

INTRINSIC ENERGY OF PARTIAL STRUCTURE*

Katsunori SAKURAI and Kichisuke NISHIMOTO

Department of Chemistry, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Received December 1st, 1987

Accepted December 30th, 1987

Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

A modified model Hamiltonian has been proposed for the analysis of a given partial structure in the molecule. With this Hamiltonian, some interesting mirror image relationships have been derived. The calculated results for the intrinsic energies of hexagons (Benzene Character) in hydrocarbons showed that the stability of hexagon is well correlated with the number of Kekulé structures.

Attempts to elucidate the electronic structure of a partial structure in the molecule are meaningful for the theoretical study of molecular design and drug design. Therefore, we are doing quantum chemical study of the partial structure (PS). The purpose of our theoretical works is to propose useful concepts associated with active electrons of a PS in the molecule, such as characteristic energy, valence, regional reactivity, redox ability, polarizability and so on.

In the previous paper¹, we proposed a new idea for the PS analysis of conjugated systems. We introduced a new type of model Hamiltonian and applied to the analysis of Benzene Character of the hexagons in conjugated systems. Benzene is one of the most important PS which is closely related to aromaticity. The calculated results were in accord with previously proposed indices of aromaticity²⁻¹¹.

A molecule can be divided into a given PS and a residual part which is obtained by deleting all the bonds in the PS. For example in naphthalene, if we choose the l.h.s. hexagon as a PS, this molecule is divided into the hexagon and the residual part with five bonds shown in Scheme 1.



SCHEME 1

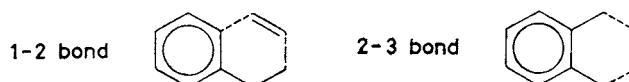
* Part II in the series Partial Structure Analysis of Conjugated Systems; Part I see ref.¹

The simplest PS is, of course, an atom in the molecule, and many concepts, such as charge density, frontier electron density¹², free valence¹³, and so on, are well established with this PS. In naphthalene, some possible PS's can be written as depicted in Scheme 2.

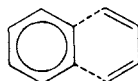
Atomic Structure



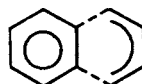
Ethylene Structure (or Double Bond Structure)



Butadiene Structure



Benzene Structure



SCHEME 2

For the convenience, the solid lines in PS are called as inner bonds and the dashed lines as outer bonds.

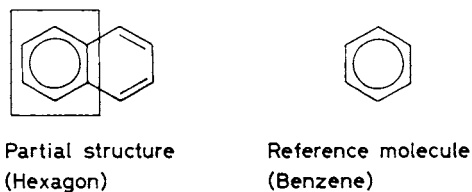
With our model Hamiltonians, one can see that the whole molecule can be stabilized by the deformation of the residual part. Our model Hamiltonians calculates not only the intrinsic energy of a given PS but also an extra energy coming from the deformation of the residual part. Our next attack is the calculation of the intrinsic stabilization or destabilization energy of a given PS. For this purpose, the residual part should be unchanged in the calculation using these model Hamiltonian. In this paper, we propose a modified model Hamiltonian which calculates only the intrinsic Π -electronic energy of a given PS.

THEORETICAL

At first, we summarize briefly the previous results. We introduce a following model Hamiltonian;

$$\mathbf{h}_e = \mathbf{h} - \sum_k \varepsilon_k |k\rangle \langle k|, \quad (1)$$

where \mathbf{h} represents Hückel Hamiltonian and $|k\rangle$ and ε_k (given by $\varepsilon_k = E_k - \alpha$) denote the k -th MO and MO energy of a reference molecule, respectively. Reference molecule means an isolated molecule which has the same molecular Π -electronic skeleton as the PS of interest (e.g. benzene for the analysis of Benzene Character of the hexagon, see Scheme 3).



