REVISIT TO THE ELECTRON DENSITY, BOND ORDER, AND AROMATICITY

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Abstract——Spatial distribution of electrons in a molecule is analyzed by several different approaches, *i.e.*, MO, VB, and graph-theoretical methods. Quantum chemical interpretation of the concept of the oxidation number was obtained by *ab initio* MO calculation. The concepts of the local structure character and partial electron density are proposed and discussed.

INTRODUCTION

Although the concepts of electron density q_r and bond order p_{rs} are generally thought to be established, the analysis and interpretation of these quantities have been done mainly through the conventional definitions in terms of LCAO coefficient, C_{nr}, as

$$q_r = 2 \sum_{n}^{occ} c_{nr}^2 \tag{1}$$

$$p_{rs} = 2 \sum_{n}^{occ} c_{nr} c_{ns} \tag{2}$$

but not through the spatial distribution of electrons. Further, Mulliken's population analysis is a formal but somewhat arbitrary extension of these definitions (1). In these formalisms the coefficient C_{nr} gives us only point-information but not space-information. Thus no matter how the *ab initio* type wavefunctions of highest quality is used, there is an inevitable limit of understanding the electronic distribution as long as the population analysis technique is chosen.

On the other hand, the concept of the oxidation number has long been used favoritely in inorganic chemistry for predicting and interpreting the various aspects, including the electron distribution, of molecules during the oxidation-reduction reactions (2). In some cases this non-quantum mechanical quantity could give much more information than the more sophisticated calculation affords by conventional procedures. Graph-theoretical consideration also provides us some useful parameters which are quite easily calculable but give considerably reliable results for predicting the electronic properties of conjugated hydrocarbons (3-11). On the global and local aromaticity in benzenoid aromatic hydrocarbons several useful indices have been proposed both from the resonance-theoretical and graph-theoretical considerations (4-6,11-13). The molecular orbital analyses on the spatial electron distribution in these systems have not been performed until recently (14-20).

These apparent disadvantages of the molecular orbital theories might come from the fact that we really do not yet know how to squeeze the very essence out of the molecular orbital wavefunctions. The purposes of the present paper are to expose some of the important issues of the analysis of electronic distributions and to introduce some of our trials in these problems mainly on hydrocarbons and the related compounds.

ELECTRON DENSITY AND OXIDATION NUMBER

Several studies have been performed on the spatial distribution of electrons with direct numerical integration of the squares of the molecular orbital wavefunctions (14-17). Attempts to draw the contour maps of electron density of various sections have also been reported (18-20). However, none of these studies is suitable for a systematic and detailed analysis for clarifying the nature of the oxidation state. Recently Iwata (21) has obtained analytical expressions for the number and density of electrons in a sphere centered at an arbitrary point for the cases where the wavefunctions are written in terms of Gaussian type functions (GTF's). By using this technique we have calculated with the *ab initio* wavefunctions of varying quality the difference electron number $\Delta N(R)$ and difference spherically averaged electron density $\Delta \rho_0(R)$ relative to the sum of the free atom contributions,

$$\Delta N(R) = N(R) - \sum_{i}^{\text{atom}} N_i(R) \tag{3}$$

$$\Delta \rho_0(R) = \rho_0(R) - \sum_{i}^{\text{atom}} \rho_{0i}(R) \tag{4}$$

for a sphere of radius R around the sulfur and chlorine atoms for a series of molecules where the classical oxidation numbers of sulfur and chlorine atoms change stepwise (22). It was found that there is no dramatic change in the electron number $N(R)$ but a subtle and stepwise change in $\Delta N(R)$ and $\Delta \rho_0(R)$, especially in the latter quantity, can be detected in parallel

