

A simple treatment to design NBMO degenerate systems in alternant and non-alternant hydrocarbons

Yuriko Aoki and Akira Imamura

Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 724, Japan

Received October 24, 1991/Accepted February 12, 1992

Summary. A simple treatment for systems with many degenerate non-bonding molecular orbitals (NBMO's) in alternant and non-alternant hydrocarbons without performing computer calculations is presented at the Hückel level. Using Hückel theory, we have proven that the linkage between carbon atoms with coefficients of zero in an NBMO does not present any substantial action to the original NBMO. By using this simple rule, many polycyclic conjugated hydrocarbons possessing high spin multiplicity are hypothesized. We term these NBMO degenerate systems "NBMO network systems". This treatment can be expected to provide information for designing novel organic high-spin molecules including possible ferromagnetic substances in particular those consisting of non-alternant polycyclic conjugated hydrocarbons.

Key words: NBMO degenerate system – Non-alternant polymer – Hückel method

1 Introduction

In many π -conjugated compounds, all π electrons are accommodated in the available bonding molecular orbitals and provide an appreciable amount of resonance energy. Alternant hydrocarbon ring systems are all even-membered rings. The carbon atoms can be alternately starred and unstarred about the ring that each starred C* atom is surrounded only by unstarred C atoms, and vice versa. It is easily shown by means of the NBMO method [1] that the orbitals with coefficients on the starred atoms correspond to the non-bonding molecular orbital at the zero level. According to the theorem of Coulson and Rushbrooke [2], a system has at least $|n^* - n|$ degenerate NBMO's; where n^* and n are the number of the starred and unstarred carbon atoms, respectively. The fundamental properties of neutral alternant hydrocarbons in Hückel theory have been extensively described.

Ovchinnikov [3] has shown for large alternant hydrocarbons with conjugated bonds that if the numbers of starred and unstarred carbon atoms differ from each other the full spin of the molecule is greater than zero. He has presented

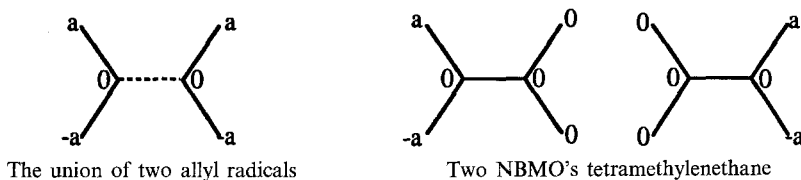
some possible planar and linear molecules with the full spin shown to be ring size dependent. Tyutyulkov and his co-workers [4–6] have investigated the band structures of alternant, non-alternant, and heteroatomic nonclassical polymers [7] and shown that, although they are polyradicals, these polymers have considerable delocalization energy which may determine their relative stability. They have also proposed a concrete model and shown that magnetic ordering at finite temperatures occurs when interchain interactions in a quasi-one-dimensional nonclassical alternant polymer are taken into account [8]. Their studies on polyradical polyconjugated systems are extended to networks containing heteroatoms [9, 10]. Furthermore, they have studied the energy dispersion of the lowest elementary excitation from the ferromagnetically aligned state of quasi-one-dimensional alternant hydrocarbon networks, utilizing an extended Hubbard-type Hamiltonian which incorporates both nearest-neighbor Coulomb repulsion and exchange interactions [11].

Unfortunately, there are few studies on non-alternant ring systems containing odd numbers of carbon atoms since it is more difficult to derive a simple relationship between the energies and the orbital coefficients of the NBMO's than for the alternant hydrocarbon case. In general, the energy change of the molecular orbitals of interacting π systems may be estimated by using Dewar's PMO treatment [12–14] on the basis of NBMO's of alternant conjugated hydrocarbons [15]. Recently, Dewar and his co-worker [16] have shown that the PMO calculation is useful in predicting the orientation of substitution in non-alternant polycyclic aromatic hydrocarbon derivatives of fluoroanthene. Zahradnik [17] has reported a quantum chemical study on the electronic structure and properties of non-alternant hydrocarbons. The aromaticity of pentalene, heptalene and related bicyclic hydrocarbons was studied by Boyd [18], using an internally consistent LCAO-MO method. We have also presented a simple perturbational analysis of degenerate NBMO's in a previous article [19]. This method has been successfully applied to bicyclic hydrocarbons, pentalene, and phenalene derivatives [20]. The results obtained were consistent with the classification proposed by Refs. [17] and [18]. However, a simple rule for determining NBMO's and their electron occupancies in non-alternant hydrocarbons without calculations has not been reported.

With respect to high-spin molecules, such attention has been paid to organic ferromagnetic substances, since the first high-spin molecule was reported by Itoh [21], and subsequently by Wasserman et al. [22]. Teki et al. [23–25] have studied the spin state and molecular conformation of a novel alternant hydrocarbon, *m*-phenylene-bis[(diphenyl-methyl-3-yl)methylene] by electron-spin resonance. They have reported the unusually high spin multiplicity of this compound and postulated that pseudo-one-dimensional organic ferromagnets may be expected with measured chain length. Mataga [26] and Itoh [27] have discussed a possible electronic structure for such polymers on the basis of simple molecular orbital theory. The high spin multiplicity of the above-mentioned organic molecules arises from a characteristic property of NBMO's in alternant hydrocarbons. However, the spin multiplicities of long chain alternant hydrocarbons possessing NBMO's cannot readily be predicted and, moreover, those of non-alternant ones are likely to be even less predictable.

Borden and Davidson [28] have classified conjugated diradicals into two types according to whether their Hückel NBMO's can be confined to disjoint sets of atoms. In one class, the Hückel NBMO's can be chosen so that they are confined to different sets of carbon atoms, as is the case in the cyclobutadiene

([4*n*] annulenes). In other classes, the Hückel NBMO's cannot be so confined, as in the case of trimethylenemethane. They applied PMO analysis to both types of conjugated diradicals by treating them as the union of an allyl radical and a carbon atom bearing a *p*- π orbital and showed both molecules are diradicals. The results also indicated that when the effect of CI is included, the singlet is found to lie below the triplet in cyclobutadiene, the reverse of that which is found in trimethylenemethane. Furthermore, the SCF and full π space CI calculations were performed on tetramethylenethane and showed the singlet to have the same energy as the triplet in SCF calculations and to lie below the triplet in the CI calculations. The Hückel MO treatment based on the PMO analysis implies that the inactive carbons of two allyl radicals can be joined. The resulting two NBMO's are clearly confined to separate sets of atoms, like cyclobutadiene.



This suggests that the configuration interaction of this type may cause a singlet to become the ground state.

In this article, at first, we demonstrate on the basis of the *MO based variational principle* that the connection between two fragments of hydrocarbons at inactive positions gives two NBMO's. This will provide a general method of obtaining many Hückel NBMO's via the use of connections between various fragments at inactive sites. The advantages are that (a) all the higher order terms neglected in the PMO treatment are incorporated in the variational treatment and (b) this method should be applicable to all types of hydrocarbons, and especially useful for non-alternant hydrocarbons. Although the investigation concerning the singlet-triplet gap as proposed by Borden et al. [28] is essential in designing realistic high spin molecules, our treatment will provide, as a first step, a convenient guide to designing novel "NBMO Network" systems which should be of importance in connection with the molecular design of organic ferromagnetic substances.

The concept of our treatment is briefly reviewed and applied to intermolecular interactions of alternant conjugated hydrocarbons in order to predict their one- and two-dimensional NBMO degenerate systems. Next, a series of non-alternant cata- and peri-condensed polycyclic hydrocarbons having NBMO's are shown using 4*n*-monocyclic hydrocarbons and their derivatives as starting molecules. By using these NBMO systems as parent molecules, some one- and two-dimensional non-alternant NBMO networks are studied. Furthermore, our treatment is extended to large NBMO networks by using radical bridging between molecules having NBMO's. The predictions obtained by this treatment for the adopted systems are confirmed by simple Hückel calculations.

2 Method

Our approach is performed in the framework of the simple Hückel method. However, the general form of the secular determinant (outside the frame):

$$|H_{rs} - S_{rs}\epsilon| = 0 \quad (r, s = 1, 2, \dots, n), \quad (1)$$

is used in our treatment. In the case of the usual simple Hückel theory, the matrix elements H_{rs} and S_{rs} are written as $H_{rr} = \alpha_r$ ($r = s$), $H_{rs} = \beta_{rs}$ (r, s are neighboring), $H_{rs} = 0$ (otherwise), and $S_{rs} = \delta_{rs}$. If the molecular orbitals for particular parent alternant hydrocarbons having NBMO's are defined as zero order wave functions:

$$\psi_i^{(0)} = \sum_r^n C_{ri}^{(0)} \chi_r, \quad (2)$$

the secular determinant for the wave function is represented as:

$$|H_{rs}^{(0)} - \delta_{rs} \varepsilon^{(0)}| = 0. \quad (3)$$

Suppose that a new bond is created in the alternant hydrocarbon by a cross-linkage between two carbon atoms as a perturbation ΔH . The new solution for the perturbed system is obtained by solving the following secular equation:

$$|(H_{rs}^{(0)} + \Delta H_{rs}) - \delta_{rs} \varepsilon| = 0. \quad (4)$$

Since simple Hückel theory has not been well studied from the point of view of the molecular orbital basis, this investigation presents a novel usage of the Hückel method. The determinant can be represented on the basis of molecular orbitals Eq. (2) for the parent alternant hydrocarbons as follows:

$$|H_{ij} - \delta_{ij} \varepsilon| = 0, \quad (5)$$

where the H_{ij} is a matrix element between particular MOs i and j , that is:

$$H_{ij} = \sum_r^n \sum_s^n C_{ri}^{(0)} C_{sj}^{(0)} (H_{rs}^{(0)} + \Delta H_{rs}) = \varepsilon_i^{(0)} \delta_{ij} + \Delta H_{ij},$$

$$\delta_{ij} = \sum_r^n \sum_s^n C_{ri}^{(0)} C_{sj}^{(0)} \delta_{rs}.$$

If ΔH_{rs} is a perturbation term arising from the linkage between two carbon atoms with zero coefficients in an NBMO's, i.e. between unstarred and unstarred, then all the perturbation terms with respect to the NBMO's become zero. That is,

$$\Delta H_{iN} = \sum_r^n \sum_s^n C_{ri}^{(0)} C_{sN}^{(0)} \Delta H_{rs} = 0 \quad (i = 1, 2, \dots, n), \quad (6)$$

since $C_{sN}^{(0)} = 0$ if $\Delta H_{rs} \neq 0$, and $\Delta H_{rs} = 0$ if $C_{sN}^{(0)} \neq 0$.

