

Vibrational Spectra, Conformations, and Potential Functions of Cycloheptane and Related Oxepanes¹

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Abstract: The vibrational spectra of cycloheptane, oxepane, and 1,3-dioxepane are presented and assigned with particular emphasis on the skeletal bending vibrations. The assignments and normal coordinate calculations show that the three molecules have twist-chair conformations as their lowest energy forms. The cycloheptane and 1,3-dioxepane exist as twist-chairs (C_2 symmetry) and the oxepane exists as two asymmetric (C_1 symmetry) *dl* pairs of twist-chairs of approximately equal energy. The vibrational spectra can be interpreted on the basis of rigid conformations. A model potential is developed which is used in the following paper to calculate the conformational properties of these ring molecules.

I. Introduction

The conformations of saturated ring compounds have long been of interest to chemists and many methods have been employed in an attempt to determine their geometries and relative energies. The equilibrium structures of a large number of three-, four-, five-, and six-membered rings have been well characterized by the powerful techniques of electron diffraction and microwave spectroscopy, and more indirectly, by vibrational analysis. Although the equilibrium structures of small saturated ring molecules have been characterized by these methods, the seven-membered rings present difficulties that have, so far, prevented an experimental determination of their lowest energy conformations. However, extensive conformational energy calculations have been done on the seven-membered rings and these have led to an identification of four basic conformations²⁻⁶—the chair, boat, twist-chair, and twist-boat. The determination of the relative energies and geometries of these four forms has proved extremely difficult; consequently, we have undertaken a detailed vibrational investigation of cycloheptane and the cyclic ethers oxepane and 1,3-dioxepane (Figure 1).

We discuss the vibrational analysis in a number of steps. First we present the experimental spectra and provide an assignment of the low-frequency skeletal modes based on the potential functions and structures we have previously used to fit some preliminary data.⁷ We then refine the potential function to give a better fit to the skeletal frequencies. This potential function also provides a basis for describing the conformations of the seven-membered rings and this detailed description is to be found in the following paper.⁸ Finally, the calculated geometries of the conformations are used together with standard vibrational potential functions⁹⁻¹¹ (quadratic terms only) to assign the entire vibrational spectrum of each molecule. In practice, of course, we went through several cycles of this procedure to arrive at our final results. We conclude that the lowest energy conformations of these molecules are the twist-chairs illustrated in Figure 1.

II. Vibrational Spectra and Assignment of Vibrational Frequencies

There have been no detailed infrared or Raman studies of cycloheptane or the oxepanes. Several investigators have, however, reported vibrational spectra of these molecules and offered some very qualitative interpretations. No Raman spectrum of oxepane appears to have been reported, and reports of the Raman spectra of the other molecules lack polarization data.

Our starting point is to characterize the eight ring-bending modes of the three molecules studied. These deformations are

shown schematically for cycloheptane in Figure 2, which is drawn as if the ring were planar (D_{7h} symmetry). In this representation there are four vibrations whose motion is essentially out-of-plane (ω_1 – ω_4) and four whose motion is in-plane (ω_5 – ω_8). Despite the fact that the seven-membered rings deviate greatly from planarity, the designations “in-plane” and “out-of-plane” remain approximately correct and will be retained. A summary of the irreducible representations of the ring-bending deformations is presented in Table I along with their infrared and Raman selection rules in several relevant symmetries.

The approximate separability of the low-frequency motions of the ring from other vibrations in the molecule has been demonstrated by normal coordinate calculations on cyclohexane and other six-membered rings.¹⁰⁻¹² The calculations indicate that five of the six lowest frequency vibrations of these molecules are almost entirely associated with bending deformations of the ring. The sixth is also primarily a ring-bending vibration, but contains appreciable contributions from the motions of the methylene groups. This information can be extrapolated to predict that only the two highest frequency deformations of a seven-membered ring will show significant mixing with the higher frequency vibrations. The validity of this hypothesis is verified by the full normal coordinate calculations which will be discussed later.

Before presenting the vibrational spectra of the seven-membered rings in detail, it is useful to state some conclusions: A summary of the ring-bending assignments for all three molecules is presented in Tables II–IV. Also included in the tables are the calculated ring-bending frequencies and the observed and calculated far-infrared intensities. The calculated vibrational frequencies are those of the minimum energy twist-chair conformers whose structures are shown in Figure 1. For each of the structures, the *C* axis of inertia is approximately the out-of-plane coordinate and for the forms with C_2 symmetry, the *A* inertial axis corresponds to the symmetry axis. The exact geometries of the lowest energy forms as well as their energies relative to the other conformations of the ring can be found in the following paper.⁸ Both the frequencies and the structures of the twist-chairs were determined from our ring-bending potential function, whose exact form will be discussed at length later. The vibrational frequencies were calculated as in our work on six-membered rings.^{12,13a} Since the potential function is based on a model in which the low-frequency vibrations are treated as pure ring-bending motions, no attempt was made to fit the ω_7 and ω_8 vibrations, which are appreciably mixed with motions of the methylene groups. For all three molecules, the calculated frequencies of ω_7 and ω_8 are higher than those observed. This is consistent with the con-

Table I. Symmetry Correlation Table for the Ring-Bending Vibrations

Vibration	Planar cycloheptane			Planar heterocycles			Boat and chair conformers for all rings ^b			Twist-boat and twist-chair conformers for all rings		
	D_{7h}^a	IR	Raman	C_{2v}	IR	Raman	C_s	IR	Raman	C_2	IR	Raman
ω_1	E_2''	I ^c	I	B_1	A	A	A'	A	Ap	B	A	A
ω_2	E_2''	I	I	A_2	I	A	A''	A	A	A	A	Ap
ω_3	E_3''	I	I	B_1	A	A	A'	A	Ap	B	A	A
ω_4	E_3''	I	I	A_2	I	A	A''	A	A	A	A	Ap
ω_5	E_2'	I	A	A_1	A	Ap	A'	A	Ap	A	A	Ap
ω_6	E_2'	I	A	B_2	A	A	A''	A	A	B	A	A
ω_7	E_3'	I	I	A_1	A	Ap	A'	A	Ap	A	A	Ap
ω_8	E_3'	I	I	B_2	A	A''	A''	A	B	B	A	A

^a The notation of ref 9 is used in the table. ^b For the nonplanar heterocycles there are also boat, twist-boat, chair, and twist-chair conformers which have no symmetry. For these cases all eight vibrations are both IR and Raman active and belong to the irreducible representation A of the symmetry group C_1 . ^c The designations "A" and "I" indicate active and inactive vibrations, respectively. The polarized Raman bands are marked with a lower case "p".