with the oxidation numbers which are assigned according to the standard but yet unproved recipe, *i.e.*, so as to attain the electrical neutrality for the whole molecule with hydrogen (+1) and oxygen (−2) atoms as the standard. For example, as seen in Fig. 1 the $\Delta \rho_0(R)$ values
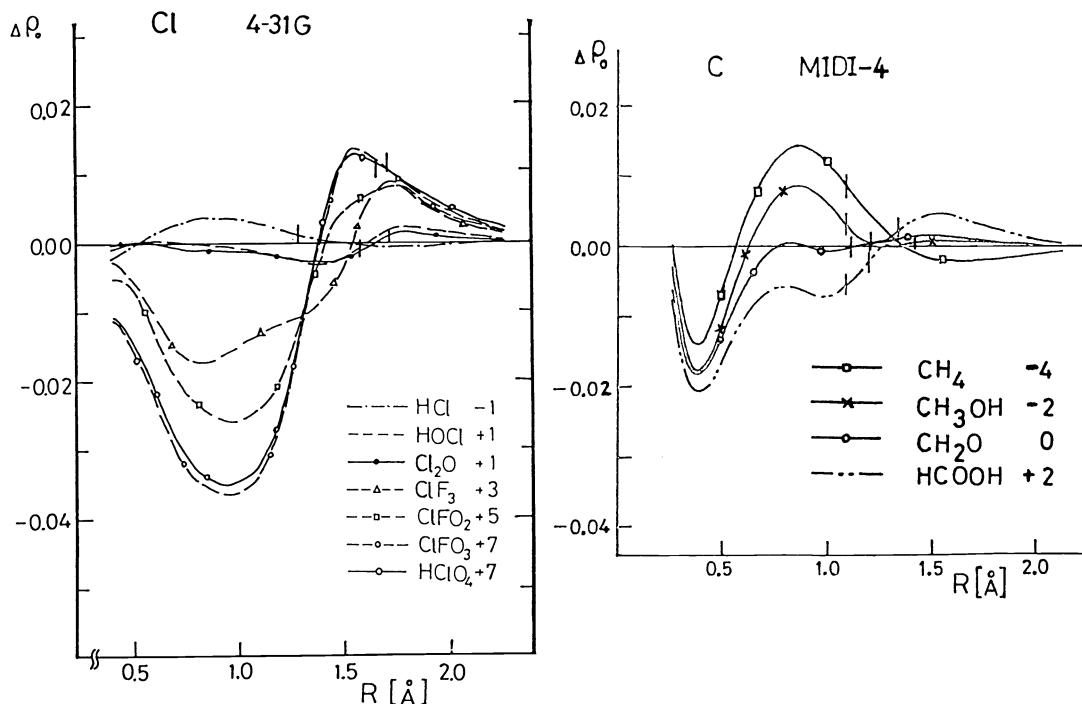

Fig. 1. Difference electron density $\Delta \rho_0(R)$ of Cl and C atoms in a series

of compounds. The signed number refers to their oxidation number.

for chlorine atoms in HCl (−1), HOCl (+1), Cl_2O (+1), ClF_3 (+3), $ClFO_2$ (+5), $ClFO_3$ (+7), and $HClO_4$ (+7) in the range around $R=1.0$ Å calculated with 4-31G wavefunctions are roughly proportional to the assigned oxidation numbers (in parentheses above). The actual change $\Delta N(R)$ in the number of electrons in the bonding region is almost one tenth of the classically assigned oxidation numbers, whose notion thus should be modified.

On the other hand, in organic chemistry the concept of the oxidation number has been abondoned ever since this concept was vigorously discussed in 1930's, although in most of the organic chemistry textbooks and courses the following series of changes,

$$CH_4 \text{ ---- } CH_3OH \text{ ---- } H_2CO \text{ ---- } HCO_2H \text{ ---- } CO_2$$
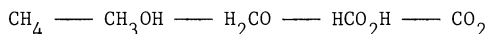
are explained as the changes of the oxidation state of the carbon atom.