$$\Delta H_{Nj} = \sum_r^n \sum_s^n C_{rN}^{(0)} C_{sj}^{(0)} \Delta H_{rs} = 0 \quad (j = 1, 2, \dots, n), \quad (7)$$

since $C_{rN}^{(0)} = 0$ if $\Delta H_{rs} \neq 0$, and $\Delta H_{rs} = 0$ if $C_{rN}^{(0)} \neq 0$. The N indicates all of the non-bonding levels included in the original alternant hydrocarbon. The secular equation to be solved is shown as follows.

$$\begin{array}{c} \text{NBMO} \\ \left| \begin{array}{cccc} (\varepsilon_1^{(0)} + \Delta H_{11}) - \varepsilon & \Delta H_{12} & \cdots & \Delta H_{1n} \\ \Delta H_{21} & (\varepsilon_2^{(0)} + \Delta H_{22}) - \varepsilon & \cdots & \cdots \\ \cdots & \cdots & \ddots & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{array} \right. \\ \text{NBMO} \left| \begin{array}{cccc} \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{array} \right. \\ \left. \begin{array}{cccc} \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \Delta H_{n1} & \cdots & \cdots & (\varepsilon_n^{(0)} + \Delta H_{nn}) - \varepsilon \end{array} \right| = 0 \quad (8) \end{array}$$

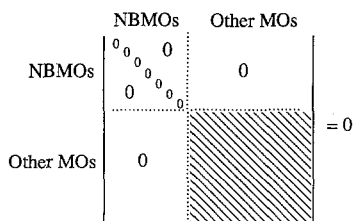


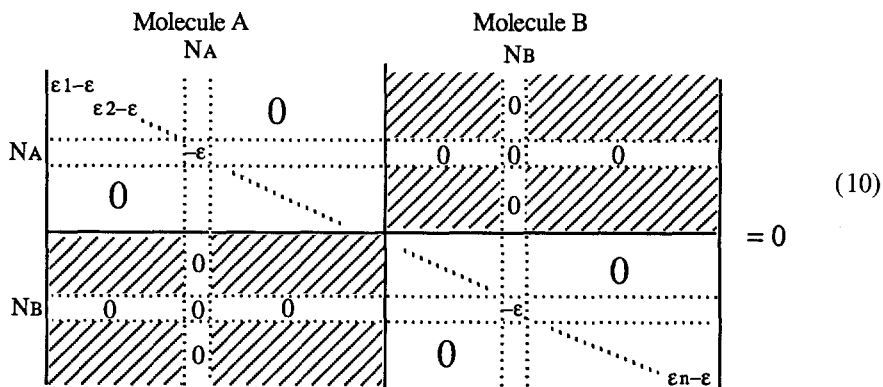
Fig. 1. Schematic representation for Eq. (8)

From this representation, it can be seen that the matrix to be diagonalized is already block diagonalized into two types: matrix elements based on NBMO's and those on the others as shown in Fig. 1. All the matrix elements in the NBMO block are zero. Therefore, this ensures that the non-bonding levels are retained after a perturbation corresponding to a linkage between atoms having coefficients of zero. If f degenerate NBMO's exist in the adopted systems, the f solutions are retained as NBMO's:

$$\epsilon_i = \epsilon_N^{(0)} = 0 \quad (i = 1, 2, \dots, f). \tag{9}$$

It should be pointed out that all of the higher order terms in the perturbation expansion are incorporated in the solutions thus obtained from the secular determinant based on the MO's. By using this simple treatment, the existence of NBMO's in many polycyclic hydrocarbons, even including odd membered rings, can be easily determined.

Apparently, a similar principle holds for interactions between molecules as well. For example, we consider a supermolecule composed of molecule A and molecule B by linking carbon atoms with coefficients of zero. The secular determinant to be solved is written as follows on the basis of molecular orbitals.



N_A and N_B indicate NBMO's of molecule A and molecule B, respectively. The off-diagonal elements with respect to N_A or N_B remain to be zero by the following relations:

$$\begin{aligned} \Delta H_{iN_A} &= \left(\sum_r^{\text{on A}} + \sum_r^{\text{on B}} \right) \left(\sum_s^{\text{on A}} + \sum_s^{\text{on B}} \right) C_{ri}^{(0)} C_{sN_A}^{(0)} \Delta H_{rs} \\ &= \sum_r^{\text{on B on A}} \sum_s^{\text{on A}} C_{ri}^{(0)} C_{sN_A}^{(0)} \Delta H_{rs} = 0 \quad (i = 1, 2, \dots, n) \end{aligned} \tag{11}$$

$$\begin{aligned} \Delta H_{N_{Aj}} &= \left(\sum_r^{\text{on A}} + \sum_r^{\text{on B}} \right) \left(\sum_s^{\text{on A}} + \sum_s^{\text{on B}} \right) C_{rN_A}^{(0)} C_{sj}^{(0)} \Delta H_{rs} \\ &= \sum_r^{\text{on A}} \sum_s^{\text{on B}} C_{rN_A}^{(0)} C_{sj}^{(0)} \Delta H_{rs} = 0 \quad (j = 1, 2, \dots, n) \end{aligned} \quad (12)$$

$$\begin{aligned} \Delta H_{iN_B} &= \left(\sum_r^{\text{on A}} + \sum_r^{\text{on B}} \right) \left(\sum_s^{\text{on A}} + \sum_s^{\text{on B}} \right) C_{ri}^{(0)} C_{sN_B}^{(0)} \Delta H_{rs} \\ &= \sum_r^{\text{on A}} \sum_s^{\text{on B}} C_{ri}^{(0)} C_{sN_B}^{(0)} \Delta H_{rs} = 0 \quad (i = 1, 2, \dots, n) \end{aligned} \quad (13)$$

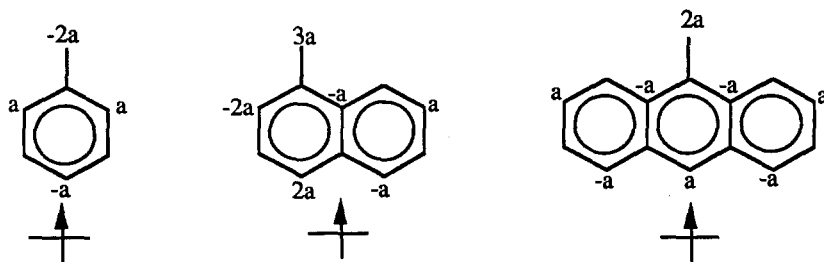
$$\begin{aligned} \Delta H_{N_{Bj}} &= \left(\sum_r^{\text{on A}} + \sum_r^{\text{on B}} \right) \left(\sum_s^{\text{on A}} + \sum_s^{\text{on B}} \right) C_{rN_B}^{(0)} C_{sj}^{(0)} \Delta H_{rs} \\ &= \sum_r^{\text{on A}} \sum_s^{\text{on B}} C_{rN_B}^{(0)} C_{sj}^{(0)} \Delta H_{rs} = 0 \quad (j = 1, 2, \dots, n) \end{aligned} \quad (14)$$

because the NBMO coefficient on the r -th or s -th atom is zero when the ΔH_{rs} has a value. As a result, the original NBMO's of the molecules A and B are retained. This means that m degenerate NBMO's appear by linking the carbon atoms with coefficient of zero between m molecules having one half-filled NBMO.

Consequently, NBMO's of non-alternant hydrocarbons can be obtained from Eq. (8) and one- and two-dimensional NBMO degenerate systems (NBMO networks) are predicted by Eq. (10). With these rules we can proceed to various designs of NBMO degenerate systems in alternant and non-alternant polycyclic conjugated hydrocarbons. First, a few NBMO networks of alternant hydrocarbons are shown as follows.

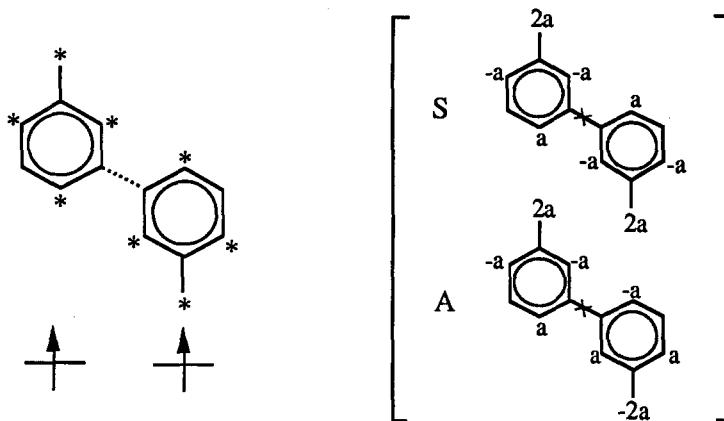
3 An example of applications to alternant hydrocarbons

Polybenzenoid closed shell systems generally have no NBMO's. Therefore, open-shell structures such as in benzyl, naphthyl, anthracenyl, and phenalenyl radicals and their diradical species are depicted as parent molecules and the above-mentioned method is applied to intermolecular interactions of these molecules for construction of NBMO network systems. Benzyl, naphthyl, and anthracenyl radicals have the following half-filled NBMO's, respectively.



For example, at first, consider the benzyl radical polymer in which the benzyl radical has a half-filled NBMO. It is evident from Eq. (10) that the dimerization by a linkage between two carbon atoms with zero coefficients retains the NBMO's in the original molecule. As the result, the dimer has the following two

half-filled NBMO's; one is symmetric about a rotational axis and the other is antisymmetric (shown in right side of the following figure).



