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MOLECULAR MECHANICS CALCULATIONS ON THE STRUCTURES AND CONFORMATIONAL PROPERTIES OF [8]CIRCULENE AND SOME RELATED PHANE COMPOUNDS

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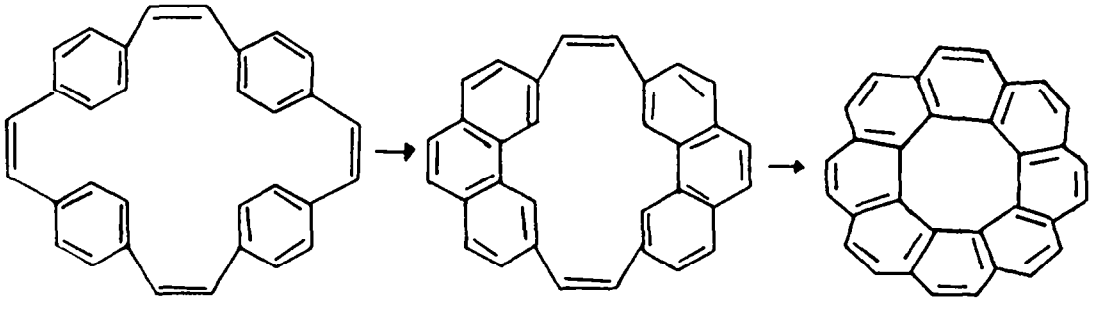
Abstract—Molecular mechanics calculations on [8]circulene and some related compounds have been performed in order to gain insight into the geometrical and conformational properties of these molecules. [8]Circulene is predicted to undergo a facile "bond-shift" process between two saddle shaped conformations. The relation between the geometrical and conformational properties of **1** and **2** and the so far unsuccessful attempts to synthesize [8]circulene is discussed.

The investigation of the aromatic behaviour of organic molecules and the theoretical foundation for it has contributed considerably to the development of modern organic chemistry. A planar arrangement of the atoms is required for efficient overlap between neighbouring π-orbitals, maximizing the resonance energy of the compound. Nevertheless, aromatic compounds are flexible and may deviate considerably from planarity without loosing all their resonance energy. Many examples of this are found among the cyclophanes[1] and helicenes.[2] An interesting group of compounds in this context is the circulenes,[3] compounds built by the condensation of aromatic nuclei to give *ortho*-fused ring systems without internal atoms. The few known examples are corannulene or [5]circulene,[4] coronene or [6]circulene,[5] some thia[7]circulenes[3] and tetraoxo[8]circulene.[6] Corannulene has a bowl-shaped structure while coronene and tetraoxo[8]circulene are planar. The thia[7]circulenes may deviate from planarity but no experimental structure has been reported. We have been engaged in an attempted synthesis of [8]circulene (**3**) by successive photocyclization of [2$_4$]paracyclophanetetraene (**1**) and [2.2]-(3,6)phenanthrenophanediene (**2**).

The first photocyclization has been achieved with a diiodo derivative of **1**,[7a] whereas photocyclizations of unsubstituted **1** and of **2** have failed so far. In order to gain some insight into the geometrical and conformational properties of compounds **1**–**3**, we have carried out molecular mechanics calculations on these compounds using a well-tested method developed by Allinger *et al.*[8] In particular, we wish to predict the geometry and the conformational behaviour of the hitherto unknown [8]circulene (**3**). In addition, it was hoped that an elucidation of the preferred conformations of **1** and **2** would shed some light on the failures of the photocyclization processes **1** → **2** and **2** → **3**.

Method of calculation. A molecular mechanics method for compounds containing delocalized electronic systems was used in the present calculations. This method, developed by Allinger *et al.*, has been described in detail.[8] Its main feature is the incorporation of a quantum mechanical π-system calculation (VESCF) in the energy minimization scheme. The VESCF calculation provides bond orders from which stretching and torsional constants are evaluated. These π-electron calculations are repeated several times during the energy



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minimization process in order to ensure consistency between the energy-minimized geometry and its force field. For each molecule, several trial structures were energy minimized in order to find the lowest energy geometry.