We have performed the analysis of the $\Delta \rho_0(R)$ around the carbon and oxygen atoms of these molecules with five different basis sets of varying quality, *i.e.*, STO-6G, 4-31G, 4-31G** by Pople *et al.* (23) and MIDI-4 and MIDI-4* by Tatewaki and Huzinaga (24). As is evident from Fig. 1 with MIDI-4 basis, the subtle but stepwise change in $\Delta \rho_0(R)$ are observed in the bonding region around the carbon atom in proportion to the formally assigned oxidation numbers. The absolute magnitude of $\Delta \rho_0(R)$ for carbon per unit oxidation number is only a little smaller than in the case of chlorine and sulfur compounds. No significant change in $\Delta \rho_0(R)$ around the oxygen atom is observed, supporting the assumption that the oxygen is chosen as the standard. The basis set dependency is found to be small as long as a series of compounds are to be compared. This is a very important finding because it has long and widely been overlooked that

the carbon atoms in different surroundings even in the same molecule are actually different in the oxidation states as well as in the case of heavier atoms capable of showing various oxidation numbers. Analysis of the possible change of the electron density around the carbon atoms due to the hybridization, unsaturation, and ionicity (carbonium ion and carbanion) are being in progress. Our preliminary calculation shows that the oxidation state and oxidation number of the carbon atom in these molecules are largely determined by the number of =O (-2) and -OH (-1) bonded to it, and less dependent on the number of the bonding hydrogen atoms.

Correlation between the oxidation states of the carbon atoms and ^{1}H and ^{13}C NMR shift will be given fairly quantitative interpretation by extending this study.

On the other hand, owing to the pairing theorem by Coulson and Rushbrooke (25) there has not actually been fruitful discussion on the π-electron density on the carbon atom of unsaturated, especially alternant, hydrocarbons. For non-alternant hydrocarbons, however, the deviation of the π-electron density from unity can be well explained by the graph-theoretical consideration (10). From the molecular orbital standpoint, interesting features of the electron distribution in hydrocarbons, irrespective of their alternancy, will be demonstrated in the last part of this paper in terms of the "partial electron density".

MATHEMATICAL RELATIONS AMONG VARIOUS BOND ORDERS

Contrary to the above problem, the distribution of π-electrons in an unsaturated hydrocarbon network is known to be well understood by a rather simplified model. If we confine ourselves to the Hückel molecular orbital, the so-called Coulson bond order, p_{rs}^C, defined in Eq. (1) is shown to be analytically related to some other bond orders based on different theoretical grounds, such as resonance theory (RT) and graph-theory (GT). Namely, we have Ham-Ruedenberg bond order, p_{rs}^{HR} (26), Pauling bond order, p_{rs}^P, and topological bond order, p_{rs}^T (8,9), as

$$p_{rs}^{HR} = 2 \sum_n^{occ} (c_{nr}c_{ns}/x_n) \qquad \text{(HMO)} \qquad (5)$$

$$p_{rs}^P = K(G \ominus rs)/K(G) \qquad \text{(RT)} \qquad (6)$$

$$p_{rs}^T = Z_{G \ominus rs}/Z_G \qquad \text{(GT)} \qquad (7)$$

where x_n stands for the orbital energy (or $\varepsilon_n = \alpha + x_n\beta$) of n-th HMO, $K(G)$ is the number of the Kekulé structures for graph G, or the carbon atom skeleton of an unsaturated hydrocarbon, Z_G is the topological index of G, and $G \ominus rs$ means the subgraph of G obtained by deleting bond rs together with all the bonds adjacent to rs. The topological index is an index defined for characterizing the topological structure of a graph (27). A number of interesting properties and application of the topological index have been discovered (7-10,28). The p_{rs}^{HR} has been shown to be identical to p_{rs}^P for alternant hydrocarbons (29). This is one of the most dramatic relations showing the equivalence between the Hückel molecular orbital and resonance theories. By using the contour integral over the complex plane, as has been done by Coulson and Longuet-Higgins (30), the mathematical relations among the three different bond orders were obtained (9). Namely, if one defines the function $F_{G,rs}(y)$ as

$$F_{G,rs}(y) = \Delta_{r,s}(iy)/\Delta_G(iy) \qquad (8)$$

for a given bond rs in G, all these bond orders are shown to be expressed commonly through this function as

$$p_{rs}^C = \frac{1}{\pi} \int_{-\infty}^{\infty} F_{G,rs}(y) \, dy \qquad (9)$$

$$p_{rs}^P = F_{G,rs}(0) \qquad (10)$$

$$p_{rs}^T = F_{G,rs}(1) \qquad (11)$$

where Δ_G is the characteristic polynomial, or the determinant of the adjacency matrix of G, and Δ_{rs} is the cofactor, or adjunct, obtained from Δ_G by striking out row r and column s. From Eqs. (9)-(11) and after a little numerical calculations we get the following relation among the three different bond orders as

$$p_{rs}^C = c(p_{rs}^T + \lambda \, p_{rs}^P) \qquad (\lambda = 0.16). \qquad (12)$$

