

# Partial structure analysis of conjugated systems I

## Benzene character

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(Received August 5, revised September 24/Accepted September 25, 1985)

A new method for analysing the partial structure of conjugated systems is proposed. The present method is applied to the most important partial structure, benzene, which is closely related to aromaticity. The calculated results are in accord with the previously proposed indices of aromaticity.

**Key words:** Benzene character — Aromaticity — Benzenoid hydrocarbon

### 1. Introduction

Aromaticity is the most beautiful concept in organic chemistry. This concept is originally related to so called Hückel's  $4n + 2$  rule, in which benzene is the first member of aromatic hydrocarbons. The origin of extra stabilization has been paid a special attention to organic chemists. Molecular orbital (MO) theory is well recognized as the most useful method for the investigation of aromaticity. However MO theory usually calculates the total energy of a molecule. From the chemical point of view, it might be very useful to obtain "the energy of the partial structure of a given molecule". Hexagon is one of the important partial structure in aromatic compounds. There are two kinds of hexagon in anthracene and five kinds of that in 3,4-benzopyrene. Benzene has been regarded as a key molecule for aromatic compounds. It might, therefore, be interesting to consider the energy difference between benzene and hexagons in a molecule. Many methods have been proposed [1-9] to estimate "benzene character of hexagon" and the topological dependency is discussed in detail [7]. In this paper we propose a new method which calculates the energy of the partial structure in a given conjugated molecule by introducing a model hamiltonian. We apply the present method to the analysis of benzene character in various alternant hydrocarbons. The following discussions

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will be restricted within the framework of Hückel theory, although our theory may be applicable for any MO method.

## 2. Method

We introduce a following model hamiltonian,

$$h_e = h - \sum_i \varepsilon_i' \beta |i\rangle \langle i| \quad (1)$$

where  $h$  represents Hückel hamiltonian, and  $|i\rangle$  and  $\varepsilon_i'$  denote the  $i$ th molecular orbital and the orbital energy of reference molecule, respectively. Reference molecule means an isolated molecule which has the same molecular  $\pi$ -electronic skeleton as the partial structure of interest. We conveniently use the following  $\beta$  unit.

$$\varepsilon_i = (E_i - \alpha) / \beta. \quad (2)$$

For instance if we take the hexagon as a partial structure, benzene is taken to be a reference molecule. The second term of Eq. (1) represents an energy weighted projection operator, therefore it works to remove the MOs of reference molecule by the orthogonality condition. If the summation of  $i$  runs over the bonding orbitals of reference molecule, we call this model hamiltonian as bonding orbitals extracted hamiltonian  $h_b$  (abbreviated as bonding extracted hamiltonian). Similarly if the summation of  $i$  runs over the antibonding orbitals of reference molecule, we call it as antibonding orbitals extracted hamiltonian  $h_a$  (abbreviated as antibonding extracted hamiltonian).

In order to clarify the physical meaning of  $h_b$  we perform a following unitary transformation of basis set,

$$\begin{array}{ccc} \{\chi_\mu\} & \xrightarrow{I} & \{\chi_\mu, \phi_i^r\} \\ & \searrow \text{II} & \swarrow \text{III} \\ & \{\psi_i\} & \end{array}$$

where  $\{\chi_\mu\}$  represents the AO basis set and  $\{\chi_\mu, \phi_i^r\}$  represents AO plus MO basis set, in which MO's of reference molecule  $\phi_i^r$  are used as MO basis set.  $\{\psi_i\}$  represents MO's of a given molecule. For the transformations I, II and III, there exist following unitary matrices  $C_I$ ,  $C_{II}$  and  $C_{III}$ , respectively.

$$\mathbb{H}_{\text{AO+MO}} = C_I \mathbb{H}_{\text{AO}} C_I^\dagger \quad (3)$$

$$\mathbb{H}_{\text{diag}} = C_{II} \mathbb{H}_{\text{AO}} C_{II}^\dagger \quad (4)$$

$$\mathbb{H}_{\text{diag}} = C_{III} \mathbb{H}_{\text{AO+MO}} C_{III}^\dagger \quad (5)$$

$$C_{II} = C_{III} C_I \quad (6)$$

where  $\mathbb{H}_{\text{AO}}$ ,  $\mathbb{H}_{\text{AO+MO}}$  and  $\mathbb{H}_{\text{diag}}$  denote the representation matrices of a hamiltonian using  $\{\chi_\mu\}$ ,  $\{\chi_\mu, \phi_i^r\}$  and  $\{\psi_i\}$ , respectively. Therefore the transformation I transforms  $\{\chi_\mu\}$  into  $\{\chi_\mu, \phi_i^r\}$ . On the other hand the transformations II and III