SCHEME 3

The second term of r.h.s. of Eq. (1) represents an energy weighted projection operator. Therefore it transforms the bonding or antibonding MO's of the reference molecule to nonbonding MO's. If the summation of k runs over the bonding MO's of reference molecule, we call this model Hamiltonian as bonding MO's extracted Hamiltonian \mathbf{h}_b (abbreviated as bonding extracted Hamiltonian). Similarly if the summation of k runs over the antibonding MO's of the reference molecule, we call it as antibonding MO's extracted Hamiltonian \mathbf{h}_a (abbreviated as antibonding extracted Hamiltonian).

We define the degree of PS character, P_C , which is a measure of stabilization or destabilization energy of PS as follows;

$$P_C = P_{Cb} + P_{Ca} \quad (2)$$

$$P_{Cb} = (E - E_b)/E \quad (3)$$

$$P_{Ca} = (E - E_a)/E, \quad (4)$$

where E , E_b , and E_a are the total Π -electronic energies (in β unit) associated with \mathbf{h} , \mathbf{h}_b , and \mathbf{h}_a , respectively. The first term of r.h.s. of Eq. (2) represents the stabilization energy of PS by taking in the bonding MO's of reference molecule. On the other hand, the second term of r.h.s. of Eq. (2) represents the destabilization energy of PS by taking in the antibonding MO's of the reference molecule.

In this paper, we normalize these energies by E (total π -electronic energy of the reference molecule). This definition gives 1 for P_{Cb} , if the PS is isolated in the molecule (as the case of reference molecule). In this case, P_{Ca} becomes to be zero. In the case of alternant hydrocarbons, we obtained the following relation

$$P_{Cb} - P_{Ca} = 1. \quad (5)$$

Therefore, when we calculate P_{Cb} , the value of P_{Ca} is immediately obtained by Eq. (5).

We also found out that the pairing theorem is hold for the ψ_i and ε_i associated with \mathbf{h}_b and the ψ_{N-i+1} and ε_{N-i+1} associated with \mathbf{h}_a . It should be noted that the well known pairing theorem of Coulson and Rushbrooke¹³ is only hold for the parent Hamiltonian \mathbf{h} of an alternant hydrocarbon.

As an example, we apply the extracted Hamiltonian to the analysis of Benzene Character for the hexagon in naphthalene. The calculated bond orders associated with \mathbf{h} , \mathbf{h}_b , and \mathbf{h}_a are given in Table I, where the l.h.s. hexagon is analysed. We shall discuss the origin of the change in bond orders by using the unitary transformation of basis set. We represent MO's associated with \mathbf{h}_b by a linear combination of the parent MO's of naphthalene. The results are given in Table II.

It is seen from this table that occupied MO's associated with \mathbf{h}_b include the vacant MO's of naphthalene. This is due to the following reasons. In the variational procedure, the extracted Hamiltonian \mathbf{h}_b can operate on the full space of naphthalene MO's, which are spanned by five bonding MO's and five antibonding MO's. Therefore the calculated results by \mathbf{h}_b are not restricted within the variational space spanned by the occupied MO's of parent molecule (occupied MO's of naphthalene). Since the bonding MO's of benzene become to the nonbonding MO's in the calculation with \mathbf{h}_b , the bonding MO's of benzene cannot contribute to the stabilization of hexagon.

TABLE I
Calculated bond orders associated with \mathbf{h} , \mathbf{h}_b , and \mathbf{h}_a (atom numbering see Fig. 2)

Bond	\mathbf{h}	\mathbf{h}_b	\mathbf{h}_a
1-2	0.725	0.753	0.753
2-3	0.603	0.599	0.599
1-6	0.555	0.412	0.412
5-6	0.518	0.376	0.376
6-10	0.555	0.708	0.708
8-9	0.603	0.681	0.681
9-10	0.725	0.606	0.606

Contrary to the case of \mathbf{h} , the vacant (antibonding) MO's of naphthalene work to lower the total Π -electronic energy associated with \mathbf{h}_b . In other words, this means that the residual part deforms and causes the stabilization of the whole molecule. Thus occupied MO's associated with \mathbf{h}_b cannot be obtained by the unitary transformation of occupied MO's (bonding MO's) of the parent molecule associated with the parent Hamiltonian \mathbf{h} . Therefore, the occupation number of bonding MO's associated with \mathbf{h}_b is slightly different from that of occupied MO's associated with \mathbf{h} . This indicates that MO's associated with \mathbf{h}_b are slightly different in character from that with \mathbf{h} .

