

## Stabilizing cyclacene molecules

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It is shown that introducing a single methylene group into each trannulene ring of a cyclacene molecule compels the formation of a non-bonded molecular orbital, NBMO, in the ring. The union of both trannulenes conforms to a first order perturbation change in the total energy according to Dewar's PMO theory. The NBMO coefficients can be calculated then according to Coulson's pairing theorem. The PMO calculated new HOMO-LUMO energies of the cyclacene indicate the relative stabilization of the singlet over the triplet state of the cyclacene. The results are confirmed by the DFT calculation of differently substituted bis, methylene cyclacenes. The same arguments apply to the introduction of 2 (donor + acceptor) substituents, e.g.  $\text{NH}_2$  +  $\text{BH}_2$  groups. Stabilizing the singlet state should facilitate the synthesis of the cyclacene.

### Introduction

Theoretical and quantum mechanical studies of cyclacenes (Figure 1) yielded interesting magneto-electrical properties for this class of molecules and suggested their possible future application in different technological fields.<sup>1-3</sup>

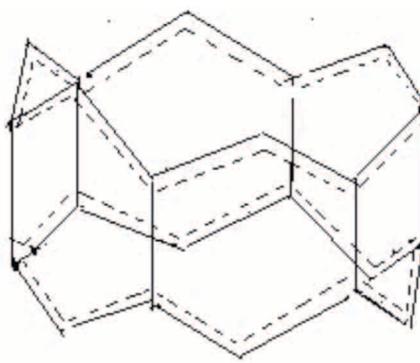


Figure 1. Cyclacene-6.

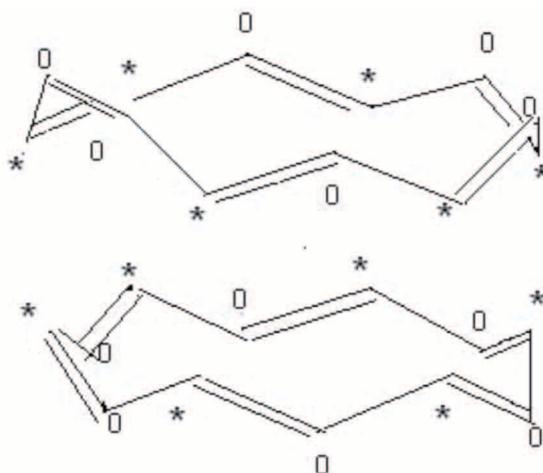
Attempts to synthesize cyclacenes remained unsuccessful obviously due to the nonstability of the endproducts.<sup>4,5</sup> Gleiter et al. pointed out that the cause of instability is the small energy difference between the singlet and triplet states of these molecules ( $\Delta E_{S-T}$ ).<sup>6</sup> It was possible for the same group to synthesize topologically different cyclacenes, composed of 4- and 8- membered rings (3xCOT-c.But), stabilized through binding to Co-cyclopentadienyl (CoCp) groups.<sup>7</sup> Applying a methylation reaction to C<sub>60</sub> fullerene, Nakamura et al. synthesized 6-cyclacene, but embedded in the fullerene cage.<sup>8</sup> Being more appropriate to future applications than the restrained cyclacenes, the free ring molecules are worthy of formal and a priori study. In the present work we suggest a method for stabilizing cyclacenes, such that their singlet- triplet energy differences are big enough to stabilize the singlet ground states, making their chemical synthesis possible.

## Methods of treatment

Semi-quantitative description of the energetically highest MOs of cyclacenes is done applying Dewar's first order perturbation molecular orbital (PMO) method.<sup>9</sup> The basis for the perturbation treatment is the  $\pi$ - nonbonded molecular orbitals (NBMO) of conjugated odd alternant hydrocarbons as defined according to Coulson's pairing theorem.<sup>10</sup> The correct values of the NBMO coefficients of the hydrocarbon are determined by the symmetry and topology of the molecule.<sup>9</sup> As for the quantitative evaluation of the energies of the cyclacenes, the Gaussian03 program of Pople et al. was applied.<sup>11</sup> The method of calculation was the unrestricted B3LYP- density-functional theory (DFT) method.<sup>12</sup> This type of treatment should distinguish correctly among electronic states of different multiplicities.