Table II. Observed and Calculated Ring-Bending Frequencies of Cycloheptane

Vibration	ν_{obsd}			Intensity (IR)	
	IR _{gas}	Raman _{liquid}	ν_{calcd}	Obsd	Calcd
ω_1	123		130	0.16	0.15
ω_2	190 ^a	182 p	182	0.04 ^a	0.03
ω_3	335	332 dp ^c	344	0.20	0.30
ω_4	315 ^a	320 p	317	0.05 ^a	0.20
ω_5	395	400 p	377	0.09	0.06
ω_6	273		275	1.0	1.0
ω_7	515	515 p	518 ^b	0.90	0.30
ω_8	490	490 dp	495 ^b	1.2	0.40

^a These numbers are taken from the liquid spectra. ^b These frequencies were not fit with ring-bending potential function; see text. ^c Depolarized band.

Table III. Observed and Calculated Ring-Bending Frequencies of 1,3-Dioxepane

Vibration	ν_{obsd}			Intensity (IR)	
	IR _{gas}	Raman _{liquid}	ν_{calcd}	Obsd	Calcd
ω_1	175	182 dp	173	1.2	1.0
ω_2	215	219 p	211	0.25	0.19
ω_3	377	377 dp	391	0.18	0.30
ω_4	350	350 p	337	0.07	0.15
ω_5	437	437 p	445	0.45	0.38
ω_6	273	275 dp	274	1.0	1.0
ω_7	610	606 p	632 ^a	0.45	0.31
ω_8	516	516 dp	595 ^a	1.0	0.63

^a These frequencies were not fit with ring-bending potential function; see text.

straints imposed on the ring-bending motions by our model, since inclusion of the methylene motions can only shift the calculated frequencies of ω_7 and ω_8 downward. The far-infrared intensities were calculated using a bond-dipole model which includes both C-H and C-O dipoles. The C-H dipole is assumed to be $-\frac{1}{3}$ that of a C-O dipole. For the oxygen-containing compounds only minor changes in the intensities result if the C-H dipole contributions are neglected.

Experiment. Cycloheptane and 1,3-dioxepane were obtained as reagent-grade solvents from Aldrich Chemical Co., Inc., and oxepane was obtained as a reagent-grade solvent from Chemical Samples Co., Inc. Gas chromatographic analysis revealed no impurities and all spectra were recorded without further purification of the chemicals. The samples used for

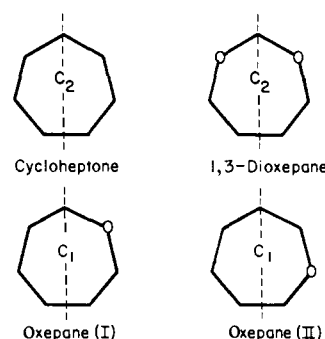


Figure 1. Structures of the minimum energy twist-chair conformers. The dashed line represents the C_2 axis in cycloheptane and 1,3-dioxepane and the pseudo- C_2 axis for the oxepane conformers. The two oxepane conformers are of approximately equal energy and only one enantiomer of each of them is shown.

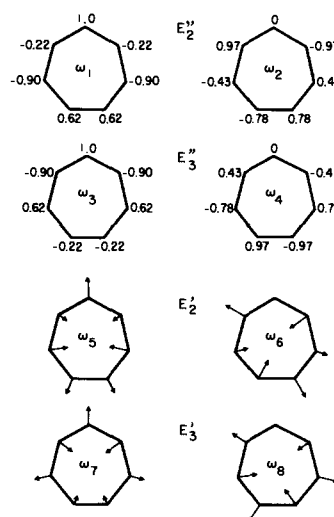


Figure 2. Definition of the eight ring-bending modes for a hypothetical planar seven-membered ring. The numbers on the first four diagrams represent displacements above and below the plane of the molecule.

gas-phase spectra were stored under vacuum after the air had been removed from the compounds by several freeze-pump-thaw cycles.

All infrared spectra in the region $4000\text{--}400\text{ cm}^{-1}$ were recorded on a Beckman IR-12 infrared spectrometer. The vapor-phase spectra were taken at a sample pressure of approximately 10 Torr at path lengths varying from 10 cm to 10 m in a Beckman variable path-length multipass cell equipped

Table IV. Observed and Calculated Ring-Bending Frequencies of Oxepane

Vibration ^a	ν_{obsd}		ν_{calcd}	Intensity (IR)		
	IR _{gas}	Raman _{liquid}		Obsd	Calcd	Calcd I + calcd II
ω_1	I	135	149	0.58	0.53	0.70
	II		136		0.17	
ω_2	I	185	190 p	0.38	0.07	0.35
	II		192		0.28	
ω_3	I	357	352 ~dp	0.15	0.07	0.10
	II		367		0.03	
ω_4	I	325 ^b	323 p	1.0 ^c	0.06	0.19
	II	310			0.13	
ω_5	I	417	410 p	0.50	0.32	0.60
	II		411		0.28	
ω_6	I	273	270	1.0 ^c	0.37	0.81
	II	297	298		0.44	
ω_7	I	550	560 p	1.0	0.34	0.81
	II	560			0.47	
ω_8	I	505	510 ~dp	0.25	0.11	0.19
	II	512	560 ^d		0.08	

^a The Roman numerals refer to Figure 1. ^b These frequencies are taken from the spectra of the liquid. ^c These bands are severely overlapped and their individual intensities cannot be measured. The observed intensity is the sum of the intensities of the ω_4 and ω_6 bands for both conformers. ^d These frequencies were not fit with ring-bending potential function; see text.

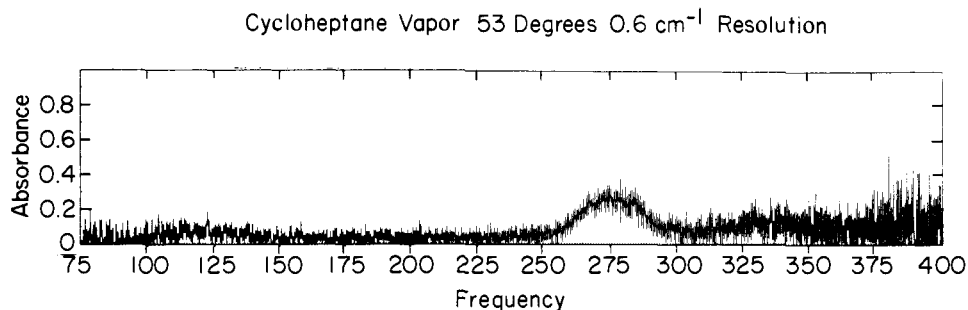


Figure 3. Far-infrared spectrum of cycloheptane (400–75 cm^{-1}). Average of six samples and six background spectra: 17-Torr pressure; 39-m path length; temperature 53 °C. The bands at 123, 335, and 395 cm^{-1} are barely visible on this spectrum.