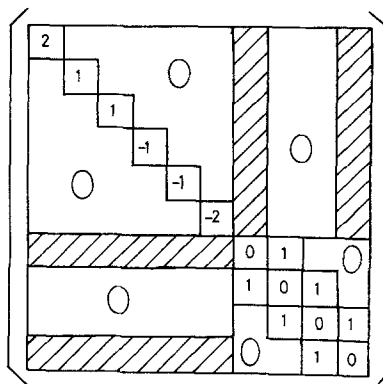


Fig. 1. Representation matrix associated with  $h$  for naphthalene using AO plus MO basis set. Shaded part has non-zero matrix elements

diagonalize a hamiltonian, thus  $H_{diag}$  is a diagonal matrix. As an example representation matrix  $H_{AO+MO}$  of  $h$  for naphthalene is shown in Fig. 1, where we use the MO of benzene for the left-hand side hexagon as the MO basis set (Fig. 2). It is noted that the diagonal terms of  $6 \times 6$  sub matrix have orbital energies of benzene in AO plus MO representation. The representation matrix  $H_{AO+MO}$  of  $h_b$  is shown in Fig. 3. The energy weighted factors are added to the diagonal terms of the representation matrix. Since we are interested in a hexagon as a partial structure, the values of them are taken to be the energies of bonding orbitals of benzene. Then diagonal elements of  $3 \times 3$  sub matrix become to be zero. This implies that in the variational calculation using  $h_b$  the corresponding left-hand side hexagon does not contribute to stabilize the molecule. Bonding orbitals of benzene in the left-hand side hexagon play a role of nonbonding molecular orbitals. It can be expected that the orbitals whose orbital energies are located in the neighbourhood of zero may have large bonding MO character of benzene.

Next we consider the total  $\pi$ -electronic energy of  $h$ ,  $h_b$  and  $h_a$ . As an example total  $\pi$ -electronic energy of naphthalene is given by

$$E = N\alpha + 2 \sum_j^{\text{occ}} \sum_{i=1}^6 \varepsilon_i^r C_{ji}^2 \beta + 2 \sum_{\mu > \nu} P_{\mu\nu} \beta \tag{7}$$

$$P_{\mu\nu} = 2 \sum_j^{\text{occ}} C_{j\mu} C_{j\nu} \tag{8}$$

where the second term gives the energy of the left-hand side hexagon, and the third term is that of the residual hexatriene structure. The total  $\pi$ -electronic

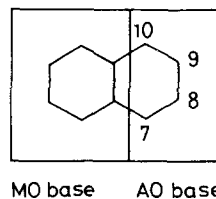


Fig. 2. Numbering of naphthalene using AO plus MO representation

MO base      AO base

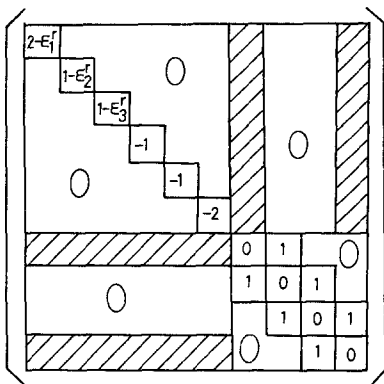


Fig. 3. Representation matrix associated with  $h_b$  for naphthalene using AO plus MO basis set. Shaded part has non-zero matrix elements

energy of  $h_b$  is given by

$$E = N\alpha + 2 \sum_j^{\text{occ}} \sum_{i=4}^6 \varepsilon_i^r C_{ji}^{\prime 2} \beta + 2 \sum_{\mu>\nu} P'_{\mu\nu} \beta. \quad (9)$$

The prime is added, since the coefficients may be different from Eq. (7) due to the inclusion of the energy weighted projection operator term. It should be noted that in the second term the summation runs over only the antibonding orbitals of benzene, so that this term works as a destabilization of hexagon. Naphthalene can be stabilized by taking in the hexatriene type orbitals. The total  $\pi$ -electronic energy of  $h_a$  is given by

$$E = N\alpha + 2 \sum_j^{\text{occ}} \sum_{i=1}^3 \varepsilon_i^r C_{ji}^{\prime\prime 2} \beta + 2 \sum_{\mu>\nu} P''_{\mu\nu}. \quad (10)$$

The double prime is used to distinguish from Eq. (7) and Eq. (9). Contrary to the case of  $h_b$ , the summation runs over only the bonding orbitals of benzene, so that this term works as a stabilization of hexagon.

