

# The effect of boron substitution on cyclacenes

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## Abstract

AM1-type semiempirical molecular orbital treatment was performed on the Hückel-type cyclacenes having certain number of boron atoms at the peri-positions and at the fusion sites of the arenoid rings. The effect of boron atoms is generally destabilizing in all the cases as compared to their unsubstituted cyclacene counterparts. The AM1 results revealed that certain properties of the boron-substituted cyclacenes are affected not only by the number of arenoid rings they have but also by the nature of their peripheral circuits. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Cyclacenes (Fig. 1) constitute a topologically interesting system because the planar  $\pi$ -skeleton of the parent acenes are bent in the cyclacene structure. The bent structure should somewhat distort the  $\pi$ -conjugation depending on the size of the system considered.

Recently, many of the theoretical and experimental chemists have been keen on investigating cyclacenes [1–17] to get an insight into the structural properties of these interesting systems or to find out some synthetic routes to obtain hitherto unknown compounds.

Structurally, cyclacenes are a special subclass of corannulenes (Fig. 1) and have identical peripheral circuits. Cyclacenes possess two types of  $\pi$ -systems embedded in their skeletons: (1) benzenoid rings

constituting the main backbone of the molecule; (2) the peripheral rings (the top and bottom), which become either  $4m$ - or  $4m + 2$ -type depending on the number of benzenoid rings ( $R$ ) present. Some theoretical studies have revealed that the peripheral circuits ( $4m$ - or  $4m + 2$ -type) of cyclacenes determine some of their properties [15,16,18,19]. The effect is called “cryptoannulenic effect” in general due to the obvious analogy to annulenes.

In addition to the classification based on the types of the peripheral circuits, cyclacenes can be further classified as the Hückel-type and the Möbius-type [16]. The main difference between these types of cyclacenes is the number of phase dislocations ( $k$ ) on the basis molecular orbitals [20] i.e. the Hückel-type possesses *even* values of  $k$  (including zero) whereas the Möbius-type is characterized by *odd* number of phase dislocations.

On the other hand, boron atom ( $1s^2 2s^2 2p^1$ ) may form aromatic ring compounds, hence it is unique in the sub-group III of the periodic table [21]. Boron in these structures undergoes trigonal ( $sp^2$ ) hybridization

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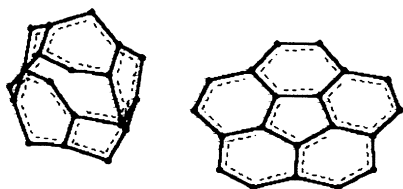


Fig. 1. Structures of a cyclacene and a corannulene having the same number of benzenoid rings.

and uses the third 2p orbital to form  $\pi$ -bond, which may become part of a non-localized orbital system of a six-membered ring, e.g. borazine and boron nitride.

In the present study, boron substituted cyclacenes having 3–8 arenoid rings ( $R$ ) are considered for AM1-type semiempirical molecular orbital calculations. Boron substitutions at the peri-positions as well as at the certain fusion sites of the ring system are considered in the following two positions: (i) only two of the peri-positions of an arenoid ring occupied by boron atoms and (ii) all the peri-positions of the system occupied by boron. Boron substitutions at the fusion points of an arenoid ring are considered also in two groups: (i) two borons are on the same peripheral circuit and (ii) two boron atoms are on the different peripheral circuits and opposite sites of an arenoid ring. The case with borons on adjacent fusion points

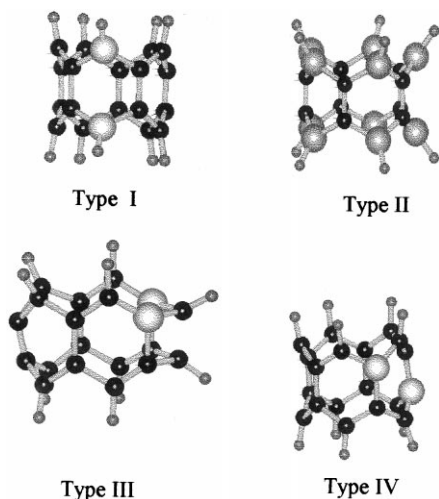


Fig. 2. The representative structures for the boron substituted cyclacenes (Types I–IV,  $R = 5$ ; Carbon, boron and hydrogens are black, big grey and small grey balls, respectively).