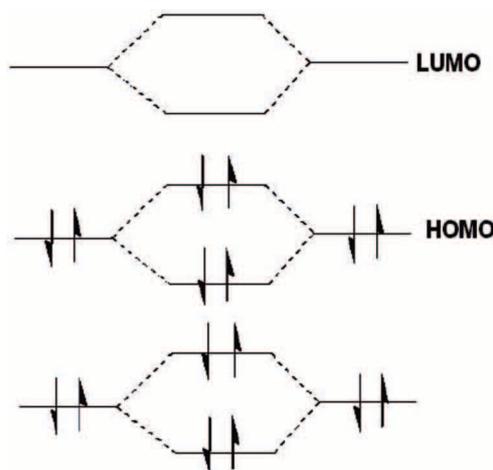
## Results and discussion

As was shown previously cyclacenes may be considered as being formed of 2 very similar conjugated rings, the so-called trannulenes.<sup>1</sup> Considering their constitutional and topological similarities (Figure 2), both trannulenes should possess 2 very similar sets of molecular orbitals.



**Figure 2.** The 2 alternate trannulenes from which the cyclacene-6 is formed.

Since the number of C atoms in such trannulenes, being part of the normal cyclacenes, is always even, they must be alternate in the sense of Coulson's pairing theorem.<sup>10</sup> This statement is valid for both  $2k$  and  $2k + 1$  cyclacenes, where  $k$  is the number of the 6-membered rings in the molecule. Accordingly, such trannulenes should have an even number of MOs that are symmetrically displaced relative to a central energy level, i.e. the  $\alpha$  level in the term of the Hückel MO theory. However, no non-bonded MO (NBMO) exists for such ring hydrocarbons. Connection of the 2 trannulenes to each other via 1 or more bonds causes a symmetric split in the energy levels for each 2 similar and energetically degenerate MOs on both trannulenes (Scheme 1).



Scheme 1.

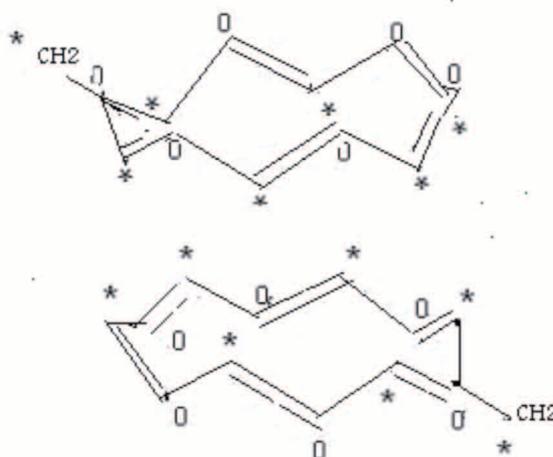
Since all the bonding MOs of both trannulenes are doubly occupied with electrons, all the newly formed MOs, due to the bond formation between the 2 trannulenes, are doubly occupied as well, and the netto first order change in energy is nil. The change in energy is of a second order perturbation term. It causes the formation of essential single bonds between the trannulenes. This is seen in the calculated longer bonds being formed, as compared with the C-C bonds of the trannulene rings in cyclacenes.<sup>1,2</sup> Repeating the DFT calculations for various cyclacenes and applying a bigger basis (6-311++G) we could confirm the previously cited results.<sup>1,2</sup>

As a consequence of the equal displacements of MOs from a central energy level, a fact inherent within the Coulson's pairing theorem,<sup>10</sup> and of the equivalent splitting in the MO energy levels (Scheme 1), the difference between the newly formed HOMO and LUMO energy levels is expected to be small. This small HOMO-LUMO energy difference compels a small energy gap between the singlet and the triplet ground states, which might be viewed in the formerly reported  $\Delta E_{S-T}$  values. In fact repeating the DFT calculations for various cyclacenes and applying a bigger basis (6-311++G), even smaller  $\Delta E_{S-T}$  values were calculated (Table 1).