If we consider a long chain extension of the unit, the linkages between m benzyl radicals produce m half-filled NBMO's as shown in Fig. 2(1). All of the coefficients on starred atoms (*) of m molecules are determined under the condition that m NBMO's should be orthonormal to each other. In such a case where m electrons occupy m NBMO levels, a parallel spin state is preferred by

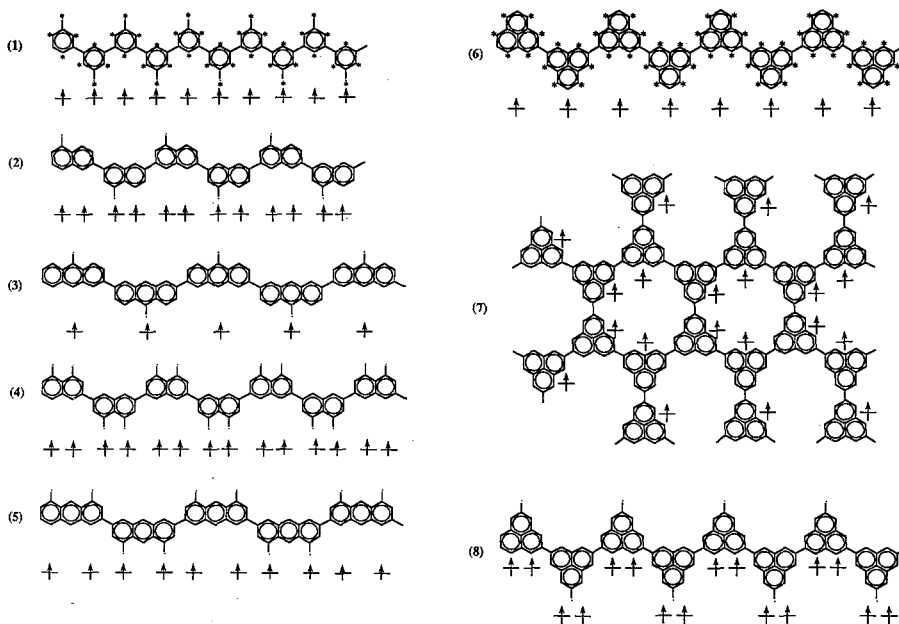
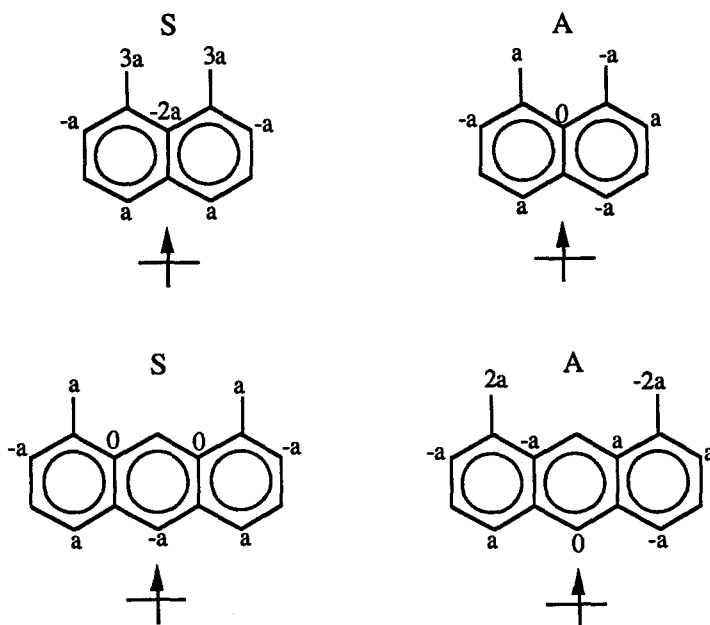


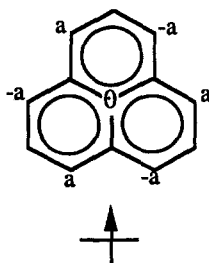
Fig. 2. Examples of NBMO networks composed of (1) benzyl radicals, (2) naphthyl radicals, (3) anthracenyl radicals, (4) naphthyl diradicals, (5) anthracenyl diradicals, (6)(7) phenalenyl radicals and (8) phenalenyl diradicals

Hund's rule. This suggests that the polybenzyl radicals linked to each other by meta substitution could reveal high spin multiplicity leading to ferromagnetism. For naphthyl and anthracenyl radicals, the one-dimensional NBMO network systems such as shown in Fig. 2 (2) and (3) are produced in a similar manner. The naphthyl and anthracenyl diradicals have two half-filled NBMO's as shown in the figure below.

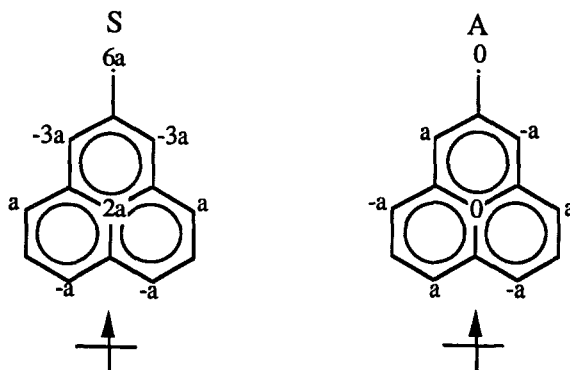


The positions of the inactive carbon atoms of the two-fold degenerate symmetric and antisymmetric NBMOs are not changed even after linear combination between the two NBMO's. Therefore, one-dimensional polymers constituted from their m molecules can produce $2m$ half-filled NBMO's as shown in Fig. 2 (4) and (5). In these alternant systems, it is clear that meta-substitutions are essential for producing a large high spin system by maintaining the NBMO's of parent molecules.

For peri-fused alternant hydrocarbons such as phenalene and its derivatives, a one-dimensional NBMO network system can be also produced. Phenalene has a half-filled NBMO. The oligomer is made up of linkages between m phenalenes



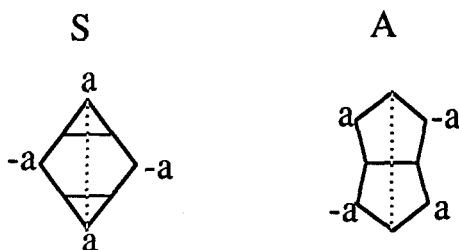
at the carbon atoms with coefficients of zero and yields m half-filled NBMO's as shown in Fig. 2(6). Furthermore, two-dimensional NBMO network systems formed in Fig. 2(7) by linkages between phenalenes at three points are also possible. In the case of phenaleny radical, there are two symmetric and antisymmetric NBMO's as in the cases of naphthyl and anthracenyl diradical species. The oligomer of phenalene formed by linkages between m molecules gives two kinds of half-filled NBMO's as shown in Fig. 2(8).



Many other alternant NBMO network systems of cata- and peri-fused polycyclic molecules can be considered. These results are easily obtained without performing the usual Hückel calculations which require diagonalization of the large Hückel matrices. It is remarkable that high spin multiplicity of the above-mentioned organic molecules is easily visualized and predicted by a simple treatment.

4 Cata-fused non-alternant systems from $[4n]$ -annulenes and their NBMO networks

The treatment of $4n$ monocyclic systems ($[4n]$ -annulenes) at the simple Hückel level generates in each case a half-filled degenerate pair of NBMO's. By using such compounds as starting molecules, the existence of NBMO's is proposed for cata-fused non-alternant hydrocarbons which contain a peripheral π -electron system perturbed by cross-linkages. The cross-linkages which retain the NBMO's of $[8]$ -annulene generate the following symmetric NBMO (HOMO) and an antisymmetric NBMO (LUMO).



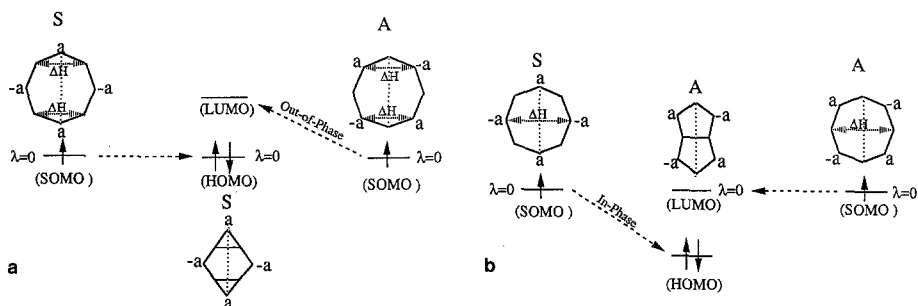
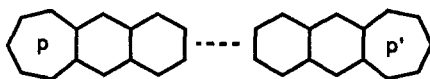


Fig. 3. Schematic energy diagram for cata-fused NBMO systems generated by cross linkages of [8]-annulene

In Fig. 3(a) and (b), energy diagram of such kinds of perturbations is schematically represented. For the former perturbation (Fig. 3(a)), the symmetric MO remains unchanged to remain the NBMO, since the perturbation term is that between two atoms with zero coefficients. At the same time, the energy of the antisymmetric MO is elevated by the perturbation between two atoms with out-of-phase coefficients and becomes an empty level. The reverse is true for the latter perturbation (in Fig. 3(b)). The former case has filled NBMO's which reveal high electron-donating abilities and the latter has empty NBMO's which reveals high electron-accepting ability. This is naturally derived from the previously mentioned method and confirmed by the simple Hückel calculations.

This procedure has been applied to [12]-annulene and [16]-annulene systems, which are shown in Fig. 4 including the derived tetracyclic cata-fused systems. From this figure, we conclude that the systems with ring size of $p = 4m + 3$ and $p' = 4m' + 3$ ($m, m' = 1, 2, 3, \dots$) as shown below have a filled symmetric NBMO, whereas those of $p = 4m + 1$ and $p' = 4m' + 1$ have an empty antisymmetric NBMO.



This property is retained even in poly-benzenoids and is consistent with our previous results [19] obtained using perturbation theory for degenerate systems.

By analogy with alternant hydrocarbons, pseudo-one-dimensional non-alternant NBMO network systems can be considered. Pentalene, whose NBMO coefficients are shown in Fig. 3, has an empty NBMO (pentalenoid system [29]). From the principle we have established that a linkage between two atoms with coefficients of zero maintains the NBMO, pentalenoid oligomers such as Fig. 5(1) can be generated which conserve their NBMO levels $\lambda = 0$ in succession by the bonding between top and tail carbons with coefficients of zero of the pentalenes. The degree of degeneracy at $\lambda = 0$ is proportional to the pentalenes included. Linkages between m pentalenes produce m degenerate empty NBMO's and result in revealing high electron accepting ability.

