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A MOLECULAR ORBITAL STUDY ON THE ELECTRON DONATING AND ACCEPTING ABILITIES OF NON-ALTERNANT POLYCYCLIC CONJUGATED HYDROCARBONS

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Electronic properties of non-alternant polycyclic conjugated hydrocarbons are investigated by using the perturbation theory for degenerate systems on the basis of NBMOs of alternants. The HOMO and the LUMO energy levels are represented as a function of the size of the odd membered-ring included in the non-alternant polycyclic hydrocarbon.

I. Introduction

Some cyclic conjugated systems are much more stable than open-chain analogues, which are termed aromatic compound. In these systems, all π-electrons in a molecule can be accommodated in all the available bonding molecular orbitals. This extra stabilization has naturally a profound effect on chemical reactivity and much attention has been paid perennially to discuss on the definition of aromaticity1). Antiaromatics such as planar 4N monocyclic systems2), on the other hand, are unstable in their electronic states but are interesting because of the possibility that a novel charge transfer complex may be produced by inter-molecular interaction between their extremely high HOMO and low LUMO energy levels.

Alternant hydrocarbons are planar conjugated hydrocarbons, having no odd-membered rings in which the carbons can be divided into two sets; starred and unstarred. It is easily proved by means of the NBMO method3) that the orbital with coefficients on the starred atoms only corresponds to the non-bonding molecular orbital with zero level. The fundamental properties of neutral alternants in Hückel theory are described in many articles.

However, in non-alternant conjugated hydrocarbons that contain odd-membered rings, there is no simple relationship between the energies and the orbital coefficients, as there is in the case of alternant hydrocarbons. It seems therefore very important to predict the degree of aromatic stabilization in non-alternant conjugated hydrocarbons and characterize the ability of the molecule as a whole to give or accept a π–electron. The chemistry to be associated with such systems mainly derives from a consideration of their frontier orbitals. Dewar's PMO treatment4) has been used very generally in discussing chemical problems such as structure or reactivity and so on5), of organic compounds. Here we will introduce a simpler perturbational procedure for estimating HOMO and LUMO energies with respect to the size of the odd-membered ring in polycyclic non-alternant hydrocarbons by means of the perturbation theory for degenerate NBMOs of alternant hydrocarbons. The simple Hückel calculations for the adopted systems are presented together with our perturbation calculations to make sure the reliability and the applicability of the present treatment. This study will provide a simple method to design some novel hydrocarbons possessing high electron-donating or high electron-accepting nature and then, furthermore, revealing a property as a charge transfer complex. The concept of our treatment is briefly reviewed as follows.

Suppose that there are two orthogonal eigenfunctions Ψ_S and Ψ_A with the same eigenvalue E_{NBMO} ($\lambda = 0$) for an unperturbed Hamiltonian H_0

$$\begin{aligned} H_0\,\Psi_S &= E_{NBMO}\Psi_S \\ H_0\,\Psi_A &= E_{NBMO}\Psi_A. \end{aligned} \tag{1}$$

Putting the perturbed Hamiltonian between adjacent atoms by ΔH, the approximate solutions for the Schrodinger equation

$$(H_0+\Delta H)\,\Psi = E\,\Psi \tag{2}$$

is given by expanding the eigenfunction and the eigenvalue as a perturbation series

$$\psi = (C_S\,\psi_S^{(0)} + C_A\,\psi_A^{(0)}) + \psi^{(1)} + \psi^{(2)} + \cdots \;, \tag{3}$$

$$E = E_{NBMO} + E^{(1)} + E^{(2)} + \cdots \;. \tag{4}$$

The linear combination $C_S\,\psi_S^{(0)} + C_A\,\psi_A^{(0)}$ is also a eigenfunction of H_0 and its zero order solution can be obtained by solving the following secular equation from the perturbation theory for degenerate systems.

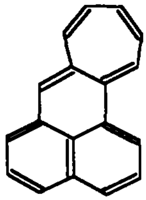
$$\begin{vmatrix} \langle \psi_S|\Delta H|\psi_S\rangle - E^{(1)} & \langle \psi_A|\Delta H|\psi_S\rangle \\ \langle \psi_S|\Delta H|\psi_A\rangle & \langle \psi_A|\Delta H|\psi_A\rangle - E^{(1)} \end{vmatrix} = 0 \tag{5}$$

If off-diagonal matrix elements have non-zero values, one of the two (symmetric and antisymmetric) NBMOs becomes anti-bonding LUMO and the other becomes bonding HOMO after perturbation. Now suppose that a biradical structure having two NBMOs is known, the HOMO and LUMO energy levels for its corresponding closed shell structure can be estimated from the two solutions of secular equation (5). In this case, the linear combination of the two NBMOs is used as a starting wave function and the matrix elements of the perturbed Hamiltonian between the linked carbons as a perturbation. In the case that the f NBMOs exist in a open shell structure, f energy levels in the vicinity of zero level($\lambda = 0$) are obtained after perturbation by solving f-by-f secular equation in a similar manner.