The calculated P_{Cb} consists of two terms. One is the intrinsic energy of a given PS, another is a relaxation energy of residual parts. This relaxation represents the flexibility of residual structure, when the PS cannot be stabilized by taking in the bonding MO's of the reference molecule. The flexibility may increase with the number of outer bonds and the strength of those connected between the PS and residual parts, and also the size of residual parts.

When the inner bonds in the PS are destroyed in the course of chemical reaction, this flexibility plays an important role for the lowering of the activation energy. Thus orbital deformation due to the participation of the vacant MO's associated with \mathbf{h} into the occupied MO's associated with \mathbf{h}_b plays a role of "energy buffer" in the chemical reaction, if it takes place at the region of PS.

In this paper, in order to calculate the intrinsic energy of PS, we introduce modified extracted Hamiltonians, in which we reinforce some requirements to insure that

TABLE II

LCMO coefficients for the MO's associated with \mathbf{h}_b , where the MO's of parent molecule (naphthalene) are used as MO basis set

MO	Occupied MO					Vacant MO				
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9	φ_{10}
φ_1	0.706	-0.664	0.000	0.240	0.000	-0.046	0.000	-0.025	0.000	0.000
φ_2	0.000	0.000	-0.857	0.000	-0.516	0.000	0.000	0.000	-0.007	0.005
φ_3	0.472	0.234	0.000	-0.800	0.000	-0.266	0.000	-0.112	0.000	0.000
φ_4	0.482	0.708	0.000	0.516	0.000	-0.064	0.000	-0.033	0.000	0.000
φ_5	0.000	0.000	-0.515	0.000	0.856	0.000	0.000	0.000	-0.036	0.022
φ_6	-0.174	-0.071	0.000	-0.158	0.000	0.942	0.000	0.229	0.000	0.000
φ_7	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000
φ_8	0.131	0.051	0.000	-0.106	0.000	0.189	0.000	0.966	0.000	0.000
φ_9	0.000	0.000	-0.024	0.000	0.027	0.000	0.000	0.000	0.999	0.001
φ_{10}	0.000	0.000	0.016	0.000	-0.017	0.000	0.000	0.000	-0.006	1.000

occupied MO's associated with \mathbf{h}_b and \mathbf{h}_a can be obtained by the unitary transformation of occupied MO's (bonding MO's) associated with \mathbf{h} . In the same way, the vacant MO's associated with those Hamiltonians can be obtained by the unitary transformation of the vacant MO's (antibonding MO's) associated with \mathbf{h} .

The modified extracted Hamiltonian can be expressed as follows

$$\mathbf{h}_{re} = \mathbf{h} - \sum_i^{\text{occ}} \sum_j^{\text{occ}} \sum_k \varepsilon_k C_{ik} C_{jk} |i\rangle \langle j|, \quad (6)$$

where C_{ik} and C_{jk} stand for the overlap between i -th and j -th occupied MO's of the parent molecule and k -th MO of the reference molecule, respectively. In the modified bonding extracted Hamiltonian \mathbf{h}_{rb} , the summation of k runs over all of the bonding MO's of the reference molecule, while in the modified antibonding extracted Hamiltonian \mathbf{h}_{ra} , the summation of k runs over all of antibonding MO's of the reference molecule. The summations of i and j run over the occupied MO's of the parent molecule.

It should be noted that if the summations of i and j run over the all of the MO's of the parent molecule, then the modified Hamiltonians, \mathbf{h}_{rb} and \mathbf{h}_{ra} become to be the same with the previously proposed extracted Hamiltonians, \mathbf{h}_b and \mathbf{h}_a , respectively, because of the completeness of these MO's.

Comparing Eq. (1) with Eq. (6), one can see that the MO's of the parent molecule are introduced as the projection operator in the modified extracted Hamiltonians. If we use these Hamiltonians, the vacant MO's of the parent molecule cannot contaminate the occupied MO's associated with \mathbf{h}_{rb} or \mathbf{h}_{ra} .

