a (1962).
(18) P. Tarte, P. A. Laurent, and C. Rogister-Paris, *Bull. Soc. Chim. Fr.*, 365 (1960).
(19) A. Kirrmann and N. Hamaide, *Bull. Soc. Chim. Fr.*, 789 (1957).
(20) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules I, II, III", Shell Development Co., Emeryville, Calif., 1962.
(21) H. M. Pickett and H. L. Strauss, *J. Am. Chem. Soc.*, **92**, 7281 (1970).
(22) T. C. Rounds and H. L. Strauss, to be submitted for publication.
(23) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).
(24) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).
(25) A. Warshel and S. Lifson, *Chem. Phys. Lett.*, **4**, 255 (1969).
(26) B. Hudson, private communication.

Conformational Structure and Energy of Cycloheptane and Some Related Oxepanes[1]

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Abstract: Calculations of the low-energy conformations of cycloheptane, 1,3-dioxepane, and oxepane are presented. The calculations use the potential function derived using the vibrational information in the preceding paper. The various paths for conformational interconversion are characterized and the chair–twist-chair pseudorotation paths are mapped. The results of the calculations are compared with NMR results and with rotational Raman spectra, and with the results of previous calculations. The available evidence leads to a consistent picture of the seven-membered rings, with the twist-chairs as the lowest energy conformations.

I. Introduction

The determination of the relative energies and geometries of the cycloalkanes has been an ongoing challenge to chemists. The conformations of the smaller ring molecules have been well characterized, but the determination of the properties of molecules of seven ring atoms and larger has proved to be more difficult. Calculations based on empirically determined potential functions have suggested the main features to be expected in the seven-membered rings[2-6] and have identified four basic conformations—the chair, the boat, the twist-chair, and the twist-boat.[7] In a previous paper,[7] we presented a detailed account of the conformational properties of cycloheptane using a potential function derived from an analysis of the vibrational spectra of six-membered rings.[8] Now we have been able to analyze the vibrational spectra of cycloheptane, 1,3-dioxepane, and oxepane. The vibrational spectra show that each of these molecules exist in twist-chair conformations. Oxepane exists as a set of *dl* pairs of two different twist-chairs with no elements of symmetry; 1,3-dioxepane and cycloheptane exist as single twist-chairs containing single twofold symmetry axes. We have used this information and the vibrational frequencies to modify our original potential function. In this paper, we present calculations of the conformational properties of these molecules using our new potential function. The transformations among the conformations are visualized using methods we described previously.[7]

Comparison is made to new NMR data and to other experiments that contain some structural information. We first present the results of the conformational energy calculations, then an account of the details of the determination of the potential function, and finally, an account of comparison with other data. We have interpreted the spectrum of one other seven-membered ring molecule, cycloheptanone. The barrier to pseudorotation in cycloheptanone is significantly lower. The same model we present here also fits the properties of cycloheptanone in detail, but we discuss the cycloheptanone in a separate paper because the lower barrier changes the observable spectra dramatically.[10]

II. Conformational Energy Surfaces

In our previous paper on cycloheptane,[7] we described a set of coordinates for the seven-membered rings which are especially suited for conformational calculations. These coordinates are similar to those which have been described in detail for cyclopentane,[11] cyclohexane,[12,13] and for rings in general.[14] In this coordinate system, the z or out-of-plane displacements

Table I. Sets of Values of ϕ_2 and ϕ_3 Giving Identical Conformations

	Cycloheptane[a]	
	$C_7{}^k$	$S_7{}^k$
ϕ_2:	$\phi_2 + 2\pi 2k/7$	$\phi_2 + \pi + 2\pi 2k/7$
ϕ_3:	$\phi_3 + 2\pi 3k/7$	$\phi_3 + \pi + 2\pi 3k/7$
	$lC_2{}'$	$l\sigma_v$
ϕ_2:	$-\phi_2 + \pi + 4\pi 2l/7$	$-\phi_2 + 4\pi 2l/7$
ϕ_3:	$-\phi_3 + \pi + 4\pi 3l/7$	$-\phi_3 + 4\pi 3l/7$
	Heterocycles	
	E	C_2
ϕ_2:	ϕ_2	$-\phi_2 + \pi$
ϕ_3:	ϕ_3	$-\phi_3 + \pi$
	σ_v($\perp$ to plane of ring)	$\sigma_{v'}$(plane of ring)
ϕ_2:	$-\phi_2$	$\phi_2 + \pi$
ϕ_3:	$-\phi_3$	$\phi_3 + \pi$

[a] From ref 8. The indices k and l both go from 1 to 7.

of the ring atoms from the positions they have in the planar ring are written in the following manner:

$$z_j = \rho[\cos\theta \cos(2\pi 2j/7 + \phi_2) + \sin\theta \sin(2\pi 3j/7 + \phi_3)] \quad (1)$$

$0 \leq \theta \leq \pi/2$, $0 \leq \phi_2, \phi_3 \leq 2\pi$. Here the index, j, labels the ring atom, ρ specifies the amount by which the conformation deviates from planarity, θ specifies the amount of boat-like and chair-like character, and the two ϕ's specify the amount of bent and twisted character in a given conformation. In this coordinate system, it turns out that the energy has a sharp minimum with respect to ρ and all of the interesting conformations have nearly the same value of ρ. There are several minima in the energy as a function of θ and these will be discussed below. At a fixed value of ρ and θ variation of either of the ϕ's leads to a periodic variation of the energy.

