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BOAT AND CHAIR BENZENES

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Recently Misumi et al. found in the course of the studies on the multilayered [2.2]metacyclophanes that isomer I in which the central benzene ring is forced to have a boat conformation and destabilization due to non-bonded interaction is expected is at least 4 kcal/mol more stable than isomer II with its central ring bent to a chair conformation.1) This observation together with the trend that the unconstrained ends of the benzene rings in [2.2]metacyclophanes are bent to make the benzene rings a boat2) led us to speculate that the boat conformation of benzenes is extraordinarily favored over the chair one in contrast to the well-established conformational preference of chair cyclohexane. It seemed, therefore, of interest to study the different stability between the boat and chair benzenes and to seek its origin. Since distorted benzene nuclei can not be an energy minimum spieces and therefore should be present only when they are incorporated into the strained compounds such as cyclophanes, it is of special significance to scrutinize the parent system theoretically. We have carried out semi-empirical SCF MO calculations by using the MINDO/2 approximations.3)

As the models for boat and chair benzenes, i.e., the central rings of I and II, we assume that they maintain C_{2v} and C_{2h} symmetry, respectively. Geometrical parameters α, β and γ are chosen to determine the direction and

Fig. 1

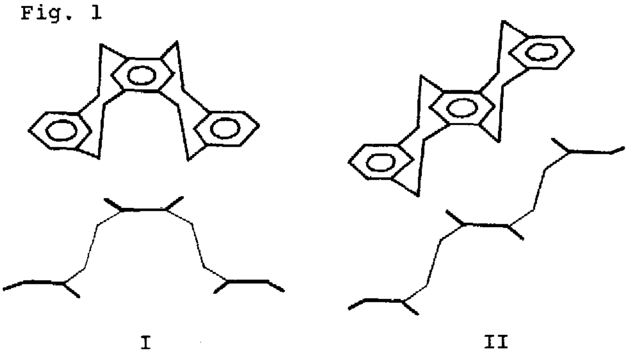


Fig. 2

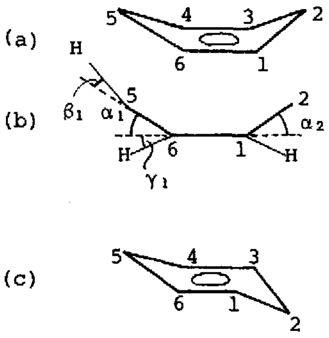
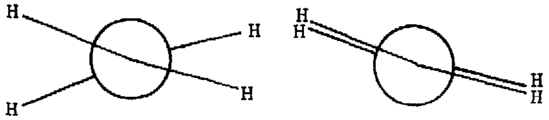
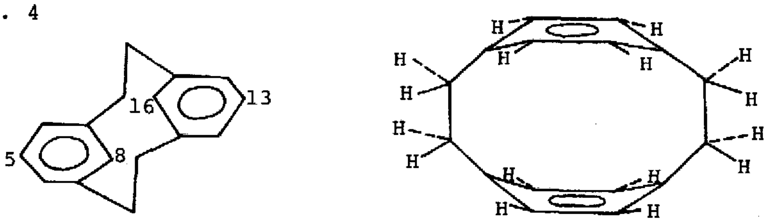


Fig. 3



Staggered Eclipsed

Fig. 4



[2.2] metacyclophane [2.2] paracyclophane

Table 1. Dissected Energy Terms (in kcal/mol) for Distorted Benzenes III and IV (γ=-14° and $|\alpha|$=12°) Expressed in Terms of Difference from the Values for Flat Hexagon Benzene.