In order to understand the effect of the second term of r.h.s. of Eq. (6), we re-

0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	ε_6	0	0	0	0
0	0	0	0	0	0	ε_7	0	0	0
0	0	0	0	0	0	0	ε_8	0	0
0	0	0	0	0	0	0	0	ε_9	0
0	0	0	0	0	0	0	0	0	ε_{10}

FIG. 1
Matrix representation of \mathbf{h}_{rb} using MO basis set of parent MO's (MO's of naphthalene). $\varepsilon_6 \sim \varepsilon_{10}$ represent the energies of vacant MO's of naphthalene. The shaded parts represent the non-zero matrix elements

present \mathbf{h}_{rb} using MO basis set of parent MO's. The matrix elements for the analysis of the l.h.s. hexagon in naphthalene are schematically shown in Fig. 1. In \mathbf{h}_{rb} , the couplings between occupied MO's and vacant MO's are completely removed. Thus vacant MO's associated with \mathbf{h} cannot mix into the occupied MO's associated with \mathbf{h}_{rb} . The same situation occurs for the case of \mathbf{h}_{ra} .

Figs 2 and 3 give the calculated matrix elements of matrix representations associated with \mathbf{h}_b and \mathbf{h}_{rb} , respectively, in AO basis set for the analysis of the l.h.s. hexagon in naphthalene. In these figures, the matrix elements are very similar to each other. It should be noted that matrix elements exist not only between the

	1	2	3	4	5	6	7	8	9	10
1	-0.667									
2	0.500	-0.667								
3	-0.167	0.500	-0.667							
4	0.000	-0.167	0.500	-0.667						
5	-0.167	0.000	-0.167	0.500	-0.667					
6	0.500	-0.167	0.000	-0.167	0.500	-0.667				
7	0.000	0.000	0.000	0.000	1.000	0.000	0.000			
8	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000		
9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	
10	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	1.000	0.000

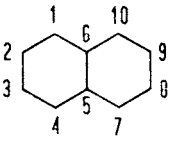


FIG. 2

Matrix representation of \mathbf{h}_b using AO basis set for naphthalene and the numbering of atoms. Only lower triangle matrix elements are shown

	1	2	3	4	5	6	7	8	9	10
1	-0.642									
2	0.473	-0.666								
3	-0.179	0.515	-0.666							
4	0.026	-0.179	0.473	-0.642						
5	-0.121	-0.036	-0.196	0.573	-0.543					
6	0.573	-0.196	-0.036	-0.121	0.597	-0.543				
7	-0.049	0.011	-0.008	-0.085	0.840	-0.143	-0.052			
8	0.015	-0.013	0.010	0.058	0.052	0.073	1.029	-0.017		
9	0.058	0.010	-0.013	0.015	0.073	0.092	0.027	0.986	-0.017	
10	-0.085	-0.008	0.011	-0.049	-0.143	0.840	-0.050	0.027	1.029	-0.052

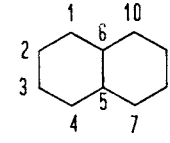
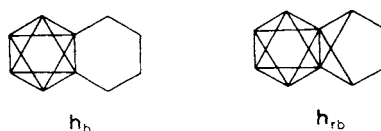


FIG. 3

Matrix representation of \mathbf{h}_{rb} using AO basis set for naphthalene and the numbering of atoms. Only lower triangle matrix elements are shown

nearest neighbour sites but also between the other non-neighbouring sites. Some main matrix elements can be graphically shown as in Scheme 4.



SCHEME 4

In this graph, the matrix elements from non-neighbours are given. We call these non-neighbour matrix elements as "phantom interaction", because they originally come from the propagation of electrons to the non-neighbour sites through the delocalized MO's of the reference molecule and the parent one.