As a comparison, heptalene (Fig. 4) is shown to have a filled NBMO (heptalenoid system [29]) since one of the two degenerate NBMO's of [12]-annulene remains at $\lambda = 0$ even after producing heptalene and the other is elevated by

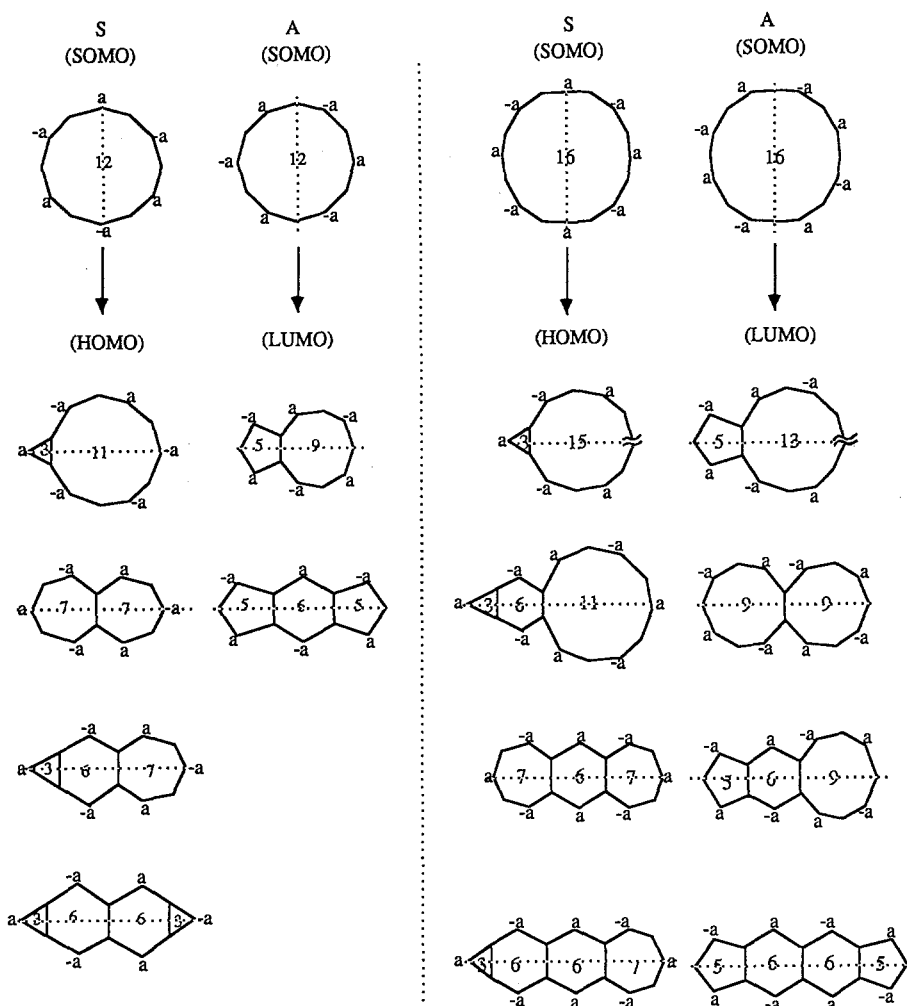


Fig. 4. Cata-fused NBMO systems generated by cross-linkages of [12]- and [16]-annulenes

the perturbation between two atoms with an out-of-phase interaction. As opposed to the pentalenoid oligomer, it is obvious that heptalenoid oligomers produced by linkages between carbon atoms and zero coefficients of m heptalenes have m filled NBMO's as shown in Fig. 5 (2)–(4), and high electron-donating ability should result. Although this observation is not interesting from the view point of ferromagnetism, the combination of the pentalene system, having an empty NBMO, and the heptalene system, having a filled NBMO, produces a new system possessing partially occupied degenerate NBMO's by the consecutive charge transfer interaction from heptalene to pentalene. If m pentalenes and m heptalenes are linked, N half-filled NBMO's are produced as shown in Fig. 5 (5) for one-dimensional and (6) for two-dimensional systems. Random mixed polymers of pentalenes and heptalenes (1:1) will be expected to reveal high spin multiplicity if the molecules are linked of carbon atoms with coefficients of zero.

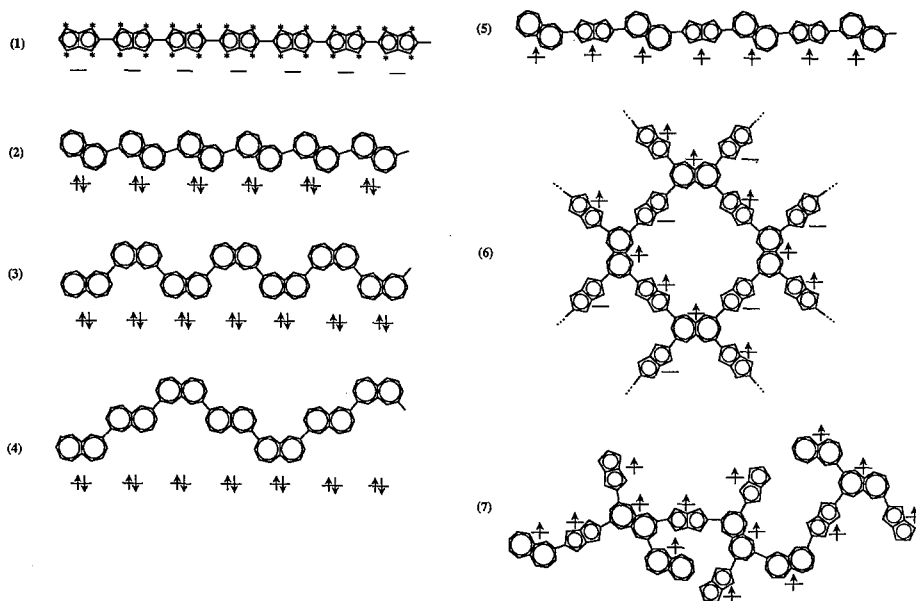


Fig. 5. (1) Pentalenoid and (2)–(4) heptalenoid oligomers produced by linkages such as retaining their NBMO levels and examples of NBMO networks composed of pentalenes and heptalenes for (5) one-dimensional regular, (6) two-dimensional regular, and (7) random systems

An example is shown in Fig. 5 (7). Many networks composed of non-alternant cross-linked hydrocarbons having NBMO's are possible.

5 Peri-fused non-alternant systems from $[4n]$ -annulenes and their NBMO networks

An intriguing perturbation arises from insertion of an internal π -system into a $4n$ monocyclic periphery to produce a peri-fused polycyclic system. If we choose to insert a pentalene system into a larger ring system, the NBMO's of the pentalenoid derivatives can be derived, as indicated in Fig. 6, and [8] annulene would appear a reasonable parent molecule. The coefficients of the two NBMO's of [8]-annulene cannot be written by dividing the carbon atoms into starred and unstarred groups because of their degeneracy. For that reason, they are adopted as the zero order solutions for performing the perturbational treatment. For the symmetric NBMO, the bridging by a carbon between two carbon atoms with zero coefficients does not change the energy of the symmetric NBMO of the parent molecule. For the antisymmetric NBMO, the bridging also has no effect on the energy because of the difference in symmetry of the atomic orbital coefficient on the added carbon atom (symmetric around the carbon atom) and the coefficients of the two carbon atoms which the added carbon atom bridges (antisymmetric with respect to the normal line through the added carbon atom).

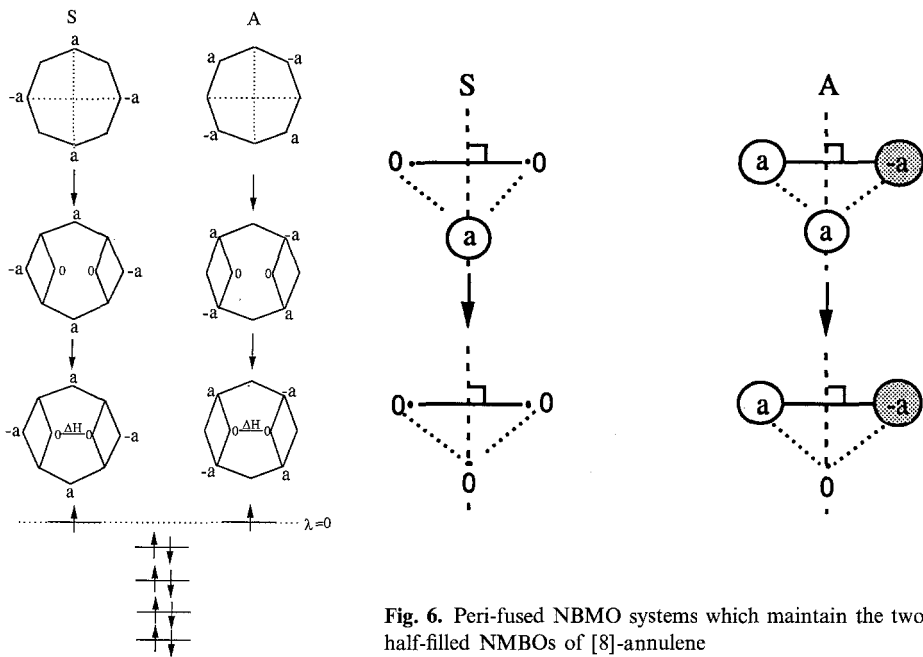


Fig. 6. Peri-fused NBMO systems which maintain the two half-filled NBMOs of [8]-annulene

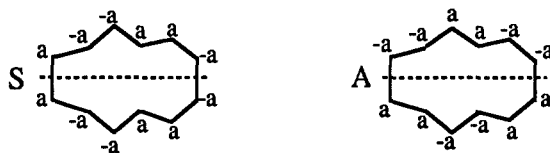
Consequently, the corresponding matrix element vanishes and the MO of the added carbon atom does not contribute to the original NBMO's. The structure of the secular determinant is shown as in Eq. (15) defining the added radical MO as the k -th MO.

$$\begin{vmatrix}
 \epsilon_1 - \epsilon & \epsilon_2 - \epsilon & \epsilon_3 - \epsilon & \dots & 0 & N(S) & N(A) & k & & \\
 0 & \dots & \dots & \dots & \dots & 0 & 0 & & & 0 \\
 N(S) & 0 & \dots & \dots & \dots & \epsilon_{N(S)}^{(0)} - \epsilon & 0 & 0 & & 0 \\
 N(A) & 0 & \dots & \dots & \dots & 0 & \epsilon_{N(A)}^{(0)} - \epsilon & 0 & & 0 \\
 k & & & & & 0 & 0 & \epsilon_k^{(0)} - \epsilon & & \\
 & & & & & & & & & \epsilon_{N+1} - \epsilon & 0 \\
 & & & & & 0 & 0 & & & 0 & \dots & \epsilon_n - \epsilon
 \end{vmatrix} = 0 \quad (15)$$

where $N(S)$ and $N(A)$ correspond to symmetric and antisymmetric NBMO's, respectively. It is clear from the above that the two original NBMO's do not mix with the atomic orbital on the added atom. Next, the formation of the central bond can be viewed as the perturbation between two atoms with coefficients of zero and has no effect on the energy of the two NBMO's as shown in the lower part of Fig. 6. Therefore, the two NBMO's generated from [8]-annulene are

conserved even by these perturbations; one becomes a SOMO with $\lambda = 0$ in which the coefficients are symmetric with respect to the axes denoted by the vertical and horizontal dotted lines, and the other becomes a SOMO with $\lambda = 0$ in which the coefficients are antisymmetric. This treatment can be extended in general to $[4n]$ -annulenes and a number of NBMO systems can be produced. In Fig. 7, the pentalenoid derivatives generated from [12]- and [16]-annulenes are listed for the systems containing two even-membered rings. From this figure, it can be seen that a two-fold SOMO and a LUMO are formed from [12]-annulene, and two two-fold SOMO's and a LUMO from [16]-annulene.