	Total	One-center	Resonance	Exchange	Electrostatic
Boat Form (III)	6.30	-2.70	11.32	1.51	-3.82
Chair Form (IV)	11.31	-2.38	16.22	1.55	-4.09

	bond C_1-C_2	bond C_1-C_6	C_2-C_5
Boat Form (III)	2.87	-1.01	0.45
Chair Form (IV)	2.92	1.44	0.26

$$\Sigma E_{\mathrm{Total}} = \Sigma E_{\mathrm{One\text{-}center}} + \Sigma E_{\mathrm{Resonance}} + \Sigma E_{\mathrm{Exchange}} + \Sigma E_{\mathrm{Electrostatic}}$$ 5)

amount of deformation of the ring. Other bond lengths and angles are varied accordingly in order to get the energy minimized theoretical structure.[4] α is defined as the angle between the planes C_1-C_2-C_3 and C_1-C_3-C_4-C_6 (bow elevating angle) and γ stands for the angle between bond C_1-H_1 and plane C_1-C_3-C_4-C_6 (See Fig. 2). When the value of γ is fixed at 14° which corresponds to the experimental value (obtained by X-ray diffraction) of the benzene contained in [2.2]cyclophanes, the structure with α=6° gives the minimum energy on MINDO/2 calculations. The experimental values for α are 12~14°.[2] The potential energy curve is, however, rather shallow in these regions and the energy difference between the structure with α=6° and that with α=13° is only 0.5 kcal/mol. The difference could be easily cancelled out by any additional steric repulsion. The value of α is thus set to be 12° and an energy partitioning analysis is made on distorted model benzenes III and IV to give the results summarized in Table 1. Notice that boat benzene (III) is much more stable than chair benzene (IV) and their difference in the total energy values corresponds mostly to the difference in the resonance integral terms. Furthermore, twice the energy difference of the C_1-C_6 (C_3-C_4) bond is equal to that of the total energy.

The reason why the difference in the C_1-C_6 bonds between boat and chair benzenes is such a large one is easily understood when the Newman projections about the C_1-C_6 bond axis for both are examined. We find the twisted ethylene suited as an approximate model for the case. It is well known that the twist ethylene is considerably unstable and the high barrier to rotation about the ethylenic double bond is based on the destabilization due to the lack of effective overlap of each π orbital on two carbon atoms in the transition state where the both p orbitals are perpendicular. It is also the case for the conformation around the C_1-C_6 bond axes of boat and chair benzenes. The eclipsed form in boat benzene in which both p orbitals can overlap rather efficiently is much more favored than the staggered(twist) form in chair benzenes on similar grounds discussed above. This situation prevails for the torsion of other pivot bond, e.g., the C_1-C_2 bond. The C_2-H_2 bond tends to move in a direction so that the energetically favored eclipsed orientation of the π-orbitals may be attained as high as possible. The MINDO/2 calculations lead to β of -9° for energy optimized structure of boat benzene. The value is in good agreement with -9.4° or -10°, the results of X-ray analysis.[2b] It is concluded that, while torsional strain in eclipsing of the $-CH_2-CH_2-$ moiety makes boat cyclohexane less stable than the chair conformer, twisting of the pπ orbitals are responsible for less stable chair benzene compared to boat benzene.

Similarly, other apparently unusual phenomena in cyclophane chemistry are readily explained. In the case of metacyclophanes, for example, unconstrained carbon atoms, C_5 and C_{13} (Fig. 4), bend in the same direction as the inside carbon atoms, C_8 and C_{16} to make benzene rings a pseudo boat. When α_1 was fixed at 13°, the calculated energy attains to a minimum at α_2=4.5°(Fig. 2b) in harmony with the observed values of 4.5° (or 3.8°)[2a] and 4.9°.[2b] It has been pointed out that the aromatic hydrogen atoms fall slightly inside of the cage in [n] and [n.n]paracyclophanes (Fig. 4).[6] When the values of α and β were fixed at 13° and 11°, respectively, H_1(and H_3, H_4, and H_6) is found nearly on the C_1-C_3-C_4-C_6 plane in the MINDO/2 energy optimized structure. These results explain the situation of [n]paracyclophanes quite nicely, but we can not rule out the contribution of re-hybridization of the aromatic carbon atoms as a result of repulsion between the π electron clouds of the facing two benzene rings in the case of [n.n]paracyclophanes;[7] the calculated geometry is only a half way to the observed inward bending of the aromatic C-H bonds.

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