

CONFORMATIONAL ANALYSIS—CVI

ON THE 1,5-CYCLOOCTADIENE RING^{1,2}

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Abstract—1,5-cyclooctadiene and the corresponding dibenzo derivatives have been studied by means of force-field calculations. The relative stabilities of the various conformations, and the energy surfaces which interconnect them found from the calculations are used to interpret the available experimental data. Differences between the parent diene and the dibenzo derivative are noted, and are attributed largely to the difference in torsional barriers of a saturated carbon bond when attached to a double bond, as opposed to being attached to an aromatic ring.

Recent NMR investigations of 1,5-cyclooctadiene³ and the corresponding dibenzo⁴ compound have led to unanswered conformational questions, and have shown what at first sight might seem to be unexpected differences between these compounds. These problems have prompted us to communicate calculations we have carried out on these molecules, which we believe suggest answers to these questions.

An early X-ray study of dibenzocycloocta-1,5-diene⁵ found the 8-member ring to exist in a chair conformation in the crystalline state, while subsequent studies of related molecules generally concluded that the boat conformation was at least as stable if not preferred. An electron diffraction investigation of the parent diene indicated an equilibrium mixture of chair and boat forms, with the latter predominating.⁶ The dipole moments of 1,6-dichlorocycloocta-1,5-diene⁷ and dibenzocycloocta-1,5-diene⁸ both indicate the presence of a boat form. X-ray studies of *syn*-3,7-dibromo-cycloocta-1,5-diene⁹ and (all *ax*) 2,6-dimethylcycloocta-3,7-diene-1,5-dicarboxamide¹⁰ show a twist-boat conformation; a structural feature previously reported in the X-ray analysis of several metal complexes of 1,5-cyclooctadiene,^{11,12} in which two independent sets of molecules of approximate C₂ symmetry were found.

Of special interest are the recently reported observations via NMR of conformational barriers in both 1,5-cyclooctadiene³ and the dibenzo derivative.⁴ For the diene,³ the low temperature PMR results show two spectral processes: a splitting of the methylene proton singlet into a doublet at -168° ($\Delta G^\circ = 4.9 \pm 0.1$ kcal/mole)

and a subsequent splitting of the doublet at -177° ($\Delta G^\circ = 4.4 \pm 0.1$ kcal/mole). It was suggested that the latter process involved an equilibration of twist-boat (1) forms via the boat (3) or twist (4) conformation and the first process involved either an interconversion of boat forms via the chair or one of the above twist-boat equilibria. The ¹³C NMR spectrum revealed one spectral process at -176° ($\Delta G^\circ = 4.2 \pm 0.2$ kcal/mole) which was presumed to be the sum of the processes observed in the PMR spectra.

The low temperature NMR study of the dibenzo derivative⁴ found a splitting of the aromatic signal at -72° ($\Delta G^\circ = 10.2 \pm 1.0$ kcal/mole) which was attributed to a chair \rightleftharpoons boat equilibrium, and a splitting of the methylene singlet at -115° ($\Delta G^\circ = 7.5 \pm 1.0$ kcal/mole) which was attributed to an equilibrium of equivalent conformations of the boat family.

Previously we had studied two conformations of 1,5-cyclooctadiene with the aid of a well tested molecular mechanical model¹³ and found that the chair form was favored over a boat (of C_{2v} symmetry). We now wish to report the results of a more thorough study of this conformational problem considering a number of conformations for both the parent diene and its dibenzo derivative. The enthalpy differences calculated between the conformations studied are listed in Table 1 and selected structural parameters appear in Table 2.

