Remarks on the Molecular Calculation of Naphthalene and Anthracene

By Noboru MATAGA, Kichisuke NISHIMOTO and Shizuyo MATAGA

(Received September 22, 1958)

The calculations made by Pariser and Parr[1,2] and also by Pople[3] in terms of semi-empirical molecular orbital (MO) method, have made a remarkable progress in the interpretation of the spectra of π-eletron systems. However, the agreement between the experimental and the theoretical results on the spectra of naphthalene which should come to our attention naturally next to benzene, does not seem to be satisfactory as yet. Although the results of Pople's SCF calculation[3] and Pariser's ASMOCI calculation[2] seem to be fairly well founded experimentally, the results of SCF and ASMOCI calculations of Moser and Lefebvre[4] in various degrees of approximations are in rather an unfortunate disagreement with experimental observations. Such an undesired circumstance is not restricted only to the case of electronic spectra, but, for example, the calculated bond orders of naphthalene and anthracene seem to agree hardly at all with observed values. The bond orders of naphthalene calculated with naive MO's are in a serious discrepancy with experimental values, but those of anthracene calculated in the same way are in good cor-

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[1] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); ibid., **23**, 711 (1955).

[2] R. Pariser, ibid., **24**, 250 (1956).

[3] J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

[4] R. Lefebvre and C. Moser, *J. Chem. Soc.*, **1956**, 1557, 2734.

TABLE I

CALCULATED AND OBSERVED SPECTRA OF NAPHTHALENE

State	Calcd.										Obs.	
	(i)		(ii)		(iii)		Pople		Pariser			
	hcν (e.V.)	f	hcν (e.V.)	f	hcν (e.V.)	f	hcν (e.V.)	f	hcν (e.V.)	f	hcν (e.V.)	f
$^1B_{3u}$	4.253	0.00	4.256	0.00	4.245	0.00	4.40	—	4.018	0.000	3.99	0
$^1B_{2u}$	4.503	0.33	4.465	0.25	4.680	0.29	4.65	—	4.493	0.256	4.30	0.18
$^1B_{3u}$	5.803	2.03	5.813	2.09	5.860	2.18	6.13	—	5.939	2.115	5.50	2.0
$^1B_{2u}$	6.337	0.46	6.415	0.83	6.490	0.89	6.20	—	6.309	0.699	7.30	0.6
$^3B_{2u}$	2.584	0.00	2.627	0.00	2.725	0.00	3.09	—	2.180	0.000	2.6	—
$^3B_{3u}$	3.758	0.00	3.762	0.00	3.740	0.00	4.09	—	3.639	0.000	3.7(?)	—
$^3B_{3u}$	4.253	0.00	4.256	0.00	4.245	0.00	4.40	—	4.018	0.000	—	—
$^3B_{2u}$	4.334	0.00	4.269	0.00	4.380	0.00	4.83	—	4.220	0.000	—	—

TABLE II

CALCULATED AND OBSERVED SPECTRA OF ANTHRACENE

State	Calcd.								Obs.	
	(i)		(iii)		Pople		Pariser			
	hcν (e.V.)	f	hcν (e.V.)	f	hcν (e.V.)	f	hcν (e.V.)	f	hcν (e.V.)	f
$^1B_{2u}$	3.279	0.26	3.481	0.39	3.72	—	3.648	0.386	3.30	0.1
$^1B_{3u}$	3.898	0.00	3.908	0.00	4.15	—	3.715	0.000	3.50	0
$^1B_{3u}$	5.098	2.74	5.185	3.00	5.64	—	5.499	3.229	4.80	2.20
$^1B_{2u}$	6.648	1.03	6.441	0.81	6.44	—	6.586	0.644	5.64	0.65
$^3B_{2u}$	1.713	0.00	1.691	0.00	2.23	—	1.660	0.000	1.8	—
$^3B_{3u}$	3.595	0.00	3.585	0.00	3.96	—	3.503	0.000	—	—
$^3B_{3u}$	3.898	0.00	3.908	0.00	4.15	—	3.715	0.000	—	—
$^3B_{2u}$	4.793	0.00	4.824	0.00	5.39	—	5.230	0.000	—	—

respondence with experiment. The application of the semiempirical SCFMO method of Pople to these molecules leads to a nice agreement with experiment in the case of naphthalene[5] but at the same time to a wrong prediction in the case of anthracene[6]. However, employing the values of molecular integrals which we have been using for studying the electrostructures of nitrogen heterocycles[7], the electronic spectra and other properties of naphthalene and anthracene seem to be satisfactorily interpreted. In the present report, the results of our calculation on the aromatic hydrocarbons will be described with some critical discussions comparing our results with those of other authors.