### 3. Benzene character

We define a benzene character (BC) as follows,

$$BC = BC_b + BC_a \quad (11)$$

$$BC_b = (E - E_b)/8 \quad (12)$$

$$BC_a = (E - E_a)/8 \quad (13)$$

where  $E$ ,  $E_b$  and  $E_a$  denote the  $\pi$ -electronic energy associated with  $h$ ,  $h_b$  and  $h_a$ , respectively. The first term in Eq. (11) represents the stabilization energy of hexagon by taking in the bonding orbitals of benzene, whereas the second term represents the destabilization energy of that by taking in the antibonding orbitals of benzene. According to the definition, benzene character of benzene itself is 1, since the first term is to be 1 and the second term is zero. Since there is a following

relationship for alternant hydrocarbons in MO basis set associated with  $h$ ,

$$[h_b]_{i,j} = -[h_a]_{N+1-i, N+1-j} \quad (14)$$

we can obtain using the property of trace

$$BC_b - BC_a = 1. \quad (15)$$

It is interesting to note that there are following mirror relationships between the eigenvalue  $\varepsilon_i^b$  and eigenvector  $\psi_i^b$  associated with  $h_b$  and  $\varepsilon_{N+1-i}^a$  and  $\psi_{N+1-i}^a$  associated with  $h_a$ ,

$$\varepsilon_i^b = -\varepsilon_{N+1-i}^a \quad (16)$$

$$\psi_i^b = \sum_{\mu}^* C_{i\mu} \chi_{\mu} + \sum_{\mu}^{\circ} C_{i\mu} \chi_{\mu} \quad (17)$$

$$\psi_{N+1-i}^a = \sum_{\mu}^* C_{i\mu} \chi_{\mu} - \sum_{\mu}^{\circ} C_{i\mu} \chi_{\mu} \quad (18)$$

where \* and  $\circ$  mean the starred and unstarred atoms in a given alternant hydrocarbon, respectively. This is similar to the pairing theorem of Coulson and Rushbrooke [10]. As an example the orbital energies of naphthalene with  $h$ ,  $h_b$  and  $h_a$  are shown in Fig. 4. It is seen that the orbital energies of  $h_b$  have the opposite sign of those associated with  $h_a$  from Eq. (16). Molecular orbitals for naphthalene associated with  $h_b$  and  $h_a$  are shown in Fig. 5 and Fig. 6, respectively. The first three bonding orbitals in Fig. 5 are hexatriene like orbitals. One nonbonding orbital appears at  $\varepsilon = 0$ , which is expressed only by a linear combination of bonding orbitals of benzene. The last five orbitals are almost the same with those of  $h$ . Figure 6 shows that the first five orbitals associated with  $h_a$  closely resemble those with  $h$ . However the last five orbitals of  $h_a$  are quite different from those of  $h$ . This fact becomes very important in the case of anions.

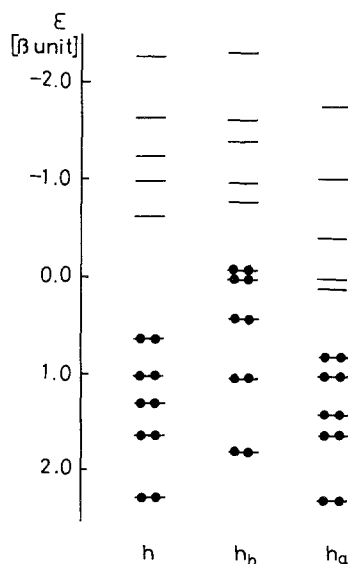


Fig. 4. MO energy diagram for naphthalene associated with  $h$ ,  $h_b$  and  $h_a$

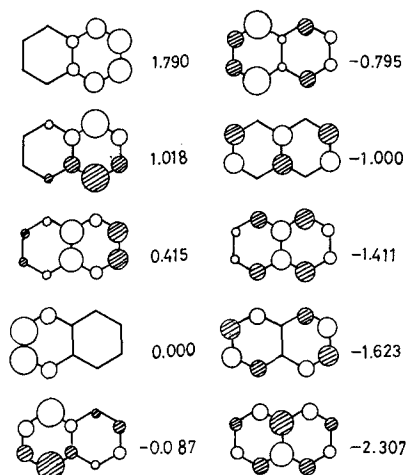
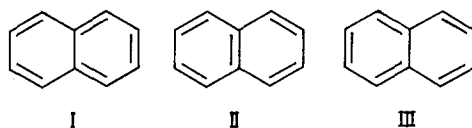


Fig. 5. Orbital energies (in  $\beta$  unit) and schematic MO's for naphthalene associated with  $h_b$ .

