LCAO SCF Calculation on Anthracene and Reactivity Indexes in SCF Method

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In order to interpret chemical reactivity of conjugated molecules, there have been proposed several quantum-mechanical methods in LCAO MO treatment, such as the frontier electron method (frontier electron density and superdelocalizability as reactivity indexes[1]), the static method (total π-electron density and self-polarizability for an ionic reaction and free valence for a radical reaction)[2]), the localization method (localization energy)[3]), and so on.

Within the scope of the simple LCAO MO treatment, where electronic interaction is not explicitly considered, total π-electron density of an alternant hydrocarbon is unity for all the positions[4]), and accordingly in terms of the static method the ionic reactivity is to be determined by self-polarizability of each position. But once electronic interaction is taken into account, the uniformity of total π-electron distribution is immediately extinguished, so that its magnitude comes to correspond to the ionic reactivity in a molecule in the static method. For *trans*-butadiene the coefficients of AO's in MO's, calculated in semi-empirical SCF method[5]), in non-empirical SCF method[6]) and in non-empirical SCF CI method[7]), show the larger π-electron density, i. e., the larger electrophilic reactivity, at the position 2, contradictory to the experiments. Further, semi-empirical SCF calculation on naphthalene leads to an erroneous prediction of electrophilic reactivity[8]).

For the purpose of obtaining more information on reactivity indexes, in the first two paragraphs of the present paper, we determine the coefficients of AO's in MO's of anthracene by semi-empirical LCAO SCF method and discuss on some physico-chemical properties. In the last paragraph it is examined whether or not each of total π-electron density, free valence and frontier electron density remains a good index of chemical reactivity in SCF treatment.

Method

Roothaan has developed in detail the general formalism of LCAO SCF method for the closed configuration of a molecule[9]). This will not be repeated here for the sake of brevity. Using his theory with only π-electrons considered explicitly, we numerically calculate the coefficients of AO's in SCF MO's of the ground state of anthracene.

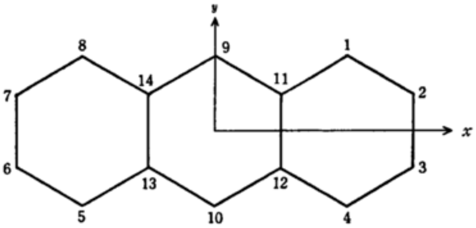

Fig. 1. The numbering of atoms and the coordinate of symmetry operation of anthracene.

The numbering of atoms and the coordinate of symmetry operation are shown in Fig. 1. The bond distances are taken to be 1.370 Å for the bond 1—2, 1.396 Å for 9—11, 1.408 Å for 2—3, 1.423 Å for 1—11 and 1.436 Å for 11—12, and all the bond angles are assumed in a good approximation to be 120° [10]).

Necessary numerical evaluation of the reasonance integral, $\beta_{\mu\nu}$, and the coulomb repulsion integral, $\gamma_{\mu\nu}$, are carried out on the semi-empirical formulae proposed by

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[1] K. Fukui et al., *J. Chem. Phys.*, **20**, 722 (1952); **22**, 1433 (1954); This Bulletin, **27**, 423 (1954).

[2] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947); F. H. Burkitt et al., *Trans. Faraday Soc.*, **47**, 553 (1951).

[3] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1940).

[4] C. A. Coulson and S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

[5] C. M. Moser, *Compt. rend.*, **238**, 1585 (1954).

[6] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.* **18**, 1338 (1950).

[7] A. Pullman and J. Baudet, *Compt. rend.*, **238**, 241 (1954); A. Pullman *J. chim. phys.*, **51**, 188 (1954).

[8] C. M. Moser, ibid., **52**, 24 (1955).

[9] C. C. J. Roothaan, *Revs. Mod. Phys.*, **23**, 69 (1951).

[10] A. McL. Mathieson et al., *Acta Cryst.*, **3**, 245 (1950); V. C. Sinclair et al., ibid., **3**, 251 (1950). Deviations of all the observed bond angles from 120° are about 1~2°.