Next, we consider pentalenoid derivatives characterized by two odd-membered rings that are linked laterally. For example, the [12]-annulene can be reduced to a pentalenoid derivative containing a five-membered ring and a seven-membered ring and has the following two half-filled NBMO's.



The NBMOs will be taken as the two degenerate S and A NBMO's of [12]-annulene to suit the symmetry for the horizontal axis, since the final structure will be symmetric or antisymmetric with respect to the horizontal line. The bridging by a carbon atom thus results in stabilization of the original symmetric NBMO because of an in-phase interaction and the conservation of the original antisymmetric NBMO.

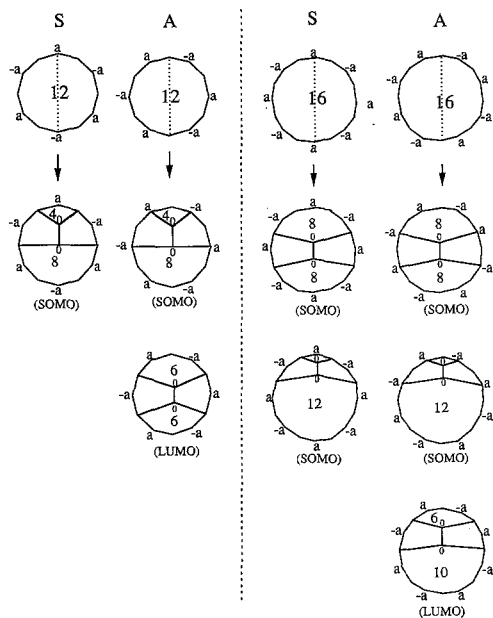
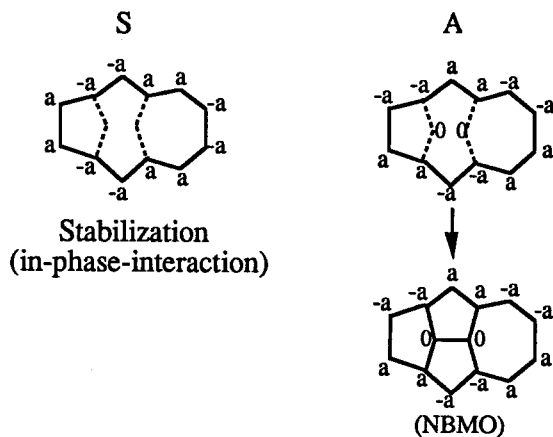


Fig. 7. NBMO systems of pentalenoid derivatives with two even-membered rings generated from [12]- and [16]-annulenes



The pentalenoid derivative having five-membered and seven-membered rings is generated with an empty NBMO (LUMO). The two electrons, which individually occupied the original two NBMO's of [12]-annulene, occupy the stabilized symmetric orbital. However, such a type of NBMO system is not appropriate as a parent molecule for preparing NBMO degenerate systems by inter-molecular bridges, because the coefficients of the NBMO's are spread out to the surroundings.

The classification system used thus far will be convenient in a systematic treatment, and can be readily applied to larger systems. NBMO systems derived from [12]- and [16]-annulenes are listed in Fig. 8 as well as some of those derived

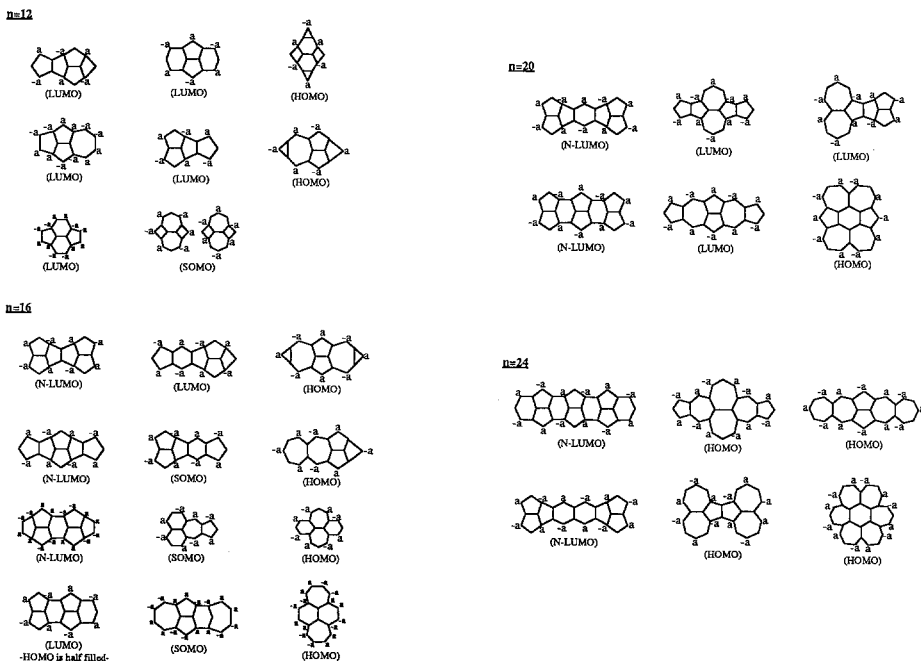
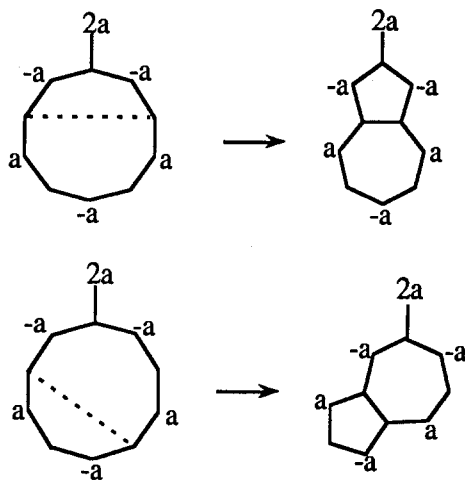


Fig. 8. Peri-fused NBMO systems generated from [12]-, [16]-, [20]-, and [24]-annulenes

from [20]- and [24]-annulenes. In the figure, N-LUMO, LUMO, SOMO, and HOMO indicate that the NBMO levels having those coefficients are next-HOMO, LUMO, SOMO, and HOMO, respectively. The electron occupancies of the NBMO's are determined by the symmetry of the two atoms, which are perturbed by cross-linkages and relate to the difference between the numbers of pentalenoid and heptalenoid structures included. With respect to the N-LUMO, more detailed analysis of the orbital interaction is required. The coefficients of these NBMO series can be easily found out by using the previously mentioned procedure without performing the usual Hückel calculations. By taking these NBMO systems as parent molecules, we can make many one- and two-dimensional NBMO network systems. Some examples of NBMO networks resulting from subsequent inter-molecular charge transfer interactions from the HOMO-NBMO to the LUMO-NBMO are shown in Fig. 9.

6 NBMO networks from other parent molecules

It is difficult to find an NBMO network composed of an azulenoid structure because of its aromatic stabilization. However, an azulenoid derivative possessing an extra carbon radical may possibly have an NBMO. The following linkages via a central bond conserve the NBMO of the [10]-annulenyl radical.



Therefore, the NBMO network oligomers exemplified by these molecules can be generated as shown in Fig. 10.

From phenyl $4n$ monocyclic hydrocarbons, many NBMO systems of non-alternant hydrocarbons are produced as well as the cases of previously mentioned cata- and peri-condensed polycyclic hydrocarbons. NBMO systems derived from mono-phenyl [8]- and [12]-annulenes are shown in the upper part of Fig. 11 and those from di-phenyl [18]- and [12]-annulenes are shown in the lower part of the figure. Some of their NBMO networks are presented in Fig. 12. It is of interest that all of the coefficients on the benzene ring of the antisymmet-

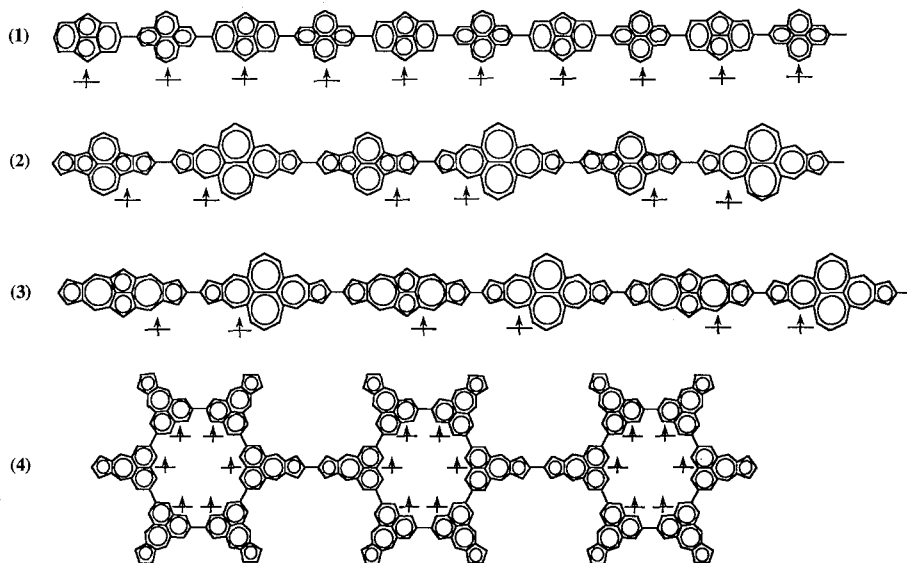


Fig. 9. Examples of NBMO networks composed of peri-fused NBMO systems

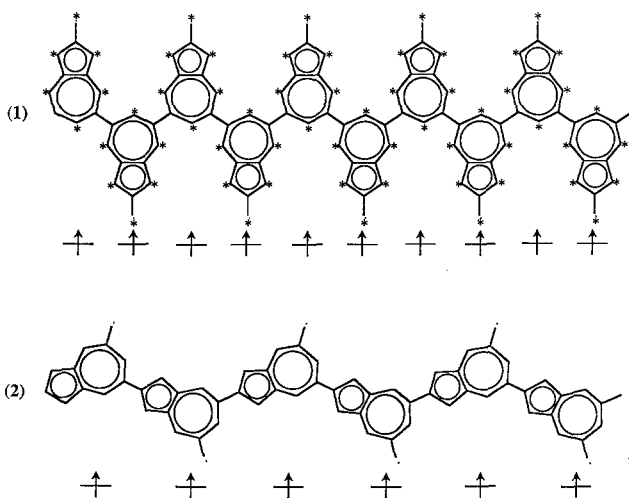


Fig. 10. NBMO networks composed of azulenoic radicals

ric NBMOs in Fig. 11 are zero and, therefore, every carbon atom in the benzene rings can take part in making NBMO networks. In Fig. 13, NBMO systems derived from [8]- and [12]-annulenes having two benzene rings are shown. Their NBMO networks obtained by combining a structure possessing an empty NBMO with that possessing a filled NBMO are presented in Fig. 14. It can be seen that the properties NBMO's are the same as in the case of the [4*n*]-annulenes, even when phenylenes or benzenes are included.