The four coordinates ρ, θ, ϕ_2, and ϕ_3 provide a complete set of coordinates with which to describe the conformations of the seven-membered rings. However, these coordinates must be written in terms of the geometrical parameters of the ring (bond angles and such) in order to carry out calculations. The transformation between the ρ, θ, ϕ_2, ϕ_3, and the ring parameters is described in ref 7 and 15. The z_j of eq 1 are rather nonlinear functions of the ring parameters and this causes the calculated values of ρ, θ, ϕ_2, and ϕ_3, which specify the various conformations to differ somewhat from ideal relationships such as those of Table I. The equivalence of various conformations was assured in our calculations by working when necessary in actual geometrical coordinates rather than in the ρ, θ, ϕ_2, and ϕ_3.

The coordinates ρ, θ, ϕ_2, and ϕ_3 define a toroidal surface[7] (Figure 1) and the pseudorotation paths form closed curves on tori with fixed values of the two radii or of ρ and θ. The pseudorotation path is the lowest energy path which connects the geometrically equivalent conformations of Table I and is thus essentially a function of ϕ_2 and ϕ_3 alone (but with small adjustments in ρ and θ to take into account the nonlinear nature of the coordinates and the nonexact symmetry of the ethers). The chair–twist-chair has a value of θ of about 66° and on this "chair–twist-chair torus", the pseudorotation path is defined by an angle ϕ such that[7]

$$\phi_2 = \phi_2{}^0 + 3\phi$$
$$\phi_3 = \phi_3{}^0 + \phi \quad (2)$$

The chair form of cycloheptane is specified by $\theta_0 \approx 66°$, $\phi_2{}^0 = 0°$, and $\phi_3{}^0 = \pi$. This form has a plane of symmetry, and so the symmetry operations of Table I generate only 14 equivalent forms. For the ethers, the coordinates $\phi_2{}^0 = 0°$ and $\phi_3{}^0 = \pi$ also specify a chair conformer with a plane of symmetry. The ethers also have only 14 geometrically similar chair forms, since all of their asymmetric chair conformers have a pseudoplane of symmetry. The next equivalent chair form for cycloheptane is reached by movement along the helical pseudorotation track specified by $\phi_2{}' = \phi_2{}^0 + 3\pi/7$, $\phi_3{}' = \phi_3{}^0 + \pi/7$. The twist-chair conformers are found just halfway between the chairs; that is, the first twist-chair is given by $\phi_2{}^T = \phi_2{}^0 + 3\pi/14$, $\phi_3{}^T = \phi_3{}^0 + \pi/14$. For the ethers, a twist-chair with C_2 symmetry is found at the coordinates $\phi_2 = 90°$, $\phi_3 = 90°$.

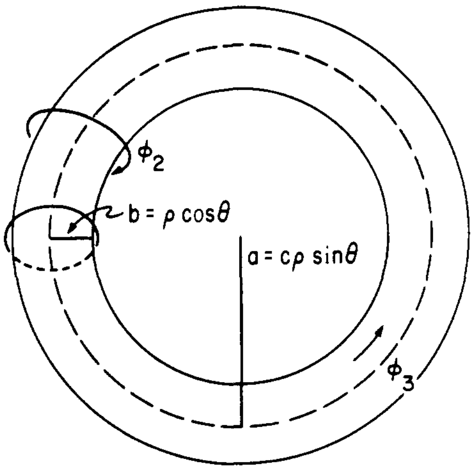

Figure 1. Plane section of the torus defined by the coordinates of eq 1. The constant c can be chosen to give the torus a convenient shape. The various pseudorotation paths form closed curves on tori with both radii fixed. (Note that in the torus pictured in ref 7, the angles ϕ_2 and ϕ_3 were inadvertently switched.)

The variation of the energy can be mapped as a function of ϕ_2 and ϕ_3 only, if a torus of fixed radii is projected onto a rectangle.[7] The detailed results of our conformational calculations are plotted as contour lines on such unfolded tori in Figures 2–4. The pseudorotation pathway connecting the 14 equivalent chair and twist-chair forms of cycloheptane is represented by the sinusoidal variation of the energy along the long continuous valley across the energy surface, while the mechanical inequivalence of the chair and twist-chair conformers of the ethers is shown by the nonsimple variation of the energy through this valley. Cuts of the energy surface along the pseudorotation tracks of the two ethers are shown in Figures 5 and 6. Comparison of these cuts with the maps illustrates some of the unique features of the conformational energetics of each molecule. The minimum energy twist-chair conformer of 1,3-dioxepane ($\phi_2 = 90°$, $\phi_3 = 90°$) is observed as the 4-kcal/mol deep hole in the pseudorotation track, while two of the low energy asymmetric twist-chair forms of oxepane are located at $\phi_2 = -61°$, $\phi_3 = 35°$ and $\phi_2 = 14°$, $\phi_3 = 64°$. The other pair of enantiomers is located at $\phi_2 = 119°$, $\phi_3 = 145°$ and $\phi_2 = 166°$, $\phi_3 = 116°$, respectively. The positions of the geometrically equivalent chairs and twist-chairs are labeled on the contour maps and pseudorotation pathways of the two ethers. The position of the oxygen atom relative to the "plane" or "axis" of symmetry for each of the conformers is shown in Figure 7.

The boat and twist-boat conformers have $\theta \approx 0°$, so the energy is just a function of ϕ_2 and this defines the pseudorotation path. For cycloheptane, the boat-like forms are freely pseudorotating and are approximately 3.4 kcal/mol above the twist-chair. The variation of the energy along the boat–twist-boat pathways of the two ethers are shown in Figures 5 and 6.