Table 1

The symmetries of the structures considered

Type	$R$					
	3	4	5	6	7	8
I	$C_{2v}$	$C_{2v}$	$C_{2v}$	$C_{2v}$	$C_{2v}$	$C_{2v}$
II	$D_{3h}$	$D_{4h}$	$D_{5h}$	$D_{3d}$	$C_1$	$C_{2h}$
III	$C_s$	$C_s$	$C_s$	$C_1$	$C_1$	$C_1$
IV	$C_2$	$C_1$	$C_2$	$C_2$	$C_2$	$C_2$

is not considered because B–B bonds are experimentally rare [21].

## 2. Method

In the present treatise, the geometry optimizations of all the structures leading to energy minima were achieved by using AM1 (Austin model 1) self-consistent field molecular orbital (SCF MO) [22] method at the restricted Hartree–Fock (RHF) level. The optimizations were obtained by the application of a conjugate gradient method, Polak–Ribiere (convergence limit of  $4.18 \times 10^{-4}$  kJ/mol (0.0001 kcal/mol) and RMS gradient of  $4.18 \times 10^7$  kJ/(mol) (0.001 kcal/(Å mol))). All these calculations were performed by using the HyperChem (release 5.1) package program.

## 3. Results and discussion

Since, in the  $sp^2$ -hybridized state, boron atom possesses an empty orbital,  $\pi$ -skeleton of boron-substituted cyclacenes have odd (or even) number of electrons when the number of boron atoms in the system is odd (or even). Thus, the above systems (Fig. 2) having even number of borons are deliberately chosen to carry out AM1-type calculations at the level of RHF approach for the singlet states.

Table 1 shows the molecular point groups of the structures considered. As seen in the table, all the Type I systems are characterized by the same molecular point group. Whereas, for the other systems, the symmetries are probably dependent on certain fine topological factors, thus they should have been affected by the geometry optimizations.

Table 2  
Various energies (in kJ/mol) of the boron substituted cyclacenes

Energy	<i>R</i>					
	3	4	5	6	7	8
Type I						
Total	– 143457	– 195634	– 247904	– 300084	– 352212	– 404308
Binding	– 7992	– 11341	– 14783	– 18135	– 21435	– 24703
Heats of formation	1601	1548	1402	1347	1343	1370
Type II						
Total	– 121186	– 162017	– 202757	– 242884	– 283462	– 324718
Binding	– 7758	– 10780	– 13710	– 16028	– 18797	– 22249
Heats of formation	1246	1227	1297	1981	2214	1768
Type III						
Total	– 143409	– 195469	– 247610	– 299742	– 351852	– 403948
Binding	– 7944	– 11176	– 14489	– 17793	– 21075	– 24343
Heats of formation	1650	1713	1697	1689	1702	1730
Type IV						
Total	– 143269	– 195354	– 247549	– 299749	– 351771	– 403954
Binding	– 7804	– 11061	– 14428	– 17800	– 20994	– 24350
Heats of formation	1790	1829	1757	1681	1783	1724

### 3.1. Stabilities

Table 2 shows various energies of the systems considered. The total and the binding energies become more and more negative as the size of the structure increases in each group. An increase in the number of boron atoms (Type I → Type II) causes the total and the binding energies to be less negative for the structures having the same number of arenoid rings, which is the indication of the destabilizing effect of the boron atoms. All these systems are electron-deficient  $\pi$ -structures so that Types I, III and IV are two-electron deficient and Type II is  $2R$ -electron-deficient systems as compared to the unsubstituted cyclacenes.

Table 2 indicates that the boron substitution at the

fusion sites is more destabilizing as compared to the peri-substituted case having the same numbers of boron atoms (Types III, IV and I, respectively) and arenoid rings ( $R$ ). However, Type III structures, which have two borons along the same peripheral circuit, are expected to be more stable than their isomeric set in which borons occupy different peripheral circuits (Type IV) with the exception of the  $R = 8$  case.

On the other hand, comparison of the data in Tables 2 and 3 shows unsubstituted cyclacenes to be more stable than the presently considered boron compounds.

As for the heats of formation ( $\Delta H_f$ ), in the case of the Hückel-type unsubstituted cyclacenes, as  $R$  increases  $\Delta H_f$  values regularly fluctuate, resulting in

Table 3  
Various energies (in kJ/mol) of unsubstituted cyclacenes

Energy	<i>R</i>					
	3	4	5	6	7	8
Total	– 154548	– 206638	– 259049	– 310778	– 363347	– 519509
Binding	– 8064	– 11326	– 14910	– 17810	– 21552	– 31230
Heats of formation	1824	1858	1570	1605	1520	1545

Table 4

The frontier molecular orbital energies for the structures considered. (Energies of the order of  $10^{-19}$  J. The first and the second entries for each  $R$  are the LUMO and HOMO energies, respectively.)