TABLE I. SCF MO'S AND THEIR ORBITAL ENERGIES OF ANTHRACENE

Symmetry	Orbital energy[a]	MO	
b_{1u}	$\varepsilon_1=-5.762$	$\phi_1=0.4887\sigma_4+0.4448\sigma_5+0.3323\sigma_6+0.6730\sigma_7$	occupied
b_{2g}	$\varepsilon_2=-5.190$	$\phi_2=0.5818\sigma_8+0.6276\sigma_9+0.5174\sigma_{10}$	
b_{1u}	$\varepsilon_3=-3.350$	$\phi_3=0.3108\sigma_4+0.7098\sigma_5-0.3717\sigma_6-0.5113\sigma_7$	
b_{3g}	$\varepsilon_4=-3.196$	$\phi_4=0.6278\sigma_{11}+0.3465\sigma_{12}+0.4423\sigma_{13}+0.5386\sigma_{14}$	
a_{1u}	$\varepsilon_5=-2.433$	$\phi_5=0.7932\sigma_1+0.4861\sigma_2+0.3668\sigma_3$	
b_{2g}	$\varepsilon_6=-1.9935$	$\phi_6=0.0792\sigma_8+0.5894\sigma_9-0.8039\sigma_{10}$	
b_{3g}	$\varepsilon_7=-0.2930$	$\phi_7=0.5130\sigma_{11}+0.4221\sigma_{12}-0.6793\sigma_{13}-0.3117\sigma_{14}$	
b_{1u}	$\varepsilon_8=+7.1389$	$\phi_8=0.4431\sigma_4-0.3746\sigma_5-0.7573\sigma_6+0.2997\sigma_7$	unoccupied
a_{1u}	$\varepsilon_9=+7.6451$	$\phi_9=0.0811\sigma_1+0.5125\sigma_2-0.8548\sigma_3$	
b_{2g}	$\varepsilon_{10}=+9.124$	$\phi_{10}=0.8095\sigma_8-0.5087\sigma_9-0.2932\sigma_{10}$	
b_{1u}	$\varepsilon_{11}=+9.668$	$\phi_{11}=0.6843\sigma_4-0.3974\sigma_5+0.4219\sigma_6-0.4425\sigma_7$	
b_{3g}	$\varepsilon_{12}=+9.726$	$\phi_{12}=0.1781\sigma_{11}-0.5967\sigma_{12}-0.5090\sigma_{13}+0.5943\sigma_{14}$	
a_{1u}	$\varepsilon_{13}=+11.747$	$\phi_{13}=0.6035\sigma_1-0.7079\sigma_2-0.3671\sigma_3$	
b_{3g}	$\varepsilon_{14}=+12.069$	$\phi_{14}=0.5576\sigma_{11}-0.5880\sigma_{12}+0.2895\sigma_{13}-0.5095\sigma_{14}$,	

where[b]

$\sigma_1=(1/2)(\phi_1-\phi_4+\phi_5-\phi_8)$, $\sigma_2=(1/2)(\phi_2-\phi_3+\phi_6-\phi_7)$, $\sigma_3=(1/2)(\phi_{11}-\phi_{12}+\phi_{13}-\phi_{14})$,
$\sigma_4=(1/2)(\phi_1+\phi_4+\phi_5+\phi_8)$, $\sigma_5=(1/2)(\phi_2+\phi_3+\phi_6+\phi_7)$, $\sigma_6=(1/\sqrt{2})(\phi_9+\phi_{10})$,
$\sigma_7=(1/2)(\phi_{11}+\phi_{12}+\phi_{13}+\phi_{14})$, $\sigma_8=(1/2)(\phi_1+\phi_4-\phi_5-\phi_8)$, $\sigma_9=(1/2)(\phi_2+\phi_3-\phi_6-\phi_7)$,
$\sigma_{10}=(1/2)(\phi_{11}+\phi_{12}-\phi_{13}-\phi_{14})$, $\sigma_{11}=(1/2)(\phi_1-\phi_4-\phi_5+\phi_8)$, $\sigma_{12}=(1/2)(\phi_2-\phi_3-\phi_6+\phi_7)$,
$\sigma_{13}=(1/\sqrt{2})(\phi_9-\phi_{10})$, $\sigma_{14}=(1/2)(\phi_{11}-\phi_{12}-\phi_{13}+\phi_{14})$

a) W_{2p} as standard. In units of eV. b) ϕ_i is the AO on the i-th atom.