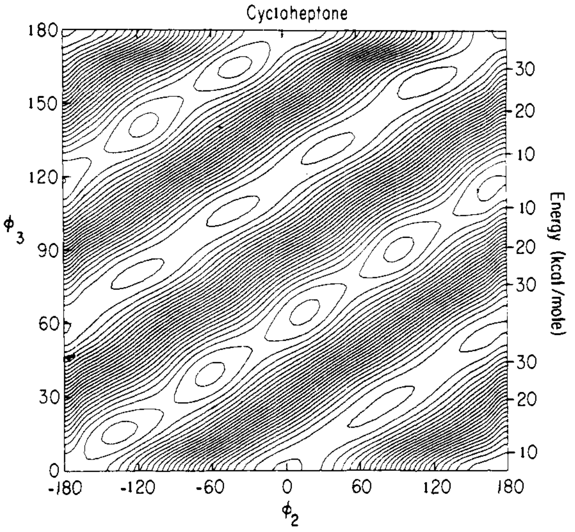

Figure 2. Contour map of the chair-twist-chair pseudorotation surface of cycloheptane. The value of θ is about 66° and the contour interval is 1 kcal/mol. Only half of the energy surface is shown. The other half for $0 \geq \phi_3 \geq -180°$ may be obtained by rotating the diagram 180° about the origin ($\phi_2 = 0$, $\phi_3 = 0$). The 14 equivalent twist-chair conformations (only seven actually shown) are at the minima within the 8-kcal/mol contours. The chair conformers are halfway between the twist-chairs along the pseudorotation path.

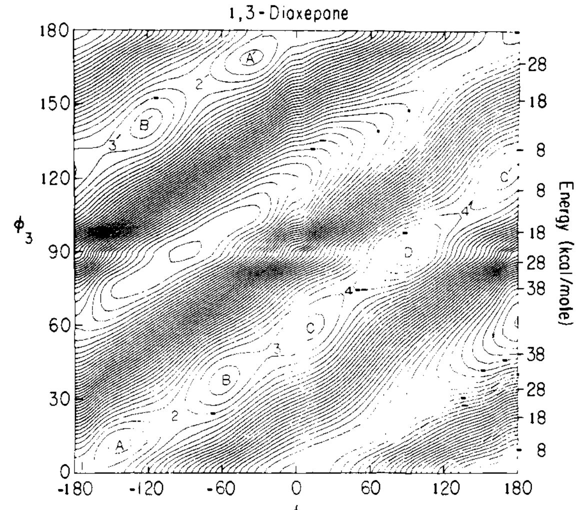

Figure 3. Contour map of the chair-twist-chair pseudorotation surface of 1,3-dioxepane. The diagram is similar to that for cycloheptane (Figure 2) and the part for $0 \geq \phi_3 \geq -180°$ is obtained in the same way. The positions of the chair conformers are labeled by numbers and of the twist-chairs by letters both here and in Figure 5. The position of the oxygen atoms for each of these forms is illustrated in Figure 7.

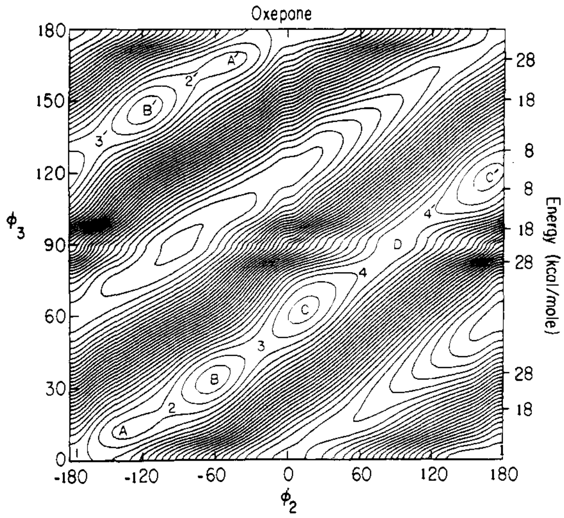

Figure 4. Contour map of the chair-twist-chair pseudorotation surface of oxepane. The notation is the same as in Figure 3. See also Figure 6.

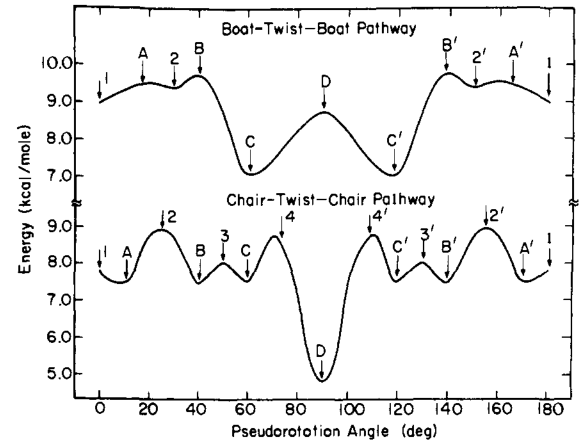

Figure 5. The energy as a function of pseudorotation angle for 1,3-dioxepane. The chair-twist-chair curve represents a cut along the surface of Figure 3. The boat-twist-boat curve is a cut from the boat-twist-boat surface, which is not shown. The notation indicates the position of the oxygen atoms in the various forms as shown in Figure 7.

The positions of several of the boat and twist-boat forms are labeled on the pathways and their respective positions correlated in Figure 7.

