STRAIN ENERGY CALCULATION OF CONFORMATIONS

AND CONFORMATIONAL CHANGES IN CYCLOOCTANE

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A number of strain energy calculations for the conformations of cyclooctane have been published.[1-4] However, the interconversion paths linking these conformations have not been extensively investigated, although Hendrickson[1] has reported the energy profiles for certain paths where at least one element of symmetry is forced to be maintained. This restriction may give paths which are not the lowest in energy,[1,5] and, furthermore, it prevents the making of any calculation of the conformationally important pseudorotation path of the boat-chair via the twist-boat-chair.[6] We now report some new calculations made with Boyd's iterative program MOLBUILD,[7] which was modified to allow conformational changes to occur by "driving" the dihedral angles, as described by Wiberg and Boyd.[8]

The excess strain energies for different conformations (Fig. 1) are listed in Table 1. In Table 2 are listed maximum energy conformations for various interconversions. No corrections for vibrational zero point energy and thermal energies of translation, rotation and vibration have been made. On the whole, the present results for conformations in Table 1 are in agreement with previous calculations and the experimental data. The BC, TBC and TCC are energy minima with respect to all small distortions. The BB and TB are separated from one another by an extremely small barrier but the BB - TB considered as one system is stable towards small distortions. A reasonably complete investigation of interconversion paths requires a very large number of calculations and it is thus difficult to be sure that the lowest path between two conformations has been found. Interconversions within the crown family are found to have very low barriers, in agreement with Hendrickson's calculations, and will not be discussed further.

There are four different kinds of dihedral angles in the boat-chair and the effect of driving each one separately towards zero, was investigated. By driving ω_2 and ω_3 (i.e. the torsional angles about the 2,3 and 3,4 bonds respectively), the BC goes smoothly to the TBC over a barrier of 3.3 kcal/mol. The TBC is an intermediate in the BC pseudorotation originally
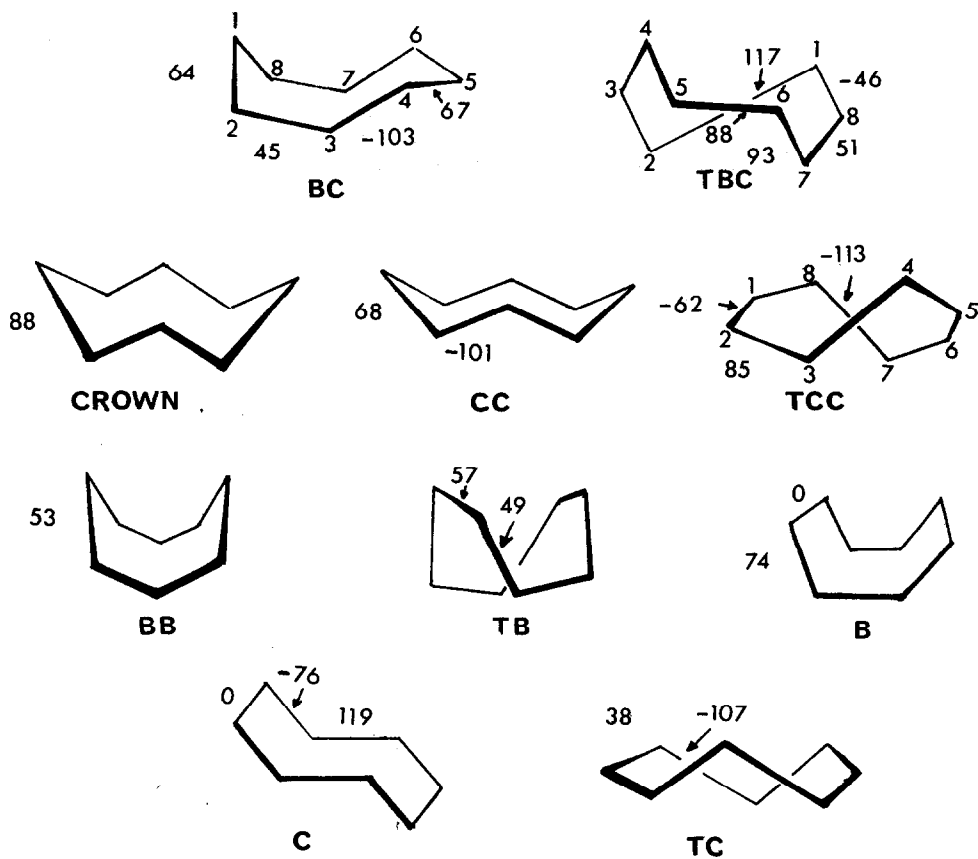
Figure 1