I. Electronic Spectra.—As indicated in Tables I and II, the calculated spectra of naphthalene and anthracene employing our parameters[7] are in a satisfactory agreement with experimental values. In these tables the results obtained by Pople and Pariser, respectively, are also given for the purpose of comparison. In both of these tables, "i" is the result of the ordinary Hartree-Fock SCF calculation with the approximation of zero differential overlap, and "ii" is obtained by an approximate SCF calculation in which $F_{\mu\nu}$'s for the neighbors more distant than the nearest are neglected, and in "iii" the naive MO's are used for the calculation of excitation energies and oscillator strengths. The calculated results in "iii" are close to those "i" or "ii", and the agreement with the observed values is satisfactory. This fact is in accordance with the circumstance that, as pointed out by Dewar and Longuet-Higgins[8], owing to the uniform charge distribution in aromatic hydrocarbons, their naive MO's themselves are fairly close to SCFMO's.

Now, the results obtained by Lefebvre and Moser are collected in Table III. In this table, A is the result of the calculation which involves the penetration integrals to hydrogen atoms, in addition to other parameters which are the same as used by Pariser and Parr. Accordingly, the pairing property between the bonding and the antibonding orbitals is lost in this

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

[6] H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.*, **A226**, 128 (1954).

[7] N. Mataga and K. Nishimoto, *Z. physik. Chem. N. F.* **13**, 140 (1957); N. Mataga, This Bulletin, **31**, 453, 459, 463 (1958).

[8] M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.*, **A67**, 795 (1954).

case. In B, $F_{\mu\mu}$, the diagonal element of Fock's Hamiltonian in terms of AO, has been assumed to be constant regardless of the position of carbon atoms, resulting in the pairing property, and all the off-diagonal elements, $F_{\mu\nu}$'s for nearest neighbors have been assumed to be equal to each other. For more distant neighbors, $F_{\mu\nu}$ is calculated by $F_{\mu\nu}=H_{\mu\nu}-1/2\ P_{\mu\nu}\gamma_{\mu\nu}$, where $H_{\mu\nu}$ is the off-diagonal element of core Hamiltonian, $P_{\mu\nu}$ is the bond order and $\gamma_{\mu\nu}$ is the electronic Coulomb repulsion integral. In C, it has been assumed that all values of $H_{\mu\nu}$ for nearest neighbors are equal.

TABLE III

SPECTRA OF NAPHTHALENE CALCULATED BY LEFEBVRE AND MOSER (SINGLET STATES)

(A)

MO's state	$hc\nu$ (e.V.)			f		
	Hückel	Cyclic	SCF	Hückel	Cyclic	SCF
B_{3u}	4.668	3.819	4.696	0.02	0.02	0.13
B_{2u}	4.984	4.180	4.995	0.05	0.00	0.00
B_{3u}	6.655	6.799	6.333	2.47	3.43	1.51
B_{2u}	6.542	5.939	6.538	1.28	1.01	1.15

(B)

MO's state	$hc\nu$ (e.V.)		f	
	Hückel	Cyclic	Hückel	Cyclic
B_{3u}	4.722	4.586	0.00	0.00
B_{2u}	4.161	4.086	0.30	0.35
B_{3u}	7.563	7.466	2.54	3.80
B_{2u}	6.762	6.993	1.11	0.59

(C)

MO's state	$hc\nu$ (e.V.)		f	
	Hückel	Cyclic	Hückel	Cyclic
B_{3u}	4.403	4.120	0.00	0.00
B_{2u}	4.289	4.314	0.20	0.20
B_{3u}	6.343	7.000	2.36	3.56
B_{2u}	6.597	5.834	1.05	0.71

The most important difference of our calculation from Lefebvre's and Moser's is in the choice of parameters, especially of $\gamma_{\mu\nu}$ values. In this respect, some discussions will be given in the latter part of this paper.

II. Bond Orders.—As mentioned in the introductory part of the present paper, Pople's self-consistent treatment as applied to the calculation of bond orders gave good agreement with the experiment for naphthalene, but not for anthracene, whereas with the simple treatment without the inclusion of electronic interaction, the situation was reversed. In view of this circumstance, Pritchard and Sumner9) tried to hit the experimental values calculating the bond orders of naphthalene and anthracene by various approximations. This was, however, a rather hard task. Among various approximations (six approximations), only one (their approximation 5) gave results for both molecules free from significant error. In this approximation, Pople's self-consistent MO method was used with variation of α , the diagonal element of core Hamiltonian in terms of μth AO; the correction used was $\Delta\alpha=\beta$ in the sense that atoms labelled 3 in Fig. 1 are more electronegative than other atoms in the system.