As we have previously described for cycloheptane,[7] variation of the coordinate θ carries the chair to a boat conformation. Plots of the energy vs. θ at two different points along the cycloheptane tori are shown in Figure 8. The transition state for boat-to-chair interconversion is approximately 9 kcal/mol above the minimum energy twist-chair. For the substituted rings, the paths between chair and boat tori are more complicated. Simple pathways in θ have different energy profiles depending on their points of origin along the pseudorotation track. Since the lowest energy boat does not generally occur at the same values of ϕ_2 and ϕ_3 as the lowest energy chair, the minimum energy pathway will involve simultaneous variation in θ, ϕ_2, and ϕ_3. The energies of the transition states of the two ethers are also about 9 kcal/mol above the lowest energy twist-chair(s) and their θ coordinates are approximately the same as that of cycloheptane. The calculated energies and geometries of the various conformations of the seven-membered rings are summarized in Tables II-V.

III. Potential Function and Details of the Calculations

In the preceding paper,[9] we examined the vibrational spectra and normal coordinates of the molecules we are considering. We were able to show that the ring-bending motions separate from the other possible modes of motion to a great degree. We then fit a potential function to these vibrational frequencies and to the conformational information and arrived at the form:

$$\begin{aligned} V = \sum_{i=1}^{7} \Big[& H(\psi_i - \psi_i{}^0)^2 + F(\psi_{i+1} - \psi_{i+1}{}^0)(\psi_i - \psi_i{}^0) \\ & + T\cos 3\tau_i + D\cos 2\tau_i + K(\psi_{i+1} - \psi_{i+1}{}^0) \\ & \times (\psi_i - \psi_i{}^0)\cos\tau_i \\ & + \sum_{\substack{j=i+3 \\ \mathrm{mod}\ 7}}^{\substack{i+4 \\ \mathrm{mod}\ 7}} \sum_{m=1}^{4} \left(Ae^{-r_{ijm}/r_0} - B/r_{ijm}{}^6\right)\Big] \end{aligned} \qquad (3)$$

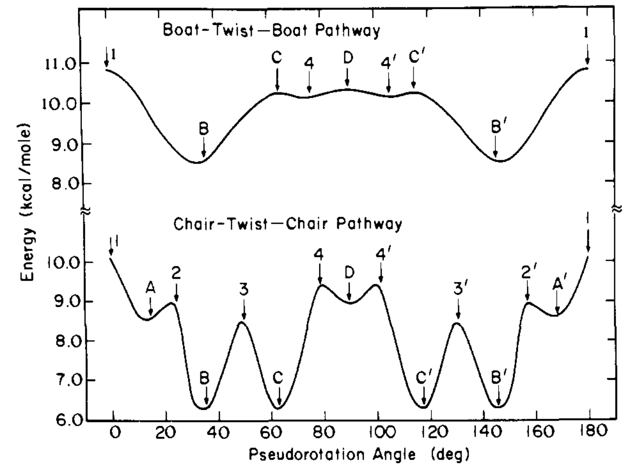

Figure 6. The energy as a function of pseudorotation angle for oxepane. The notation is the same as in Figure 5.

Table II. Coordinates of the Cycloheptane, 1,3-Dioxepane, and Oxepane Conformations

Conformation	Coordinate[a] θ	ϕ_2[b]	ϕ_3[b]	ρ
	Cycloheptane			
Twist-chair	64.8	90.0	90.0	40.1
Chair	68.1	0.0	180.0	38.9
Twist-boat	2.8	90.0	−95.0[c]	36.8
Boat	2.1	0.0	180.0[c]	36.8
Twisted transition state	30.0	90.0	90.0	37.8
Bent transition state	32.0	0.0	180.0	33.1
	1,3-Dioxepane			
Twist-chair	59.1	90.0	90.0	41.4
Chair	69.4	0.0	180.0	39.2
Twist-boat	8.2	64.3	138.3[c]	38.6
Boat	6.2	51.5	122.8[c]	39.0
Transition state	27.0	92.1	87.8	39.0
	Oxepane			
Twist-chair C,C′[d]	63.1	14.0	64.0	42.6
Twist-chair B,B′[d]	64.2	−61.2	35.0	41.6
Chair	69.9	−91.9	21.6	39.6
Twist-boat	10.4	38.6	175.8[c]	39.4
Boat	8.0	25.7	177.5[c]	40.1
Transition state	35.0	29.8	−57.9	39.9

[a] All values in degrees. [b] The values of ϕ_2 and ϕ_3 for the 13 other equivalent forms of cycloheptane and the other equivalent forms of the ethers can be obtained using Table I. For the ether conformers with no symmetry, the minimum energy form does not always occur at the ideal value of these coordinates; see text. [c] For these conformers, ϕ_3 varies widely because of the small value of θ. [d] See Figure 7.

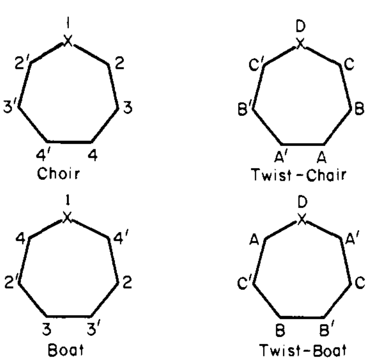

Figure 7. This diagram gives the position of the oxygen atoms relative to the pseudoplane or axis of symmetry of the various ether conformers in the notation used in Figures 3-6. The X represents the O atom in oxepane or the 2-methylene group in 1,3-dioxepane. In conformer 1 the plane of symmetry passes through this group, in conformer 2 the pseudoplane passes one ring position away in the chair and two ring positions away in the boat. The conformers are labeled in order of increasing pseudorotation angle. Successive equivalent conformers are reflected through the plane of the ring: if 1 represents a boat with its bow up, 2 is a boat with its bow down, etc.