proposed by Anet and St. Jacques.[12] On the basis of substituent additivity effects the barrier to pseudorotation has recently been estimated to be 3.7 kcal/mol,[6] in reasonable agreement with present calculations. The transition state $(BC \rightleftharpoons TBC)^{\ddagger}$ for this process is shown below and has ω_2 nearly eclipsed. Any interconversion of the BC-TBC system with the
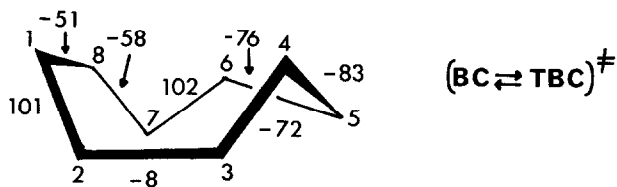
Table 1. Conformational Energies for Cyclooctane.

Family	Name	Symmetry Group	This Study	H[a]	BL[b]	W[c]	A[d]	Obs.
boat-chair	boat-chair (BC)	C_s	0[e]	0	0	0	0	
	twist-boat-chair (TBC)	C_2	1.7	2.0	–	–	–	
crown	twist-chair-chair (TCC)	D_2	0.8	1.7	1.89	–0.25	2.20	1.7[f]
	crown	D_{4d}	1.5	2.8	3.62	0.25	2.09	
	chair-chair (CC)	C_{2v}	1.8	1.9	–	–	2.25	
boat	boat-boat (BB)	D_{2d}	2.8	1.4	–	4.44	–	
	twist-boat (TB)	S_4	2.8	0.9	–	–	–	> 2.0[g]
	boat (B)	D_{2d}	11.2	10.8	–	8.96	–	
chair	chair (C)	C_{2h}	7.5	8.3	–	–	–	
	twist-chair (TC)	C_{2h}	7.7	8.7	–	6.09	–	

a)ref.1, b) ref.2, c) ref.3, d) ref.4, e) The strain energy is calculated to be 13.9 kcal/mol.

f) ref.9, g) ref.9.

Table 2. Maximum-Energy Conformations for Various Interconversions.

Conformation	Driven Angle	Symmetry Group	This Study	H[a]	Obs.
(BC ⇌ TBC)‡	ω_2 or ω_3	C_1	3.3		< 4[b]
(TBC ⇌ TC)‡	ω_2 or ω_3	C_1	7.9	(11.6)	
(TBC ⇌ C)‡ (≡ C)	ω_1 and ω_5	C_{2h}	7.5	8.3	8.1[c]
(BC ⇌ TB)‡	ω_4	C_1	10.8		
(BC ⇌ BB)‡	ω_4 and ω_5	C_s	10.7	≃ 20	
(TBC⇌TCC)‡	ω_1	C_2	10.3	(11.4)	10.5[d]
(BB ⇌ B)‡ (≡ B)	ω_1, ω_3, ω_5, and ω_7	D_{2d}	11.2		
(BB ⇌ TB)‡	ω_1 and ω_5	S_4	< 0.2		

a) ref. 1, b) ref. 10, c) ref. 11, d) ref. 9.

TC, C, BB, TB or B is a mechanism for ring inversion[1] in the boat-chair. As can be seen in

Table 2, the unsymmetrical ring inversion paths, TBC⇌TC and BC⇌TB, as obtained by driving

a single dihedral angle are actually higher in energy than the paths, TBC⇌C and BC⇌BB,

where two dihedral angles have been driven in a symmetrical fashion. The BC $\rightleftharpoons$ TB path obtained by driving one dihedral angle is dependent on the direction of the conversion, but the energy maxima are virtually the same for both directions. This means, of course, that there are two independent paths of nearly equal energies for this interconversion. The result of driving ω_1 in the BC is not interesting since the end result is the same as the BC $\rightleftharpoons$ TBC pseudorotation, but with a much higher barrier (7.0 kcal/mol).

The lowest energy path found between the boat-chair and the crown family is obtained by driving ω_1 of the TBC. The barrier for (TBC $\rightleftharpoons$ TCC)$^+$ is 10.3 kcal/mol and the system closely maintains a C_2 axis, although this is not required by the calculations. Hendrickson's calculations of this barrier involves a transition state of forced D_2 symmetry, which is more restrictive than necessary. Other paths of potential interest were also investigated and are summarized in Table 2.

<div align="center">References</div>

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6. For a more thorough discussion of dynamics of cyclooctane see F. A. L. Anet, "Dynamics of Eight-membered Rings in the Cyclooctane Class". Fortschr. Chem. Forsch., in press.

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