Pariser and Parr[11]. In the expression of the coulomb integral, α_μ,

$$\alpha_\mu=W_{2p}-\sum_{\nu(\neq\mu)}\{\gamma_{\mu\nu}+(\nu:\mu\mu)\} \qquad (1)$$

no particular values of the coulomb penetration integral, $(\nu:\mu\mu)$, have been given by Pariser and Parr, and on the theoretical consideration[12] we have determined its average value as 0.85 eV. when the atoms μ and ν are adjacent, as 0.08 eV. when μ and ν are separated by a single atom, and as zero otherwise. W_{2p} in Eq. 1 is as usual the electronic energy of a carbon atom in its valence state and is regarded as a constant.

Results and Discussion on Anthracene

The obtained SCF MO's, ϕ_i, of the ground state of anthracene and their orbital energies, ε_i, are collected in Table I, together with non-occupied MO's.

Ionization Potential. — Putting $W_{2p}=-11.28$ eV.[11], we obtain 11.57 eV. as the first ionization potential of anthracene, which is, though no experimental results are available, much larger than the estimated value, 7.23 eV., by Matsen[13]. Giving too large calculated value is not particular to the case of anthracene, but the general tendency of SCF calculation[5,6,8]; on this point a discussion shall be made in near future.

Electronic Spectra. — The energies of configurations, the values of interconfigurational matrix elements and wave functions of the excited states are listed in

TABLE II. THE ENERGIES OF CONFIGURATIONS, THE VALUES OF INTERCONFIGURATIONAL MATRIX ELEMENTS AND THE EXCITED STATES WAVE FUNCTIONS[a]

B_{2u}: $[66\mid 99]=5.535$, $[69\mid 96]=0.551$,
$[77\mid 88]=5.419$, $[78\mid 87]=0.885$.
$E(\mathrm{V}_{78})-E_0=3.782$, $E(\mathrm{V}_{69})-E_0=5.206$,
$E(\mathrm{T}_{78})-E_0=2.013$, $E(\mathrm{T}_{69})-E_0=4.104$.
$[67\mid 89]=-0.094$, $[69\mid 87]=0.369$.
$\langle\mathrm{V}_{78}\mid\mathrm{V}_{69}\rangle=0.833$, $\langle\mathrm{T}_{78}\mid\mathrm{T}_{69}\rangle=0.094$.
$\Psi({}^1B_{2u}^-)=0.908\ \mathrm{V}_{78}-0.418\ \mathrm{V}_{69}$,
$\Psi({}^1B_{2u}^+)=0.418\ \mathrm{V}_{78}+0.908\ \mathrm{V}_{69}$,
$\Psi({}^3B_{2u}^-)=0.999\ \mathrm{T}_{78}-0.045\ \mathrm{T}_{69}$,
$\Psi({}^3B_{2u}^+)=0.045\ \mathrm{T}_{78}+0.999\ \mathrm{T}_{69}$.
B_{3u}: $[66\mid 88]=5.145$, $[68\mid 86]=0.348$,
$[77\mid 99]=5.198$, $[79\mid 97]=0.502$.
$E(\mathrm{V}_{79})-E_0=3.743$, $E(\mathrm{V}_{68})-E_0=4.684$,
$E(\mathrm{T}_{79})-E_0=2.740$, $E(\mathrm{T}_{68})-E_0=3.987$.
$[76\mid 89]=-0.094$, $[79\mid 86]=-0.415$.
$\langle\mathrm{V}_{79}\mid\mathrm{V}_{68}\rangle=-0.736$, $\langle\mathrm{T}_{79}\mid\mathrm{T}_{68}\rangle=0.094$
$\Psi({}^1B_{3u}^+)=0.877\ \mathrm{V}_{79}+0.480\ \mathrm{V}_{68}$,
$\Psi({}^1B_{3u}^-)=0.480\ \mathrm{V}_{79}-0.877\ \mathrm{V}_{68}$,
$\Psi({}^3B_{3u}^-)=0.997\ \mathrm{T}_{79}-0.075\ \mathrm{T}_{68}$,
$\Psi({}^3B_{3u}^+)=0.075\ \mathrm{T}_{79}+0.997\ \mathrm{T}_{68}$.

a) In units of eV.