We can understand the decrease of benzene character of hexagons in naphthalene from the stand point of the Kekulé structure. There are three Kekulé structures in naphthalene. Benzene character of left-hand side hexagon can be represented by superposition of II and III, whereas that of right-hand side of hexagon can



be represented by the superposition of I and II. This means that both hexagons compete each other to take in structure II. This competition is the origin of decrease of  $BC$  of the hexagon. As the result,  $BC$  of the hexagon of naphthalene is calculated to be  $BC = 0.853$ .

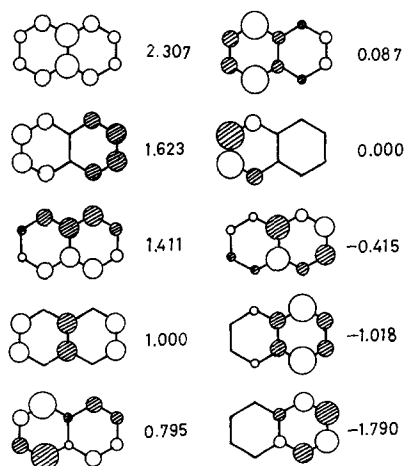


Fig. 6. Orbital energies (in  $\beta$  unit) and schematic MO's for naphthalene associated with  $h_a$ .

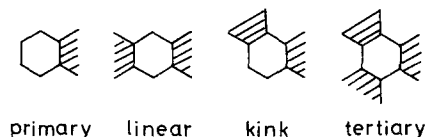


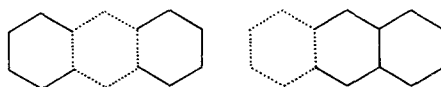
Fig. 7. Classification of hexagons in catacondensed hydrocarbons

#### 4. Results and discussion

In the following discussions we are concerned with neutral alternant hydrocarbon. Since there is the relationship between  $BC_b$  and  $BC_a$  from Eq. (15), only  $BC_b$  will be discussed.

##### A. Classification of hexagon

We use the classification for the hexagons in catacondensed hydrocarbons [7] (see Fig. 7). The calculated orbital energies for anthracene associated with  $h$  and  $h_b$  are shown in Fig. 8. The characters of bonding orbitals for the linear hexagon and the primary one correspond to the bonding orbitals of the following residual structures, respectively.



$BC_b$  for the primary hexagon ( $BC_b = 0.911$ ) is larger than that of the linear one ( $BC_b = 0.851$ ). Decrease of  $BC_b$  in a given hexagon is caused by the competition for forming benzene like bonds at hexagon (inner bonds) and breaking those by neighbouring bonds (outer bonds), where outer bonds mean the bonds which connect the neighbouring conjugated systems. For instance the hexagon in biphenylene has one outer bond and that in naphthalene has two outer bonds.

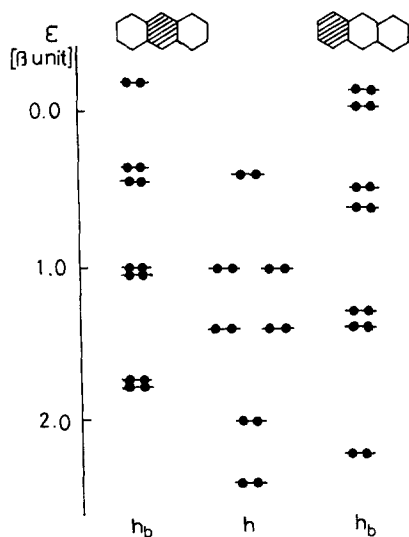


Fig. 8. MO energy diagram related to two kinds of hexagon in anthracene associated with  $h$  and  $h_b$

