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CONFORMATIONAL ANALYSIS—CXIII

THE ISOMERIC CYCLOOCTADIENES[1,2]

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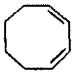
Abstract—1,3-Cyclooctadiene, and the 1,4- and 1,5-isomers were studied by the force field method. The former is calculated to be a mixture of two conformations, one of which has a C_2 axis, and one is irregular (C_1). There are for the 1,4-isomer two conformations, a boat-boat and a boat-chair, both of which have C_s symmetry. The 1,4-isomer is substantially all in the boat-chair conformation, while the 1,5-isomer is known to be preferentially a twist-boat (C_2) conformation. The calculations indicate the 1,3-isomer is much more stable, followed in turn by the 1,4- and the 1,5. An experimental measurement of the equilibrium between the isomers was also made, and is in semi-quantitative agreement with the calculations.

There are four consititutional isomers which are properly considered to be cyclooactadienes. The 1,2-cyclooctadiene, an allene, will not be considered here. The remaining 3 isomers are dienes in the usual sense, respectively, 1,3-cyclooctadiene (**1**), the conjugated isomer, 1,4-cyclooctadiene (**2**) and 1,5-cyclooctadiene (**3**). While there are known or possible several geometric isomers of these structures, we will consider here only the *cis,cis*-isomers. The conformational characteristics of **3** have been dealt with at length previously,[3] and in the present work will be concerned mainly with the other two isomers (**1** and **2**).



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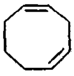

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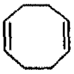

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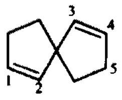
One might naively suppose that of these three isomers, the conjugated one would, by virtue of said conjugation, be the thermodynamically stable one. Things are not really quite that simple, because the structure of the 8-membered ring prevents the diene system from being coplanar, and hence any resonance stabilization is expected to be relatively small in this molecule. Nonetheless, the naive prediction is indeed correct, the 1,3-cyclooctadiene is more stable than the other two isomers, both by calculation and by experiment.

In the present work, molecular mechanics calculations were undertaken to try to ascertain the preferred conformations of the molecules mentioned, and their relative energies. Experimentally, the equilibrium constants between the various isomers were measured. These items will be discussed in turn.

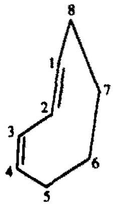
Calculations. The general method and details are those previously described,[4a] and the parameters are those given earlier.[4b] One additional parameter is also needed. For dienes which are not conjugated, the heat of formation can be calculated as described.[4b] For a conjugated diene, this calculation can be carried out with our force field except for one term, the bond energy of the single bond between the diene carbons. A numerical value for this bond energy was arrived at by taking the compounds butadiene, *cis*-, and *trans*-pentadiene, 2-methylbutadiene, cyclopentadiene, and cyclohexadiene, and calculating their heats of formation, using the unknown bond energy as a parameter. An optimized fit gave a value of −7·80 kcal/mole for the parameter, which was then used for the 1,3-cyclooctadienes. (The nonplanarity of the molecules is automatically taken into account,[4] the bond energy applies to the planar structure.)

1,3-*Cyclooctadiene.* In 1954, Braude[5] considered the conformations of a number of conjugated cycloalkadienes. Models indicated that in order to obtain a reasonably strainless structure, the double bonds in 1,3-cyclooctadiene could not be coplanar. The ultraviolet absorption maximum for this compound appeared at a lower wavelength (228 nm) than the corresponding maxima for the smaller homologous 1,3-cycloalkadienes, which appeared to have planar or near-planar diene systems (about 250 nm). Braude estimated a dihedral angle of 41° between the C=C bonds in 1,3-cyclooctadiene. Studies by Merkel[6] supported the existence of a large angle between the planes defined by the ethylene groups. In 1970 Traetteberg[7] published the molecular structure of 1,3-cyclooctadiene as determined by electron diffraction. Her conclusion was that the molecule had a rather irregular conformation, which we will simply refer to as C_1 symmetry. The dihedral angle between the planes of the double bonds which she determined was 38°.

Models also show a conformation having C_2 symmetry which seems to be reasonable. According to our calculations (summarized in Table 1), the C_1 conformation has a somewhat larger dihedral angle between the double bonds than was reported by Traetteberg, 47°. The C_2 conformation has a still larger angle, 57°. The energies of these two structures are calculated to be very nearly the same.