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[11] P. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 465, 767 (1953).
[12] R. G. Parr and B. L. Crawford, ibid., **16**, 1049 (1948).
[13] F. A. Matsen, ibid., **24**, 602 (1956).

TABLE III. THE EXCITATION ENERGIES AND THE OSCILLATOR STRENGTHS OF ANTHRACENE

Symmetry	Excitation energy (eV.)		Oscillator strength	
	Calcd.	Obsd.	Calcd.	Obsd.
$^1B_{2u}^-$	3.40	3.30[a]	0.15	~0.1[a]
$^1B_{3u}^+$	3.34	3.50[a]	0.20	~0[a]
$^1B_{3u}^-$	5.09	4.80[a]	1.94	2.20[a]
$^1B_{2u}^+$	5.59	5.64[a]	1.01	0.65[a]
$^3B_{2u}^-$	2.01	1.8[b]	0.00	—
$^3B_{3u}^-$	2.73	—	0.00	—
$^3B_{3u}^+$	3.99	—	0.00	—
$^3B_{2u}^+$	4.11	—	0.00	—

a) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

b) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); S. P. McGlynn, M. R. Padhye and M. Kasha, *J. Chem. Phys.*, **23**, 593 (1955).

Table II, where only four lower excitations are considered. The calculated excitation energies and oscillator strengths are given in Table III, together with the observed values. The agreement with experiments is good, but for the inversion of excitation energies of $^1B_{2u}^-$ band and $^1B_{3u}^+$ band, which will be improved by the inclusion of more possible configurations.

Bond Order and Bond Distance. — Our SCF bond orders and observed bond distances are collected in Table IV, in comparison with the SCF bond orders by Pritchard and Sumner in a rough approximation[14] and with the bond orders in simple LCAO treatment. It is seen in Table IV that SCF bond orders in the present calculation are parallel with the observed bond distances except for the bond 11—12, in accordance with Pritchard and Sumner's result. The discrepancy in the bond 11—12 seems to indicate that the bond order of a bonding is not determined only by its length but by its nature; namely, whether the ending carbons of this bonding are primary, secondary or tertiary.

TABLE IV. THE BOND ORDERS AND OBSERVED BOND DISTANCES OF ANTHRACENE

Bond	Bond order			Obsd. bond distances (Å)[b]
	Present treatment	Pritchard and Sumner[a]	Simple LCAO	
1—2	0.8347	0.8422	0.7374	1.370
9—11	0.6107	0.6318	0.6061	1.396
2—3	0.4542	0.4493	0.5859	1.408
1—11	0.4383	0.4178	0.5354	1.423
11—12	0.5533	0.5484	0.4849	1.436

a) Ref. 14.

b) Ref. 10.

SCF Reactivity Indexes

First of all we define SCF frontier electron density in the same way as in simple LCAO treatment[1], where the frontier orbital denotes the highest occupied one for an electrophilic reaction, the lowest unoccupied one for a nucleophilic reaction, and both for a radical reaction.

The calculated results of total π-electron density, free valence and frontier electron densities of anthracene are given in Table V. Values of these reactivity indexes in SCF method of naphthalene and *trans*-butadiene are collected in Tables VI and VII, respectively.

Total π-electron density of anthracene is the largest at the position 11 and decreases in the order of 2, 1 and 9. The position 11 being out of the question because of its lack of hydrogen to be substituted, an electrophilic substitution should take place at the position 2 and a nucleophilic substitution at the position 9 on the basis of the static method. This prediction contradicts experimental results that the position 9 is the most reactive in an electrophilic substitution. Concerning naphthalene the position 2, where SCF total π-electron density has the largest value as shown in Table VI, does not actually suffer from an electrophilic substitution. Furthermore, as for butadiene Table VII shows that total π-electron densities by semi-empirical SCF method, by non-empirical SCF method and by non-empirical SCF CI method lead to the same erroneous prediction that the position 2 is the most susceptible to an electrophilic reaction. Thus SCF total π-electron density is no longer a good index for chemical reactivity.