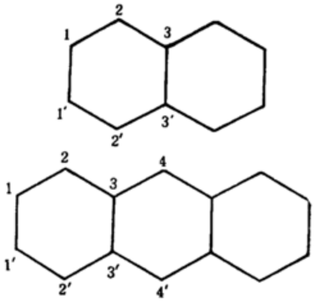

Fig. 1. Numbering of atoms in naphthalene and anthracene.

Now, as indicated in Table IV, the bond lengths calculated by the self-consistent field MO method using our parameters, are in good correspondence with experiment, where the results of Pritchard and Sumner by approximation 5 (abbreviated as P.S.) are also indicated for the purpose of comparison. In this table, the calculated

TABLE IV

CALCULATED AND EXPERIMENTAL BOND LENGTHS OF NAPHTHALENE AND ANTHRACENE (IN A)

Naphthalene

	Calcd.			Expt.
bond	(i)*	(ii)*	P.S.	
1—2	1.374	1.369	1.369	1.365±0.006
2—3	1.414	1.417	1.420	1.425±0.005
3—3'	1.412	1.406	1.409	1.393±0.010
1—1'	1.405	1.412	1.413	1.404±0.009

Anthracene

	Calcd.		Expt.
bond	(i)*	P.S.	
1—2	1.370	1.365	1.371±0.006
2—3	1.423	1.430	1.424±0.005
3—4	1.396	1.403	1.396±0.004
3—3'	1.436	1.432	1.436±0.007
1—1'	1.408	1.422	1.408±0.010

* The meaning of i and ii is the same as those in Tables I and II.

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9) H. O. Pritchard and F. H. Sumner, *Trans. Faraday Soc.*, 51, 457 (1955).

bond lengths were obtained from the bond orders using the equation

$$R_{\mu\nu}=S-\frac{S-D}{1+\kappa\left(\dfrac{1-P_{\mu\nu}}{P_{\mu\nu}}\right)}$$

where S is taken to be 1.54 Å, $D=1.33$ Å and $\kappa=0.765$.

None of the calculated values using our parameters differs from the experimental mean by more than two and a quater times the " estimated standard deviation," and may be regarded as correct.

III. Ionization Potentials and Electron Affinities.—The ionization potentials and electron affinities are important quantities for studying the molecular sturctures. We have examined whether our calculation can predict correctly the ionization potentials and electron affinities of naphthalene and anthracene. The calculated values have been standardized to the observed values of benzene, i.e., after adding $\Delta I=I_{\text{benz.}}^{\text{obs.}}-I_{\text{benz.}}^{\text{calc.}}$ or $\Delta A=A_{\text{benz.}}^{\text{obs.}}-A_{\text{benz.}}^{\text{calc.}}$ to the calculated ionization potentials or electron affinities, respectively; the theoretical values have been compared with experiment. As shown in Table V, the calculated values agree satisfactorily with observed values.

TABLE V

CALCULATED AND OBSERVED IONIZATION POTENTIALS OF NAPHTHALENE AND ANTHRACENE (IN e.V.)

Ionization Potential

Molecule	Calcd.			Obsd.
	(i)*	(ii)*	(iii)*	
Benzene	(9.24)			9.24
Naphthalene	8.116	8.125	8.068	8.12 (a)
Anthracene	7.414	—	7.400	—

Electron Affinity

Molecule	Calcd.			Obsd.
	(i)*	(ii)*	(iii)*	
Benzene	(−0.54)			−0.54 (b)
Naphthalene	0.595	0.585	0.643	0.65 (b)
Anthracene	1.297	—	1.310	1.19 (b)

* The meaning of i, ii and iii is the same as in other tables.

(a) K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957).

(b) Blackedge and Hush, quoted in, N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