The parameters used in this work (Allinger's 1973 force field) are given in Ref. 9. The molecular mechanics method has previously been successfully employed in calculations on aromatic compounds with distorted geometries.[8d,9]

RESULTS AND DISCUSSION

[2$_4$]*Paracyclophanetetraene* (**1**). The calculated minimum energy geometry of **1** is shown in Fig. 1. The molecule belongs to the symmetry point group D_{2d}. The four bridges joining the phenyl rings are almost coplanar. Maximum deviation from a least-squares plane through the bridging atoms is only 0.30 Å. A preliminary X-ray investigation of **1**[10] supports the calculated shape of the molecule. The X-ray structure shows a maximum deviation from coplanarity of 0.20 Å, in good agreement with the calculated value. In a planar geometry, the angles at the bridging double bonds must open up. The molecule avoids this increase of angle strain by small twists of the double bonds.

There is a strong similarity between the calculated structure of **1** and that of four superimposed *cis*-stilbene units.[11] The phenyl rings in **1** are calculated to be twisted 33.4° with respect to the bridges, while the preliminary X-ray structure shows an average twist of 34.2°. The corresponding value for *cis*-stilbene is 43.2 ± 3.2°.[11] A planar or almost planar geometry of the four bridges is necessary for a local *cis*-stilbene arrangement of all phenyl rings. In this arrangement, the repulsive interactions between the aromatic rings are minimized. Significant deviations from planarity result in rapidly increasing repulsive interactions between the inner *ortho* hydrogens and *ortho* and bridge-end carbons on adjacent phenyl rings.

The symmetry for the calculated structure of **1** is D_{2d}. If substituents are introduced into two opposite benzene rings, or if they are exchanged for other aromatic rings, e.g. thiophene, furan, biphenyl, the symmetry of the resulting [2$_4$]cyclophanetetraenes is reduced. Such cyclophanes could exist as separate enantiomers. In order to estimate the barrier to racemization of such cyclophanes and the barrier of inversion of [2$_4$]paracyclophanetetraene, we have calculated the energy for a planar structure of the latter (D_{4h} symmetry; all bridging atoms in one plane). This conformation is found to be 5.8 kcal/mol higher in energy that the minimum energy conformation. The calculated value may be regarded as an upper limit for the inversion barrier. The molecule may instead invert by a multistep pathway of lower energy, avoiding the angle strain at the double bonds, which is the dominant component of the energy barrier, to be introduced simultaneously at all bridge double bonds. The low height of the barrier thwarted our initial hope that properly substituted [2$_4$]paracyclophanetetraenes may function as chiral multidentate ligands.

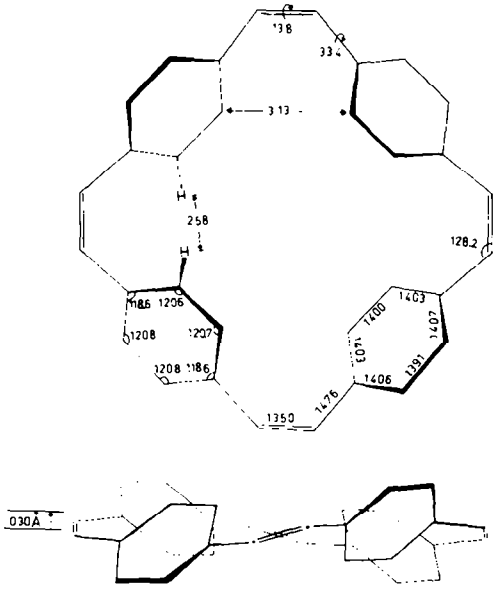


Fig. 1. Calculated geometry of [2$_4$]paracyclophanetetraene (**1**). (Bond lengths and non-bonded distances in Å, bond angles and torsional angles in degrees.)

An attempted photocyclization of **1** in the presence of air and iodine led to the slow formation of mixture of various aldehydes from oxidations of the double bonds.[7a] Compound **2** was not detected as an intermediate when the reaction was followed by UV spectroscopy. Several other attempted photocyclizations of [2$_4$]cyclophanetetraenes with two or more thiophene or furan rings, bridged in the 2 and 5 positions, have also been unsuccessful.[7b,c] If two opposite benzene rings in **1** are exchanged for biphenyls, as in [2.2.0.2.2.0]paracyclophanetetraene, the product is also rather stable on irradiation in the presence of air and iodine. No products from photocyclizations were observed, although the expected product, which can easily be prepared from a diiodo derivative, is quite stable under the reaction conditions.[7d] These rather surprising results are difficult to rationalize from a conformational and geometrical point of view. The photocyclization of *cis*-stilbene to phenanthrene is a general and synthetically useful reaction. The calculated geometrical features of **1** are favourable for a symmetry-allowed electrocyclic photocyclization **1**→**2**. The distance between *ortho* carbons in adjacent phenyl rings is calculated to be 3.13 Å; in *cis*-stilbene the distance between *ortho* carbons involved in photocyclization is 3.2 ± 0.3 Å,[11] the same as in **1**. The failure of **1** to undergo photocyclization to **2** may be due to a high activation energy for the ring-closure process. The creation of a carbon–carbon bond on one side of the molecule forces the opposite phenyl rings to approach each other, causing repulsive interactions. If a concerted cyclization **1**→**2** is considered, the inner hydrogen on the non-reacting aromatic carbons are forced into close proximity along the reaction pathway. Photocyclization of a *diiodo* derivative of **1**, however, gives **2** in 15% yield.[7a] This reaction may proceed *via* a homolytic cleavage of iodine–carbon bonds followed by a ring-closure and hydrogen abstraction by I atoms.