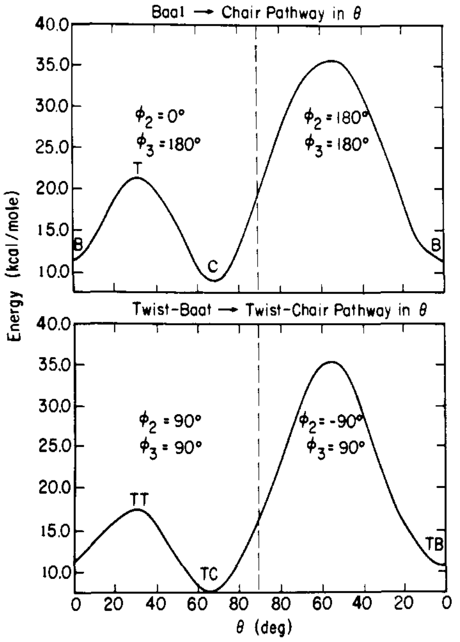

Figure 8. Boat to chair pathway for cycloheptane (top) and twist-boat to twist-chair pathway (bottom). The boat is marked by B, the chair by C, and the bent transition state by T. The twist-boat, twist-chair, and twisted transition state are marked TB, TC, and TT, respectively. The energy is plotted as a function of θ at constant ϕ_2 and ϕ_3, except ϕ_2 switches at θ = 90° where $\rho_2 = 0$ and near TB, ϕ_3 changes in the manner discussed in ref 7.

In this equation, the ψ_i are the instantaneous values of the ring-bending angles and the $\psi_i{}^0$ are their equilibrium values. The seven τ_i are the values of the torsional angles defined in ref 12. The r_{ijm} are the distances between the hydrogen atoms attached to the carbon atoms indexed, i, and j. The index m labels the four distances between the hydrogens on these atoms. For the ethers, the r_{ijm} are also the distances between an oxygen atom, which can be indexed i, and the hydrogens on atom j. In this case the index m runs only from 1 to 2. The complete set of parameters for eq 3, including the geometrical parameters, is given in Table IX and the text of the preceding paper.[9] In comparing this potential function to others that have been used for conformational analysis, it is important to note that this function has been derived using the ring-bending model and that the potential constants have absorbed the effects of a large number of interactions that might otherwise be expressed by nonbonded terms.

In our preliminary conformational calculations on cycloheptane,[7] we used the potential function derived from the properties of six-membered rings[8] (H, F, T, and a onefold torsional term U) plus the nonbonded interaction term of Abe et al.[16] (eq 3). With this potential function, the twist-chair was found to be the minimum energy conformer and the boat forms were approximately 0.5 kcal/mol higher in energy. The calculated low frequencies of the twist-chair were found to be in qualitative agreement with experiment, while those of the boats were totally inconsistent.[9] Since the observed vibrational spectra could not be interpreted in terms of the boat-chair mixture predicted by our preliminary conformational calculations, several modifications were tried in the model potential.

Table III. Geometries of the Cycloheptane, 1,3-Dioxepane, and Oxepane Conformations

Conformation	Bond angles							Torsional angles						
	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	ψ_7	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7
Cycloheptane														
Twist-chair	115.0	111.5	114.9	115.1	114.9	111.5	115.0	−73.0	89.4	−40.0	−40.4	89.4	−72.7	55.4
Chair	117.3	113.6	113.6	114.4	113.5	113.6	117.2	68.5	−85.6	63.8	−63.9	85.8	−68.3	−0.2
Twist-boat	114.9	113.9	113.9	114.8	114.8	113.9	114.8	−18.8	76.2	−18.8	−65.7	46.8	45.2	−65.1
Boat	115.3	113.4	113.8	114.9	113.8	113.4	115.3	72.2	−32.4	−58.6	−58.6	32.7	−72.2	0.0
Twisted transition state	120.6	115.6	110.0	111.5	110.0	115.7	120.8	−27.6	89.1	−46.9	−47.3	88.8	−27.0	−14.9
Bent transition state	115.1	113.4	121.0	123.2	121.0	113.4	115.1	75.1	−60.3	−1.8	1.7	60.3	−75.1	0.0
1,3-Dioxepane														
Twist-chair	114.0	108.7	114.3	110.1	114.1	108.6	113.9	−68.0	98.3	−46.9	−47.3	98.8	−68.3	45.8
Chair	116.2	111.1	115.3	111.0	114.2	110.8	115.5	67.2	−88.7	70.3	−71.8	91.5	−66.0	−1.7
Twist-boat	114.1	110.9	115.9	110.1	112.1	106.8	110.0	45.6	50.1	−66.3	−31.3	93.5	−26.7	−60.0
Boat	112.9	111.0	116.1	110.8	114.0	107.4	110.3	56.2	37.3	−75.9	−8.7	86.5	−41.0	−52.0
Transition state	117.9	111.7	109.5	110.3	110.3	113.0	119.2	−26.9	94.9	−50.4	−54.4	90.4	−19.6	−20.2
Oxepane														
Twist-chair B, B′[a]	112.2	115.7	111.4	111.1	110.6	114.1	114.6	70.0	−54.3	80.2	−101.9	46.6	34.2	−83.7
Twist-chair C, C′[a]	114.4	115.0	110.0	116.3	112.2	114.3	110.1	50.8	−72.9	96.4	−43.0	−44.4	90.9	−67.7
Chair	115.5	114.5	111.5	114.0	109.7	116.0	116.6	−79.5	62.4	−73.0	97.2	−71.1	2.1	62.8
Twist-boat	113.9	112.3	108.2	115.3	112.7	114.6	113.5	64.2	22.3	−91.4	33.5	56.7	−40.8	−48.3
Boat	112.8	112.3	109.5	114.3	110.7	113.6	112.2	73.5	1.7	−86.0	46.5	53.1	−55.6	−34.3
Transition state	115.7	121.6	116.0	114.3	106.1	109.2	109.1	23.8	8.5	44.4	−104.8	47.4	47.4	−83.5

[a] See Figure 7.