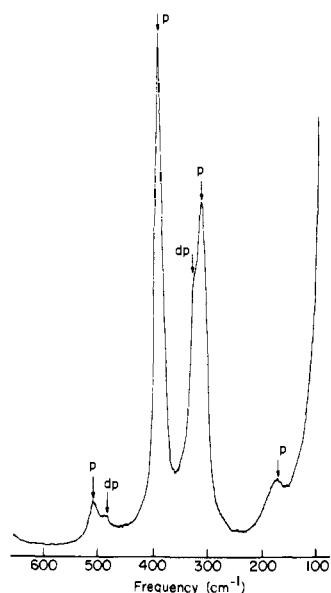


Figure 4. Low-frequency Raman spectrum of cycloheptane. The very weak shoulder at 347 cm^{-1} is not visible on this drawing.

with KBr windows. All liquid-phase spectra were recorded as neat films on CsI plates, with the exception of cycloheptane, whose spectrum was recorded at a path length of 1 mm in KBr cells.

The liquid-phase spectra in the region 400–33 cm^{-1} were recorded on a Beckman IR-11 far-infrared spectrometer. The spectra of oxepane and 1,3-dioxepane were recorded in 1-mm path length Beckman polyethylene liquid cells on 20% (by volume) solutions in cyclohexane. The spectrum of cycloheptane was obtained on the neat liquid in 5-mm path length polyethylene cells. For oxepane and 1,3-dioxepane, the reference cell contained cyclohexane, and for cycloheptane the reference cell was empty.

The vapor-phase far-infrared spectra in the region from 400 to 10 cm^{-1} were obtained on a RIIC FS-520 Michelson interferometer, which has been modified as described in the theses of Borgers, Greenhouse, and Pickett.¹³ Mylar beam splitters of $\frac{1}{4}$ - and 1-mil thickness were used to examine the regions 400–75 and 75–10 cm^{-1} , respectively. All spectra were taken at a sample pressure of approximately 10 Torr and a path length of 39 m in a specially constructed variable path-length multipass White-type cell¹⁴ with high-density polyethylene windows.

The Raman spectra of all the molecules were recorded as neat liquids at an excitation wavelength of 5145 Å. A Coherent Radiation Model CR-2 argon ion laser served as the source of incident radiation, while spectral resolution was achieved with a Spex Industries double monochromator. The spectra of cycloheptane and 1,3-dioxepane were obtained with the aid of J. M. Scherer and Sima Kint, while the spectrum of oxepane was recorded in our own laboratory.

Cycloheptane. The liquid-phase infrared and Raman spectra of cycloheptane have been reported by Wheeler and Mateos¹⁵

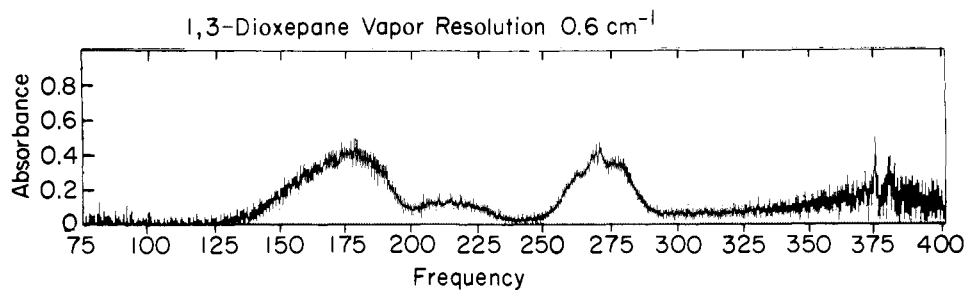


Figure 5. Far-infrared spectrum of 1,3-dioxepane (400–75 cm^{-1}). Average of six samples and six background spectra: 17-Torr pressure; 39-m path length.

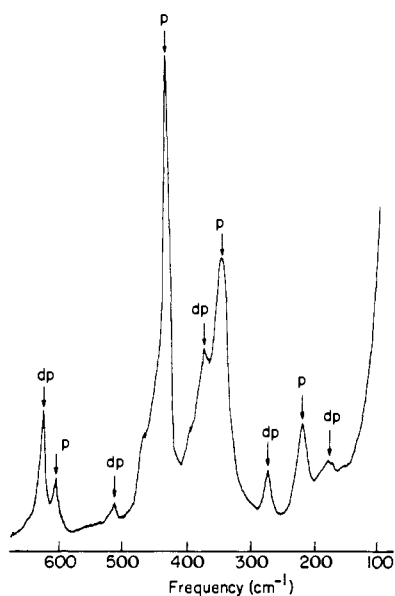


Figure 6. Low-frequency Raman spectrum of 1,3-dioxepane.

and Bazhulin et al.,¹⁶ respectively, while the liquid spectrum in the far-infrared region has been examined by Lord.¹⁷ In all cases the spectra observed in our laboratory have agreed with those reported by the previous investigators.

The vapor-phase far-infrared spectrum of cycloheptane was examined with the Michelson interferometer at room temperature. Under these conditions the vapor pressure of the molecule was found to be insufficient to yield any absorption above that of the background. In order to observe any spectral features, it was necessary to reexamine the spectrum at 53 °C, which gave a sample pressure of approximately 17 Torr. Even at this temperature the spectrum was observed to be extremely weak; a broad, moderately intense band centered at 273 cm^{-1} is its only prominent feature (Figure 3). A more careful examination of the vapor spectrum, together with an examination of the liquid far-infrared, revealed additional extremely weak absorptions centered at approximately 123, 335, and 395 cm^{-1} . No absorptions were observed in the region 75–10 cm^{-1} , the region in which absorption would be expected if the molecule were undergoing free or nearly free pseudorotation.

The low intensity of the cycloheptane spectrum can be explained in terms of approximate symmetry arguments analogous to those we used for cyclohexane.¹² For planar cycloheptane, the eight ring-bending vibrations transform in four degenerate pairs, belonging to the irreducible representations E_2'' , E_3'' , E_2' , and E_3' of the symmetry group D_{7h} (Figure 2, Table I), and are infrared inactive. Although the twist-chair conformers are distorted from a D_{7h} plane, the vibrations remain weak. Their relative intensities can be explained by examining the form of the normal coordinates. The out-of-plane

vibrations ω_1 – ω_4 have most of their motion in the out-of-plane direction parallel to the molecular C axis. The vibrations ω_2 and ω_4 are of A symmetry in the C_2 group (twist-chair) and thus can only produce dipole changes along the A molecular axis. The ω_1 and ω_3 vibrations produce dipole changes along the C molecular axis and consequently the intensities of the ω_1 and ω_3 bands are much larger than the intensities of the ω_2 and ω_4 bands. The same argument accounts for the relative intensity of the ω_1 band of 1,3-dioxepane as compared to the ω_2 band and the ω_3 band compared to the ω_4 band (Table III).