[2,2](3,6)*Phenanthrenophanediene* (**2**). The calculated minimum energy geometry of **2** is shown in Fig. 2. The molecule has two planes of symmetry, and belongs to symmetry point group C_{2v}. The geometry of the phenanthrene units is close to that of phenanthrene itself,[12] although a slight bending of the ring systems is calculated. The distances between the internal hydrogens, 2.15 and 2.24 Å, make these atoms sterically more strongly interacting than the corresponding hydrogens in in the derivative with saturated bridges, [2$_2$](3,6)phenanth-

renophane, and in phenanthrene. Accordingly, the H NMR signal for the internal protons in **2** is shifted downfield (9.45; δ ppm, $CDCl_3$)[7a] compared to the corresponding signals in [2₂](3,6)phenanthrenophane (9.16; δ ppm, $CDCl_3$)[7b] and in phenanthrene (8.93; δ ppm, $CDCl_3$).[13]

The two bridges are essentially two isolated double bonds. There is thus only a weak π-electron interaction between the two phenanthrene units. This is in accord with the UV spectrum of **2**, which is very similar to that of phenanthrene.[7a] The failure of **2** to photocyclize to **3** is understandable in view of the preferred conformation. Although the distance between 4 and 4', 3.20 Å, is the same as between the reacting carbons in *cis*-stilbene, the arrangement of the aromatic rings in **2** is not that required for a 6 π-electron, symmetry allowed photocyclization **2**→**3**. The molecule is predicted to be V-shaped (*syn*) with an angle of 67° between the phenanthrene units (Fig. 2) and with a plane of symmetry instead of the required two-fold axis. An *anti* conformation with a two-fold axis through the centers of the ethylene bridges (Fig. 3) is calculated to be 94 kcal/mol higher in energy, mainly due to severe twisting of the two bridging double bonds (125.8°). The completely planar geometry of **2**, also possessing a two-fold axis through the double bonds, lies 31 kcal/mol above the minimum energy *syn* conformation. It is thus clear that none of these conformations, which are suitable for an electrocylic photocyclization, is significantly populated at normal temperatures. A possible synthetic route to overcome some of these difficulties may be a photocyclization of a diiodo derivative of **2**, prepared *in situ* by a photocyclization of tetraiodo[2₄]paracyclophanetetraene, under an inert atmosphere, *via* homolytic cleavage of the iodine–carbon bonds. Attempts to carry out this reaction, which is analogous to the successful preparation of **2**, are now in progress.

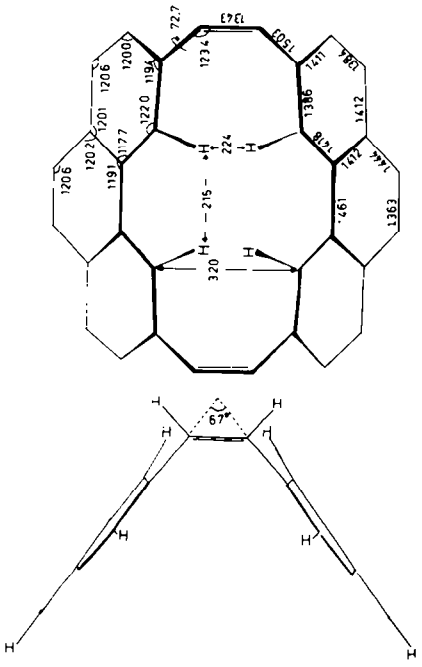


Fig. 2. Calculated geometry of [2,2](3,6)phenanthrenophanediene (**2**). (Bond lengths and non-bonded distance in Å, bond angles and torsional angles in degrees.)