Table IV. Energies of the Cycloheptane, 1,3-Dioxepane, and Oxepane Conformations[a]

Conformation	E_H	E_F	E_D	E_T	E_K	ΣE_{bond}	$E_{\text{H-H}}$	ΣE	ΔE
Cycloheptane									
Twist-chair	0.643	0.034	1.662	5.580	−0.033	7.886	−0.280	7.608	0.0
Chair	1.027	0.164	1.672	6.240	−0.080	9.023	−0.112	8.911	1.303
Twist-boat	0.480	0.098	3.161	6.674	−0.040	10.373	0.619	10.993	3.385
Boat	0.487	0.086	3.157	6.856	−0.039	10.547	0.483	11.030	3.422
Twisted transition state	3.434	0.481	3.442	10.435	−0.340	17.452	−0.179	17.273	9.665
Bent transition state	5.510	0.916	3.620	10.869	−0.581	20.334	0.923	21.256	13.648
1,3-Dioxepane									
Twist-chair	0.232	0.015	0.486	4.580	−0.001	5.312	−0.551	4.760	0.0
Chair	0.843	0.058	0.999	6.217	−0.042	8.075	−0.275	7.800	3.040
Twist-boat	0.670	−0.027	0.249	6.655	−0.017	7.530	−0.450	7.079	2.319
Boat	0.649	0.007	0.380	6.872	−0.011	7.897	−0.231	7.667	2.917
Transition state	2.253	−0.045	0.881	11.593	−0.197	14.484	−0.615	13.869	9.109
Oxepane									
Twist-chair B, B′[b]	0.495	−0.050	0.813	5.423	−0.020	6.661	−0.370	6.292	0.013
Twist-chair C, C′[b]	0.869	0.002	0.543	5.067	−0.015	6.465	−0.187	6.279	0.0
Chair	0.973	0.134	1.240	6.123	−0.067	8.403	−0.184	8.219	1.940
Twist-boat	0.594	0.063	1.204	6.437	−0.018	8.280	0.477	8.758	2.479
Boat	0.126	0.001	1.082	7.765	−0.001	8.973	−0.223	8.750	2.471
Transition state	3.883	−0.186	1.309	10.799	−0.309	15.497	−0.473	15.024	8.745

[a] In kilocalories per mole. [b] See Figure 7.

First, the effects on the relative energies and vibrational frequencies of several values of the nonbonded parameters A and $1/r_0$ were investigated. The harder interaction potentials of Hendrickson[3] and Bartell[17] were found to raise the energies of the boats by several kilocalories per mole, but had deleterious effects on the calculated out-of-plane bending frequencies. Next, the onefold torsional term U, which was found to have little effect on the properties of the seven-membered rings, was dropped, and a twofold term D was added. The effect of the twofold term is to steepen the torsional well for values of τ_i near 0°. This is exactly the effect needed to raise the energy of the boats relative to the chairs, since the average torsional angle of the boats is much nearer 0° than is that of the chairs (Table III). Unfortunately, the vibrational frequencies are rather insensitive to the twofold term and the values of D cannot be determined with any accuracy. A value of 0.5 kcal/mol was chosen for D, since this gives reasonable conformational and vibrational results. The value of D can be changed by about 35% without seriously affecting the calculated frequencies of the twist-chairs. This range of values for D places an uncertainty of approximately ±0.6 kcal/mol on the relative energies of our boat and chair-like conformations. The twofold term and the nonbonded term together give good values for the minimum energy conformations and ring-bending frequencies. Either term alone is sufficient to raise the energy of the boats to an acceptable level; but use of either term alone results in unacceptable vibrational frequencies. Use of both terms results in an estimated uncertainty in the relative energies of our boat and chair conformers of about 1 kcal/mol.

Still better fits of the vibrational frequencies were achieved by adding a bend-torsion interaction term K to the potential and making some minor changes in the values of H, F, and T for the all-carbon valence coordinates. Although these modifications do not significantly affect the relative energies of the conformations, they do have a significant effect on the structures of the molecules. The average torsional angle $|\tau_i|$ of the twist-chair is increased by about 5° and the average bond angle by nearly 4° over the values obtained in our preliminary calculations on cycloheptane.[7] These structural changes have important effects on the rotational constants, and this will be discussed further below.

We are interested in the relative energies and geometries of the four basic conformations of each of the three molecules studied, as well as all of the relatively low-energy intermediate conformations, and we therefore carried out the calculations summarized in the figures and tables.

