An LCUAO Treatment of Reactivity in Aromatic Hydrocarbons

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Several theoretical treatments of reactivity of conjugated molecules have achieved a brilliant developent in accordance with the progress of the LCAO MO method. In this procedure, the molecular orbital is represented by the linear combination of 2π atomic orbitals. By the use of these coefficients useful indices of reactivity such as electron density(1), bond order(1), and frontier electron density(2) are derived.

On the other hand, a method, the so-called LCUAO MO, in which the molecular orbital is represented by the linear combination of united-atomic orbitals in each bond of a conjugated molecule has been developed by Brown and Matsen(3). This method is an extension of united-atom approach(4) in hydrogen molecule to conjugated compounds.

This procedure may be considered to supply us more easily with information on the nature of a conjugated double bond if we introduce the frontier electron concept in LCAO MO treatment.

Theoretical

By an ordinary procedure of LCUAO MO method(3), a molecular orbital is written as

$$\psi=\sum_i a_i\phi_i \tag{1}$$

where ϕ_i is the UAO of the ith bond. The secular equation for the system can be obtained from this molecular orbital putting the matrix elements as following.

$$h_{ii}=\int\phi_i{}^*h\phi_i\mathrm{d}\tau=\alpha$$

$$h_{ij}=\int\phi_i{}^*h\phi_j\mathrm{d}\tau=\beta \text{ for adjacent bond} \tag{2}$$

$$0 \text{ for non-adjacent bond}$$

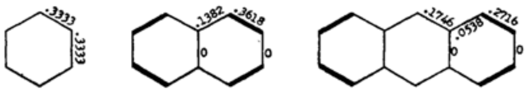
where h is the effective one electron hamiltonian, and α and β are the standard Coulomb and resonance integrals in benzene, respectively. Then all the molecular orbital coefficients are determined from the roots of the secular equation by using normalizing condition

$$\sum_i(a_i)^2=1 \tag{3}$$

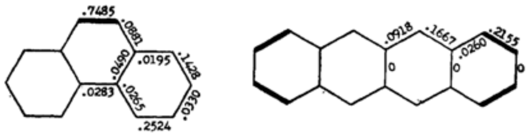
Brown and Matsen(3) has proposed that bond order, P_r, for the rth bond can be obtained by

$$P_r=\sum_j\nu_j(a_r{}^j)^2 \tag{4}$$

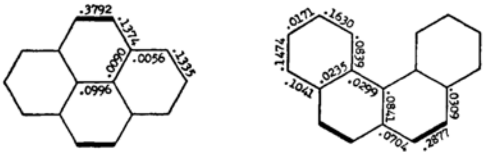
where ν_j is the occupation number for the jth molecular orbital. Then they showed that a good parallelism can be obtained between the bond orders obtained by simple LCAO MO treatment and by the present method.



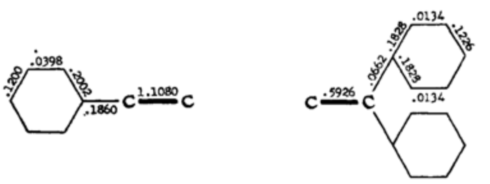
Benzene Naphtalene Anthracene



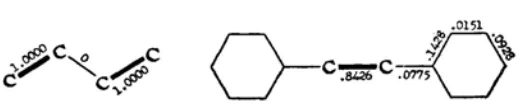
Phenanthrene Naphthacene



Pyrene 3, 4-Benzophenanthrene



Styrene 1, 1-Diphenylethylene



Butadiene Stilbene

Fig. 1. Electron densities of the highest occupied orbital.

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1) H. C. Longuet-Higgins and C. A. Coulson, *Proc. Roy. Soc.*, **A192**, 16 (1947).

2) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954).

3) R. D. Brown and F. A. Matsen, ibid., **21**, 1298 (1953).