Since the ω_2 and ω_4 vibrations are totally symmetric, they, as well as the ω_5 and ω_7 vibrations, should be observed as polarized Raman bands. The examination of the low-frequency Raman spectrum of cycloheptane (Figure 4) does, indeed, reveal two polarized bands at positions which do not correspond to bands in the gas-phase infrared, a weak band at 182 cm^{-1} and a strong, sharp line at 320 cm^{-1} . It was first thought that the 320- cm^{-1} line might be the same band as that observed at 335 cm^{-1} in the infrared, but the 335- cm^{-1} band is the depolarized shoulder which appears on the 320- cm^{-1} line. The 182- and 320- cm^{-1} bands are assigned as ω_2 and ω_4 and the infrared absorptions at 123 and 335 cm^{-1} are attributed to the other two out-of-plane vibrations ω_1 and ω_3 . Examination of the cyclohexane frequencies suggests that the E_2 frequencies are lower than the E_3 frequencies, so that the 273- cm^{-1} band is assigned as ω_6 and the strong polarized Raman band at 400 cm^{-1} as ω_5 . The two highest skeletal bending modes are assigned with ω_7 at 515 cm^{-1} , since the Raman band is polarized, and the remaining ω_8 at 490 cm^{-1} . These arguments are not unambiguous, but are confirmed by the detailed normal coordinate calculations and by consistent results for all three of the seven-membered rings.

1,3-Dioxepane. The infrared and Raman spectra of liquid 1,3-dioxepane have been reported by Tarte et al.¹⁸ and are in complete agreement with those recorded in our laboratory. As is true for cycloheptane, no vapor-phase spectra have been previously reported for 1,3-dioxepane.

The vapor-phase far-infrared spectrum of 1,3-dioxepane was examined in the region 400–10 cm^{-1} on the Michelson interferometer under the conditions previously discussed. As was the case for cycloheptane, no extremely low-frequency absorptions, which might be indicative of a freely interconverting molecule, were observed. Unlike cycloheptane, however, 1,3-dioxepane spectra recorded at room temperature at a sample pressure of 10 Torr showed fairly intense absorptions in the region 400–75 cm^{-1} . This is to be expected, since the substitution of the highly electronegative oxygen atoms for methylene groups removes the approximate electrical symmetry achieved in cycloheptane. The far-infrared spectrum of 1,3-dioxepane is shown in Figure 5 and the low-frequency Raman spectrum in Figure 6. Both of these spectra are similar to those of cycloheptane and can be assigned in an analogous fashion.

Oxepane. The mid-infrared spectrum of liquid oxepane was

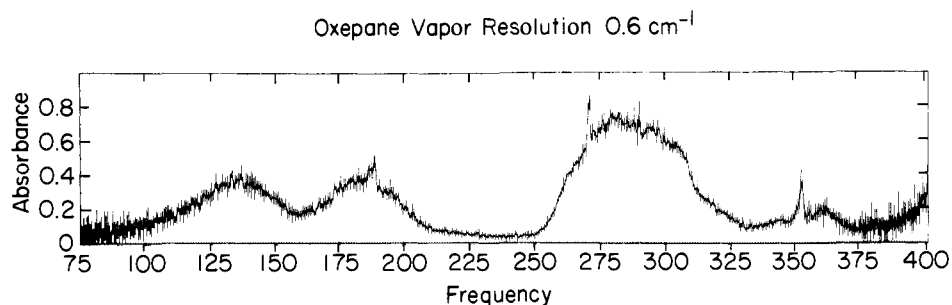


Figure 7. Far-infrared spectrum of oxepane (400–75 cm^{-1}). Average of six samples and six background spectra: 17-Torr pressure; 39-m path length.

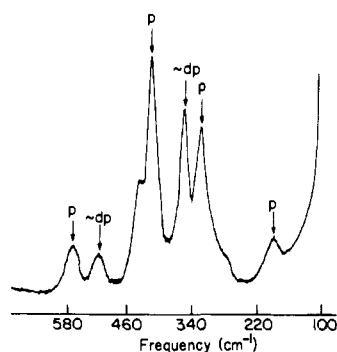


Figure 8. Low-frequency Raman spectrum of oxepane.

reported by Kirrman and Hamaide¹⁹ in 1957, but no Raman or vapor-phase infrared spectrum of this molecule is available in the literature. As was the case for cycloheptane and 1,3-dioxepane, our vapor-phase infrared spectra of oxepane below 75 cm^{-1} revealed no absorptions which might be indicative of a freely interconverting molecule. The spectrum in the region 400–75 cm^{-1} is exceptionally rich, however, and appears to be much more complex than that of either of the other two molecules (Figure 7). Prominent fine structure is evident on a number of bands and the very intense absorption centered at approximately 290 cm^{-1} appears to be a composite of three or possibly four overlapping bands. In the liquid far-infrared spectrum, the 290- cm^{-1} band splits quite clearly into two bands of approximately equal intensity at 278 and 297 cm^{-1} with much weaker shoulders at 310 and 325 cm^{-1} . The resolving of the 290- cm^{-1} band in the liquid phase is probably due to several factors, such as the collapse of vibration-rotation structure and changes in the relative intensities of the overlapping bands. In addition to the multiple bands at 290 cm^{-1} , vapor-phase mid-infrared spectra recorded at a sample pressure of 13 Torr and a path length of 1 m clearly reveal that the two highest frequency ring-bending vibrations at 555 and 508 cm^{-1} occur as doublets split by approximately 10 cm^{-1} . A number of other mid-infrared bands also appear split, and those which are not are considerably broader than their counterparts in either cycloheptane or 1,3-dioxepane. All of this evidence strongly suggests that oxepane exists in two stable conformations.

The low-frequency Raman spectrum of oxepane (Figure 8) retains many of the general features of the cycloheptane and 1,3-dioxepane spectra. In contrast to the far-infrared, no bands are clearly doubled, but several are quite broad. Attempts at splitting the 417-, 352-, and 325- cm^{-1} lines, as well as the symmetric ring-breathing vibration at 752 cm^{-1} , proved unsuccessful; but the line widths at half maximum for these bands were measured to be approximately four times those of the analogous lines in cycloheptane and 1,3-dioxepane.