C_2



C_1

A radial distribution function obtained by electron diffraction does not ordinarily furnish enough information to permit one to arrive at a unique structure for the molecule under observation, if the molecule is as

Table 1. Structural data calculated for the cycloocadienes

1,4-Cyclooctadiene

Boat-Chair		Boat-Boat			
bond lengths		bond lengths			
1-2	1.340	1-2	1.339	5-6	1.508
2-3	1.505	2-3	1.499	6-7	1.534
5-6	1.510				
7-8	1.535				
bond angles		bond angles			
1-2-3	124.1	1-2-3	125.8	5-6-7	124.0
2-3-4	105.7	2-3-4	109.9	6-7-8	116.5
4-5-6	125.4	4-5-6	130.4		
5-6-7	115.2				
6-7-8	115.8				
dihedral angles		dihedral angles			
1-2-3-4	85.7	1-2-3-4	78.6	5-6-7-8	64.0
3-4-5-6	2.7	3-4-5-6	1.3		
4-5-6-7	75.0	4-5-6-7	7.4		
5-6-7-8	82.3				

1,3-Cyclooctadiene

C_2		C_1			
bond lengths		bond lengths			
1-2	1.344	1-2	1.344	5-6	1.531
2-3	1.486	2-3	1.481	6-7	1.536
4-5	1.512	3-4	1.347	7-8	1.527
5-6	1.530	4-5	1.512	8-1	1.505
6-7	1 537				
bond angles		bond angles			
1-2-3	121.3	1-2-3	124.2	5-6-7	113.8
3-4-5	124.5	2-3-4	127.5	6-7-8	111.7
4-5-6	114.2	3-4-5	132.1	7-8-1	109.1
5-6-7	113.8	4-5-6	121.5	8-1-2	124.2
dihedral angles		dihedral angles			
1-2-3-4	55.7	1-2-3-4	47.2	5-6-7-8	56.6
2-3-4-5	4.9	2-3-4-5	3.8	6-7-8-1	52.9
3-4-5-6	98.0	3-4-5-6	0.0	7-8-1-2	93.8
4-5-6-7	83.7	4-5-6-7	78.9	8-1-2-3	2.0
5-6-7-8	52.2				

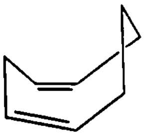
[a] The 1973 force field was used.[4b]

complicated as cyclooctadiene. This is particularly true in a case where two or more conformations are appreciably populated under the conditions of the experiment. Unless there is reason to do otherwise, an investigator analyzing such a radial distribution function generally assumes a unique conformation is present. If this is not a good assumption, then the structure deduced is, of course, of limited accuracy.

Recently, Anet and Yavari[8] have described low temperature ^{13}C NMR studies of compound 1. They found that between −120° and −170° the two conformations were present in similar amounts. Because of the small contributions of entropy at such low temperatures, this indicates that the enthalpies of these conformations must be very similar. We believe that our calculated structures in this case are better than the electron diffraction structure, which must be some kind of an average over the two conformations. This contention receives strong support from the NMR work. The details of our calculated structures are presented in Table 1.

1,4-*Cyclooctadiene.* Unlike the 1,3-isomer, this compound is relatively little known.[9] Based on our calculations and an examination of models, there appear to be two conformations which seem worthy of consideration. These we may call the boat-boat (4) and the boat-chair (5). The former is flexible in models, while the latter is rigid.

While 4 is flexible and pseudorotates in models, the calculations indicate that the structure as shown, which has a plane of symmetry, corresponds to the energy minimum. Models seem to indicate that a twisting would relieve the severe repulsion between the bridgehead hydrogens. The calculations do not bear this out. When the molecule is twisted, the energy minimization scheme undoes the twist, and brings it back to the C_s conformation. In this conformation there is significant van der Waals repulsion, but the energy suffers mainly from angle bending, which the molecule has undergone in an effort to alleviate that repulsion. Conformation 5, although torsionally somewhat poor, is energetically much more favorable than 4. At room temperature 4 only constitutes about 1% of the equilibrium mixture with 5.



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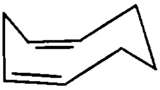

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Energy considerations. In Table 2 are summarized the calculated thermodynamic data concerning the isomeric cyclooctadienes. The more significant features can be summarized as follows. 1,3-Cyclooctadiene consists of a mixture of 2 conformations in similar proportions. The C_2 form is calculated to predominate over the C_1 form at very low temperatures, although the energy difference between them is small, probably within calculational error. At room temperature there are similar amounts of the conformations in equilibrium. Entropy favors the C_1 conformation by 1·4 e.u.