Note that the right hand side of Eq. (12) can quite easily be obtained even by a pencil and paper, we can estimate the relative magnitudes of p_{rs}^C for alternant hydrocarbons. Let us show an example in Fig. 2, where the p_{rs}^C value for 21 different bonds of benzanthracene 1 are plotted against the $p_{rs}^T + 0.16 p_{rs}^P$ value. Except for the three points (marked with ×) corres-

ponding to the bridge bonds almost all the points lie on a straight line. If one uses a different λ value (=0.22) for those three bonds the linearity will greatly be improved. The number given to each point in Fig. 2 represents the corresponding $K(G\ominus rs)$ value. The bonds having the largest and smallest bond orders are also marked with ℓ and s, respectively.

Once the correlations among these bond orders are established, we can analyze various aspects, especially the topological dependency, of the distribution of electrons in the carbon atom network more efficiently by complementary use of these quantities. Namely, taking the case of Fig. 2 as an example, we can analyze the reason why all the points lie almost in the order of the $K(G\ominus rs)$ values and further why the bond ℓ and s, respectively, have the largest and smallest p^C_{rs} value by scrutinizing the structure of the graph. Similarly we can analyze the reason why the flow of π-electrons in the central Broadway of type A network in Fig. 3 is more dense than that of type B whose structure differs from A just in the positions of the starred double bonds (*31*). The concept of the "bond notation" proposed by Vroelant and Daudel (*32*)
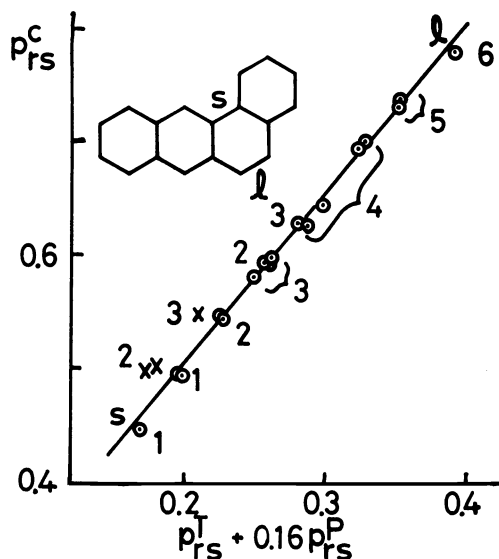

Fig. 2. Relations among Coulson, topological, and Pauling bond orders. The number refers to $K(G\ominus rs)$ value.
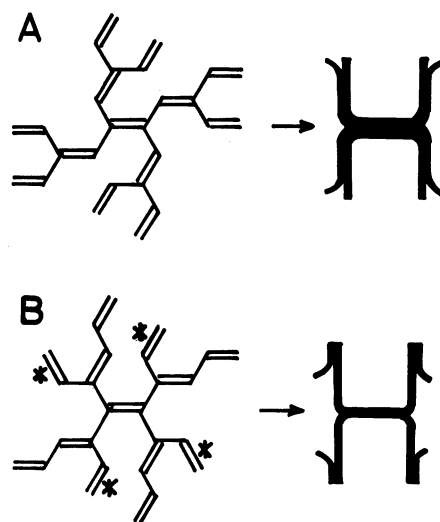
Fig. 3. Effect of branching on the flow of electrons. The central bond has large bond order in A than in B.

for discussing the topological dependency of the bond order can also be given a new light of the graph theory. By extending the graph-theoretical considerations several important consequences of the Hückel molecular orbital theory can be proved. For example, the effect of the formation of a 4n- or (4n+2)-membered ring or rings in a π-electronic network on the electron distribution and energy can fully be explained in terms of the characteristic polynomial and matching polynomial (*7,9,10,33*). This graph-theoretical discussion can be extended to the polarizability defined by Coulson and Longuet-Higgins (*29,34*). Recently Aono and his coworkers succeeded in deriving all the mathematical expressions of the Hückel molecular orbital theory in terms of the Green's function (or a propagator) and obtained a new insight into the topological nature of the π-electronic systems (*35*).