Our ring-bending potential function predicts two stable conformations for oxepane.⁸ The calculations indicate that

these forms are both twist-chairs (Figure 1), which are of approximately equal energy, and that there exists a 2-kcal/mol barrier to interconversion between the two forms. The calculated frequencies and intensities of the ring-bending vibrations of the two forms, when viewed together, successfully account for the complexities found in the oxepane spectrum. The quartet of bands is due to the overlapping ω_4 and ω_6 vibrations of both conformers, while the nondoubled bands at 417 and 357 cm^{-1} are a result of the near coincidence of the two ω_5 and ω_3 vibrations, respectively. The low-frequency normal coordinate calculations also indicate that both ω_1 and ω_2 should be doubled, but no splitting of these bands is observed. The intensity calculations reveal, however, that 80% of the intensity of the ω_2 band is due to conformer II, while 75% of the intensity of the ω_1 band is due to conformer I (Table IV). In light of this fact, it is not unreasonable that the weaker members of each of the pairs of bands are not seen.

Since both of the stable oxepane conformations have no symmetry, all Raman bands would be expected to be at least partly polarized. However, the low-frequency Raman spectrum of oxepane exhibits both polarized and approximately depolarized bands analogous to those of cycloheptane and 1,3-dioxepane.

Nonfundamental Low-Frequency Vibrations. Several nonfundamental vibrations are also observed in the low-frequency spectra of cycloheptane, oxepane, and 1,3-dioxepane. The frequencies and possible assignments of these vibrations are summarized in Table V. Several of these bands can be successfully assigned as sum and difference bands between comparable ring-bending vibrations in more than one of the molecules. For example, the spectra of both cycloheptane and 1,3-dioxepane have bands assignable as the difference between ω_7 and ω_2 , while oxepane and 1,3-dioxepane have bands assignable as the sum of ω_2 and ω_4 . In addition, the oxepane and 1,3-dioxepane spectra have bands which are not consistent with sums, differences, or overtones of the ring-bending frequencies exclusively. A weak shoulder appears in the 1,3-dioxepane spectrum at 470 cm^{-1} which has a counterpart in oxepane at 436 cm^{-1} (Figures 6 and 8). Both of these bands are assignable as the difference between ω_7 and a ring-stretching vibration. The oxepane band is quite broad, with a frequency spread of approximately 20 cm^{-1} , while the 1,3-dioxepane band is considerably narrower. This is consistent with the doubling observed for the ω_7 band in oxepane (Table IV), since the difference band is probably a composite of the bands arising from both of the stable oxepane conformers.

One other relatively intense band is observed in both the infrared and Raman spectra of 1,3-dioxepane. Although this band could be assigned as a difference frequency between any one of several of the ring-bending vibrations and a ring stretch, the band seems too strong to be a difference band. There is some possibility the band is due to an unusually low-frequency C-H rocking vibration, but the normal coordinate calculations for 1,3-dioxepane (Table VII) do not indicate that a defor-

Table V. Correlation Table for Nonfundamental Vibrations^a

Cycloheptane (1)	Oxepane (2)	1,3-Dioxepane (3)	Assignment	(1)	(2)	(3)
347, IR, R, sh	~436 R, sh 515 IR	397 IR, R, sh 470 R, sh 565 IR 630 IR, R, dp	$\omega_7 - \omega_2 =$ Ring ^b stretch - $\omega_7 =$ $\omega_2 + \omega_4 =$?	333	~425 510	387 469 565

^a IR, observed in infrared spectrum; R, Raman spectrum; sh, shoulder; dp, depolarized. ^b Oxepane ring stretches at 975 cm⁻¹ in conformer I and 982 cm⁻¹ in conformer II. 1,3-Dioxepane ring stretches at 1075 cm⁻¹.

mation of this type should occur anywhere in this frequency region. It is also unlikely that the band is one of the two highest frequency ring-bending vibrations, since the intensities and polarizations of the 1,3-dioxepane bands at 606 and 516 cm⁻¹ are much more consistent with those of the ω_7 and ω_8 vibrations in the other two molecules.

Normal Coordinate Calculations. In order to assign the higher frequency vibrations and to test the validity of the assumption concerning the separability of these vibrations from the low-frequency motions, conventional normal coordinate calculations were carried out for each of the molecules studied. The inverse kinetic energy matrix, G , was set up using the internal coordinates of Wilson, Decius, and Cross,⁹ and the geometries determined by our conformational calculations.⁸ The force fields used were the saturated hydrocarbon force field of Snyder and Schachtschneider¹⁰ and the aliphatic ether force field of Snyder and Zerbi.¹¹ The secular equation was solved using the FG matrix method of Wilson, using the computer programs of Schachtschneider.²⁰ The application of Snyder and Zerbi's force field to 1,3-dioxepane is not possible without some additional assumptions, and whenever necessary we used the force constant for the valence coordinate most like the needed force constant. For example, the force constant for the OCC angle bend was also used for the OCO angle bend of 1,3-dioxepane.

The results of the normal coordinate calculations are presented in Tables VI–VIII. The fits obtained are not nearly as good as those for the model compounds used by Snyder and Schachtschneider and Snyder and Zerbi to determine the force fields, but they are surprisingly good considering the approximations made before application to the seven-membered rings was possible. As is the case for the model compounds, the low-frequency vibrations are those whose calculated values agree most poorly with experiment. For all the molecules, however, only the two highest frequency ring-bending vibrations show significant mixing with the motions of the methylene groups. The relative separability of the in- and out-of-plane deformations of the ring is also maintained and these motions retain much of their ideal character. In the results for oxepane both stable conformations are included. The calculations indicate that many of the higher energy motions in the two conformers have frequencies which are nearly coincident, consistent with the failure to observe clearly doubled lines for many of these vibrations. Most of the bands calculated to have splittings >5 cm⁻¹ are observed to be doubled.

III. Determination of Conformation and Potential Function for Ring Bending

The determination of a ring-bending potential function for the seven-membered rings was complicated by the fact that the geometries of the minimum energy forms were not known. Although most conformational calculations indicate the twist-chair to be the most stable form,²⁻⁶ it is not clear a priori that this should be the lowest energy conformer. Conventional normal coordinate calculations are of little aid in the determination of conformation, since only very approximate fits can be obtained for those frequencies most sensitive to the con-

formation. Additionally, we have found that the higher frequency vibrations of the seven-membered rings are fairly insensitive to the conformation. Thus, mid-infrared spectra can be successfully interpreted in terms of either a boat- or chair-like conformer. None the less, some useful information can be extracted from conventional normal coordinate calculations. These show that good agreement can only be obtained with the observed Raman polarizations in the mid-frequency range if the molecule is taken to be in a twisted conformation (C_2 symmetry).