When we diagonalize h_b , h_{rb} , and h_{ra} , we obtain the modified MO's and MO energies, which are shown in Figs 4–6. It is seen that the MO's associated with h_{rb} are almost same with those associated with h_b . The reason for this is that the matrix elements associated with these Hamiltonians are very similar to each other. It should be noted that the vacant MO's and the MO energies associated with both h_{rb} and h_{ra} are exactly same with those of the parent molecule. Moreover, the occupied MO's associated with h_{ra} are very similar to those associated with h , because the hexagon slightly takes in the antibonding MO's of benzene.

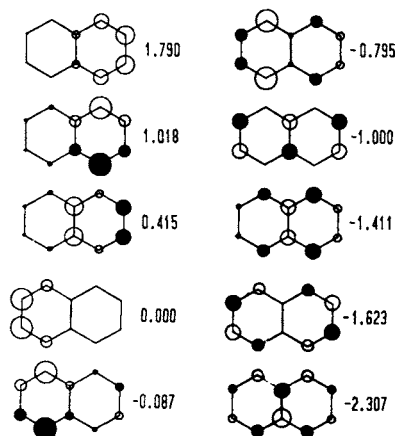


FIG. 4

MO's and MO energies associated with h_b

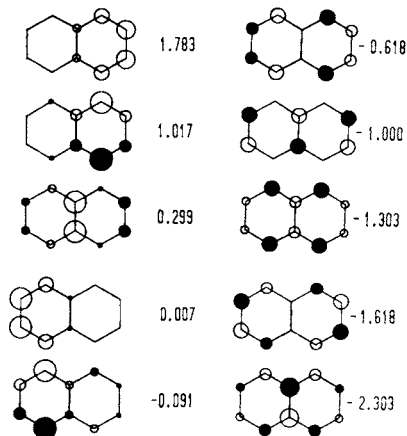


FIG. 5

MO's and MO energies associated with h_{rb}

One can obtain the occupied MO's associated with \mathbf{h}_{rb} or \mathbf{h}_{ra} by the unitary transformation of the occupied MO's of parent molecule. As an example for the analysis of l.h.s. hexagon in naphthalene, the occupied MO's associated with \mathbf{h}_{rb} can be expressed as the linear combination of occupied MO's of parent naphthalene as given in Table III. Therefore, physical properties coming from the nature of total Π -electrons such as charge densities and bond orders calculated by \mathbf{h}_{rb} are exactly same with those calculated by the parent Hamiltonian. However, since we use the different Hamiltonians, total Π -electronic energies are different.

Degree of PS character, P_{Cr} , associated with the modified extracted Hamiltonians can be written as follows:

$$P_{Cr} = P_{Crb} + P_{Cra} \quad (7)$$

$$P_{Crb} = (E - E_{rb})/E \quad (8)$$

$$P_{Cra} = (E - E_{ra})/E, \quad (9)$$

where E , E_{rb} , and E_{ra} are total Π -electronic energies (in β unit) calculated by \mathbf{h} , \mathbf{h}_{rb} , and \mathbf{h}_{ra} , respectively.

For alternant hydrocarbons, the following relation holds

$$P_{Crb} - P_{Cra} = 1 \quad (10)$$

which is similar to Eq. (5) for the case between \mathbf{h}_b and \mathbf{h}_a .

TABLE III

LCMO coefficients for the MO's associated with \mathbf{h}_{rb} , where the MO's of parent molecule (naphthalene) are used as MO basis set

MO	Occupied MO					Vacant MO				
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9	φ_{10}
φ_1	0.699	-0.670	0.000	0.251	0.000	0.000	0.000	0.000	0.000	0.000
φ_2	0.000	0.000	-0.856	0.000	-0.516	0.000	0.000	0.000	0.000	0.000
φ_3	0.476	0.173	0.000	-0.862	0.000	0.000	0.000	0.000	0.000	0.000
φ_4	0.534	0.722	0.000	0.440	0.000	0.000	0.000	0.000	0.000	0.000
φ_5	0.000	0.000	-0.516	0.000	0.856	0.000	0.000	0.000	0.000	0.000
φ_6	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000
φ_7	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000
φ_8	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
φ_9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000
φ_{10}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000

For alternant hydrocarbons, there is an interesting mirror image relationship between the occupied MO's and MO energies associated with h_{rb} and the vacant MO's and MO energies associated with h'_{ra} , where the prime means that the summations of i and j run over the vacant MO's of the parent molecule, instead of the occupied MO's in Eq. (6). This mirror image relationship is shown in Figs 5 and 7. Similarly there is a mirror image relationship between the occupied MO's and MO energies associated with h_{ra} and those associated with h'_{rb} as shown in Figs 6 and 8.