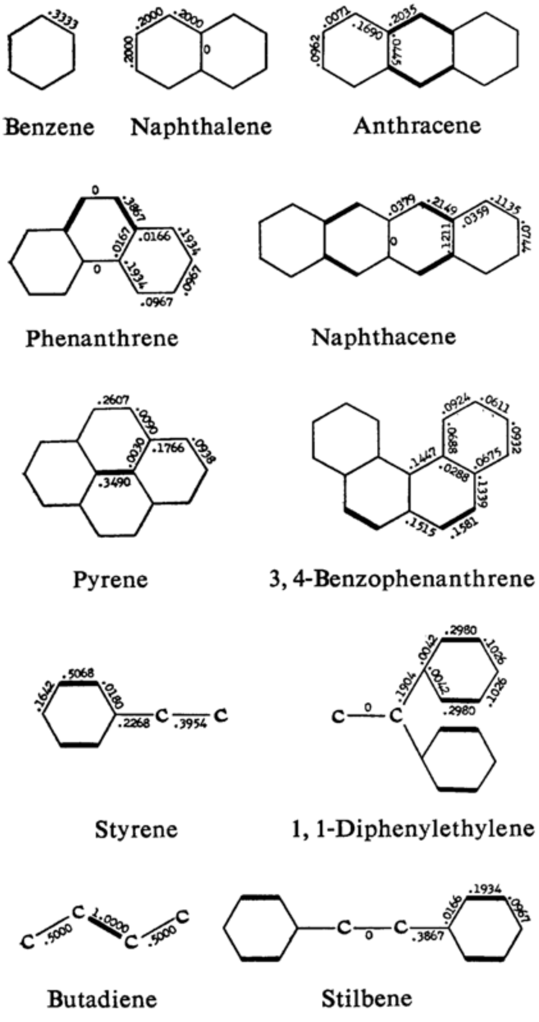
4) R. D. Brown, *J. Chem. Soc.*, **1953**, 2615.

TABLE I. REACTIVE BOND IN AROMATIC HYDROCARBONS

Compound	Experimentally most reactive bond*	Bond of largest frontier density	Bond of minimum ortho localization energy**
Benzene	1 : 2	1 : 2	1 : 2
Naphthalene	1 : 2	1 : 2	1 : 2
Anthracene	1 : 2	1 : 2	1 : 2
Phenanthrene	9 : 10	9 : 10	9 : 10
Pyrene	4 : 5	4 : 5	4 : 5
Naphthacene	1 : 2	1 : 2	1 : 2
3, 4-Benzophenanthrene (Benzo[*c*]phenanthrene)	5 : 6	5 : 6	5 : 6

* Estimated from the addition reaction of OsO_4, which is considered to be an electrophilic addition taking place simultaneously at the two adjacent carbon atoms.

** Ref. 7.



Benzene Naphthalene Anthracene

Phenanthrene Naphthacene

Pyrene 3, 4-Benzophenanthrene

Styrene 1, 1-Diphenylethylene

Butadiene Stilbene

Fig. 2. Electron densities of the lowest vacant orbital.

In these circumstances the investigation is made to elucidate whether or not the frontier electron concept by which the chemical reactivity in conjugated molecules is successfully interpreted may be applicable in LCUAO MO method. The calculation is carried out with respect to benzene, naphthalene, anthracene, naphthacene, pyrene, 3, 4-benzophenanthrene (benzo[*c*]phenanthrene), styrene, stilbene and 1, 1-diphenylethylene. The electronic distributions of the highest occupied and the lowest vacant orbitals are calculated and indicated in Figs. 1 and 2.

Results and Discussion

The bond of the largest frontier electron density for electrophilic reaction in polycondensed aromatics are indicated in the third column of the Table I. These results may give some information concerning the bond which will play a dominant role in the complex formation of aromatic hydrocarbons with Ag^+ ion⁵⁾ or H^+ ion. Furthermore the bond of the largest electron density of the highest occupied orbital in 1, 1-diphenylethylene coincides with the position pointed out by Evans and his coworkers⁶⁾ in the complex formation of this compound with H^+. In regard to styrene, butadiene and stilbene, calculated results are considered to be reasonable.

On the other hand, the electronic distribution of the lowest vacant orbital shown in Fig. 2 seems to correspond to none of the chemical reactions ever known. But since there exist no experimental data available, we must refrain here from deciding whether the results thus obtained are essentially meaningless or not. But one thing attracts our attention. That is, the most reactive position does not coincide with what is predicted from the electronic distribution of the highest occupied orbital,

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5) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938); R. E. Kofahl and H. J. Lucas, ibid., **76**, 3933 (1954).

6) A. G. Evans, D. M. S. Jones and J. H. Thomas, *J. Chem. Soc.*, **1957**, 104.

while the existing theories of these compounds predict the same position to be most reactive in both electrophilic and nucleophilic additions. A typical one of these theories is the localization theory⁷⁾. This point should be investigated in future.

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7) E. C. Kooyman and J. A. A. Ketelaar, *Rec. trav. chim.*, **65**, 859 (1946); R. D. Brown, *J. Chem. Soc.*, **1950**, 3249.