Our criteria for determining a ring-bending potential function are two: First, the potential must accurately reproduce the observed ring-bending frequencies of all three molecules. Second, this potential, when used as the basis for conformation calculations, must yield minimum energy structures consistent with the observed spectroscopic data. The actual details of the conformational calculations using our ring-bending potential function are presented in the following paper.⁸

The potential function used for our conformational and low-frequency vibrational calculations is

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

In this equation, the ψ_i are the values of the seven ring bond angles and the ψ_i^0 are the equilibrium values they would have if the ring were opened. The τ_i are the torsional angles of the ring. 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, r_{ijm} also represents the distance between the oxygen atom (indexed i) and the hydrogens on carbon atom j . For the special case of the hydrogen-oxygen interaction, the index m runs from 1 to 2.

In our calculations all the carbon-carbon bond lengths were fixed at 1.532 Å and the carbon-hydrogen bond lengths at 1.110 Å. The carbon-oxygen bond lengths were taken as 1.43 Å.^{13a} The HCH bond angle was fixed at 107°. The values of the ψ_i^0 were the same as those used by Pickett and Strauss in their determination of a ring-bending potential function for cyclohexane and a number of oxanes.¹²

The complete set of parameters for eq 1, used in our calculations, is summarized in Table IX. Since the potential constants were obtained by fitting the low-frequency vibrational motions only, they are effective potential constants which in other potential functions would be modeled by a large number of nonbonded interactions (carbon-carbon, carbon-hydrogen, carbon-oxygen, etc.). For this reason many of our constants are quite different from those determined from conventional normal coordinate calculations.^{10,11}

Pickett and Strauss found that a potential function containing only H , F , T , and a onefold torsional term, U , is sufficient for a successful conformational and low-frequency vi-

Table VI. Normal Coordinate Calculations for Cycloheptane

No.	Symmetry	ν_{calcd}	$\nu_{\text{obsd IR gas}}^a$	$\nu_{\text{obsd Raman}}^a$	Approximate motion ^b
1	B	2926			Asym CH stretch
2	B	2926			Asym CH stretch
3	A	2923			Asym CH stretch
4	B	2923	2925 vvs	2930 vvs	Asym CH stretch
5	A	2921			Asym CH stretch
6	A	2920			Asym CH stretch
7	B	2917	2917 vvs	2912 vs	Asym CH stretch
8	A	2862			Sym CH stretch
9	B	2861			Sym CH stretch
10	A	2861	2860 vvs	2862 vvs	Sym CH stretch
11	A	2860			Sym CH stretch
12	B	2860		2856 vvs	Sym CH stretch
13	A	2859			Sym CH stretch
14	B	2859			Sym CH stretch
15	A	1458	1466 vs	1468 w, p	CH scissors
16	B	1450	1450 vs		CH scissors
17	B	1446	1446 s		CH scissors
18	A	1439	1439 s	1440 m, dp	CH scissors
19	B	1436			CH scissors
20	A	1433			CH scissors
21	A	1426			CH scissors
22	B	1339	1360 m	1355 w	CH wag
23	B	1332	1350 mw	1345 w	CH wag
24	A	1322			R(22) CH wag
25	A	1307	1310 w		R(32) CH wag
26	A	1305			R(46) CH wag
27	B	1294			R(32) CH wag
28	B	1287	1275 m	1287 m, dp	CH twist
29	B	1241			CH twist
30	A	1231			CH twist and wag
31	A	1229			CH twist
32	A	1214	1210 m	1205 w, p	CH twist
33	B	1202			R(10) CH twist
34	A	1193			CH twist
35	B	1133	1125 mw	1125 w, dp	R(32) CH wag
36	A	1099			R(41) CH wag
37	A	1058		1040 mw, p	R(31) mixed CH
38	B	1018	1020 m		R(51) θ (12) CH rock
39	A	1005			R(54) CH wag
40	B	998	1005 m	1005 m, dp	R(38) θ (11) CH rock
41	B	944	950 m		θ (17) CH rock
42	A	915			R(12) θ (24) CH rock
43	A	854	850 m	845 mw, p	R(20) θ (15) CH rock
44	B	838	830 m		R(40) θ (11) CH rock
45	B	817	810 m		R(53) CH rock
46	B	804			R(53) CH rock
47	A	734	735 m	735 vvs, p	R(70)
48	B	705	690 w		CH rock
49	A	647			θ (33) CH rock
50	A	537	515 m	515 vw, p	θ (46) CH rock
51	B	437	490 mw	490 vw, dp	θ (46) CH rock
52	A	406	395 vw	400 mw, p	θ (64) τ (16)
53	B	355	335 vw	332 vw, dp	θ (58) τ (16)
54	A	334	315 vw	320 w, p	θ (42) τ (28)
55	B	311	273 mw		θ (74) τ (13)
56	A	199	190 vvw	182 vvw, p	θ (40) τ (37)
57	B	156	123 vw		θ (15) τ (65)

^a Abbreviations: v, very; s, strong; m, medium; w, weak; p, polarized; dp, depolarized. ^b Key to the notation for the vibrational motion. The motions involving the bond and torsional angles of the ring are denoted by θ and τ , respectively. R denotes the stretching of a ring bond. The motions of the methylene group are defined with respect to the plane formed by three consecutive ring atoms, where the methylene group of interest is located at the central atom. These motions are defined as follows: scissoring, the two protons move out of the plane in opposite directions; twisting, the two protons move in the plane in opposite directions; wagging, the two protons move in the plane in the same direction; rocking, the two protons move out of the plane in the same direction. Only the major contributions to the vibrational motion are listed in the tables. For the ring skeleton, numerical values are given (parentheses), and these represent the percentage contribution of the major diagonal elements of the force constant matrix to the vibrational frequency.

brational treatment of the six-membered rings.^{12,21} For cyclic molecules larger than cyclohexane, however, it is clear that more terms must be added to the potential function. Calculations on cyclooctane show that a potential with just H , F , T ,

and U terms leads to untenable conformations with unreasonably small 1,5-hydrogen-hydrogen distances.²² A 1,5-hydrogen repulsive term must therefore be added to the potential function. The terms H , F , T , and U should correlate 1,2-