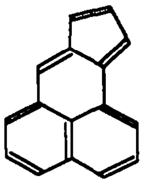
It would probably be worthwhile to attempt to apply this treatment for larger systems possessing many degenerate NBMOs. But in this article some applications for simple systems having only two NBMOs are presented to estimate the relationship between the size of odd-membered rings attached to a parent molecule and their electronic properties. In Sec. II, the difference in the electronic properties between cyclohepta[a]phenalene and cyclopenta[a]phenalene are clarified by means of above-mentioned perturbational treatment. Some applications are made in Sec. III for bicyclic hydrocarbons and those including polybenzenoid aromatics, and in Sec. IV for pentalenoid derivatives with bicyclic hydrocarbons. Finally, in Sec. V a summary and the conclusions are given.

II. Phenalene Derivatives

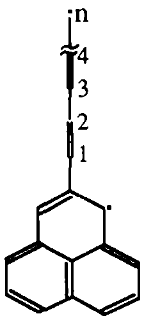
The high electron-donating nonalternant hydrocarbon, cyclohepta[a]phenalene **1**, was synthesized by Murata et al.[6)] Its high electron-donating ability was borne out experimentally by cyclic voltammetry and then confirmed by the extremely high HOMO orbital energy given by the simple Hückel method. They also pointed out that cyclopenta[a]phenalene **2** should possess high electron accepting nature since this molecule has the extremely low LUMO orbital energy. It is quite interesting that the two molecules derived from the same parent molecule **3** produce opposite chemical properties depending on the ring size.


Cyclohepta[a]-
phenalene

1

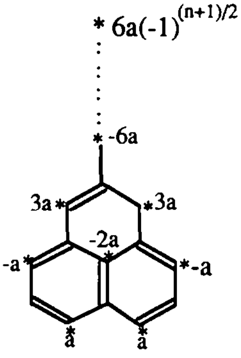

Cyclopenta[a]-
phenalene

2



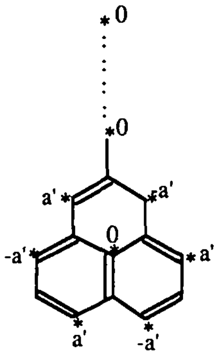
3

The neutral structure **3** with a linear chain composed of n carbons is taken as an unperturbed molecule. In the usual manner, this open shell structure has two NBMOs; one is symmetric and another is antisymmetric as follows,



ΨS

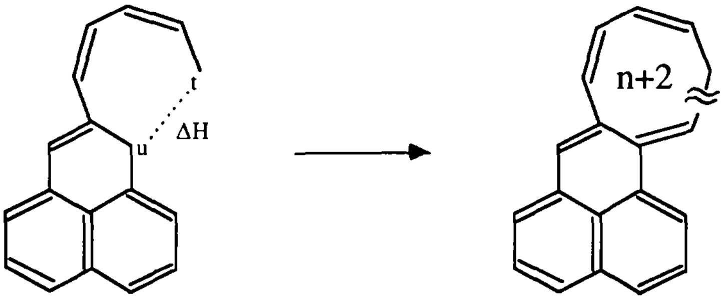
$$a = \frac{1}{\sqrt{2(9n+22)}}$$



ΨA

$$a' = \frac{1}{\sqrt{6}}$$

where a and a' are readily defined from normalization condition as a function of the chain length n. Now suppose a condensation of the radical on the atom n with that of the parent molecule. The solutions for the two NBMOs are then used in solving the perturbational problem. If the change of the Hamiltonian between the t-th AO (on the edge of the chain) and the u-th AO (on a carbon atom of the parent molecule) is given by ΔH, then the matrix element between them is defined as $\delta\beta = \langle\chi_t|\Delta H|\chi_u\rangle$.