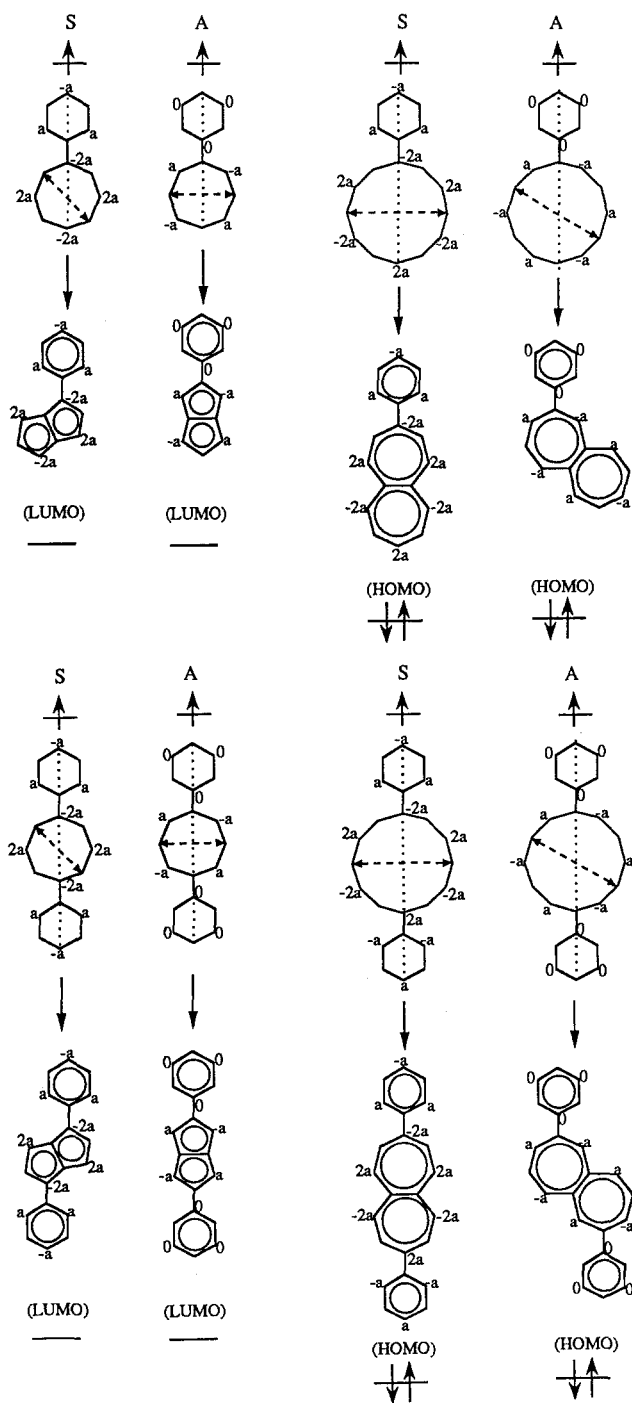


Fig. 11. Mono-phenyl pentalenoid and heptalenoid NBMO systems derived from mono-phenyl [8]- and [12]-annulenes and di-phenyl pentalenoid and heptalenoid NBMO systems derived from di-phenyl [8]- and [12]-annulenes

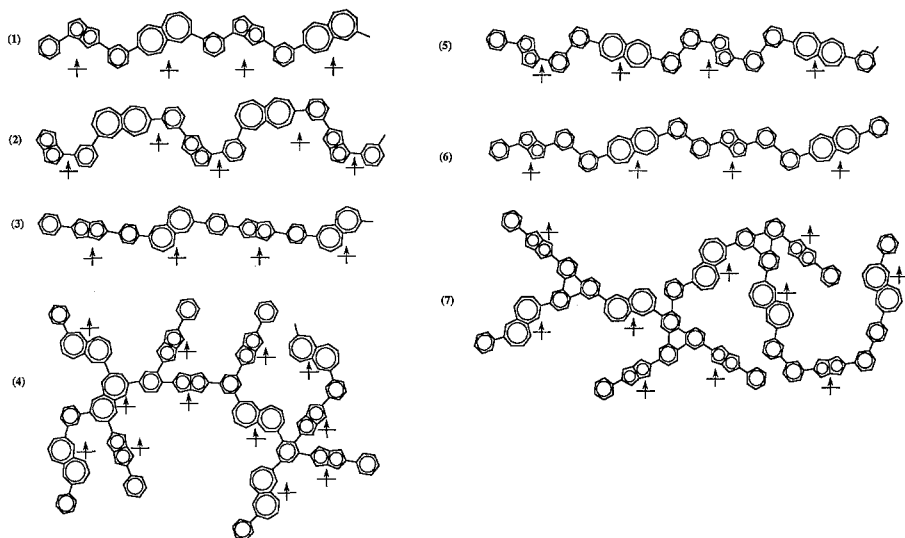


Fig. 12. NBMO networks produced by NBMO systems shown in Fig. 11

7 Radical networks

Next, we show another method to generate molecules with many half-filled NBMO's via radical insertion into periodic pentalenoid or heptalenoid oligomers. At first, we consider the case where a radical combines with an NBMO system. In this case, the original NBMO is retained even if the radical atom is attached to the carbon atom of the parent molecule with a coefficient of zero, since the MO added by a radical cannot interact with the original NBMO of the parent molecule. That is:

$$\Delta H_{kN} = \sum_r^n \sum_s^n C_{rk}^{(0)} C_{sN}^{(0)} \Delta H_{rs} = 0,$$

since $C_{sN}^{(0)} = 0$ if $\Delta H_{rs} \neq 0$. In this equation, the radical MO is defined as the k -th MO. Therefore, the MO based determinant to be solved has the following form.

		NBMO k				
NBMO	$\epsilon_1 - \epsilon$	$\epsilon_2 - \epsilon$	$\epsilon_3 - \epsilon$	0	0	= 0
				⋮	0	
k	0	0	0	0	0	(16)
		0	0	0	0	
				0	0	
				0	0	
					$\epsilon_{N+1} - \epsilon$	
					0	
					⋮	
					$\epsilon_n - \epsilon$	

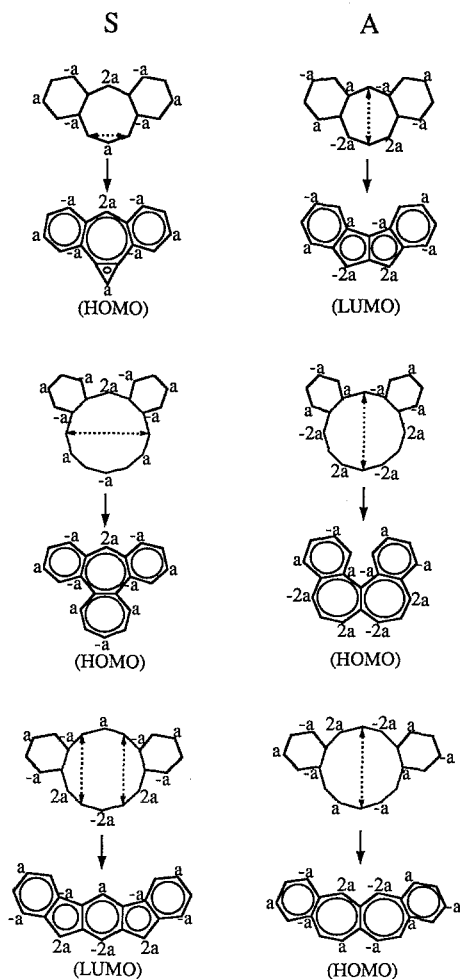


Fig. 13. Cata-fused NBMO systems derived from [8]- and [12]-annulenes with two benzene rings

It can be seen that the NBMO remains, because all of the off-diagonal matrix elements concerning the original NBMO remain zero. If several radicals are added to the original molecule, extra NBMO's are produced but the original NBMO remains unchanged. In order to investigate the electron occupancy of the NBMO level, the interacting energy diagram is shown in Fig. 15, in which pentalene or heptalene combines with a radical on a carbon atom with a coefficient of zero. In pentalene, the zero level lies closer to the occupied orbitals than to the vacant orbitals. The extent of interaction increases with the proximity of interacting levels. Because the radical NBMO interacts with occupied orbitals more strongly than with vacant orbitals, the radical NBMO is raised in energy. The original NBMO of pentalene remains and is occupied by an unpaired electron. Conversely, in heptalene, the zero level lies closer to the vacant orbitals than to the occupied orbitals. Since the radical NBMO interacts with vacant orbitals more strongly than with occupied orbitals, the radical NBMO is lowered and occupied by two electrons and the remaining original NBMO of heptalene is half-occupied. Thus, both pentalene and heptalene yield a half-filled NBMO