The twist-boat form (1) is found to be the most stable conformation in both the diene and dibenzo molecules, with a conformational preference over the chair (2) of 1.45 and 1.30 kcal/mole, respectively. The twist-boat form

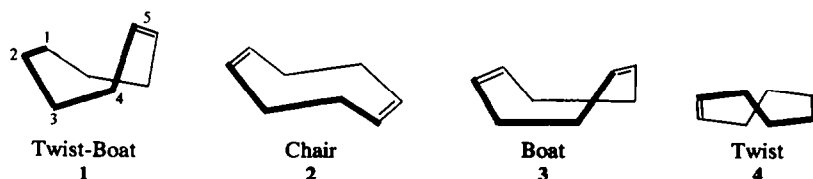
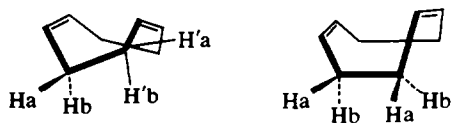


Table 1. Relative enthalpies for various conformations of 1,5-cyclooctadiene and 1,5-dibenzocyclooctadiene

Conformations	Diene	Dibenzo
Twist-Boat (1)	0	0
Chair (2)	1.45	1.30
Boat (3)	3.05	1.89
Twist (4)	5.94	6.78
"(5)	5.23	11.41



packing effects which may substantially influence the actual position of the twist-boat form (1) along a pseudorotational coordinate in the crystalline state.

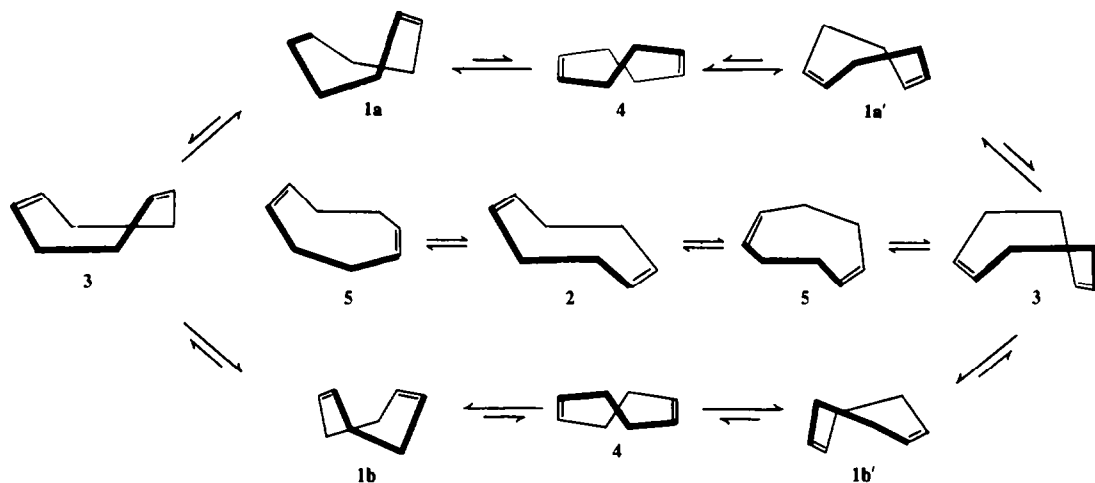
Looking at the ring dynamics of the diene, our calculations support some of the suggestions offered in

Table 2. Calculated structural features of various conformations of 1,5-cyclooctadiene and 1,5-dibenzocyclooctadiene

Diene Conformation	C=C-C	C-C-C	ω C=C-C-C	ω C-C-C-C
Twist Boat (1)	126.6, 125.6	116.3, 112.6	41.5, 88.2	37.9
Chair (2)	124.8	112.6	73.2	103.6
Boat (3)	124.1	113.3	73.0	0.0
Twist (4)	126.9	115.1	46.8	102.9
"(5)	127.0, 123.0	116.4, 112.6	62.9, 78.7	
Dibenzo Conformation				
Twist-Boat (1)	121.9, 122.1	115.6, 111.8	53.9, 89.1	26.5
Chair (2)	122.2	113.1	74.5	109.3
Boat (3)	121.7	113.6	74.3	0.0
Twist (4)	123.5	116.4	47.7	109.7
"(5)	120.5, 131.9	112.3, 128.5	88.2, 0.0	

is characterized by a ω_{2345} of 37.9° for the diene and 26.5° for the dibenzo derivative. By comparison, the X-ray diffraction value for this angle in the dibromo derivative⁹ is 65° , a value substantially larger than we calculate, indicating a geometry somewhere between our structures (1 and 4) in the pseudorotation diagram. Because of the pseudorotational flexibility of the ring, however, little can be said of this difference owing to substituent and crystal

the most recent PMR study of the hydrocarbon. The twist-boat form (1) has the two hydrogens on carbon 3 non-equivalent, and they are in addition non equivalent to the two hydrogens on carbon 4. In the boat form (3) the hydrogens on carbon 3 become equivalent with those on carbon 4, but there is one set of "inside" hydrogens (Hb) and one set of "outside" hydrogens (Ha). The smaller of the observed energy barriers (4.4 ± 0.1 kcal/mole at