The small values of  $\Delta E_{S-T}$ , which apply even for the odd numbered cyclacene-7, seem to be the cause of chemical instability of cyclacenes.<sup>6</sup> To increase the  $\Delta E_{S-T}$  energy difference one should perturb the MOs of both trannulenes through introduction of a new, singly occupied moiety to each ring and thus form a new odd-alternate ring system that possesses an NBMO according to the pairing theorem (Scheme 2).

**Table 1.** DFT calculated total energy values for the singlet and triplet ground states of various cyclacene molecules applying the 6-311++G basis. Cn refers to the cyclacene molecules with different ring size.<sup>6</sup>

Cyclacene	Singlet (Har.)	Triplet (Har.)	ES – ET (kcal/mol)
B6	-921.6429753	-921.6418855	-0.67
B7	-1075.3407725	-1075.3338220	-4.36
B8	-1228.8228765	-1228.8218819	-0.62
B10	-1536.4414268	-1536.4365569	-3.05
B12	-1843.7992189	-1843.7936279	-3.54
6xCOT-But	-1843.3198032	-1843.3130573	-4.23

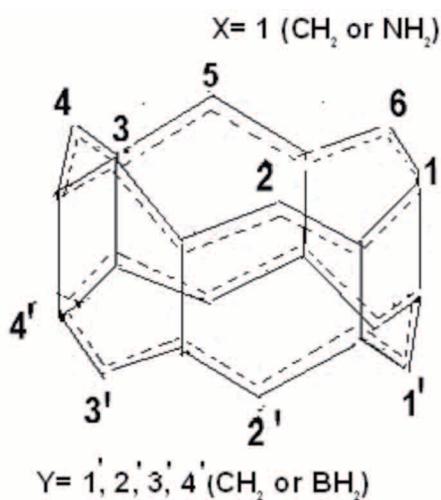
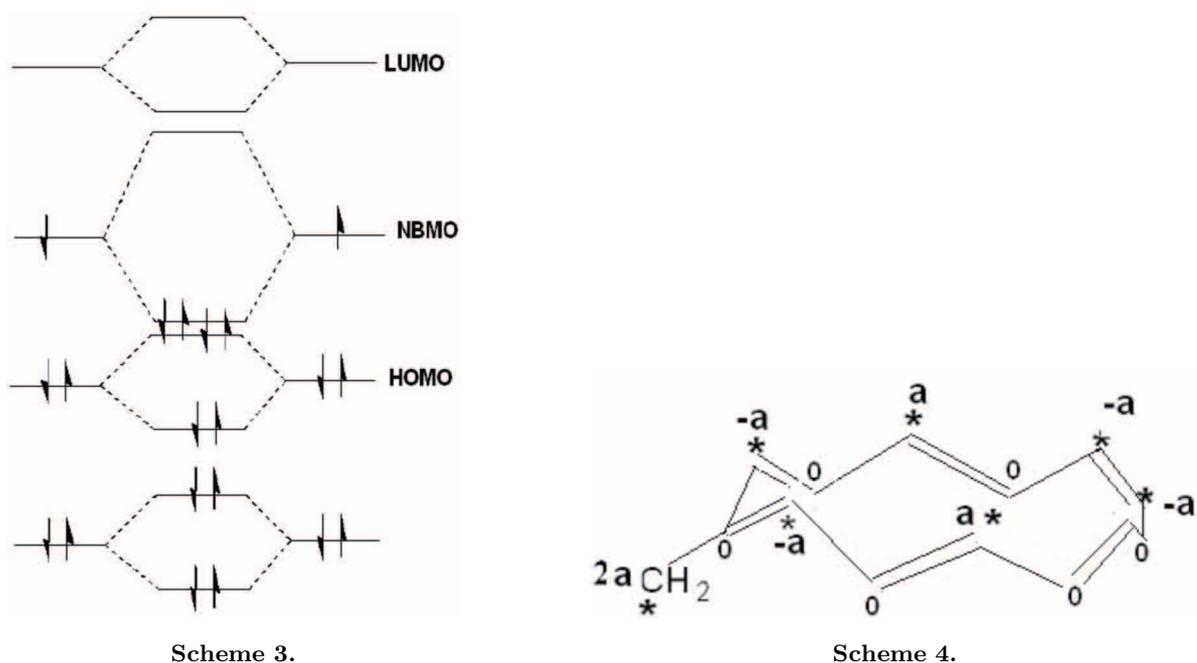
**Scheme 2.**

