AM1 and PM3 treatment of Hückel type cyclacenes

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Semi-empirical molecular orbital treatment at the level of AM1 and PM3 has been performed on the Hückel type cyclacenes. The effect of peripheral circuits on the stabilities and the interfrontier energy gaps of cyclacenes has been investigated.

Cyclacenes which are a kind of macrocyclic belt-shaped conjugated molecules and structurally related to both carbon tubules (nanotubes or microtubules) and corannulenes have been quite popular recently among the theoretical as well as experimental researchers. Kivelson and Chapman have mentioned cyclacenes in connection with a model for conducting conjugated polyacenes. The increased attention towards cyclacenes is due to their interesting structures from the point of view of pure theoretical studies but is also related to the recent achievements in the design and synthesis of nanotubes, molecular wires and possible development of similar devices for future molecular electronics.

Cyclacenes are characterized by the presence of two types of π-systems embedded in their skeletons (Figure 1). These are the benzenoid rings constituting the main backbone of a cyclacene molecule and peripheral circuits (the top and bottom rings, see Figure 1) which become 4m or 4m+2 depending on the number of benzenoid rings (R) present.

It may be noted that the size of a peripheral circuit is equal to 2R. Various properties of the π-electron systems of cyclacenes have recently been examined. Of these the cryptoannulenic effects (that is the effect of 4m or 4m+2 type nature of the annulenic peripheral circuit of a cyclacene on certain properties of the system), the possibility of superaromatism in some members of the family and the total energy-effect of cyclic conjugation (the effect of various circuits on the so-called topological resonance energy, TREA) in cyclacenes are to be cited. The peripheral circuits have quite an important role on certain properties of cyclacenes such as, the angle of total π-electron energies \[ \theta = \arccos \left( \frac{E}{2e(n)^{\frac{1}{2}}} \right) \] where E, e and n are the total π-electron energy, the number of bonds and half of the number of atoms in the π-skeleton, respectively), latitudinal and longitudinal bond lengths, heats of formation values etc. which are collectively called cryptoannulenic effect.

The previous studies on cyclacenes are theoretical and involve either purely topological treatments or studies within the framework of the simple Hückel molecular orbital theory (eg. the angle of total π-electron energies) which is also highly related to topology of the system. In the present study the Hückel type cyclacenes have been investigated by using some advanced semi-empirical molecular orbital methods (AM1 and PM3) in order to find out whether these methods predict any cryptoannulenic effect on certain properties of cyclacenes, such as heats of formation values and interfrontier energies.

Computational Methods

In the present study, cyclacenes having 3-11 benzenoid rings (R) have been considered. The geometry optimizations of cyclacenes leading to global minima were achieved by using the
simulated annealing technique involving a long cooling period. For that purpose, on the initially geometry optimized structures, a simulation protocol involving, heating period of 0.1 pico second, 1 ps. simulation at 3000 K and cooling to 298 K within 200 ps. was applied under AMBER force field. The time step of 0.5 femtosecond was used for the molecular dynamics studies. Thereafter, AM1 and PM3 methods at the restricted Hartree-Fock (RHF) level and a conjugate gradient minimization, Polak-Ribiere, approach were applied to get the optimized geometries. All these calculations were carried out using the Hyperchem (release 4) package program.

Result and Discussion

The Geometries

The cyclacenes of present interest, possessing $D_{6h}$ symmetry in unoptimized geometry generally turns into systems having lower symmetry or unsymmetrical forms when subjected to AM1 or PM3 geometry optimization. Although, for $R=3$ the symmetry is lost, again higher order symmetrical structures (e.g. $D_{4h}$ for $R=4$) arise for $R=4-8$. $C_{2v}$ symmetry is valid for each distorted benzenoid rings present in cyclacenes having $R=4, 5$ and 7. In the case of $R=5$, different rings characterized by the same symmetry group ($C_{2v}$) lead to overall symmetry of $C_{2v}$. Whereas, the symmetrical arrangements of arenoid rings each belonging to $S_2 (C_i)$ symmetry group leads to $D_{6h}$ type overall symmetry for $R=6$ and 8.