RESULTS AND DISCUSSION

We calculated the P_{Cr} 's of the hexagons in some alternant hydrocarbons using modified extracted Hamiltonians. This P_{Cr} value represents the Benzene Character of the hexagon. The results are shown in Fig. 9. It should be noted that since $E_b > E_{rb}$, by definition, the PS character calculated by h_{rb} is slightly larger than that calculated by h_b . Thus $P_{Crb} > P_{Cb}$. $\Delta P_C = P_{Crb} - P_{Cb}$ represents the flexibility of the electronic structure of the residual part due to the ability of taking in the vacant MO's of the parent molecule. Therefore it might relate closely with the polarizability of the residual part. ΔP_C increases with increasing the number of outer bonds connecting the PS and the residual part and the strength between them.

It is interesting to calculate the value of P_{Cr} of hexagons in quinones, because in these molecules the delocalization of π -electrons seems to be rather difficult and the double and single bonds are almost fixed.

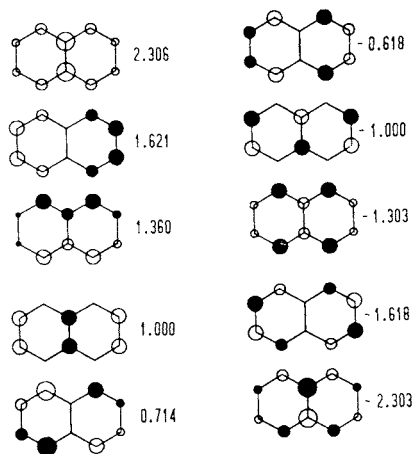


FIG. 6
MO's and MO energies associated with h_{ra}

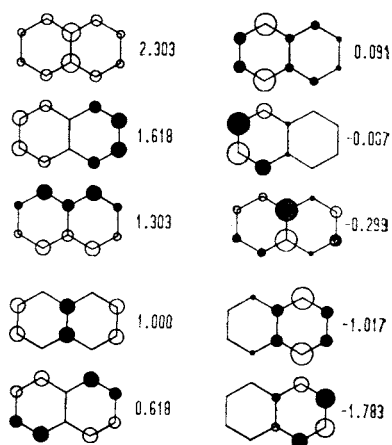
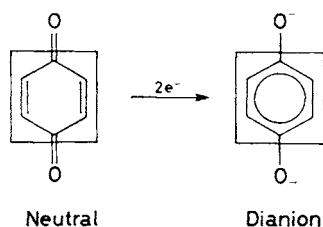


FIG. 7
MO's and MO energies associated with h'_{rb}

The calculated Benzene Characters for some hexagons in neutral quinons and corresponding dianions are shown in Figs 10 and 11. When *p*-benzoquinone receives two electrons, then two resonant Kekulé structures can be written in the hexagon part. Therefore, in *p*-benzoquinone dianion the Benzene Character is expected to be large, and it is to be small in neutral *p*-benzoquinone. The results are shown in Scheme 5.



SCHEME 5

The calculated results are in good agreement with this expectation. The major contribution to P_{Cr} is P_{Crb} . The destabilization due to P_{Cra} is very small. Detailed analysis of P_{Cr} shows that the largest contribution to P_{Crb} in dianion is φ_3 of benzene. Namely φ_2 of benzene works to form the quinoid structure of neutral *p*-benzoquinone.