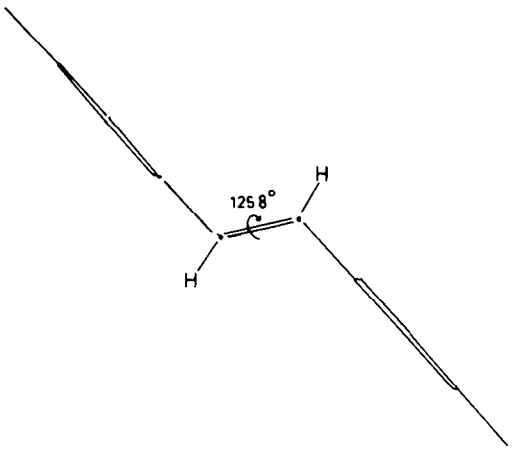


Fig. 3. *Anti* conformation of [2.2](3,6)phenanthrenophanediene (**2**).

A few phane-dienes have been shown to be conformationally flexible. In these cases, one of the rings flips by a rotation around bonds.[14,15] In cases where this motion is impossible due to high strain, the molecules are conformationally rigid. However, in phane-dienes containing large aromatic ring systems, there is a possibility that, although a one-ring rotation process is ruled out, the molecule may invert by a mechanism involving significant deformations of the aromatic system. The planar conformation of **2** lies, as mentioned above, 31 kcal/mol above the most stable conformation. This value is an upper limit for the inversion barrier. To investigate if the molecule may invert along a lower energy pathway involving deformations of the phenanthrene units, we carried out calculations on some conceivable transition state conformations along such an inversion pathway. The energetically most favorable pathways was calculated to be a two-step inversion, passing through a local minimum conformation with a C_2 axis through the phenanthrene units (Fig. 4b). This local minimum lies 20.9 kcal/mol above the global minimum. A model for the transition state between these minima (shown in Fig. 4a) is only

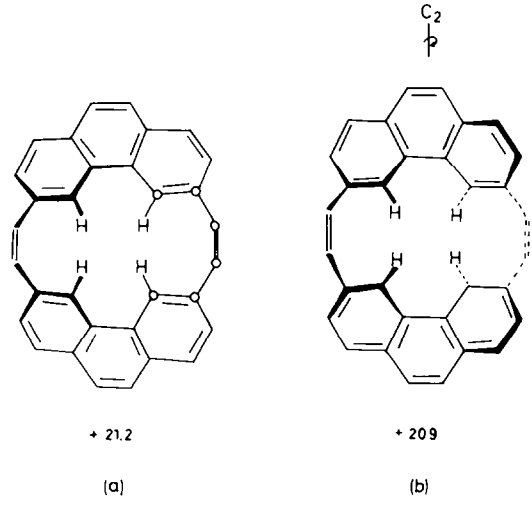


Fig. 4. Calculated conformations and conformational energies (in kcal/mol) along an inversion pathway for [2.2](3.6)phenanthrenophanediene (**2**). Encircled atoms are restricted to a plane.

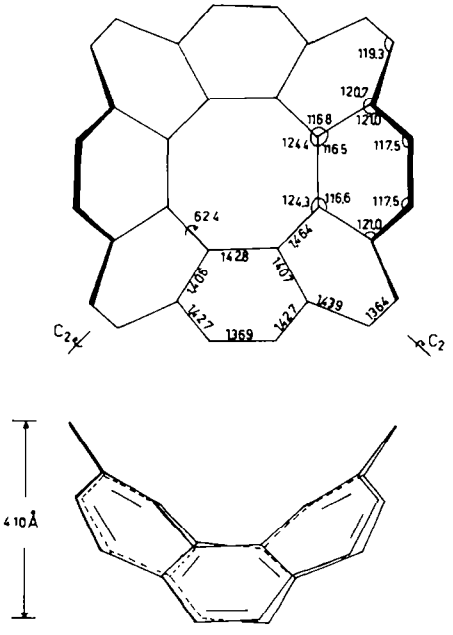
0.3 kcal/mol higher in energy than the local minimum. The calculated energy of the inversion process is thus lowered by *ca.* 10 kcal/mol by allowing the aromatic rings to be nonplanar. It should be noted that the calculated barrier to inversion of **2** is low enough to make it possible to study the inversion process with dynamic NMR provided that a prochiral substituent can be introduced in the molecule in a position where it does not interfere with the inversion process. Work along this line is in progress in our laboratories.