$R$	Type			
	I	II	III	IV
3	-2.68	-1.73	-2.09	-2.58
	-14.78	-14.36	-13.32	-13.82
4	-2.36	-1.52	-2.95	-2.26
	-12.34	-13.97	-12.75	-11.66
5	-1.47	-1.63	-2.49	-3.45
	-11.89	-14.27	-13.77	-11.26
6	-2.26	-6.16	-3.14	-2.99
	-11.81	-9.46	-11.40	-11.45
7	-2.43	-6.97	-3.59	-4.48
	-11.48	-8.81	-10.96	-9.97
8	-2.92	-2.04	-3.49	-3.39
	-11.42	-13.94	-11.07	-11.28

local maxima and minima [15]. This is because of the overwhelming effect of the peripheral circuits (cryptoannulenic effect [2]), which can be dealt as a special type of polyene system having mode 0 or 2 (modulo 4) depending on whether the peripheral circuit is of the type  $4m$  (antiaromatic) or  $4m + 2$  (aromatic) in character. The most favorable (the least endothermic) heat of formation value occurs for  $R = 7$  ( $4m + 2$ -type) case [15]. Note that the number of the peripheral carbon atoms is  $2R$ . A simi-

lar behavior is exhibited by Type II, III and IV structures whereas Type I structures are characterized by  $\Delta H_f$  values declining in magnitude up to the  $R = 7$  case, after which  $\Delta H_f$  increases for  $R = 8$ .

Within the limitations of the AM1 treatment, the  $R$ -dependent fluctuations in  $\Delta H_f$  values are more clearly exhibited by Type III and -IV structures in which boron atoms occupy certain fusion sites. However, this behavior is not a true cryptoannulenic effect because in some cases less endothermic structure coincides with  $4m$ -type peripheral circuit structure (see Table 2,  $R = 6$  case for Types III and IV). Actually, due to the presence of boron atoms, each peripheral circuit in Type I and IV structures possesses  $2R - 1$  (odd) electrons whereas the peripheral circuits in Type II structure have  $R$  electrons and Type III systems, which have nonidentical peripheral circuits, are characterized by  $2R - 2$  and  $2R$  electron-containing peripheral circuits. Thus, in the last case, the number of electrons in the unsubstituted and substituted peripheral circuits should compete with each other, one being aromatic while the other antiaromatic or vice versa depending on  $R$ . The overall effect of both of the peripheral circuits and the arenoid rings should dictate the calculated values in Table 2.

On the other hand, keeping the  $R$  constant, the electronic energies for the structures considered become less negative in the order of (algebraic values): Type I < III < IV < II., whereas core-core repulsion energies follow the same sequence but being less positive.

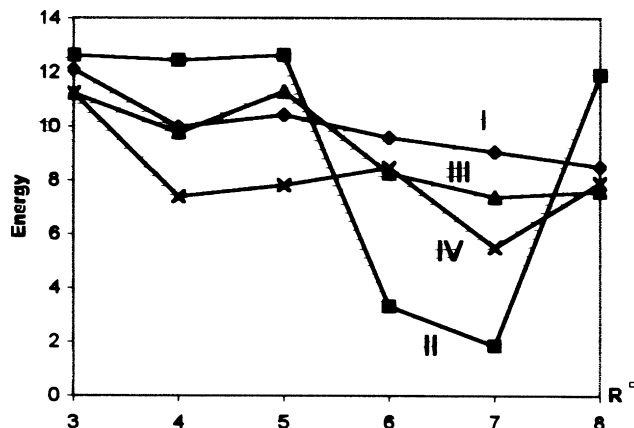


Fig. 3. The interfrontier molecular orbital energy gap vs.  $R$  graph. Energies are on the order of  $10^{-19}$  J.