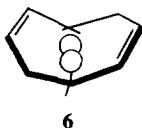
-177°K) is assigned the interconversion of **1a** and **1b** via the boat form (**3**). When the entropy correction is taken into account (**1** is *dl*, while **3** is not) the calculated ΔG^\ddagger is 3.18 kcal/mole.

The other observed process, a boat inversion, would correspond to **3(1a, 1b)** going to **3'(1a', 1b')**. In this interconversion, the inside and outside hydrogens are exchanged. This process is calculated to go through the chair form, the exact path being $1 \rightarrow 5 \rightarrow 2 \rightarrow 5' \rightarrow 1'$. This would correspond to the observed barrier of 4.9 ± 0.1 kcal/mole at -168°K . Since we go from a structure (**1a, 1b**) which has a symmetry number of 2 through a transition state which has the symmetry number of 1 (**5**), there is again an entropy effect to be taken into account. This gives us a calculated ΔG^\ddagger for this process of 5.09 kcal/mole. Transition state **5** is characterized by a propene type eclipsing of the hydrogens on C_2 (and C_1) with the outside hydrogens of C_3 (and C_8). Geometrically it would appear midway between the way structures **3** and **5** are drawn in the pseudorotation diagram. There is slight ambiguity in choosing transition states for these inversions, but the good agreement between the experimental and calculated values suggest that reasonable choices have been made in each case.

The twist form (**4**) is also a transition state for a $1 \rightleftharpoons 1'$ interconversion but this process is energetically unfavored as compared to an interconversion via **5** owing to a higher ΔH^\ddagger of the twist pathway (5.94 kcal/mole).

It was anticipated that a pseudorotational form (**6**), midway between the twist-boat and twist geometries would be at an energy maximum because of the two internal hydrogens moving past one another, however, this was found not to be the case.

For the dibenzo compounds, the calculated barrier to interconversion (or rocking) between twist boat forms (**1a** \rightleftharpoons **3** \rightleftharpoons **1b**) is quite low, $\Delta H^\ddagger = 1.89$ kcal/mole. Experimentally⁴ this inversion remains undetected down to -135°C with now lower temperature studies being reported.



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Of the two possible modes of boat-boat inversion the pathway involving the twist form (**1a** \rightleftharpoons **4** \rightleftharpoons **1a'**) is energetically preferred, with a calculated ΔH^\ddagger of 6.78 kcal/mole ($\Delta G^\ddagger = 7.0$ kcal/mole at -115° due to *d,l* entropy). This would account for the splitting of the methylene singlet observed in the NMR spectrum at -115° ($\Delta G^\ddagger = 7.5 \pm 1.0$ kcal/mole). Inversion via the chair form, the preferred pathway for the diene, is hindered in the dibenzo compound by the high relative conformational energy of transition state **5** (calculated $\Delta H^\ddagger = 11.41$ kcal/mole). This latter process is observed⁴ in the NMR spectral as a splitting of the aromatic peaks at -72° ($\Delta G^\ddagger = 10.2 \pm 1.0$ kcal/mole), due to a freezing out of the chair form. The corresponding splitting of the methylene singlet is barely visible even at -100° because of the relatively small

amounts of chair form present. The geometry of **5** in the dibenzo case is as represented in the pseudorotation diagram, with six ring atoms coplanar.

The difference in conformational behavior between the diene and dibenzo derivative is a consequence of the different type of torsional interactions found in these molecules.