3'

4

The secular equation (5) for the system 4 becomes as follows with respect to the n;

$$\begin{vmatrix} 36a^2(-1)^{\frac{n+1}{2}}\delta\beta - E^{(1)} & -6aa'(-1)^{\frac{n+1}{2}}\delta\beta \\ -6aa'(-1)^{\frac{n+1}{2}}\delta\beta & -E^{(1)} \end{vmatrix} = 0 \qquad (6)$$

The two solutions are given by

$$E_{\pm}^{(1)} = 18a^2(-1)^{\frac{n+1}{2}}\delta\beta \pm 6a(-1)^{\frac{n+1}{2}}\delta\beta\sqrt{9a^2 + a'^2}$$

$$= \frac{1}{9n+22}\{9\pm\sqrt{3(9n+49)}\}(-1)^{\frac{n+1}{2}} \quad . \tag{7}$$

These solutions are classified into two cases; n=1,5,9, ..., 4m+1 and n=3,7,11, ..., 4m+3.

If the n is 4m+1 (m=1,2, 3, ...), the LUMO energy is given by

$$E_{\mathrm{LUMO}}^{(1)} = -\frac{1}{9n+22}\{\,9 + \sqrt{3(9n+49)}\,\}\delta\beta \quad , \tag{8}$$

and the HOMO energy is

$$E_{\mathrm{HOMO}}^{(1)} = -\frac{1}{9n+22}\{\,9 - \sqrt{3(9n+49)}\,\}\delta\beta \quad . \tag{9}$$

These solutions indicate that the phenalene derivative **4** with n=1,5,9,13, ... possesses a electron-donating ability arising from the relatively high HOMO energy level.

If n is 4m+3 (m=1,2,3, ...), the LUMO energy is given by

$$E_{\mathrm{LUMO}}^{(1)} = \frac{1}{9n+22}\{\,9 - \sqrt{3(9n+49)}\,\}\delta\beta \quad , \tag{10}$$

and the HOMO energy is

$$E_{\mathrm{HOMO}}^{(1)} = \frac{1}{9n+22}\{\,9 + \sqrt{3(9n+49)}\,\}\delta\beta \quad . \tag{11}$$

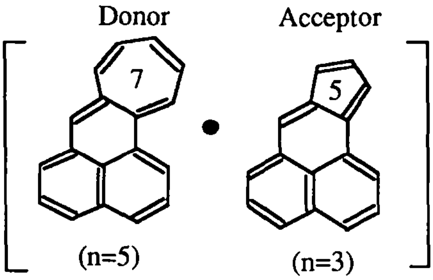
This shows that the structure **4** with n=3, 7, 11, ... , on the other hand, possesses a electron-accepting ability arising from the relatively low LUMO orbital energy level.

The results for the present method have been verified by carrying out the simple Hückel calculations on each system of non-alternant phenalene derivatives **4** with a perimeter of up to n=21 carbon atoms and with substituting β to $\delta\beta$ as shown in Table I. The relative tendency for each n+2 membered-ring is in excellent agreement with each other for the two methods, in which the absolute values of $E^{(1)}$ decrease as the conjugated system increases in size because of normalization of the coefficients.

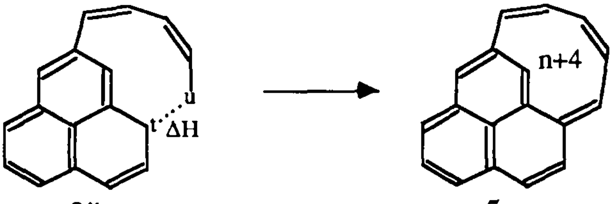
This suggests a possibility that the system with the ring size of n+2=4m+1 (corresponding to cyclohepta[a]phenalene series which will tend to give two electrons) and that of n+2=4m+3 (corresponding to cyclopenta[a]phenalene series which will tend to acquire two electrons) can mutually construct a hydrocarbon donor-acceptor charge transfer complex as shown in the following figure.

Table I Perturbational and variational energy levels as a function of n of compound **4**.

	Perturbation		Variation	
n	HOMO	LUMO	HOMO	LUMO
1	0.1352	-0.7158	0.1280	-0.5868
3	0.4918	-0.1245	0.4328	-0.1154
5	0.1163	-0.3850	0.1055	-0.3387
7	0.3215	-0.1098	0.2778	-0.0976
9	0.1044	-0.2791	0.0909	-0.2356
11	0.2485	-0.0998	0.2046	-0.0853
13	0.0958	-0.2253	0.0804	-0.1808
15	0.2070	-0.0923	0.1621	-0.0761
17	0.0892	-0.1921	0.0722	-0.1468
19	0.1797	-0.0865	0.1342	-0.0688
21	0.0840	-0.1693	0.0657	-0.1236



Next, we consider the following perturbation on a different site of the parent molecule.