In order to elaborate, further, these discussions of the topological dependency of the π-electronic systems one has to check to what extent the result of the Hückel molecular orbital theory is valid by using more sophisticated approximations and methods. Although due caution should always be necessary, rather optimistic results are obtained as long as the electronic distribution is concerned (*31,36*).


AROMATICITY AND LOCAL STRUCTURE CHARACTER

The nature of the "aromaticity" has long been discussed from several different standpoints. Polansky and Derflinger (*37*) have proposed a useful concept of "benzene character" which is the projection of the occupied π-MO's of a polycyclic aromatic hydrocarbon onto the three occupied MO's of benzene localized in a given hexagon. This quantity can be expressed as a linear combination of the Coulson bond order for the component six bonds and for the three para-bonds in the hexagon L. The original definition of the benzene character for L can be transformed into the "normalized" benzene character as

$$\bar{r}_L = (2 \sum_{r>s}^{\text{ortho in L}} p^C_{rs} - \sum_{r>s}^{\text{para in L}} p^C_{rs})/3 - 2 \tag{13}$$

where either the Hückel MO or semi-empirical PPP MO may be used for calculating the bond orders (36). The VB-benzene character can also be defined as the ratio of the numbers of the Kekulé structures as

$$\overline{b}_L = 2\, K(G \ominus L)/K(G). \tag{14}$$

For a number of polycyclic aromatic hydrocarbons these benzene characters were calculated and analyzed with particular reference to the topology dependency. The local aromaticity in polycyclic aromatic hydrocarbons was then found to be largely determined by the local topological structure, but not necessarily by the global structure of the molecule. For example, the local aromaticity of 1 is well represented by a hybrid of anthracene (2) and phenanthrene (3) as
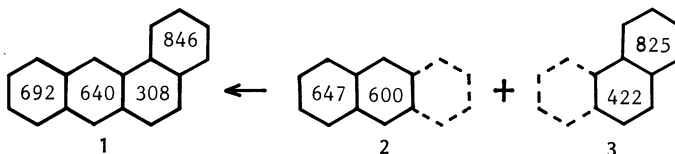

where the number in a hexagon is $1000\overline{r}_L$ calculated with the variable-β version of PPP MO.

Qualitatively almost the same conclusion can be drawn as symbolically depicted below
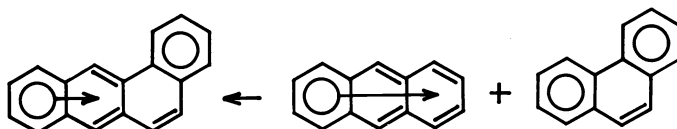
by using the concept of the aromatic sextet, induced by Clar from a large amount of experimental knowledges on the properties of polycyclic aromatic hydrocarbons (12). That this Clar's aromatic sextet has a profound mathematical meaning has been shown (38) by the aid of the graph-theoretical analysis technique, such as the sextet polynomial (11).

The local aromaticity of each of the component hexagons of 1 is roughly but quite readily deduced by enumerating the $K(G \ominus L)$ value (4-6,11,39) as
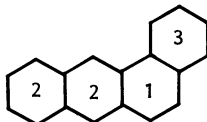
It became clear then that the local structure character, such as benzene character or local aromaticity, is well understood both by VB and GT considerations. The next question is whether it is possible to single out such a particular MO or a set of MO's for a given unsaturated hydrocarbon that could predict the distribution of π-electrons fairly well.