[8]*Circulene* (**3**). In circulenes larger that coronene ([6]circulene), the periphery of the molecule will be too long and the inner ring too short for the molecule to adopt a planar conformation. Adjustment of bond lengths in the molecule may decrease the periphery and increase the size of the inner ring. Bond length adjustments, however, require more energy than angle distortions. On the other hand, if the angle distortions become severe, some of the resonance stabilization may be lost. Circulenes are therefore interesting model compounds for studies on the flexibility of aromatic systems.

The lowest energy geometry of [8]circulene was found to be of a slightly twisted saddle shape with D_2 symmetry (**3a**, Fig. 5). A saddle structure with D_{2d} symmetry possessing in addition two perpendicular mirror planes through benzene units and with the inner "cycloctatetraene" ring in a perfect tub shape is calculated to be only 1.1 kcal/mol higher in energy. These calculations thus suggest that the molecule may oscillate about the D_{2d} structure without significant expenditure of energy.

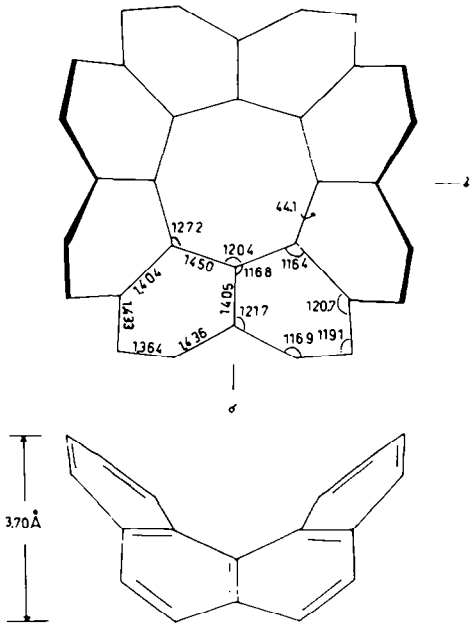
The minimum energy geometry (**3a**) shows alternating bond lengths in the inner "cyclooctatetraene" ring. Although this ring is calculated to be somewhat more puckered than in cyclooctatetraene itself[16] (the calculated C=C–C=C torsional angle is 62°), the alternation is much less pronounced in the inner ring in **3a** than in cyclooctatetraene.[16] The outer bonds in **3a** are short, 1.36–1.37 Å, but not significantly different from the corresponding bond lengths in helicenes.[17] In the saddle structure of **3a** there is thus no significant decrease in the length of the periphery. There are also no severe distortions of bond angles. All bond angles in the benzene units are within 4° of the ideal 120°. The dominant part of the strain in the molecule is rather due to torsions around the various bonds in the benzene units.

Anet[18] has found two different dynamical processes in the cyclooctatetraene system: ring inversion via a planar alternate transition state, and bond shift via a planar transition state with equal bond lengths. In **3**, an inversion of the molecule is ruled out. To investigate whether a bond shift process may be energetically feasible, although a planar conformation of the inner "cyclooctatetraene" ring cannot be adopted without introducing excessive strain, we calculated the energy of a saddle structure with two mirror planes through bonds of the benzene units. The energy minimized structure (**3b**) is shown in Fig. 6. This structure has a twisted inner "cyclooctatetraene" ring with equal bond lengths, which are approximately the average of the alternating bond lengths in **3a**. The energy of **3b** is only 4.0 kcal/mol higher than that of **3a**, indicating an energetically facile bond-shift process in [8]circulene. It should be noted that all eight benzene rings in **3b** are equivalent, while in the lowest energy geometry there are two sets of mutually nonequivalent benzene rings. The process **3a** $\rightleftharpoons$ **3b** exchanges the two nonequivalent sets of benzene rings in **3a**, resulting in a displacement of the benzene rings along a wave-like path in the [8]circulene system. As a consequence, the ^{1}H NMR spectrum of **3** is predicted to show only a single resonance signal due to the averaging process **3a** $\rightleftharpoons$ **3b**. Unfortunately, the ac-



3a

Fig. 5. Calculated minimum energy structure for [8]circulene (**3**). (Bond lengths in Å, bond angles and torsional angles in degrees.)



3b

Fig. 6. Calculated geometry for a transition state model of the bond shift process in [8]circulene. (Bond lengths in Å, bond angles and torsional angles in degrees.)

tivation energy for this interesting dynamical process is predicted to be too low, and thus the rate too fast on the NMR time scale to allow the process to be frozen out. It may be worthwhile to study whether substitution or other changes in the molecule can be devised, once a synthesis for it is found, to slow down the bond-shift process.

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