3''

5

The secular equation to be solved is written as

$$\begin{vmatrix} -12a^2(-1)^{\frac{n+1}{2}}\delta\beta - E^{(1)} & -6aa'(-1)^{\frac{n+1}{2}}\delta\beta \\ -6aa'(-1)^{\frac{n+1}{2}}\delta\beta & -E^{(1)} \end{vmatrix} = 0 \tag{12}$$

The obtained two solutions are

$$\begin{aligned} E_{\pm}^{(1)} &= -6a^2(-1)^{\frac{n+1}{2}}\beta \pm 6a(-1)^{\frac{n+1}{2}}\delta\beta\sqrt{a^2+a'^2} \\ &= \frac{1}{9n+22}\left\{ -3\pm\sqrt{3(9n+25)} \right\}(-1)^{\frac{n+1}{2}}\delta\beta \end{aligned} \tag{13}$$

If the n is 4m+1 (m=1,2,3 .....), the LUMO energy is given by

$$E_{\mathrm{LUMO}}^{(1)} = -\frac{1}{9n+22}\left\{ -3+\sqrt{3(9n+25)} \right\}\delta\beta\ , \tag{14}$$

and the HOMO energy is

$$E_{\mathrm{HOMO}}^{(1)} = -\frac{1}{9n+22}\left\{ -3-\sqrt{3(9n+25)} \right\}\delta\beta\ . \tag{15}$$

From these solutions it can be seen that the phenalene derivative **5** with n=1,5,9,13, ... possesses a electron-accepting ability by means of the relatively low LUMO energy level.

If n is 4m+3 (m=1,2,3, ...), the LOMO energy is given by

$$E^{(1)}_{\mathrm{LUMO}} = \frac{1}{9n+22}\left\{ -3 - \sqrt{3(9n+25)} \right\} \delta\beta , \tag{16}$$

and the HOMO energy is

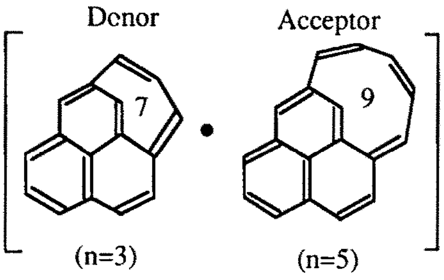
$$E^{(1)}_{\mathrm{HOMO}} = \frac{1}{9n+22}\left\{ -3 + \sqrt{3(9n+25)} \right\} \delta\beta . \tag{17}$$

This shows that the structure **5** with n=3, 7, 11, ... , on the other hand, possesses a electron-donating ability by the relatively high HOMO energy level.

The numerical results for this system **5** possessing a expanding ring (n+4) are shown in Table II in comparison with those by the simple Hückel method. The electronic properties depending on the n are in the reverse of the case of the structure **4**, while those depending on the member of the ring formed after perturbation are in the same. It can be seen in the structure **5** that the compound having the ring size of n+4=4m+3 and that of n+4=4m+1 may mutually produce a hydrocarbon donor-acceptor charge transfer complex as shown in the following figure.

Table II Perturbational and variational energy levels as a function of n of compound **5**.

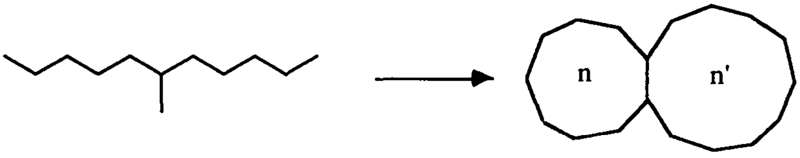
	Perturbation		Variation	
n	HOMO	LUMO	HOMO	LUMO
1	0.4226	-0.2290	0.3565	-0.2037
3	0.1937	-0.3161	0.1739	-0.2790
5	0.2611	-0.1715	0.2314	-0.1531
7	0.1559	-0.2265	0.1374	-0.1988
9	0.2023	-0.1440	0.2314	-0.1531
11	0.1346	-0.1842	0.1374	-0.1988
13	0.1701	-0.1269	0.1748	-0.1250
15	0.1204	-0.1587	0.1149	-0.1563
17	0.1492	-0.1149	0.1415	-0.1064
19	0.1101	-0.1412	0.0922	-0.1294
21	0.1343	-0.1059	0.1192	-0.0930



From these results it is pointed out that the biradical structure **3** has many possibilities to generate various closed shell structures which reveal high electron-donating or high electron-accepting properties depending on the chain length (n) and the linked site (ι). This simple perturbational treatment is considered to provide a way to design novel intermolecular charge transfer hydrocarbon complexes.