One can decompose the MO benzene character, Eq. (13), into the sum of the orbital contributions of the component MO's. For all the distinct hexagons of all the possible catacondensed aromatic hydrocarbons with three to five hexagons, the correlation coefficients, ρ's, between the MO benzene character and the orbital contribution of the component MO's and their various combinations were calculated (40). The result is that HOMO, or the frontier orbital, is nothing to do with the local aromaticity of any benzene ring in polycyclic aromatic hydrocarbons. Further, there is no such occupied MO that by itself reflects the local aromaticity reasonably well. Let us add the orbital contributions one by one successively from HOMO to the lower occupied orbitals. The combined contribution of the two highest occupied MO's still does not show high correlation with the total benzene character. However, if one takes the combined contribution of the three highest occupied orbitals, suddenly we get a high ρ value with the total benzene character, as large as 0.9, which, however, does not increase appreciably by adding further the contribution of the lower orbitals. Namely, the local aromaticity is determined largely by the combined contribution of the three highest occupied orbitals.

Among the polycyclic aromatic hydrocarbons studied the benzene character of the central hexagon of perylene 4 is the smallest, and the two double bonds and five single bonds in the central two hexagons of zethrene 5 are all fixed.
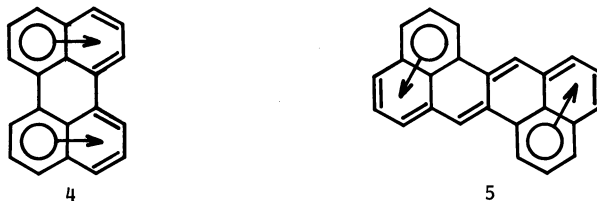
In these cases the MO naphthalene character can be defined following the discussion by Polansky and Derflinger (37). The VB naphthalene character can also be defined. Analysis of the

orbital contribution of the naphthalene character for cata- and peri-condensed aromatic hydrocarbons shows that the local naphthalene character of polycyclic aromatic hydrocarbons is largely determined by the combined contribution of the five highest occupied orbitals. The magic number 3 and 5 are no doubt the halves of the occupied π-electrons in benzene and naphthalene, respectively. One can extend this discussion to the definitions of butadiene character, hexatriene character, and so on. In this sense, to see the density of the HOMO or the frontier orbital is nothing else to see the ethylene character.

The above discussion leads one to introduce the concept of the partial electron density and also to draw its contour map in the plane above and below the molecular plane (*40,41*). The variable-β version of PPP MO was used and the distance between the plane for the contour map and the molecular plane was chosen to be one Bohr radius. In Fig. 4 are given the contour maps of the partial electron density of 1, where the orbitals are added from HOMO to the lower occupied orbitals. The number of the orbitals chosen are 1 (ρ_h), 2 ($\rho_{\bar{2}}$), 3 ($\rho_{\bar{3}}$), and 5 ($\rho_{\bar{5}}$), respectively. The ρ_h represents the frontier orbital density and predicts the possible sites of the electrophilic substitution reaction originally pointed out by Fukui *et al.* (*42*), but no aromatic character can be perceived from ρ_h. As the number of the combined orbitals increases, the shape of the molecular skeleton gradually appears. The $\rho_{\bar{3}}$ clearly indicates that the π-electron system of 1 is divided roughly into three parts, *i.e.*, naphthalene, benzene, and ethylene moieties, and further the distribution of electrons within these parts is
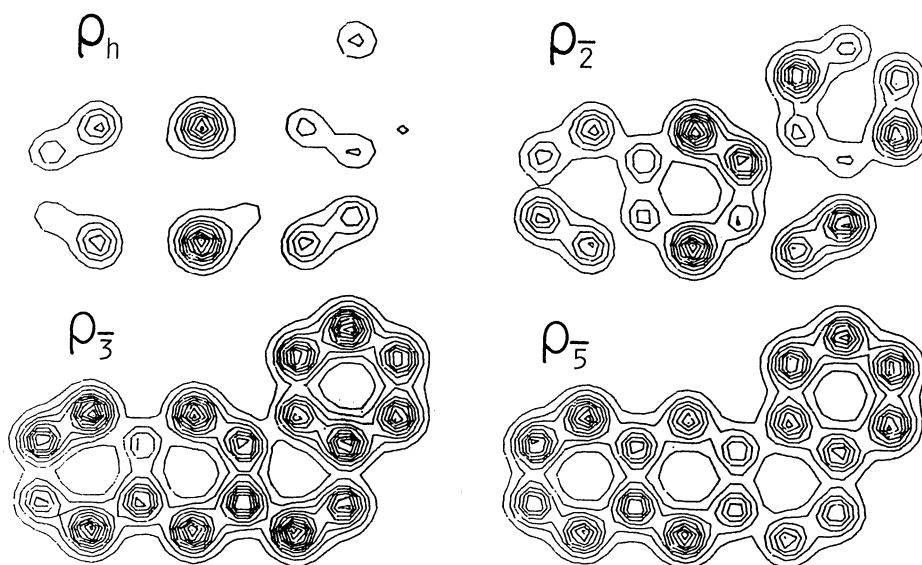