Table VII. Normal Coordinate Calculations for 1,3-Dioxepane^a

No.	Symmetry	ν_{calcd}	ν_{obsd} IR gas	ν_{obsd} Raman	Approximate motion
1	B	2966		2975 vvs	Asym CH stretch
2	B	2965			Asym CH stretch
3	B	2962	2955 vvs		Asym CH stretch
4	A	2925	2925 vvs	2918 vvs	Asym CH stretch
5	A	2920			Asym CH stretch
6	A	2868		2877 vvs	Sym CH stretch
7	A	2866	2865 vvs		Sym CH stretch
8	B	2866			Sym CH stretch
9	A	2861		2850 s	Sym CH stretch
10	B	2860			Sym CH stretch
11	A	1463	1465 s	1485 mw, p	CH scissors
12	B	1447			CH scissors
13	B	1445	1445 m	1455 m	CH scissors
14	A	1432	1432 s	1435 m	CH scissors
15	A	1427			CH scissors
16	A	1422	1410 m		CH wag
17	B	1385	1385 mw		CH wag
18	B	1370	1375 s	1370 w	CH wag
19	A	1328	1345 mw	1350 w	CH wag and twist
20	A	1319		1320 vw	CH wag and twist
21	B	1290	1295 vs	1290 m, dp	CH wag and twist
22	B	1261	1257 vs	1260 mw, dp	R(20) CH twist
23	A	1254			R(20) CH wag and twist
24	B	1231	1238 vs	1230 mw	Mixed CH
25	A	1226	1220 mw		Mixed CH
26	B	1157	1175 vs		R(56) mixed CH
27	B	1118	1118 vvs	1120 w, dp	Mixed CH
28	A	1101	1136 vvs	1140 m, p	R(65)
29	B	1083	1075 vvs	1070 m, dp	R(27) mixed CH
30	A	1047			R(65) $\theta(12)$
31	B	1006	1005 vvs	1000 mw, dp	R(55) $\theta(12)$ CH wag
32	B	977	970 s	970 m, dp	R(22) CH rock
33	A	945	925 vs	915 s, p	R(45) CH rock
34	B	876	845 m	840	R(75) $\theta(15)$ CH wag
35	A	850	830 vs	825	R(55) CH rock
36	A	814	760 vw	765 m, p	R(25) CH rock
37	A	772	805 vw	800 vvs, p	R(84)
38	A	626	610 m	606 vvw, p	$\theta(63)$ CH rock
39	B	567	516 s	516 vvw, dp	$\theta(47)$ CH rock
40	A	470	437 m	437 m, p	$\theta(71)$
41	B	423	377 mw	377 w, dp	$\theta(76)$ $\tau(13)$
42	B	360	273 mw	275 vw, dp	$\theta(60)$ $\tau(17)$
43	A	340	350 vw	350 mw, p	$\theta(65)$ $\tau(17)$
44	A	215	215 vvw	219 vw, p	$\theta(53)$ $\tau(38)$
45	B	152	175 vw	182 vvw, dp	$\tau(90)$

^a See Table VI for notation.

and 1,3-hydrogen-hydrogen interactions, but it is unclear a priori how these terms correlate the 1,4-interactions in the seven-membered rings. Calculations show, however, that 1,4-nonbonded interaction terms can have a significant effect on both the relative energies⁷ and vibrational frequencies of the various conformations. If a potential function containing only H , F , T , and U terms is used for the seven-membered rings, the boats are the preferred structures by several kilocalories per mole, while inclusion of nonbonded terms makes the chairs more favorable. Vibrational calculations for the seven-membered rings using the six-membered ring potential function reveal that the low frequencies of the chair forms are in qualitative agreement with experiment, while those of the boat are totally inconsistent. The calculated out-of-plane frequencies of the boat conformers deviate by nearly 70 cm^{-1} from those observed, while the calculated intensities of the vibrations are an order of magnitude different from their actual values. No simple adjustment of the parameters H , F , T , and U can bring the frequencies of the boats into agreement with experiment.

A number of different approaches could be taken in modi-

fying the six-membered ring potential function to provide a better fit to the data. We have chosen to add a nonbonded term, to replace the onefold torsional term, U , by a twofold term, D , and to add a bend-torsion interaction constant, K (eq 1). With minor modification, the values of H , F , and T are taken to be the same as for the six-membered rings. The parameter B of the nonbonded part of the potential is set at the value estimated for van der Waals interactions.⁷ A number of choices are available for the parameters A and r_0 ^{3,23,24} and we have used the relatively soft potential of Abe et al.,²³ which raises the boat conformers about 0.5 kcal/mol above the chair forms and has only a small effect on the calculated skeletal bending frequencies. The onefold torsional term, U , used for cyclohexane was found to have little effect on the properties of the seven-membered rings, so a twofold term was added instead. This term raises the energy of the boat forms some more and has a small effect on the frequencies. The value of D cannot be determined with much accuracy because of the insensitivity of the frequencies to changes in D . As a final adjustment to our potential function, an angle bending-torsion interaction term, K , is added. A term of this form has been used by Warshel and