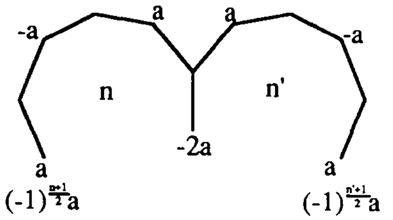
III. Non-alternant Bicyclic Hydrocarbons

The aromaticity of pentalene, heptalene and related bicyclic hydrocarbons has been studied by using an internally consistent LCAO-MO method by Boyd7). His treatment is generalized for bicyclic non-alternant hydrocarbons with a perimeter of 4N atoms by means of first-order perturbation theory and verified numerically. Our treatment is applied to bicyclic hydrocarbons **7** composed of two odd membered-rings and consistent results with those by Boyd are obtained . The n or n' indicates a number of the member of the two rings.

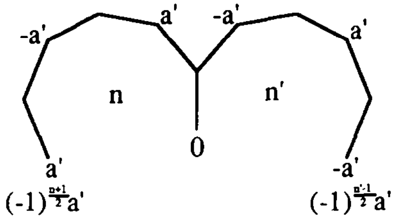


6 **7**

As a parent molecule we adopt the open ring structure **6** which has two symmetric and antisymmetric NBMOs as follows.



Ψ_S



Ψ_A

$$a = \sqrt{\frac{2}{n + n' + 6}} \qquad a' = \sqrt{\frac{2}{n + n' - 2}}$$

The HOMO and the LUMO energy levels are approximately determined as well, as functions of n and n' by solving the following two-by-two equation.

$$\begin{vmatrix} -\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'+1}{2}}\}4a^2\delta\beta - E^{(1)} & -2aa'\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'-1}{2}}\}\delta\beta \\ -2aa'\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'-1}{2}}\}\delta\beta & -E^{(1)} \end{vmatrix} = 0 \tag{18}$$

If n=4m+1 and n'=4m'+1 or n=4m+3 and n'=4m'+3 (m, m' =1,2,3,...), the eq.(18) is reduced to

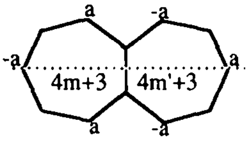
$$\begin{vmatrix} -\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'+1}{2}}\}4a^2\delta\beta - E^{(1)} & 0 \\ 0 & -E^{(1)} \end{vmatrix} = 0 \tag{18'}$$

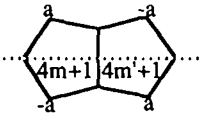
Then, the obtained solutions are

$$E^{(1)} = 0$$

$$\begin{aligned} E^{(1)} &= -\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'+1}{2}}\}4a^2\delta\beta \\ &= -\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'+1}{2}}\}\frac{8}{n + n' + 6}\delta\beta \end{aligned} \tag{19}$$

This means that only the antisymmetric orbital of the two NBMOs is retained as shown in the following figure.





If n = 4m+3 and n'=4m'+3, the remaining NBMO becomes a filled nonbonding level (HOMO) in which the coefficients are symmetric for the axis denoted by the dotted line, and then the other MO becomes LUMO. If n = 4m+1 and n'=4m'+1, on the other hand, the one of the two original NBMOs becomes an empty nonbonding level (LUMO) in which the coefficients are antisymmetric, and then the other MO becomes HOMO.

If n=4m+1 and n'=4m'+3 or n=4m+3 and n'=4m'+1 (m, m' =1,2,3,...), the eq.(18) becomes

$$\begin{vmatrix} -E^{(1)} & -2aa'\{(-1)^{\frac{n+1}{2}}+(-1)^{\frac{n'-1}{2}}\}\delta\beta \\ -2aa'\{(-1)^{\frac{n+1}{2}}+(-1)^{\frac{n'-1}{2}}\}\delta\beta & -E^{(1)} \end{vmatrix} = 0 \qquad (18'')$$

giving the following two solutions.

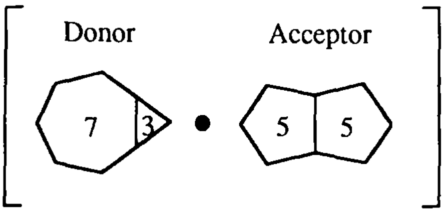
$$E^{(1)} = \pm\, 2aa'\{(-1)^{\frac{n+1}{2}}+(-1)^{\frac{n'-1}{2}}\}\,\delta\beta$$

$$= \pm\, 4\{(-1)^{\frac{n+1}{2}}+(-1)^{\frac{n'-1}{2}}\}\,\frac{1}{\sqrt{(n+n'-2)(n+n'+6)}}\,\delta\beta. \qquad (20)$$

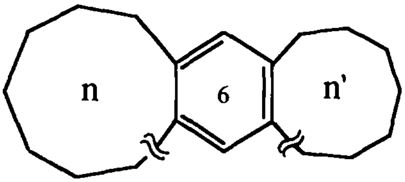
The degree of the destabilization and the stabilization after interaction between the two NBMOs are in the same order. This system reveals the properties attributed to aromatic hydrocarbons based on Hückel's 4N+2 rule. The overall agreement of the HOMO and the LUMO levels by eq.(20) with those by the simple Hückel method is shown in Table III at each n and n'. These results suggest that a series of bicyclic hydrocarbons composed of 4m+3 (the HOMO is at zero level) and those composed of 4m+1 (the LUMO is at zero level) can mutually produce a donor-acceptor charge transfer complex.