With 1,4-cyclooctadiene, the boat-chair isomer (5) is essentially the only one present. Finally, with 1,5-cyclooctadiene, the twist-boat conformation (a *dl* pair of

Table 2. Thermodynamic data calculated for the cyclootadienes

Compound	H^{b}	ΔH°	ΔS°	$\Delta G^{a}_{343^{\circ}K}$	$H_f^{\circ\,c}$	$\Delta G_{343}^{\;d}$	Equil. % (343°K)
1,3-Cyclooctadiene	-	-	-	-	21.26	0	98.9
C_2	21.05	0.00	0	0.00			
C_1	21.47	0.42	1.38	-0.05			
1,4-Cyclooctadiene	-	-	-	-	23.54	2.99	1.0
Boat–Boat	26.55	5.50	0	5.50			
Boat–Chair	23.54	2.47	0	2.49			
1,5-Cyclooctadiene	-	-	-	-			
C_2 (twist–boat)	24.73	3.68	0	3.68	24.73	4.18	0.1

[a] ΔG here is relative to the C_2 conformation of 1,3-cyclooctadiene

[b] Relative to an arbitrary zero

[c] The heat of formation of the gas at 298°K

[d] Relative to the actual (mixture of conformers) 1,3-cyclooctadiene.

C_2 symmetry), predominates to the extent of more than 90% at room temperature.[3,4]

If we consider the equilibrium between the isomeric cyclooctadienes, the 1,3-isomer is calculated to be the most stable. The 1,4-isomer is higher in energy by 2·5 kcal/mole, and the 1,5-isomer by 4 kcal/mole, and these energies are essentially identical with the free energies at low temperatures. As the temperature is raised, the free energy shifts even further in the direction favoring the 1,3-isomer because of the entropy contribution, and the calculated percentages of the isomers in the equilibrium mixture are as shown in Table 2.

This equilibrium was studied experimentally by starting with both **1** and **2**, and allowing the samples to equilibrate, using potassium t-butoxide as a catalyst in dimethyl sulfoxide as a solvent at 70°. The result of a mixture containing 99·49% 1,3-cyclooctadiene, with approx. 0·5 ± 0·1% of the 1,4-isomer noted. The 1,5-isomer amounted to slightly less than 0·01%. The agreement between calculation and experiment is qualitatively correct, although experimentally the 1,3-isomer is somewhat more stable relative to the others than we calculate. Part of the difference may be due to the fact that the calculation is for isolated molecules in the gas phase, whereas the experimental conditions for the equilibration are substantially different.

EXPERIMENTAL

1,4-Cyclooctadiene. 1,3-Cyclooctadiene was brominated with N-bromosuccinimide, and the bromide was reduced with LAH. A mixture of the 1,3- and 1,4- isomers was obtained.[9] The 1,3-isomer was separated as the silver nitrate complex. The 1,4-isomer was obtained by this procedure with a purity of 70–99%, the impurity being unreacted 1,3-cyclooctadiene. The 1,3- and 1,5-isomers were commercial samples.

Equilibration experiments. Treatment of **3** with potassium t-butoxide in dimethyl sulfoxide was reported[10] to yield pure **1**. A second report indicated isomerization, but apparently did not reach equilibrium.[11]

A 2 ml sample of **1** or **3** was dissolved in 50 ml dry dimethyl sulfoxide containing 2 g t-BuOK, and the soln was maintained at 70° for 4 hr. The mixture was then poured into water, and extracted with ether. The ether extracts were washed with water, and the soln was analyzed using a Perkin Elmer F 11 gas chromatograph, and a 100 ft capillary column of silicon (SE 60) maintained at 50° using N_2 as a carrier gas. The isomers were identified by comparison with synthetic mixtures prepared from authentic samples, and the concentrations were confirmed with authentic known mixtures. It was found that **1** predominated to a very great extent, the concentration of **2** being 0·5 ± 0·1%, and that of **3** being somewhat less than 0·01%.

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[1] This research was supported by Public Health Service Research Grant AM-14042 from the National Institute of Arthritis and Metabolic Diseases. Abstracted mainly from the M.S. Thesis submitted by JFV, submitted to the University of Georgia, August, 1974. UB is grateful to the Deutsche Akademische Austausch-Dienst for a traveling scholarship.

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