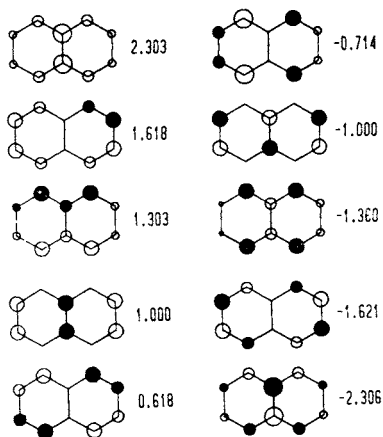


FIG. 8

MO's and MC energies associated with h'_{ra}

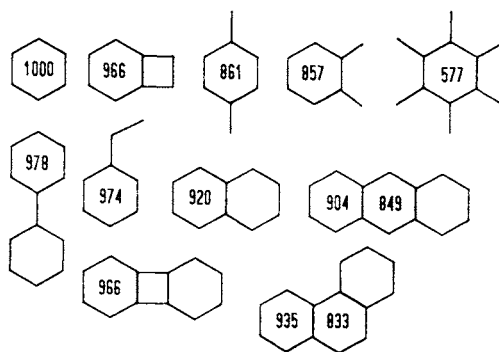
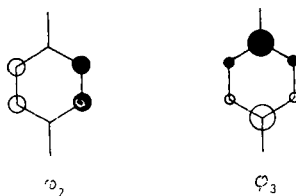


FIG. 9

Values of $P_{Cr} \cdot 10^3$ for the hexagons in some alternant hydrocarbons

Participation of φ_3 in dianion assists the delocalization of Π -electron in hexagon part and realizes the two resonant Kekulé structures (see Scheme 6).



SCHEME 6

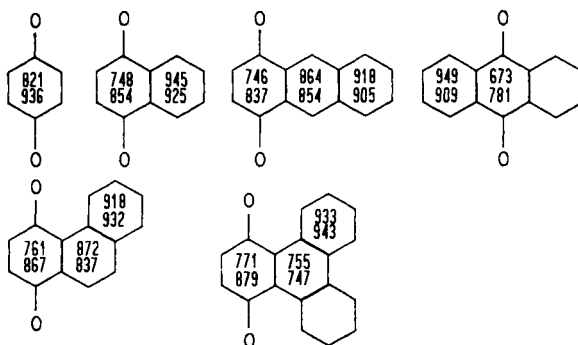


FIG. 10

Values of $P_{Cr} \cdot 10^3$ for the hexagons in *p*-benzoquinone type molecules. The upper values are for the neutral molecules and lower values for the dianions. Parameters for heteroatoms ($\alpha' = \alpha + h\beta$ for oxygen atom, $\beta' = k\beta$ for C=O bond) are $h = 1.0$ and $k = 1.1$, respectively

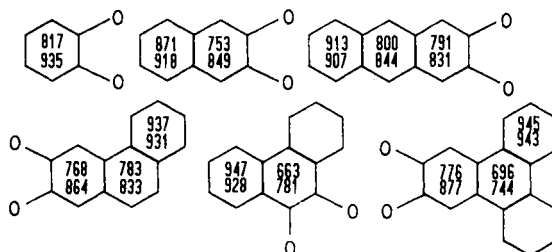
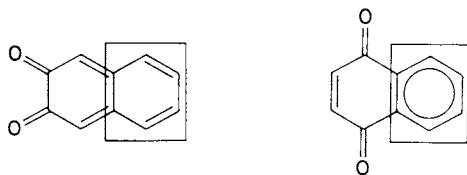


FIG. 11

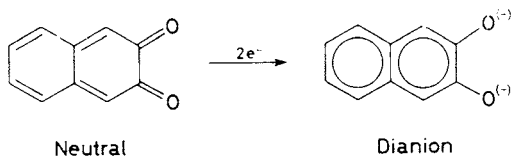
Values of $P_{Cr} \cdot 10^3$ for the hexagons in *o*-benzoquinone type molecules. The upper values are for the neutral molecules and lower values for dianions. Parameters for heteroatoms ($\alpha' = \alpha + h\beta$ for oxygen atom, $\beta' = k\beta$ for C=O bond) are $h = 1.0$ and $k = 1.1$, respectively

From Figs 10 and 11, it is found that increase of P_{Cr} in the dianion is almost localized in the area of hexagon of quinone structure. The values of P_{Cr} of hexagons in neutral quinones are well correlated with the number of possible Kekulé structures of the hexagon in a given molecule. For example, let us consider molecules shown in Scheme 7.