Table III Perturbational and variational energy levels as functions of n and n' of compound 7.

		Perturbation		Variation	
n	n'	HOMO	LUMO	HOMO	LUMO
3	3	0.0	-1.3333	0.0	-1.0000
3	5	0.8729	-0.8729	0.6180	-0.8203
3	7	0 0	-1.0000	0.0	-0.4450
5	5	1.0000	0.0	0.4707	0.0
5	7	0.5963	-0.5963	0.4773	-0.4004
5	9	0.8000	0.0	0.3033	0.0
7	7	0.0	-0.8000	0.0	-0.3111
7	9	0.3780	-0.3780	0.2950	-0.3348
7	11	0.0	-0.6667	0.0	-0.2294



These electronic properties are retained also in the case including a benzene ring as follows.



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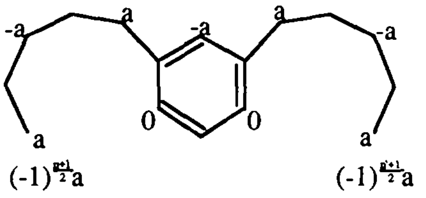
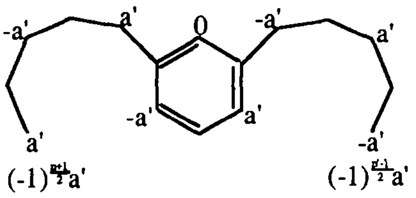
The open ring structure gives two NBMOs as is the case for bicyclic hydrocarbons.



Ψ_S



Ψ_A

$$a = \sqrt{\frac{2}{n+n'}} \qquad a' = \sqrt{\frac{2}{n+n'+2}}$$

The two-by-two equation for this structure is

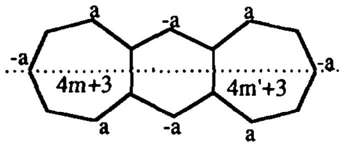
$$\begin{vmatrix} -E^{(1)} & -aa'\{(-1)^{\frac{n+1}{2}} - (-1)^{\frac{n'+1}{2}}\}\delta\beta \\ -aa'\{(-1)^{\frac{n+1}{2}} - (-1)^{\frac{n'+1}{2}}\}\delta\beta & -2\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'-1}{2}}\}a'^2\delta\beta - E^{(1)} \end{vmatrix} = 0 \qquad (21)$$

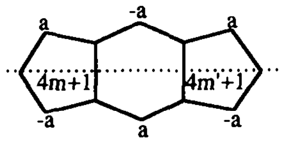
If n=4m+1 and n'=4m'+1 or n=4m+3 and n'=4m'+3 (where m, m' =1,2,3,.......), the eq.(21) gives the two solutions.

$$E^{(1)} = 0$$

$$E^{(1)} = -\{(-1)^{\frac{n+1}{2}} + (-1)^{\frac{n'-1}{2}}\}\frac{4}{n+n'+2}\delta\beta \qquad (22)$$

On the contrary to the case of the previous bicyclic hydrocarbon 7, only the symmetric orbital of the two NBMOs is retained at zero level. That generates a following symmetric filled non-bonding level for each case of n=4m+3 and n'=4m'+3 or an antisymmetric empty nonbonding level for n=4m+1 and n'=4m'+1.





The other solution becomes either the LUMO or the HOMO, respectively.

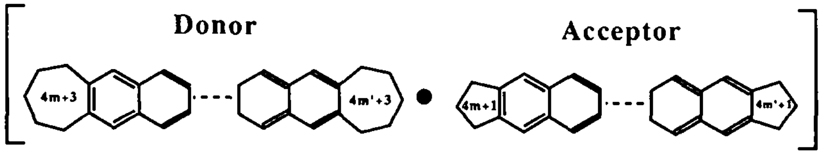
If n=4m+1 and n'=4m'+3 or n=4m+3 and n'=4m'+1 (m, m' =1,2,3,.......), the eq.(21) gives the two separated solutions.

$$E^{(1)} = \pm \{(-1)^{\frac{n-1}{2}} - (-1)^{\frac{n'-1}{2}}\}\frac{2}{\sqrt{(n+n')(n+n'+2)}}\delta\beta \tag{23}$$

Table IV Perturbational and variational energy levels as functions of n and n' of compound **8**.