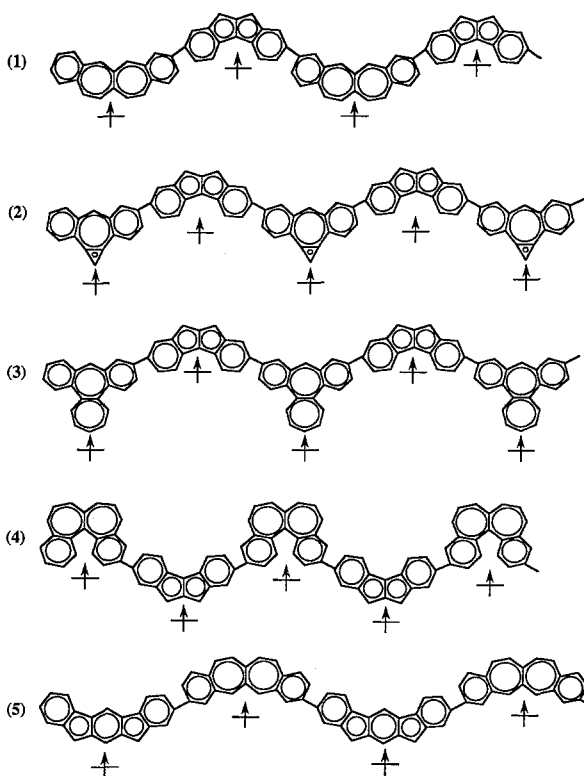


Fig. 14. NBMO networks produced by NBMO systems shown in Fig. 13

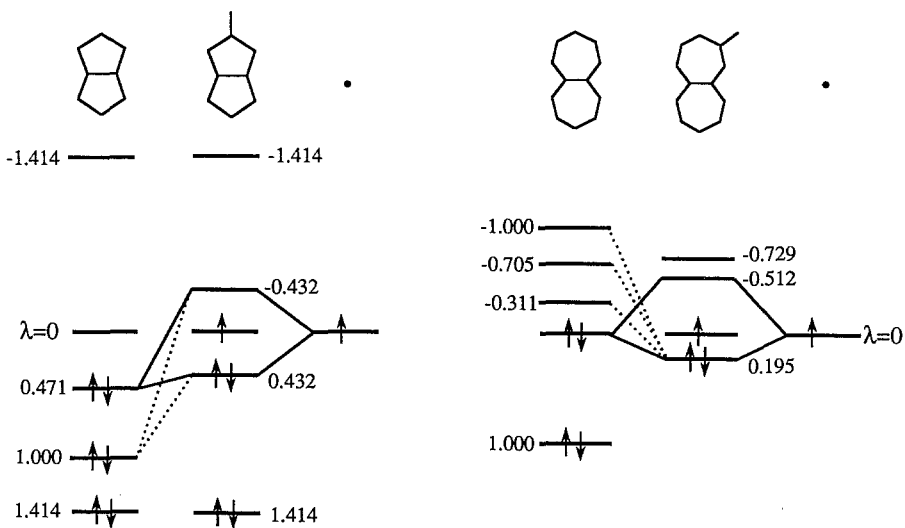


Fig. 15. Energy diagrams obtained by simple Hückel calculations for the systems that pentalene interacts with a carbon radical producing a pentalenyl radical and that heptalene interacts with a carbon radical producing a heptalenyl radical

by combining with a carbon radical on a carbon atom with a coefficient of zero. This property can be extended to one-dimensional NBMO network systems. In Fig. 16, pentalene radical oligomers (1), heptalene radical oligomers (2), and their mixture oligomers (3) are all composed of either pentalene and heptalene radicals and are shown as NBMO network systems, all of which have degenerate half-filled NBMO's proportional to the number of included molecules. Furthermore, a two-dimensional network is also produced by three-fold bridges between

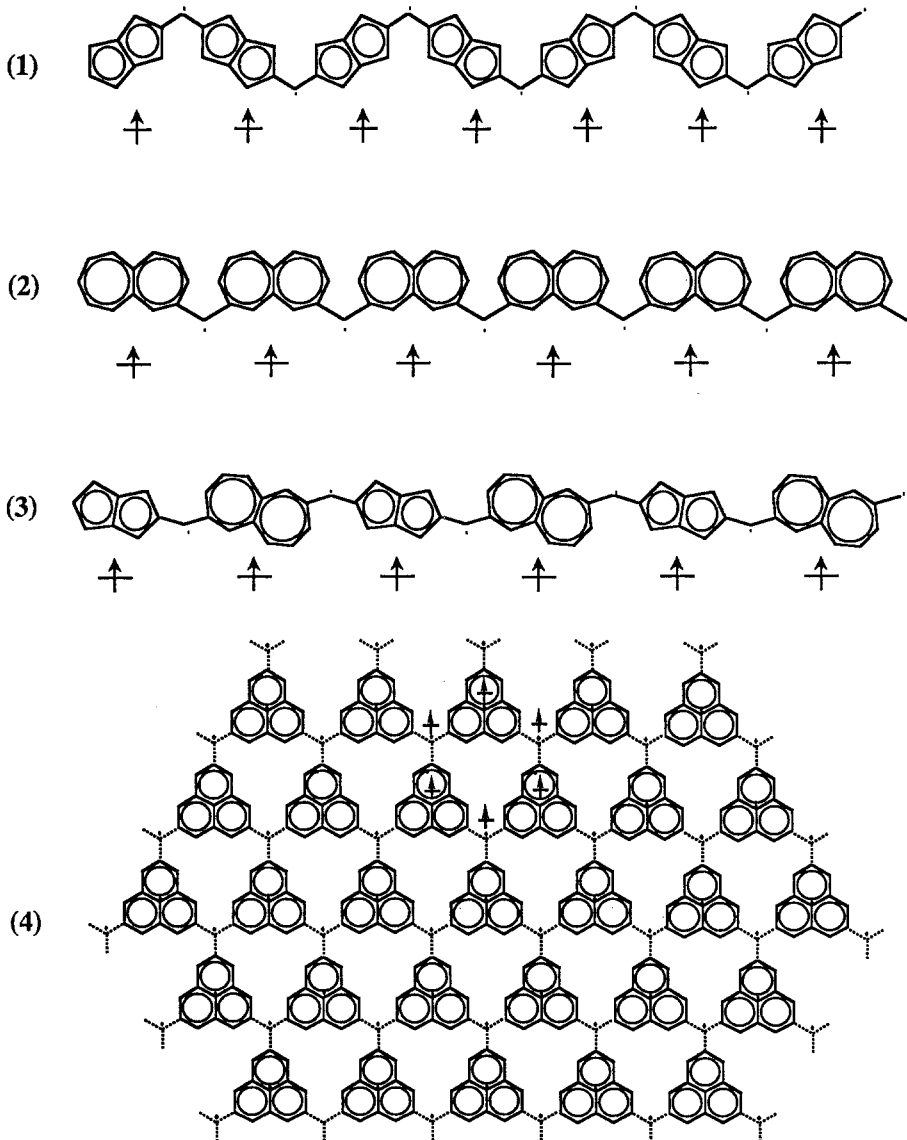
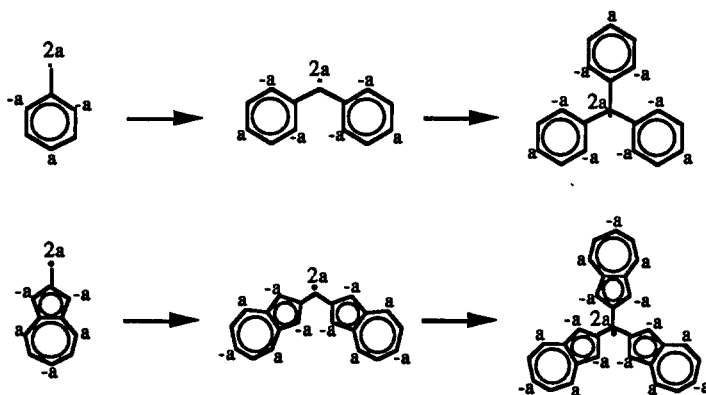


Fig. 16. (1) Pentalene radical and (2) heptalene radical NBMO networks produced by radical bridgings, (3) NBMO network produced by mixing of pentalene and heptalene radicals, (4) two-dimensional NBMO network produced by three-fold bridgings between three phenalenes

carbon atoms with coefficients of zero in phenalenes. Phenalene already has a half-filled NBMO as mentioned previously. Thus, two half-filled NBMO's per phenalene molecule are generated in the network as shown in Fig. 16(4).

8 Networks by dimerized and trimerized parent molecules

The structure having a radical NBMO can be extended by addition onto the radical site in such a way that the coefficient is retained. The following benzyl radical and azuleny radical dimers with a two-fold linkage and their trimers with a three-fold linkage are proposed as parent molecules for producing NBMO networks.



As Eq. (16) implies, the original NBMO of each molecule is unperturbed by the radical combination at the carbon atoms having zero coefficients. NBMO networks produced by inter-molecular linkage between benzyl dimer and azuleny dimer radicals are shown in Fig. 17. Those networks formed by benzyl trimer radicals and azuleny trimer radicals are presented in Fig. 18. In Fig. 18(1) a tri-phenyl methyl network is shown. The networks proposed by Mataga [26], possesses seven carbon atoms per unit and has been the object of several attempted syntheses recently [30, 31]. The band structure of this polymer was investigated by Tyutyulkov [6] and is characterized by a large energy gap, in the center of which falls the degenerate NBMO band. By our method, it can easily be shown that this molecule has one NBMO per monomer unit as a result of the meta-substituted linkages at the three points between tri-phenyl methyl radicals. It is noteworthy that the structure in Fig. 18(2) which is composed of a non-alternant tri-azuleny methyl network should also be expected to be a ferromagnetic substance as predicted by our simple treatment.