The contour maps of Figures 2-4 were obtained by specifying values of θ, ϕ_2, and ϕ_3 and then minimizing the energy with respect to ρ and the set of in-plane coordinates described in ref. 7. Although the true minimum energy conformations occur at different values of θ as ϕ_2 and ϕ_3 are varied, each of the energy surfaces is mapped with θ held constant at 66°. This is approximately the average value of θ for the various conformations on the chair–twist-chair surface of each molecule. All of the true minima are found in the range $\theta = 66 \pm 2°$ for cycloheptane and $\theta = 66 \pm 6°$ for the ethers (Table II). Since the minimum energy values of θ are quite close to 66°, all of the important features of the energy surfaces are well reproduced by mapping at the average value. In order to locate the most stable conformations and to map the energy variation along the pseudorotation pathways (Figures 5 and 6), a seven-dimensional minimization was performed. Only the relevant pseudorotation angle was specified (ϕ_3 for the chair pathway and ϕ_2 for the boats) and the energy was minimized with respect to the other pseudorotation angle, ρ, θ, and the in-plane coordinates. All of the minimizations were carried out to the nearest 0.0005 kcal/mol, and no difficulties were encountered in locating the minima. The coordinates of the various conformations of the three molecules are listed in Table II and their respective geometries are given in Table III. The contributions to the conformational energies are summarized in Table IV and the rotational parameters of the various conformations are given in Table V. The rotational parameters provide a simple means of characterizing small changes in the geometry and can be experimentally determined (next section). Since there are many different boat and chair conformers for the two ethers, the values listed in the tables are for the lowest energy bent and twisted forms on the two different pseudorotation pathways. The "transition state" listed in the tables is defined as the lowest maximum connecting the boat–twist-boat and chair–twist-chair surfaces. For cycloheptane this transition state is represented by the left maxima in Figure 8.

IV. Other Experiments

We have examined the ^{13}C NMR spectra of cycloheptane, oxepane, and 1,3-dioxepane using the proton-enhanced nuclear induction techniques of Pines et al.[18] The cycloheptane spectrum was recorded at −185 °C and the spectra of the two ethers were recorded at several temperatures down to −150 °C. These spectra failed to reveal any splittings which might be indicative of the freezing out of some mode of conformational motion and this is consistent with the experiments of Meiboom[19] and Anet.[20] The lack of splitting is also consistent with the low values of the barriers to pseudorotation given by our calculations. The spectrum of 1,3-dioxepane does, however, exhibit noteworthy behavior as the temperature is reduced from 25 to −115 °C. The 1,3-dioxepane spectrum begins to deteriorate near −95 °C. At −115 °C, the signal to noise ratio (S/N) is so unfavorable that no spectrum is observable. In proton-enhanced nuclear induction spectroscopy, the signals of dilute nuclear spins (naturally abundant ^{13}C) are enhanced by transferring polarization from a more abundant spin species (protons) to which the dilute spins are coupled.[18] In our experiments on the three rings, the same delay times were used between the measurement of successive free induction decays. For cycloheptane and oxepane this resulted in good spectra with high S/N ratios at all temperatures studied, while for 1,3-dioxepane, no spectra were obtainable below −115 °C and higher signal intensities resulted at higher temperatures when the delay times were lengthened. This suggests that the proton relaxation times, T_1, are considerably shorter in cycloheptane and oxepane than in 1,3-dioxepane. The observed NMR spectra can be related to the conformational interconversion process via transition state theory,[21] which gives the interconversion rate (R_i) as

$$R_i = (kT/h)\exp(\Delta S^{\ddagger}/R)(-\Delta H^{\ddagger}/RT) \tag{4}$$

Table V. Rotational Constants of the Cycloheptane, 1,3-Dioxepane, and Oxepane Conformations

Conformation	A^a	B^a	C^a	κ^b
	Cycloheptane			
Twist-chair	0.1061	0.09605	0.05854	0.5768
Chair	0.1049	0.09604	0.05773	0.6259
Twist-boat	0.1016	0.1011	0.06316	0.9754
Boat	0.1025	0.1004	0.06330	0.8907
Twisted transition state	0.1070	0.09552	0.06113	0.4992
Bent transition state	0.1018	0.09630	0.05841	0.7479
	1,3-Dioxepane			
Twist-chair	0.1196	0.1052	0.06474	0.4767
Chair	0.1149	0.1057	0.06275	0.6469
Twist-boat	0.1154	0.1115	0.07110	0.8253
Boat	0.1139	0.1121	0.07116	0.9177
Transition state	0.1178	0.1067	0.06718	0.5614
	Oxepane			
Twist-chair B,B′[c]	0.1114	0.1013	0.06143	0.5983
Twist-chair C,C′[c]	0.1128	0.09982	0.06134	0.4953
Chair	0.1106	0.1006	0.06016	0.5826
Twist-boat	0.1078	0.1063	0.06694	0.9255
Boat	0.1082	0.1072	0.06773	0.9480
Transition state	0.1134	0.1006	0.06451	0.4782

[a] In wavenumbers. [b] Ray's asymmetry parameter. [c] See Figure 7.

Our conformational calculations predict barriers to pseudorotation of 1.3 and 4 kcal/mol in cycloheptane and 1,3-dioxepane, respectively (Figures 2 and 3). The barrier to pseudorotation in oxepane is also on the order of 4 kcal/mol, but the interconversion barrier between the two stable, equal energy twist-chair conformers is much lower, 2.2 kcal/mol (Figure 4). If the entropy term in eq 4 is neglected, the cycloheptane and oxepane barriers predict an interconversion rate of approximately 300 MHz (at −185 and −150 °C, respectively). The 1,3-dioxepane barrier results in an interconversion rate of 10 MHz (at −115 °C, where the spectrum is no longer observable). In the NMR experiment, the Larmor frequency of the protons was 185 MHz. The 300-MHz interconversion rates of cycloheptane and oxepane are much closer to the precessional frequency of the protons than is the 10-MHz rate of 1,3-dioxepane; thus, the interconversion process in cycloheptane and oxepane can provide a much more efficient relaxation mechanism for the protons than can the interconversion process in 1,3-dioxepane. This is consistent with the observed spectra.