Table 5  
The dipole moments (of the order of  $10^{-30}$  C.M.) of the structures considered

Type	<i>R</i>					
	3	4	5	6	7	8
I	5.46	1.91	2.22	0.97	1.08	0.37
II	0.00	0.00	0.00	0.00	2.60	0.00
III	6.05	8.65	0.60	7.34	5.78	6.68
IV	5.96	4.33	0.51	5.57	15.03	4.76

### 3.2. Interfrontier molecular orbital energies

Table 4 and Fig. 3 show the frontier molecular orbital energies (FMO; HOMO and LUMO energies) and the interfrontier molecular orbital energy gaps ( $\Delta E$ ; LUMO–HOMO energy difference), respectively. In Type I series of compounds, the HOMO energy increases as *R* increases, whereas the LUMO energy first increases and then decreases from the *R* = 6 case onwards. In the case of Type II structures, both the HOMO and the LUMO energies fluctuate as *R* varies but the fluctuations in HOMO energies are more regular. Boron in  $sp^2$ -hybridized state is electron withdrawing, so does it in Type I and II structures. However, in Type I structures, which possess only two boron atoms, the effect of boron becomes less influential as *R* increases. Thus, the net effect of increase in *R* is the increased extended conjugation, which generally raises up the HOMO level and lowers the LUMO level in the direction of a narrowed interfrontier molecular orbital energy gap [23]. This is generally the case for Type I structures. In the case of Type II systems, due to their structural requirements, increase of *R* is parallel to increase in the number of borons, thus the arenoid rings extending the conjugation should not be the main factor on FMO energies.

In the case of Type III structures, both the HOMO and the LUMO energies are subject to fluctuations as *R* varies. In the case of unsubstituted cyclacenes, the HOMO energies of the systems having odd values of *R* (thus  $4m + 2$ -type peripheral circuits) stand for local minima within the homologous series [15]. Whereas, the local minima for the LUMO energies occur for systems characterized with even values of *R* (thus  $4m$ -type peripheral circuits) [15]. In the present case, Type III structures having nonidentical peripheral circuits are expected to behave, at least

partly, like unsubstituted cyclacenes if the peripheral circuits have the predominant role on FMO energies. AM1 calculations result in this direction and up to the *R* = 7 case, Type III structures mimic unsubstituted cyclacenes. The behavior of Type IV structures is irregular compared to unsubstituted cyclacenes implying that an analysis of the fact based on solely one factor such as the electronic effects due to the peripheral circuits is not appropriate. Probably, the fine topological factors including electronic and structural contributors are operative.

### 3.3. Dipole moments

Table 5 shows the dipole moments of the structures considered presently. In Type I systems, the dipole moments decrease as *R* increases, which implies that the influence of boron in the topology of this class of compounds decreases with the increasing number of arenoid rings. On the other hand, Type II structures generally have no dipole moments due to the high symmetry they have. Type III and IV structures have appreciable values of dipole moments. Type III compounds, interestingly enough have high dipole moments whenever *R* is even ( $4m$ -type peripheral circuits) and comparatively low values for odd values of *R* ( $4m + 2$ -type peripheral circuits) in a regular way. Fig. 4 shows the three-dimensional charge densities for structures I–IV having six arenoid rings. The direction of the dipole moments in Type I structures is from boron having arenoid ring to the center of the system. In Type II, it is from one of the arenoid rings to the center of the cyclacene system. Whereas, in Type III (the direction is clearly seen in Fig. 4) and IV it is from the ring, opposite to the boron-substituted ring to the boron-substituted ring.

## 4. Conclusion

The results of AM1-type semiempirical treatment of the presently considered boron-substituted cyclacenes reveals that they are less stable than the parent cyclacenes. The heats of formation values in some cases are more endothermic and in some cases less endothermic as compared to the cyclacenes having the same *R* value. On the other hand, both the frontier molecular orbital energies and the inter-frontier molecular orbital energy gaps, for all types of