The diene has H/H eclipsing of the type found in propene (1.98 kcal/mole rotational barrier)¹⁴ while dibenzocyclooctadiene has H/ C_{sp^2} eclipsing of the type found in toluene (0.5 ± 0.5 kcal/mole rotational barrier).¹⁵ In both the diene and dibenzo derivative, all relevant conformations except the boat-chair transition state (**5**), have unfavorable torsional interactions of these types. Since the H/H interaction is quite severe as compared to the H/ C_{sp^2} interaction, one would expect the boat to chair to boat conversion to be much more favorable in the diene as opposed to the dibenzo derivative, since such a process involved relief of the H/H (or H/ C_{sp^2}) eclipsing.

The dibenzo compound will therefore preferentially pseudorotate from one boat to another while the diene accomplishes this interconversion by a ring inversion via the chair.

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APPENDIX

The 1973 force field was used.¹⁶ The additional parameters required for unsaturated systems, developed according to published procedures,¹⁷ are as follows:

van der Waal Constants				Torsional Constants		
C_{sp^2}	r 1.85 Å	ϵ 0.030 kcal/mole		Angle	k_w	k_w
Bond	Stretching Constants l_0 , Å	k_1 , mdyn/Å				
$C_{sp} \equiv C_{sp^2}$	1.334	9.6		$C-C_{sp^2}-C_{sp^2}-C_{sp^3}$	2.34	
$C_{ar}-C_{ar}$	1.392 ^a	8.08 ^a		$C-C_{sp^2}-C_{sp^2}-H$	2.34	
$C_{sp^2}-C_{sp^3}$	1.496	4.4		$H-C_{sp^2}-C_{sp^2}-C_{sp^3}$	2.34	
$C_{sp^2}-H$	1.090	4.6		$H-C_{sp^2}-C_{sp^2}-H$	2.34	
Angle ^b	Bending Constants		k_0 , mdyn Å/rad ²			
Type ^c	θ_0 , deg					
$C_{sp} \equiv C_{sp^2}-C$	2	120.2	0.38	$C_{sp^3}-C_{sp^2}-C_{sp^2}-C_{sp^3}$	6.25	-1.13
$C_{sp} \equiv C_{sp^2}-C$	3	121.7	0.38	$C_{sp^3}-C_{sp^2}-C_{sp^2}-H$	6.25	
$C_{sp} \equiv C_{sp^2}-H$	1	118.8	0.24	$H-C_{sp^3}-C_{sp^2}-C_{sp^2}-H$	6.25	
$C_{sp} \equiv C_{sp^2}-H$	2	120.0	0.24	$H-C_{sp^3}-C_{sp^2}-H$	6.25	
$C_{sp^2}-C_{sp^2}-C_{sp^3}$		116.6	0.38	$X-C_{ar}-C_{ar}-X$	4.6 ^d	(X = C, H)
$C_{sp^2}-C_{sp^2}-H$		119.8	0.24			
$H-C_{sp^2}-H$		122.4	0.19			
$C_{ar}-C_{ar}-C_{ar}$		120.0	0.38			
$C_{ar}-C_{ar}-C_{sp^3}$		120.0	0.24			
$C_{ar}-C_{ar}-H$		120.0	0.24			
out-of-plane		0.0	0.05			

^a Derived according to methods outlined in Ref. 13.

^b Where carbon hybridization is not specified, the parameters apply to both C_{sp^3} and C_{sp^2} . Values for $C-C_{sp^3}-C$ and $C-C_{sp^2}-H$ are as reported in ref. 16.

^c Type refers to degree of substitution on central atom (i.e. primary, secondary or tertiary).

^d Derived according to methods outlined in N. L. Allinger, T. Liljefors and J. T. Sprague, *J. Amer. Chem. Soc.*, **96**, 5100 (1974).

^a Derived according to methods outlined in Ref. 13.

^b Where carbon hybridization is not specified, the parameters apply to both C_{sp}^3 and C_{sp}^2 . Values for $C-C_{sp}^2-C$ and $C-C_{sp}^2-H$ are as reported in ref. 16.

^c Type refers to degree of substitution on central atom (i.e., primary, secondary or tertiary).

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