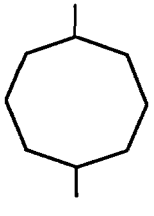
n	n'	Perturbation HOMO	Perturbation LUMO	Variation HOMO	Variation LUMO
3	3	0.0	-1.0000	0.0	-1.0000
3	5	0.4472	-0.4472	0.2950	-0.3775
3	7	0.0	-0.6667	0.0	-0.5550
5	5	0.6667	0.0	0.6180	0.0
5	7	0.3086	-0.3086	0.2607	-0.2154
5	9	0.5000	0.0	0.4184	0.0
7	7	0.0	-0.5000	0.0	-0.4450
7	9	0.2357	-0.2357	0.1694	-0.1973
7	11	0.0	-0.4000	0.0	-0.3340

As can be seen in Table IV, the behavior of the energy levels does not change essentially by including benzene ring, compared to the case of bicyclic hydrocarbons. As well as the case in the compounds of **7** and **8**, the introduction of two benzene rings into bicyclic hydrocarbons produces also symmetric or antisymmetric orbital at zero level. It is concluded that the electronic properties in the vicinity of zero level are retained even by including kata-fused polybenzene rings. A series of charge transfer complexes are considered as the following figure.

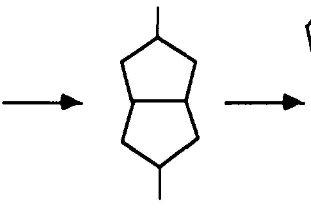


IV. Pentalenoid Derivatives

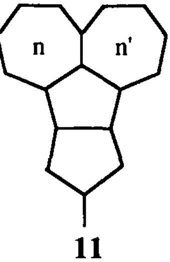
Next, we consider electronic properties of the structure **11** including n and n' odd membered-rings. The pentalenoid[8)] derivative **10** is regarded as a parent molecule, which can be produced from the monocyclic biradical structure **9**.



9

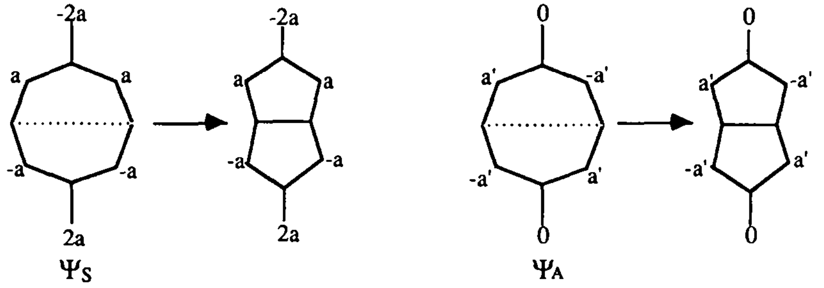


10

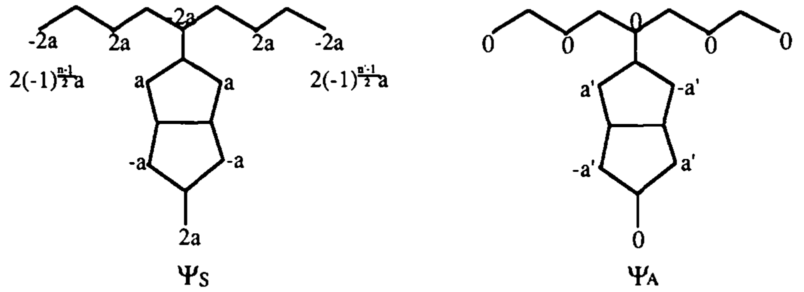


11

The biradical open shell structure **9** derived from a 4N-monocyclic system has the two symmetric and anti-symmetric NBMOs as shown in the following figure. Their symmetries are retained by cross-linkage between alternated atoms having no coefficients, i.e., unstarred and unstarred, which can be proved by means of secular equation based on molecular orbitals for the whole system. The symmetries are, therefore, preserved also in pentalenoid biradical derivative as shown in the following figure and this is confirmed by simple Hückel calculations.