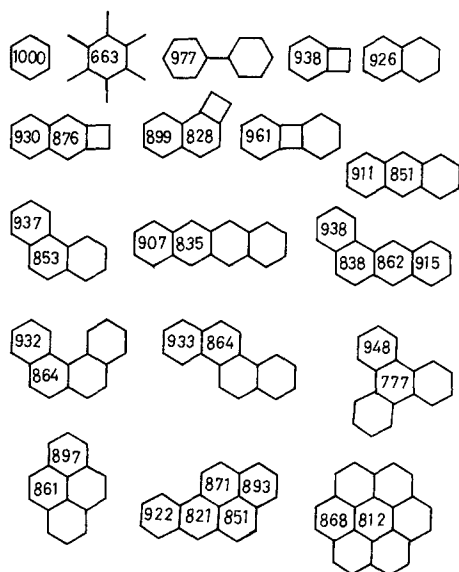


Fig. 9. Values of  $BC_b \times 1000$  for various alternant hydrocarbons

Figure 9 shows the calculated  $BC_b$  of various alternant hydrocarbons. It is seen from this figure that  $BC_b$  mainly depends on the number of outer bonds. Thus in general  $BC_b$  of the primary hexagon (with two outer bonds) is larger than that of linear ones (with four outer bonds). The calculated MO energies for triphenylene associated with  $h$  and  $h_b$  are shown in Fig. 10. The characters of bonding orbitals for tertiary hexagon and primary one correspond to the bonding orbitals of the following residual structures, respectively.

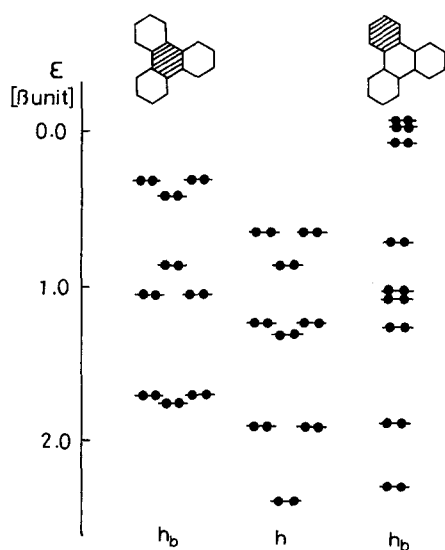
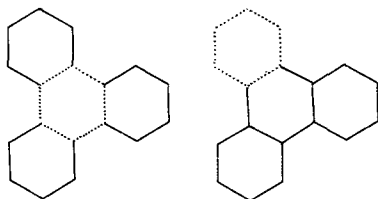
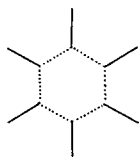


Fig. 10. MO energy diagram related to two kinds of hexagon in triphenylene associated with  $h$  and  $h_b$





The tertiary hexagon has very small  $BC_b$  compared with that of primary one, since the tertiary hexagon has six outer bonds. The calculated MO energies for [6]-radialene associated with  $h$  and  $h_b$  are shown in Fig. 11. The character of bonding orbitals for the hexagon corresponds to the bonding orbitals of the following residual structure.



$BC_b$  of [6]-radialene is the smallest of the molecules as far as we calculated, since the Kekulé structure of this molecule has six external double bonds, and benzene structure of hexagon is completely broken. The energy of three highest bonding orbitals are invariant in the calculation using  $h_b$ , since these orbitals in the hexagon are represented only by the linear combination of antibonding orbitals of benzene. These invariant orbitals make no contribution to  $BC_b$ .

The order of  $BC_b$  for catacondensed hydrocarbon is roughly

primary > linear  $\approx$  kink > tertiary.

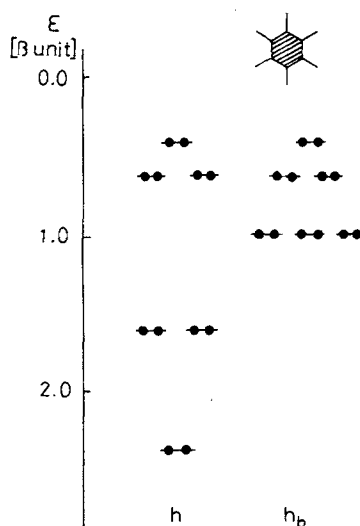
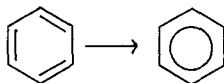


Fig. 11. MO energy diagram for [6]-radialene associated with  $h$  and  $h_b$

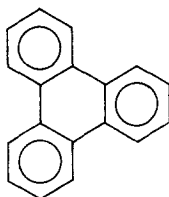
The local topological dependency of  $BC_b$  has the same tendency suggested by Aida and Hosoya [7].