According to Dewar's perturbation molecular orbital theory (PMO theory) the 2 odd alternant hydrocarbon rings, i.e. the perturbed trannulenes, may interact with each other forming 1 or more connection bonds, in the form of 1- or multi-center first order interactions.<sup>9</sup> Only 1 MO of the equally displaced NBMOs of the 2 trannulenes is occupied by the 2 electrons of the perturbed trannulenes; the other MO remains empty (Scheme 3). It can be shown that the splitting in NBMO energy levels is always bigger than that in other MOs of the trannulene ring. This is due to the fact that the NBMOs are localized at the starred, C\*, atoms of the alternating radical and have values of zero at the unstarred, C<sup>o</sup>, atoms.<sup>9</sup> Due to the smaller number of C\* atoms participating in the formation of the NBMO, and the fact that almost all C atoms participate in the formation of other MOs of the hydrocarbon radical, the calculated MO coefficients of the NBMO are usually bigger in magnitude than those of the remaining MOs (Scheme 4).

This difference in MO coefficient magnitudes causes the bigger splitting in MO energy levels, considering the fact that the 1st order as well as the 2nd order interactions are always functions of a, b, and  $\beta$ , where a and b are the coefficients at the 2 atoms of interaction and  $\beta$  is the Hückel resonance parameter.

It is easily seen then that the energy required to excite an electron from the new doubly occupied MO to any unoccupied MO of the formed cyclacene should be bigger than that in normal and unperturbed cyclacene.

To examine this we carried out DFT (6-311++G) calculations for the following perturbed cyclacene-6 in both their singlet and triplet ground states (Figure 3). The results are compiled in Table 2.



**Figure 3.** Molecular structures of the calculated substituted cyclacene-6.

Obviously, the same consideration applies for 2 or more substituents, 1 with a lone pair of electrons (such as NH<sub>2</sub>) and the other with an electron deficient heteroatom (such as BH<sub>2</sub>). The 2 lone pair electrons occupy the newly generated low MO, leaving the other, energetically higher MO empty. A similar consideration then follows as with the 2 CH<sub>2</sub> radical substituents. Table 2 includes the calculated  $\Delta E_{S-T}$  values for such NH<sub>2</sub>, BH<sub>2</sub> substituted 6-cyclacenes.

**Table 2.** Calculated singlet–triplet energy difference ( $\Delta E_{S-T}$ ) for substituted cyclacene-6 derivatives applying the density functional theory method with the 6-311++G basis. The calculated  $\Delta E_{S-T}$  value for the unsubstituted cyclacene-6 is 0.6 kcal/mol applying the same method.

Substituent	Singlet E(Hart)	Triplet E(Hart)	$\Delta E_{S-T}$ (kcal/mol)
1,CH <sub>2</sub> ; 1',CH <sub>2</sub>	-998.8835811	-998.8727703	6.70
1,CH <sub>2</sub> ; 2',CH <sub>2</sub>	-998.880345	-998.8467873	20.80
1,CH <sub>2</sub> ; 3',CH <sub>2</sub>	-998.8883824	-998.8284019	37.19
1,CH <sub>2</sub> ; 4',CH <sub>2</sub>	-998.8919348	-998.8693728	14.16
1,NH <sub>2</sub> ; 1',BH <sub>2</sub>	-1002.241215	-1002.1706308	43.76

## Conclusion

It is predicted that introducing a 1 electron CH<sub>2</sub> moiety to each of the 2 ‘trannulene’ rings of the cyclacene molecules causes the stabilization of the singlet ground state relative to the lowest triplet state of the molecules. The same conclusion applies for the introduction of an electron deficient group (BH<sub>2</sub>) along with another electron rich group (NH<sub>2</sub>). The prediction is based on a first order perturbation molecular orbital (PMO) treatment as well as on an unrestricted B3LYP/DFT calculation with a 6-311++G basis. Stabilizing the singlet ground state of the cyclacenes should facilitate their chemical synthesis.

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