9 Conclusion

A simple method to determine NBMO's in non-alternant hydrocarbons is presented using a secular determinant based on Hückel MO's theory and applied

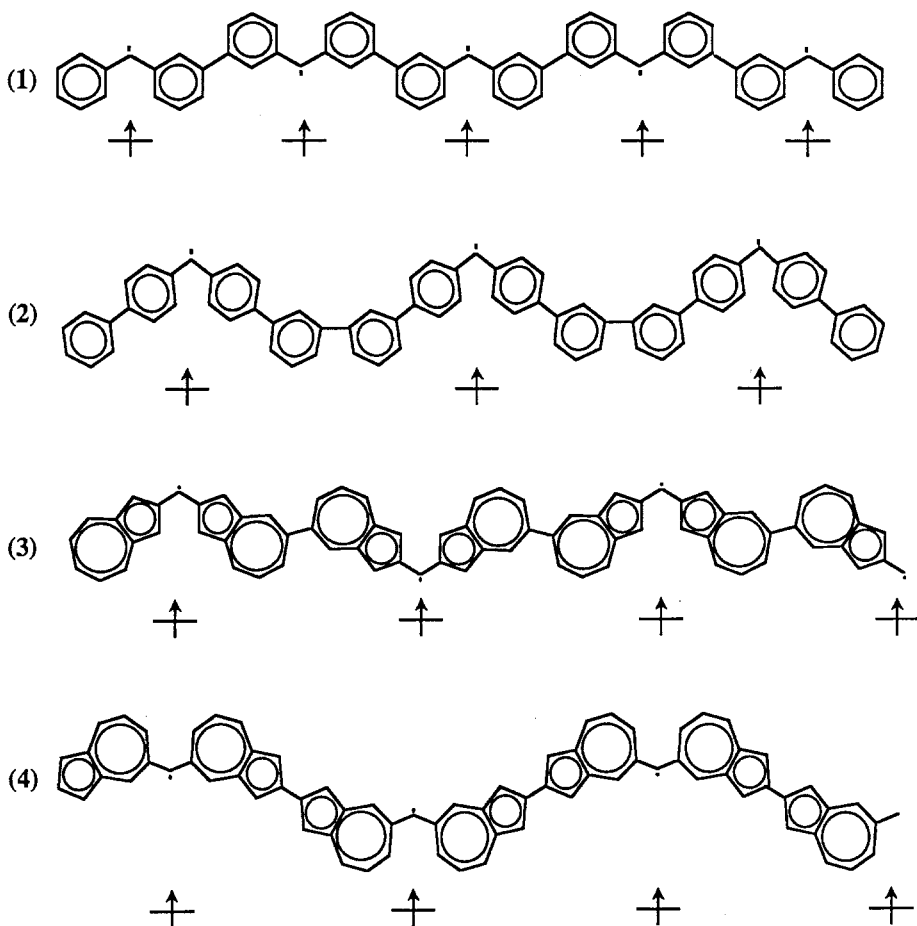


Fig. 17. NBMO networks produced by linkages between NBMO systems of (1)(2) benzyl dimer and (3)(4) azulenyl dimer radicals

to some cata- and peri-fused systems. The important concept behind the method used in this study is that a linkage between two carbon atoms with coefficients of zero conserves the NBMO levels of the parent molecule. This study represents the first investigation into this problem, although it has been previously implied in the framework of the first order perturbation theory. However, the present method is based on the variational concept of including infinite higher order terms in the perturbation expansion. The properties of the NBMO's are easily elucidated from the position of coefficients in relation to the symmetry axis. The conditions of this method are sufficient, but not necessary, for covering all NBMO systems in non-alternant hydrocarbons. However, this study should provide insight on the bonding of cata- and peri-condensed non-alternant hydrocarbons and a convenient guide for the designing novel organic ferromagnetic substances. This treatment will also be useful for examination of electronic properties in the vicinity of the zero level of large systems including heteroatoms, where calculation of the whole system directly is troublesome.

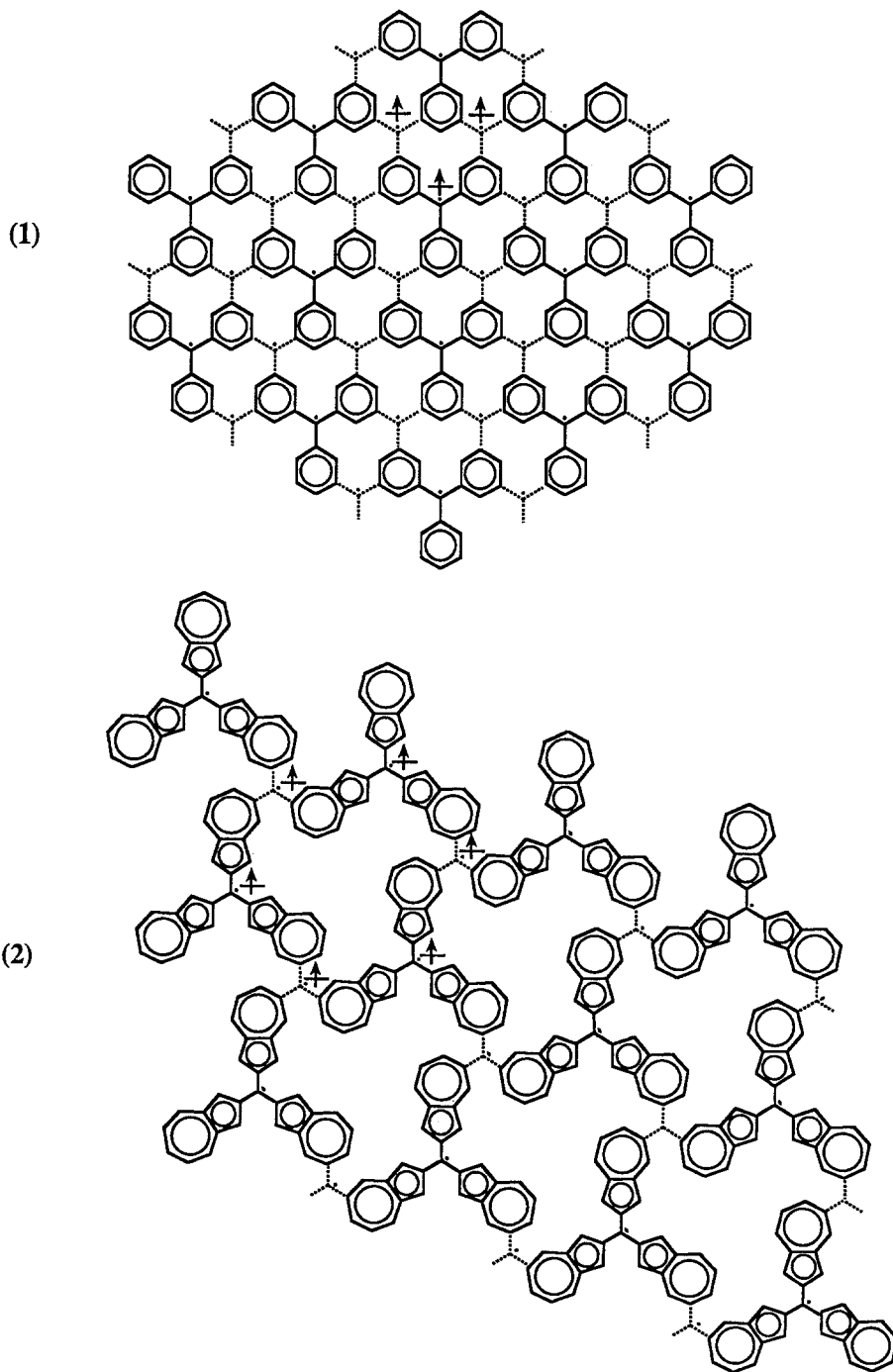


Fig. 18. NBMO networks produced by linkages between NBMO systems of (1) benzyl trimer and (2) azulanyl trimer radicals

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan, for which we express our gratitude.

References

1. Longuet-Higgins HC (1950) *J Chem Phys* 18:283; Dewar MLS (1952) *J Am Chem Soc* 74:3357; Dewar MJS (1952) *Sci Progr (London)* 40:604; (1953) *Prog Org Chem* 2:1; (1956) *Ann Rep Chem Soc* 53:126
2. Coulson CA, Rushbrooke GS (1940) *Proc Cambridge Phil Soc* 1940 36:193
3. Ovchinnikov AA (1978) *Theoret Chim Acta* 47:297
4. Tyutyulkov N, Bangov I (1974) *CR Acad Bulger Sci* 27:1517
5. Tyutyulkov N, Schuster P (1983) *Theor Chim Acta* 63:291
6. Tyutyulkov N, Polansky OE, Schuster P, Karabunarliev S, Ivanov CI (1985) *Theor Chim Acta* 67:211
7. Dewar MJS (1969) *The MO theory of organic chemistry*. McGraw-Hill, NY
8. Tyutyulkov N, Karabunarliev SC (1986) *Int J Quantum Chem* 29:1325
9. Tyutyulkov N, Ivanov CI, Schopov IS, Polansky OE, Olbrich G (1989) *Int J Quantum Chem* 34:361
10. Karabunarliev S, Tyutyulkov N (1989) *Theor Chim Acta* 76:65
11. Ivanov CI, Tyutyulkov N, Olbrich G, Barentzen H, Polansky OE (1988) *Theor Chim Acta* 73:27
12. Dewar MJS (1952) *J Am Chem Soc* 74:3341, 3345, 3359, 3353, 3355, 3357
13. Dewar MJS, Pettit R (1954) *J Chem Soc* 1617
14. Dewar MJS, Dougherty RC (1975) *The PMO theory of organic chemistry*. Plenum, New York
15. Trost BM, Bright GM (1967) *J Am Chem Soc* 89:4244
16. Dewar MJS, Dennington RD (1989) *J Am Chem Soc* 111:3804
17. Zahradnik DR (1965) *Angew Chem Int Ed* 4:1039
18. Boyd GV (1966) *Tetrahedron* 22:3409
19. Aoki Y, Imamura A, Murata I (1990) *Tetrahedron* 46:6659
20. Sugihara Y, Yamamoto H, Mizoue K, Murata I (1967) *Angew Chem Int Ed Engl* 26:1247
21. Itoh K (1967) *Chem Phys Lett* 1:235
22. Wasserman E, Murray RW, Yager WA, Trozzolo AM, Smolinsky G (1967) *J Am Chem Soc* 89:5067
23. Teki Y, Takui T, Itoh K, Iwamura H, Kobayashi K (1983) *J Am Chem Soc* 105:3722
24. Teki Y, Takui T, Yagi H, Itoh K, Iwamura H (1985) *J Chem Phys* 83:539
25. Teki Y, Takui T, Itoh K, Iwamura H, Kobayashi K (1986) *J Am Chem Soc* 108:2147
26. Mataga N (1968) *Theor Chim Acta* 10:372
27. Itoh K (1971) *Bussei* 12:635
28. Borden WT, Davidson ER (1977) *J Am Chem Soc* 99:4587
29. This is termed by Trost BM (1973) in: Nozoe T, Breslow R, Hafner K, Itoh S, Murata I (eds) *Topics in nonbenzenoid aromatic chemistry*, Vol. I. Hirokawa Publ, Tokyo, p 243
30. Torrance JB, Oostra S, Nazzari A (1987) *Synth Metals* 19:70
31. Ota M, Otani S, Igarashi M (1989) *Chem Lett* 1183