### B. Clar pattern

For the stability of benzenoid hydrocarbons Clar proposed semiempirical rules based on the structure and stability relationship [11]. The concept of the aromatic sextet is introduced as a set of three double bonds circularly conjugated as in either of two Kekulé structures of benzene and represented by a circle.



Clar defined that no two sextets can have a common bond. Clar suggested that Kekulé structure with the largest number of sextets represents the electronic structure of the ground state of a polycyclic hydrocarbon and the stability increases with the number of the sextets. This structure is called Clar pattern [7] or sextet formula [6]. It is interesting to note that the hexagons which correspond to the sextets in a Clar pattern have large  $BC_b$ . For triphenylene  $BC_b$  of three primary hexagon is larger than that of the tertiary hexagon. This result is pictorially represented by the following Clar pattern.



This is due to the result that since the primary hexagons take in the bonding orbitals of benzene, benzene structure of tertiary hexagon is completely broken. Thus triphenylene is stabilized by peripheral three primary hexagons.

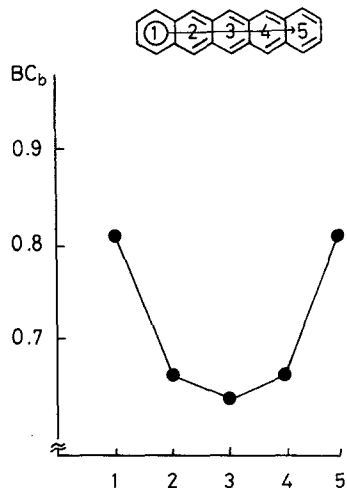


Fig. 12. Values of  $BC_b$  for hexagons in tetracene

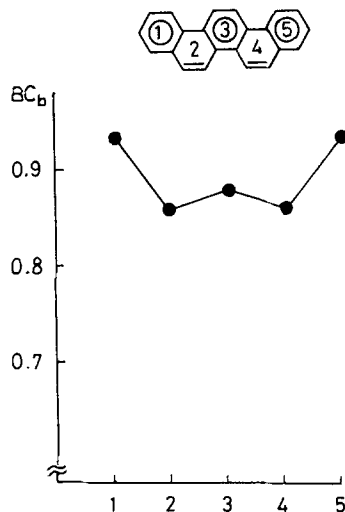


Fig. 13. Values of  $BC_b$  for hexagons in picene

### C. Linear and zig-zag benzenoid hydrocarbon

We consider linear and zig-zag benzenoid hydrocarbons. It can be seen that  $BC_b$  of hexagons in zig-zag benzenoid hydrocarbon are much larger than those in linear one (see Figs. 12 and 13). This result is in accord with the prediction from the number of Kekulé structures.

### D. [6]-Annuleno [ $N$ ]-annulene

We apply the present method to [6]-annuleno [ $N$ ]-annulene.  $BC_b$  of hexagons varies zig-zag with small differences and converges to a certain value (see Fig. 14). Even if the size of [ $N$ ]-annulene becomes large, the hexagon retains large  $BC_b$ .  $BC_b$  of benzocyclobutadiene is larger than that of naphthalene. It is noted that  $BC_b$  of the hexagon with  $4n$ -membered rings and  $4n+2$ -membered rings are on different curves. In general the hexagon with  $4n$ -membered ring effectively

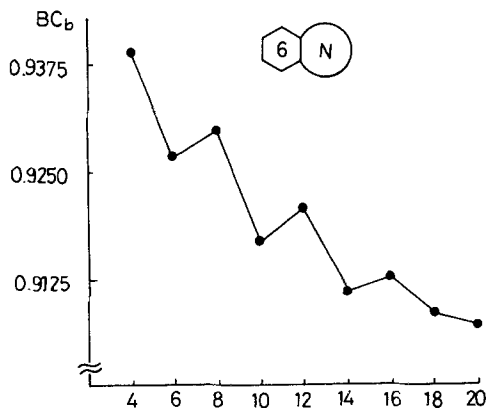


Fig. 14. Values of  $BC_b$  for hexagons in [6]-annuleno [ $N$ ]-annulene

takes in the bonding orbitals of benzene to stabilize the molecule, while the hexagons with  $4n + 2$  membered ring compete with each other.  $BC_b$  of hexagon is almost unchanged with the size of [ $N$ ]-annulene.

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