Fig. 4. Contour maps of the partial electron densities of 1.

very smooth. The relative magnitudes of the VB-benzene character can also be estimated from the $\rho_{\bar{3}}$ map. Namely, the electron distribution in each of the two hexagons of anthracene moiety is less smooth than that in the terminal hexagon of phenanthrene moiety, while in the kink hexagon the electron distibution is divided into three subunits showing small benzene character. On the other hand, from the $\rho_{\bar{5}}$ map fairly smooth electron distribution is perceived in the naphthalene moiety in the left half of 1. Thus by the complementary use of $\rho_{\bar{3}}$ and $\rho_{\bar{5}}$ maps we cna easily deduce that the ground state of 1 is well represented by the so-called Clar's diagram shown above.

Similarly the characteristic features of the electronic distribution of 4 and 5 as depicted above can be embossed from the $\rho_{\bar{3}}$ and $\rho_{\bar{5}}$ maps as shown in Fig. 5. Note that in these compounds highly localized naphthalene moieties can be seen from the $\rho_{\bar{5}}$ map, while the distribution of electrons in each of the benzene rings is a little distorted in the $\rho_{\bar{3}}$ map. We have succeeded in visualizing the characteristic features, such as local aromaticity and localized double bond character, of a number of polycyclic aromatic hydrocarbons by drawing the contour maps of various partial electron densities (*40,41*). Except for some cases the Clar's hypothesis of assigning aromatic sextets in these compounds is thus generally supported.

As the last examples we will show the $\rho_{\bar{3}}$ maps of the typical non-benzenoid hydrocarbons in Fig. 6. These maps are not necessarily the replicas of the electronic distributions of these molecules but represent their interesting features. Namely, 6, 7, and 10 are polyene-like,

whereas **8**, **9**, and **11** are aromatic or pseudo-aromatic. The electronic properties of these molecules will be more clearly understood if information from other $\rho_{\bar{n}}$ maps is supplemented.

It was confirmed that the choice of parameters, *i.e.*, choice of AO, height of the contour map plane, exact location of the carbon atoms, the spacings between the contour lines, or even
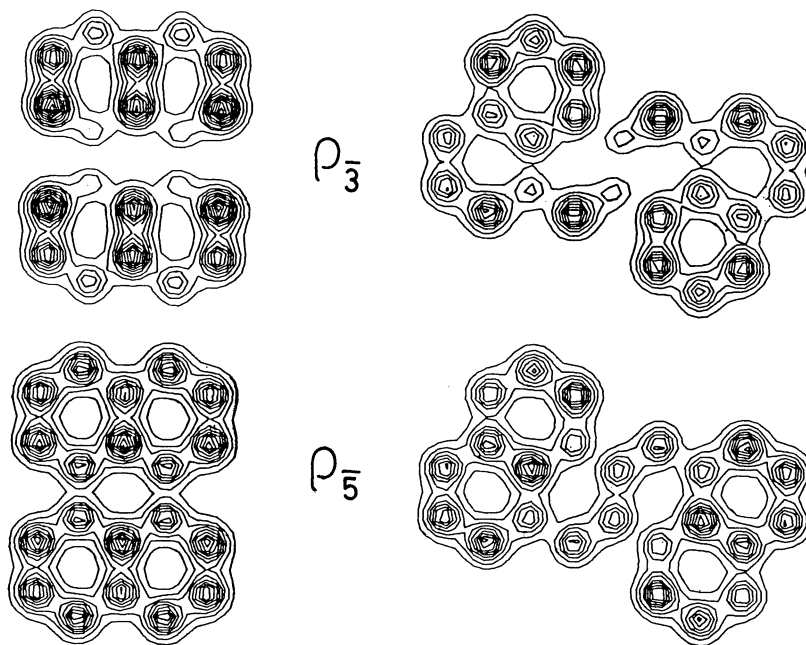