The existence of the following two NBMOs is turned out because the individual symmetry is conserved by a elongation of a radical site in the parent molecule **10** with the polyene chain.



$$a=\frac{1}{\sqrt{2(n+n')}} \qquad a'=\frac{1}{2}$$

The previously-mentioned perturbational procedure can be applied to these orbitals. The two-by-two secular equation is given by

$$\begin{vmatrix} 4\{(-1)^{\frac{n-1}{2}}+(-1)^{\frac{n'-1}{2}}\}a^2\delta\beta\ -\ E^{(1)} & 2\{(-1)^{\frac{n-1}{2}}-(-1)^{\frac{n'-1}{2}}\}aa'\delta\beta \\ 2\{(-1)^{\frac{n-1}{2}}-(-1)^{\frac{n'-1}{2}}\}aa'\delta\beta & -E^{(1)} \end{vmatrix}=0 \qquad (24)$$

If n=4m+1 and n'=4m'+1 or n=4m+3 and n'=4m'+3 (m, m' =1,2,3,.......), the eq.(24) gives the two solutions.

$$E^{(1)} = 0$$

$$E^{(1)} = \{(-1)^{\frac{n-1}{2}} + (-1)^{\frac{n'-1}{2}}\}\frac{2}{n + n'}\delta\beta$$

As is the case for the compound **7** or **8**, one of the two NBMOs remains as either the HOMO (n= 4m+3 and n'=4m'+3) or the LUMO(n=4m+1 and n'=4m'+1) and the other becomes either the LUMO or the HOMO, respectively.

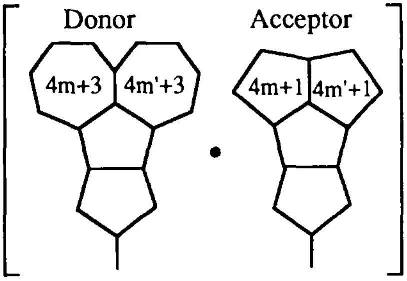
If n=4m+1 and n'=4m'+3 or n=4m+3 and n'=4m'+1 (where m, m' =1,2,3,.......), the eq.(24) gives the two separated solutions.

$$E^{(1)} = \pm\{(-1)^{\frac{n-1}{2}} - (-1)^{\frac{n'-1}{2}}\}\frac{1}{\sqrt{2(n+n')}}\delta\beta$$

From Table V, it can be seen that the behavior of the energy levels thus obtained is similar to the case of bicyclic hydrocarbons. That is, their electronic properties with respect to the HOMO and the LUMO levels are retained even by including pentalenoid derivative **10**. The charge transfer complexes are considered as the following figure. As well as the case of the bicyclic hydrocarbons, the HOMO of the donor series is at zero level and the LUMO of the acceptor series is at zero level.

Table V Perturbational and variational energy levels as functions of n and n' of compound **11**.

		Perturbation		Variation	
n	n'	HOMO	LUMO	HOMO	LUMO
3	3	0.0	-0.6667	0.0	-0.2108
3	5	0.2500	-0.2500	0.3608	-0.2203
3	7	0.0	-0.4000	0.0	-0.2019
3	9	0.2041	-0.2041	0.2622	-0.2175
5	5	0.4000	0.0	0.4311	0.0
5	7	0.2041	-0.2041	0.3086	-0.2015
5	9	0.2857	0.0	0.2811	0.0
5	11	0.1768	-0.1768	0.2688	-0.1776
7	7	0.0	-0.2857	0.0	-0.1879
7	9	0.1768	-0.1768	0.2300	-0.1959
7	11	0.0	-0.2222	0.0	-0.1701
7	13	0.1581	-0.1581	0.1807	-0.1895
9	9	0.2222	0.0	0.2173	0.0
9	11	0.1581	-0.1581	0.2059	-0.1694
9	13	0.1818	0.0	0.1732	0.0
9	15	0.1443	-0.1443	0.1864	-0.1446
11	11	0.0	-0.1818	0.0	-0.1510
13	13	0.1538	0.0	0.1463	0.0
15	15	0.0	-0.1333	0.0	-0.1178



V. Conclusion

It is shown that a series of charge transfer complexes of polycyclic non-alternant hydrocarbons are easily predicted by applying perturbation method for degenerate systems. It is concluded that most of polycyclic hydrocarbons including 4m+3 membered-rings indicate electron-donating ability and those including 4m+1 membered-rings electron-accepting ability, and then a complex composed of them is considered to be bounded by charge transfer interaction. On the other hand, the system including both of the 4m+1 and the 4m+3 membered-rings indicates an azulenoid-like aromatic stabilization by itself. These results seem natural in terms of the Hückel's 4N+2 rule. However, in our treatment, the intensities of electron-donating or electron-accepting abilities are numerically given by solving a simple determinant derived from the perturbation theory for degenerate systems. This method will be useful for predicting the electronic properties in the vicinity of zero level of complicated systems such as including many of odd membered-rings.

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