Subject to PM3 geometry optimization, all the cyclacenes studied possessed certain symmetry groups all having $\sigma_h$ and $\sigma_v$ symmetry planes. For both AM1 and PM3 cases, the overall symmetry for $R=9-11$ are CS, C2 and CS, respectively.

The latitudinal bond lengths in all the cases fall in between $1.35-1.54\times10^{-10}$ m, whereas the longitudinal bond lengths lie in between $1.32-1.47\times10^{-10}$ m. It may be noted that for AM1 treatment a statistical study has been reported by Stewart about the reliability of the molecular geometries. For second row elements, the calculations of bond lengths are accurate to an average of approximately $1.0\times10^{-12}$ m, and for third row elements the error is about twice that of the second row elements. Bond angles are predicted correctly to within a few degrees for almost all organic molecules.

The Stabilities

Table I tabulates the total energy/R values

<table>
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<th>$R$</th>
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<th>PM3 method</th>
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</table>

*Energies in kJ/mol

Figure 2 displays the heats of formation ($\Delta H_f$) values of various cyclacenes as $R$ varies. Cyclacenes are characterized with endothermic heats of formation values. Moreover, the Figure 2 reveals that AM1 method estimates the heats of formation values of cyclacenes in such a way that alternatingly fluctuating values emerge (the first order cryptoannulenic effect). However, AM1 method predicts less endothermic structures whenever $4m+2$
type peripheral rings arise as compared to 4m type. On the other hand, PM3 method exhibits the regular cryptoannulenic effect of the first kind for R=4 onwards. The ΔH/R values based on calculations of both types, steadily decrease as R increases, indicating that no cryptoannulenic effect of second order exists on heats of formation values. It may be noted that for most organic molecules, AM1 calculations report heats of formation accurate to within a few kilo Joules per mol. Also, that PM3 is functionally similar to AM1 but uses an alternative parameter set. In many cases, PM3 method is an improvement over AM1.

The Frontier Molecular Orbital energies of cyclacenes

The frontier molecular orbital energies (FMO) of conjugated molecules play a very important role on various properties, especially on UV-Vis absorption bands. Table II displays the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energies of various cyclacenes whereas Figure 3 shows the variation of their interfrontier energy gap (ΔE; LUMO - HOMO energy difference) as a function of R.

Inspection of the Table II and the Figure 3 reveals that AM1 method predicts a cryptoannulenic effect on the interfrontier energy gaps of cyclacenes. For systems having 4m+2 type peripheral circuits, ΔE values within the homologous series exhibit a local maximum, consequently local minima happen whenever 4m type (for even values of R) peripheral rings arise (inverse cryptoannulenic effect). Since, the interfrontier energy gap narrows as the extended conjugation occurs, the results of AM1 type calculations imply that in cyclacenes of 4m+2 type a strong conjugation along the peripheral circuits should occur at the expense of the conjugation in benzenoid rings. The same type of interfrontier energy gap narrowing is expected by PM3 method. However, in each case (AM1 or PM3 type calculations) as the number of benzenoid rings increases, AE tends to decrease in general, although there exist local extremum points.

Actually for R<4, strain energies should distort the benzenoid rings causing unusual behaviour. Further, the delocalization within the benzenoid rings and on the peripheral circuit compete and the effects of the peripheral circuit show up only when the periphery is larger than 6 that is at R>3.

Conclusion

The present study reveals that in general AM1 and PM3 methods predict the similar results for cyclacenes of the Hückel type. In both cases, more stable systems should be obtained by increasing the size of the cyclacene. The geometrical constraints of cyclacenes at the global minima (which have been obtained by the simulated annealing technique followed by a conjugate-gradient geometry optimization) results in emergence of the first order cryptoannulenic effect on the heats of formation values and interfrontier energy gaps. Cyclacenes...
having 4m+2 type peripheral circuits are predicted to be relatively less endothermic. The influence of the peripheral circuits is also evident on the interfrontier energy gaps in such a way that cyclacenes with even number of benzenoid rings should absorb at longer wavelengths as compared to homologous systems having odd number of benzenoid rings.

References
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