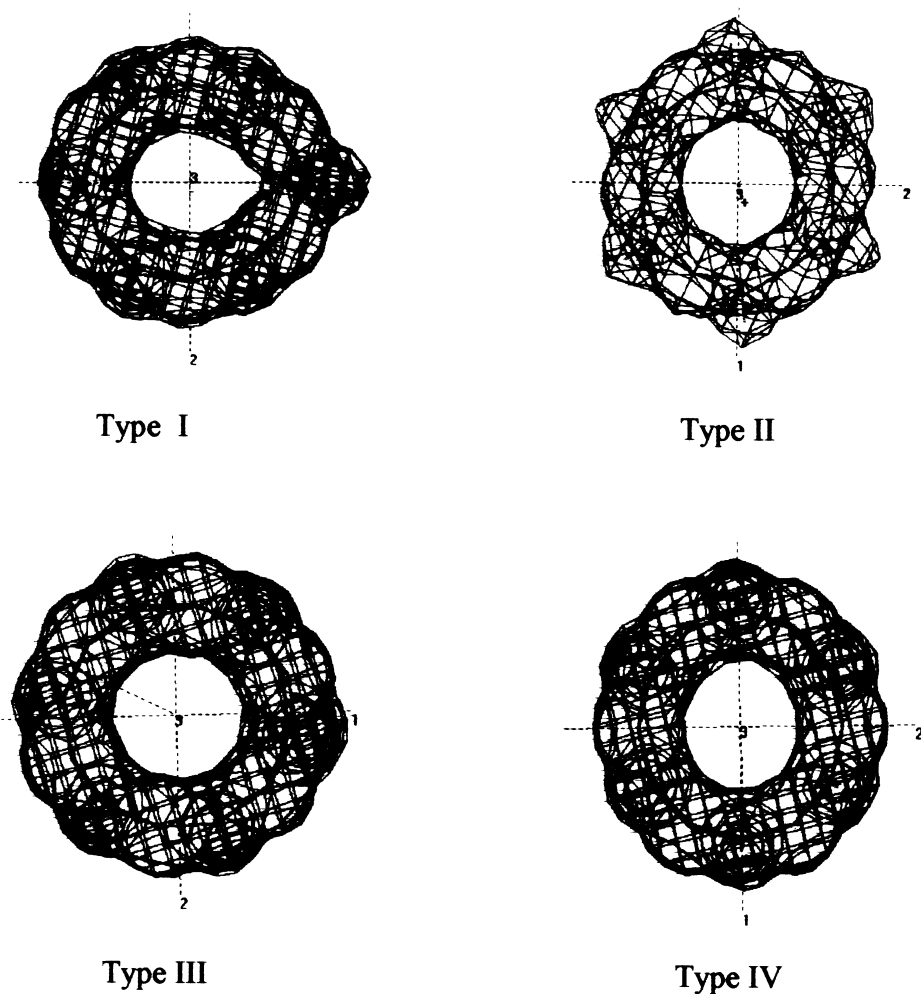


Fig. 4. Three-dimensional charge density plots for the structures having  $R = 6$ . Vertical dashed lines stand for the axes of inertia.

structures, do not exhibit any smooth behavior depending on  $R$ .

## References

- [1] I. Agranat, B.A. Hess Jr., L.J. Schaad, *Pure Appl. Chem.* 52 (1980) 1399.
- [2] J.L. Bergan, B.N. Cyvin, S.J. Cyvin, *Acta Chim. Hung.* 124 (1987) 299.
- [3] G. Ege, H. Vogler, *Theor. Chim. Acta* 35 (1974) 189.
- [4] E. Heilbronner, *Helv. Chim. Acta* 37 (1954) 921.
- [5] G. Derflinger, H. Sofer, *Monatsh. Chem.* 99 (1968) 1866.
- [6] S. Kivelson, O.L. Chapman, *Phys. Rev.* 28 (1983) 7236.
- [7] F.J. Zhang, S.J. Cyvin, B.N. Cyvin, *Monatsh. Chem.* 121 (1990) 421.
- [8] P.R. Ashton, N.S. Isaacs, F.H. Kohnke, A.M.Z. Slawin, C.M. Spencer, J.F. Stoddart, D.J. Williams, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 966.
- [9] R.W. Alder, R.B. Sessions, *J. Chem. Soc., Perkin Trans. 2* (1985) 1849.
- [10] R.O. Angus Jr., R.P. Johnson, *J. Org. Chem.* 53 (1988) 314.
- [11] L. Türker, *Polycyclic Aromatic Comps* 4 (1994) 191.
- [12] L. Türker, *Polycyclic Aromatic Comps* 8 (1996) 67.
- [13] L. Türker, *Polycyclic Aromatic Comps* 4 (1995) 231.
- [14] L. Türker, *Polycyclic Aromatic Comps* 8 (1996) 203.
- [15] L. Türker, *J. of, Mol. Struct.* 407 (1997) 217.
- [16] L. Türker, *J. Mol. Struct. (Theochem)* 454 (1998) 83.
- [17] I. Gutman, P.U. Biederman, V.I. Petrovic', I. Agranat, *Polycyclic Aromatic Comps* 8 (1996) 189.
- [18] L. Türker, *Indian J. Chem.* 37B (1998) 230.
- [19] L. Türker, *Polycyclic Aromatic Comps* 12 (1997) 213.

- [20] A. Groavac, I. Gutman, N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules*, Springer, Berlin, 1977.
- [21] P.J. Durant, B. Durant, *Introduction to Advanced Inorganic Chemistry*, Longman, London, 1970.
- [22] M.J.S. Dewar, E.G. Zoebisch, E.F. Healey, J.J.P. Stewart, *J. Am. Chem. Soc.* 107 (1985) 3902.
- [23] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London, 1976.