Brookeman and Rushworth have made detailed NMR line shape and relaxation and measurements on the various crystalline phases of cycloheptane.[22] They find an activation energy of 1.7 kcal/mol for a process that may be pseudorotation. This energy is close to the 1.3-kcal/mol barrier we predict, but further interpretation is difficult in the absence of accurate structural information on the crystals.

A good rotational Raman spectrum of cycloheptane has been obtained by Kainnady and Weber.[23] Their experiments show a symmetric top-like spectrum and their data come from states with high rotational quantum numbers, J. Their analysis gives

$$B_{\mathrm{eff}} = 0.099\,380\,1 \pm 0.000\,004\,7\ \mathrm{cm}^{-1}$$

$$D_J = (4.08 \pm 0.17) \times 10^{-8}\ \mathrm{cm}^{-1}$$

The effective rotational constant $B_{\mathrm{eff}} \approx (A + B)/2$ and this quantity is listed in our tables. However, the effective rotational constant, B_{eff}, is not a precisely defined structural constant. It is a function of the asymmetry of the molecule and is also an average over the rotational properties of the various thermally accessible conformers. We have estimated the effect of asymmetry by calculating detailed band shapes for a molecule with approximately the rotational constants of cycloheptane. We find the maximum of the rotational band gives a value of B_{eff} about 0.2% lower than the value of $(A + B)/2$ and so we estimate

$$(A + B)/2,\ \mathrm{exptl} = \sim 0.0996\ \mathrm{cm}^{-1}$$

The value of $(A + B)/2$ for the cycloheptane twist-chair is calculated to be 0.1011 (Table V). The value for all the other conformers is very close to this value. The value for the chair is 0.1004 and even the boat forms have values of $(A + B)/2$ of 0.1015. The value of $(A + B)/2$ provides a measure of the overall flatness of the ring and does not change appreciably with conformation, in contrast to the value of C which changes 10%. The predicted value of $(A + B)/2$ adjusted for the thermal distribution of conformers is then very close to 0.1011. This is about 1% higher than the experimental value and very close to the values of $(A + B)/2$ calculated from the geometries of Hendrickson and Bixon and Lifson.[7] Our new value is also larger than our previously calculated value[7] and, indeed, our new geometries are much closer to those of both Hendrickson[3] and Bixon and Lifson[6] than are our previous ones. It is difficult to account for the discrepancy between the various results of these calculations and the experimental value of the rotational constant. Uncertainties in quantities such as the correct value of the H–C–H angle cannot account for the discrepancy.[7] Most likely, the experimental rotational constant contains contributions from Coriolis interactions and other rotation–vibration interactions we have not been able to take into account.

The relative order of the energies of the various conformers of cycloheptane is similar in our present calculations and in those of the other authors. However, the chair–twist-chair pseudorotation barrier calculated by Bixon and Lifson is approximately half as large as our barrier. This difference is significant, since the lower barrier would result in very low frequencies for the out-of-plane ring-bending bending vibrations in cycloheptane and this is not observed.

Little other structural information on these seven-membered rings is available. We have attempted to obtain a low-resolution microwave spectrum of 1,3-dioxepane, but were not able to observe any prominent bands.

V. Conclusions

A satisfyingly consistent picture of the conformations of the saturated seven-membered rings emerges from our calculations, the calculations of others, and the various spectroscopic experiments. For cycloheptane, this picture gives the twist-chair as the lowest energy conformation with a 1.3-kcal/mol barrier to pseudorotation. The boat forms are a few kilocalories per mole higher in energy. The various calculations agree remarkably well on the geometry of the twist-chair. The oxygen-substituted seven-membered rings have more complicated conformational energy surfaces which also fit the framework developed for cycloheptane and which are described in detail in the figures and tables.

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References and Notes

(1) Supported in part by the National Science Foundation.
(2) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).
(3) J. B. Hendrickson, *J. Am. Chem. Soc.*, **89**, 7036 (1967).
(4) J. B. Hendrickson, *J. Am. Chem. Soc.*, **89**, 7047 (1967).
(5) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. van-Catledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968).
(6) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967).
(7) D. F. Bocian, H. M. Pickett, T. C. Rounds, and H. L. Strauss *J. Am. Chem. Soc.*, **97**, 687 (1975). Drawings of the basic conformations of cycloheptane appear in this paper.
(8) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **53**, 376 (1970).
(9) D. F. Bocian and H. L. Strauss, *J. Am. Chem. Soc.*, preceding paper in this issue.
(10) D. F. Bocian and H. L. Strauss, *J. Chem. Phys.*, in press.
(11) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947).
(12) H. M. Pickett and H. L. Strauss, *J. Am. Chem. Soc.*, **92**, 7281 (1970).
(13) H. L. Strauss, *J. Chem. Educ.*, **48**, 221 (1971).
(14) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **55**, 324 (1971).
(15) D. F. Bocian, Ph.D. Dissertation, University of California, Berkeley, 1976.
(16) A. Abe, R. L. Jernigan, and P. F. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).
(17) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1962).
(18) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
(19) S. Meiboom, private communication.
(20) F. A. L. Anet, private communication.
(21) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, N.Y., 1966.
(22) J. R. Brookeman and F. A. Rushworth, *J. Phys. C*, **9**, 1043 (1976).
(23) J. V. Kainnady and A. Weber, *J. Raman Spectrosc.*, **4**, 275 (1976).