Discussion

As has been described so far, the electronic spectra, bond lengths, ionization potentials and electron affinities calculated with our parameters are in an excellent agreement with experimental values, and the main difference of our calculation from that of other authors' is in the choice of $\gamma_{\mu\nu}$ values. Our values are somewhat smaller than those used by Pariser and Parr and by Pople. The procedure employed by Pariser and Parr for evaluating $\gamma_{\mu\mu}$ is analogous to the Moffitt's method of " atoms in molecules "[10] which takes into account accurately the energy difference between the separated pairs of ions and neutral atoms. In other words, it may also be regarded as an appropriate consideration of the effect of electronic correlation for the one-center interaction integral $\gamma_{\mu\mu}$, by the use of the experimental values of atomic valence state ionization potential and electron affinity[11]. In Moffitt's method, $\gamma_{\mu\nu}$'s where $\mu\neq\nu$, are calculated theoretically using, for example, Slater type AO's. In the procedure used by Pariser and Parr, $\gamma_{\mu\nu}$'s for neighbors more distant than the nearest are calculated in terms of Slater type AO's or by uniform charge sphere approximation. $\gamma_{\mu\nu}$'s for nearest neighbors are evaluated by interpolation formula of the type: ar^2+br+c, where r is the interatomic distance and $c=\gamma_{\mu\mu}$. When atoms are combined to form a molecule, however, the effective charges for σ-electrons may be rather increased compared with the case of isolated atoms and the electron clouds associated with σ-bonds may somewhat contract.

In contrast to this, the effective changes for π-electrons may by decreased. Owing to this circumstance, one should use a little smaller values of $\gamma_{\mu\nu}$'s than those used by Pariser and Parr and by Pople, which may be a cause of the excellent agreement of our calculated results with experiment. In addition, our procedure for evaluating $\gamma_{\mu\nu}$'s is very simple and straightforward. One can easily obtain them if one can only know the values of valence state ionization potentials and electron affinities of the atoms involved. Another reason for the use of our $\gamma_{\mu\nu}$ values may be as follows, although it might be essentially the same as described above. When applied to some simple molecules such as hydrogen[12,13] and lithium molecules[14], the method of Moffitt gives

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[10] W. Moffitt, *Proc. Roy. Soc.*, **A210**, 245 (1951): *Report Progr. Phsics*, **17**, 173 (1954).

[11] W. Kotos, *Acta Phys. Polon.*, **16**, 299 (1957).

[12] C. W. Scherr, *J. Chem. Phys.*, **22**, 149 (1954).

[13] A. C. Hurley, *Proc. Phys. Soc.*, **A68**, 149 (1955).

[14] A. Rahman, *Physica*, **20**, 623 (1954).

rather unsatisfactory results. For example, it leads to the conclusion that the ground state of the hydrogen molecule is almost completely ionic[13]. A similar conclusion is also reached in the case of the diamond[15]. In the latter case, however, if one calculate non-empirically the energies and wave functions employing Slater AO's, one can obtain the result that the ground state is homopolar even if the agreement between the calculated and the observed cohesive energy is very unsatisfactory.

Then, one may be able to improve the results in the following way. For example, if $\gamma_{\mu\mu}$ calculated with Slater AO's is κ times the $\gamma_{\mu\mu}$ evaluated by Moffitt's method, one divides by κ all $\gamma_{\mu\nu}$'s calculated with Slater AO's and one uses $\gamma_{\mu\nu}=(1/\kappa)\gamma_{\mu\nu}$ (Slater) in the calculation of molecular energy and wave function. Actually, in the case of the diamond, a satisfactory improvement has been brought about in this way[15]. Although the real theoretical ground for doing it in this way is not very clear, the physically unsatisfactory results at which Moffitt's method arrives originate from the inconsistent use of, for example, $\gamma_{\mu\mu}$ values which are obtained empirically on the one hand and $\gamma_{\mu\nu}$ $(\mu \neq \nu)$ values which are calculated with ordinary orbital functions on the other hand. Thus, even if the interatomic part of energy is very small compared with its intra-atomic part, the former still affects the calculated results to such an extent as described above.

When studing the π-electronic structures, such a circumstance may not be very serious as in the case of σ-electronic structures. Nevertheless, our calculation in the present paper seems to indicate that such a circumstance still exists in the case of π-electronic structures. Actually, the ratio $\gamma_{\mu\nu}$ (Slater)$/\gamma_{\mu\nu}$, where $\gamma_{\mu\nu}$ is the value we have used, is approximately constant and close to κ when μ-th and ν-th atoms are one or two bond distances apart from each other and approaches gradually to unity as they become more distant.

Summary

Electronic structures of naphthalene and anthracene have been studied by the self-consistent field MO method employing our semiempirical parameters. The calculated electronic spectra, bond lengths, ionization potentials and electron affinities are in a good agreement with expriment. Some discussions have been given in connection with the method of "atoms in molecules" and others.

We are grateful to Professor R. Fujishiro for his encouragement. One of the authors (N.M.) expresses with pleasure his cordial thanks to Mr. T. Yamaguchi of Osaka University for his helpful discussions.

Institute of Polytechnics
Osaka City University
Kita-ku, Osaka

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[15] T. Yamaguchi, Private communication.