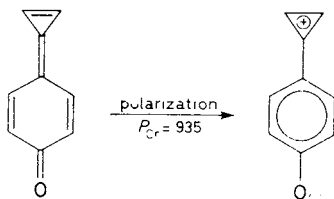
SCHEME 7

In case of 1,4-naphthoquinone, the l.h.s. hexagon has resonant two Kekulé structures. Therefore the calculated Benzene Character is quite large, while in 2,3-naphthoquinone, the l.h.s. of hexagon cannot have resonant Kekulé structures and the calculated Benzene Character is very small. In dianion, the l.h.s. hexagon of 2,3-naphthoquinone has two Kekulé structures. Therefore, in this case the Benzene Character becomes very large compared with the neutral species (see Scheme 8).



SCHEME 8

The following molecule is very interesting, because if an electron is transferred from the three-membered ring to the oxygen, it makes to form stable Hückel $4n + 2$ Π -electron systems each other (see Scheme 9).



SCHEME 9

Therefore, if this molecule is polarized easily, the Benzene Character of the hexagon becomes very large. The calculated results support this tendency.

The sum of bond orders of inner bonds in a given PS generally increases with the value of P_{Cr} of the PS of interest. This can be easily understood in the case of the hexagons in quinone molecules. In neutral *p*-benzoquinone, there exist only two double bonds in the hexagon part, however in dianion we can draw three double bonds in two resonant Kekulé structures for the hexagon.

The decrease of the number of the inner double bonds in the partial structure is nothing but the indication of weakening of bonds in it and then it causes the decrease of the value of P_{Cr} . By compensation for the weakening of bonds of hexagon in neutral quinone, the PS can form outer double bonds with oxygen. Thus we can conclude that formation of strong outer double bonds decreases the value of P_{Cr} . This suggests an alternative method to estimate the stabilization of the partial structure. The stabilization of PS (forming inner bonds) and that of whole molecule (forming outer bonds) compete with each other in a molecule. In actual molecules these two factors are well-balanced.

This work was partly supported by the Grant-in-Aid for Special Research Projects on the fundamental study on molecular design (No. 62124035) from Ministry of Education, Science and Culture.

REFERENCES

1. Sakurai K., Kitaura K., Nishimoto K.: *Theor. Chim. Acta* 69, 23 (1986).
2. Polansky O. E., Derfringer G.: *Int. J. Quantum Chem.* 1, 379 (1967).
3. Herndon W. C., Ellzey M. L., jr: *J. Am. Chem. Soc.* 96, 6631 (1974).
4. Randić M.: *Tetrahedron* 30, 2067 (1974).
5. Randić M.: *Tetrahedron* 31, 1477 (1975).
6. Hosoya H., Yamaguchi T.: *Tetrahedron Lett.* 1975, 4659.
7. Aihara J.: *Bull. Chem Soc. Jpn.* 49, 1429 (1976).
8. Aida M., Hosoya H.: *Tetrahedron* 36, 1317 (1980).
9. Shobu M., Hosoya H.: *Nat. Sci. Rep., Ochanomizu Univ.* 32, 55 (1981).
10. Shobu M., Hosoya H.: *Tetrahedron* 36, 1317 (1980).
11. Hosoya H., Shobu M., Takano K., Fujii Y.: *Pure Appl. Chem.* 55, 269 (1983).
12. Fukui K., Yonezawa T., Shingu H.: *J. Chem. Phys.* 20, 722 (1952).
13. Burkitt F. H., Coulson C. A., Longuet-Higgins H. C.: *Trans. Faraday Soc.* 47, 553 (1951).
14. Coulson C. A., Rushbrooke G. S.: *Proc. Cambridge Phil. Soc.* 36, 193 (1940).