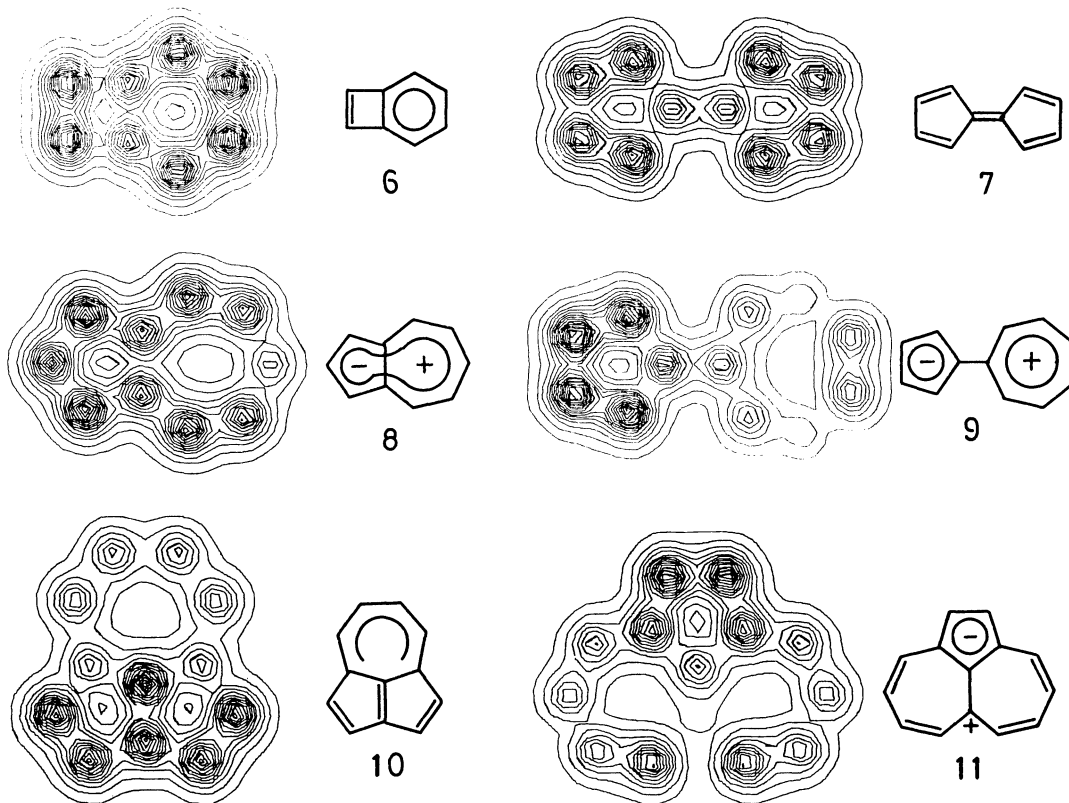Fig. 5. Contour maps of the partial electron densities of **4** and **5**.

Fig. 6. Contour maps of the partial electron densities, $\rho_{\bar{3}}$, of **6-11**.

the quality of MO (*i.e.*, HMO wavefunctions give essentially the same information), is not essential for discussing the 2-dimensional features of the local structure characters. The most important factor is how to select a set of orbitals out of the occupied orbitals. As one scrutinizes the combined distribution of π-electrons one by one from the HOMO to the lower occupied orbitals, various aspects of the π-electronic properties of the molecule gradually come out.

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