Table VIII. Normal Coordinate Calculations for Oxepane

No. ^a	Symmetry	ν_{calcd}	ν_{obsd} IR gas	ν_{obsd} Raman	Approximate motion
1a	A	2967			Asym CH stretch
b	A	2965			
			2960 vvs	2950 vs	
2a	A	2962			Asym CH stretch
b	A	2961			
3a	A	2925			Asym CH stretch
b	A	2926			
4a	A	2923			Asym CH stretch
b	A	2923			
			2930 vvs	2930 vvs	
5a	A	2921			Asym CH stretch
b	A	2922			
				2910 vs	
6a	A	2919			Asym CH stretch
b	A	2920			
7a	A	2866			Sym CH stretch
b	A	2868			
8a	A	2866			Sym CH stretch
b	A	2866			
9a	A	2862			Sym CH stretch
b	A	2862			
10a	A	2861	2863 vs	2860 vvs	Sym CH stretch
b	A	2860			
11a	A	2860			Sym CH stretch
b	A	2860			
12a	A	2859			Sym CH stretch
b	A	2859			
13a	A	1467	1470 s	1478 w, p	CH scissors
b	A	1470			
14a	A	1452	1455 s		CH scissors
b	A	1455			
15a	A	1449	1450 s	1450 s	CH scissors
b	A	1450			
16a	A	1442			CH scissors
b	A	1444			
17a	A	1424		1432 s	CH scissors
b	A	1429			
18a	A	1417			CH scissors
b	A	1423			
19a	A	1393	1382 m	1390 vw	CH wag
b	A	1381	1375 m		CH wag
20a	A	1385		1375 w	CH wag
b	A	1376	1365 m	1360 w	CH wag
21a	A	1320	1323 w	1330 w	R(14) mixed CH
b	A	1320			R(14) mixed CH
22a	A	1304	1308 w	1310 m, ~dp	R(32) CH wag and twist
b	A	1300			R(32) CH wag and twist
23a	A	1280	1288 m	1284 m, ~dp	R(25) CH wag and twist
b	A	1276	1280 m		R(35) CH wag and twist
24a	A	1270	1262 m	1260 m, ~dp	R(11) CH wag and twist
b	A	1270			R(23) CH twist and twist
25a	A	1264	1257 m		R(24) CH wag and twist
b	A	1266			R(14) CH twist
26a	A	1255	1253 m	1244 w	R(15) CH twist
b	A	1248	1247 m		R(19) mixed CH
27a	A	1235			CH wag and twist
b	A	1233			CH wag and twist
28a	A	1227	1220 m	1220 vw	CH twist
b	A	1227			CH twist
29a	A	1210		1205 vvw	CH twist
b	A	1207			CH twist
30a	A	1203	1188 w	1185 w, p	Mixed CH
b	A	1193			CH wag and twist
31a	A	1131	1144 s	1144 m, p	R(69)
b	A	1142	1152 s		R(73)
32a	A	1104	1115 s	1111 m, p	R(56) CH mixed
b	A	1097	1106 s		R(49) mixed CH
33a	A	1049	1035 m	1033 s, ~dp	R(42) θ (10) mixed CH
b	A	1043			R(46) θ (14) mixed CH
34a	A	1042	1020 m		R(53) mixed CH
b	A	1038			R(66) mixed CH

Table VIII (Continued)

No. ^a	Symmetry	ν_{calcd}	ν_{obsd} IR gas	ν_{obsd} Raman	Approximate motion
35a	A	1023	1000 m	1000 s, ~dp	R(43) CH rock
b	A	1023			R(27) CH rock and twist
36a	A	1013	982 m	975 mw	R(31) mixed CH
b	A	1017	975 m		R(48) CH rock
37a	A	936	935 w	940 vs, p	R(26) θ (16) CH rock
b	A	939			R(12) θ (15) CH rock
38a	A	903	900 vw	895 w, p	R(31) θ (25) CH rock
b	A	907			R(27) θ (19) CH rock
39a	A	879	887 w	882 s, p01r)27) CH rock	
b	A	868			R(39) θ (15) CH rock
40a	A	840	837 mw	845 w, p	R(80)
b	A	839			R(74)
41a	A	823	825 mw	820 m, p	R(47) CH rock
b	A	816	812 mw	808 m, p	R(39) CH rock
42a	A	753	752 w	753 vvs, p	R(70) CH rock
b	A	741			R(62) CH rock
43a	A	724			R(12) CH rock
b	A	782			R(33) CH rock
44a	A	612	560 m	560 vvw, p	θ (58) CH rock
b	A	606	550 m		θ (54) CH rock
45a	A	552	512 mw	510 vvw, ~dp	θ (49) CH rock
b	A	541	505 mw		θ (49) CH rock
46a	A	437	417 mw	410 m, p	θ (71)
b	A	447			θ (72)
47a	A	396	357 vw	352 w, ~dp	θ (66)
b	A	399			θ (78)
48a	A	370	310 ^b	323 w, p	θ (68) τ (10)
b	A	347	325 vvw		θ (66) τ (12)
49a	A	332	297 m		θ (65) τ (16)
b	A	334	273 m		θ (55) τ (27)
50a	A	194	185 mw	190 vw, p	θ (49) τ (39)
b	A	206			θ (51) τ (38)
51a	A	144	135 w		τ (91)
b	A	145			τ (88)

^a The lettering "a" and "b" refers to conformers II and I, respectively. ^b These frequencies are taken from the spectra of the liquid. See Table VI for notation.

Table IX. Parameters Used in Equation 1

H , kcal/(mol-rad ²)	F , kcal/(mol-rad ²)	T , kcal/mol
CCC	68.0	CCCC 1.65
CCO	83.0	CCCO 2.43
COC	73.3	CCOC 1.01
OCO	119.6	COCO 1.85

D , kcal/mol	K , kcal/(mol-rad ²)	ψ_i^0 , deg
CCCC	0.5	CCC 112.6
CCCO	0.	CCO 109.5
CCOC	0.	COC 112.6
COCO	0.	OCO 109.5

$1/r_0$, Å ⁻¹	B , (kcal-Å ⁶)/mol	A , kcal/mol
4.55	45.2	9950

Lifson in their conformational and vibrational treatment of cyclopentane, cyclohexane, and a number of n -alkanes,²⁵ and inclusion of terms in $K(\text{CCCC})$ and $K(\text{CCCO})$ results in a general improvement of the fits of the in-plane frequencies. No significant improvements were noted upon inclusion of $K(\text{CCOC})$ or $K(\text{COCO})$ terms, however, so these are not included in our potential function.

In order to obtain the calculated ring-bending frequencies listed in Tables II-IV, a few additional modifications are necessary in the six-membered ring potential function. These involve small adjustments in the values of H , F , and T for the

valence coordinates involving only the carbon atoms. Our CCC angle bending force constant is about 10% larger than that of Pickett and Strauss,¹² while our threefold CCCC torsional parameter is approximately 40% smaller. The large change in T is somewhat artificial, however, occurring for the most part because of the addition of the twofold term. The barrier height of our torsional well is only 14% less than that of Pickett and Strauss. The six-membered ring potential function does not differentiate between the angle bending interaction terms CCC-CCC and CCC-CCO. For the seven-membered rings, the fits of the in-plane frequencies improve considerably if the sign of the CCC-CCC term is reversed and its absolute value increased by about 50%. No adjustments were found necessary in the potential constants H , F , or T for any of the valence coordinates involving the oxygen atoms.

IV. Conclusions

We conclude that the lowest energy conformation of cycloheptane, 1,3-dioxepane, and oxepane are the twist-chair forms shown in Figure 1. The skeletal bending modes are fit by the potential function of eq 1 and Table IX, and this potential function also determines the structures and relative energies of the various conformations. Using our calculated structures, standard vibrational potential functions fit the entire range of vibrational frequencies. It should be emphasized that the conclusion that the molecules are twist-chairs does *not* depend on the details of the potential function. Indeed, a rather different potential function developed by Warshel²⁶ gives similar results for the low frequencies and the conformations. The low frequencies are used to further refine our potential

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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Conformational Structure and Energy of Cycloheptane and Some Related Oxepanes¹

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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 rings²⁻⁶ 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