On the contrary, it will be valuable to emphasize that SCF frontier electron density correctly predicts the most reactive positions, that is, the position 9 in anthracene, 1 in naphthalene and 1 in

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[14] H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.*, **A226**, 128 (1954); H. O. Pritchard, private communication. Their assumptions are the same as those that are presented by Pople[15], the main points of which are (1) neglect of the coulomb penetration integral, and (2) assumption of equi-bond-length and of regular hexagone of carbon ring, and (3) that the coulomb repulsion integral, $\gamma_{\mu\nu}$, is expressed in the following form.

$\gamma_{\mu\nu}=e^2/R_{\mu\nu}$ ($R_{\mu\nu}$: distance between the atoms μ and ν)

[15] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

TABLE V. VALUES OF SCF REACTIVITY INDEXES OF ANTHRACENE

Position	Total π-electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
1	0.983	0.459	0.132	0.098	0.115
2	0.989	0.443	0.089	0.070	0.080
9	0.906	0.511	0.461	0.574	0.517
11	1.075	0.130	0.049	0.045	0.047

TABLE VI. VALUES OF SCF REACTIVITY INDEXES OF NAPHTHALENE[a]

Position	Total π-electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
1	0.967	0.453	0.334	0.339	0.343
2	1.003	0.435	0.166	0.162	0.157
9	1.062	0.158	0	0	0

a) Ref. 8.

TABLE VII. VALUES OF SCF REACTIVITY INDEXES OF *trans*-BUTADIENE

Position	Total π-electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
A) Semi-empirical SCF method[a]					
1	0.938	0.757	0.575	0.606	0.637
2	1.062	0.545	0.425	0.394	0.363
B) Non-empirical SCF method[b]					
1	0.975	—	0.620	0.633	0.645
2	1.025	—	0.380	0.367	0.355
C) Non-empirical SCF CI method[c]					
1	0.978	—	—	—	—
2	1.022	—	—	—	—

a) Ref. 5. b) Ref. 6. c) Ref. 7.

TABLE VIII. VALUES OF SCF FREE VALENCE OF HYDROCARBONS IN ROUGHER APPROXIMATION[a]

Molecule	Position	Free valence
Naphthalene	1	0.447
	2	0.420
Anthracene	1	0.473
	2	0.441
	9	0.468
Phenanthrene	1	0.431
	2	0.408
	3	0.409
	4	0.428
	9	0.474
Chrysene	1	0.461
	2	0.464
	3	0.439
	4	0.434
	5	0.435
	6	0.436
Pyrene	1	0.432
	2	0.395
	4	0.485

a) Ref. 14.

butadiene for all the three kinds of reactions. It may be, therefore, concluded that frontier electron density remains a good reactivity index even when the electronic interaction is explicitly included.

So far as our approximation is concerned, free valence seems to give correct results in the three hydrocarbons, as shown in Tables V, VI and VII. In comparison with this, we have collected in Table VIII values of free valence of some hydrocarbons, which have been derived from the SCF bond orders obtained by Pritchard and Sumner[14]. It can be seen in Table VIII that this free valence leads to a seriously erroneous conclusion for anthracene and for pyrene: anthracene is, as is well known, the most susceptible to a radical attack at the position 9, and pyrene is so at 1. On inspection of these and other results of SCF calculation[16], it

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[16] G. Berthier, *J. chim. phys.*, **50**, 344 (1953); I. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 218 (1954); H. O. Pritchard and F. H. Sumner, *Trans. Faraday Soc.*, **51**, 457 (1955); etc.

may be said that the value of bond order, or that of free valence, varies very easily depending on the degree or approximation employed and on the semi-empirical method of evaluating atomic integrals. Such an unstable quantity would probably not deserve a reliable reactivity index.

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