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Predictions of Molecular Geometries and Electronic Spectra of Complex Unsaturated Molecules from MC-LCAO-MO Method with Particular Reference to Triplet-Triplet Transitions of Naphthalene

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An MC-LCAO-MO approach which has been proposed for open-shell systems of unsaturated hydrocarbons having degenerate MO's is applied to naphthalene, calculating its molecular geometry and electronic spectrum. The results are compared with those obtained by the usual semi-empirical SCF-CI method and with experiment. As for benzene, anthracene, phenanthrene and triphenylene, the bond lengths and the π-electron energies in their ground states are calculated in the same manner. Most of the calculated bond lengths are in fairly good agreement with experiment. The total π-electron energies of the ground states obtained by the MC-LCAO-MO and SCF-CI methods agree within about 0.01 eV when CI is included and within about 0.1 eV when CI is not invoked. It is found that the electronic spectrum of naphthalene obtained by the present method is in good agreement with that derived from the SCF-CI method and also explains most part of experiments. A detailed discussion is given on the calculated triplet-triplet absorption spectrum and its intensity distribution of naphthalene.

Key words: MC-LCAO-MO method, semi-empirical – Naphthalene, triplet-triplet transitions – Polyacenes, molecular geometry prediction of ~

1. Introduction

In previous papers [1–3], a semi-empirical multi-configuration (MC) LCAO-MO method was proposed for calculations of electronic spectra and prediction of molecular geometry in each electronic state of unsaturated hydrocarbons which have open-shell molecular orbitals (MO). The method was applied to the benzene mono-negative and mono-positive ions and further to the triphenylene mono-negative ion in order to examine a static Jahn-Teller effect. For open-shell systems having degenerate MO's, there has not been a consistent theory which can be applied with the same accuracy and easiness as the usual semi-empirical LCAO-SCF method with configuration interaction (CI) for closed-shell systems. The MC-LCAO-MO method is designed to include CI in each iterative computation process wherever a π-electron approximation is used, and has the advantage that it can be applied in-

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dependently of whether configurations are made up of closed shells or open shells and whether MO's are degenerate or non-degenerate. In a previous series, however, we were unable to guarantee that the calculated bond lengths of the ground states of these ions are about right, since they are experimentally unknown.

In the present study, we examine the applicability of the method to the systems which have closed-shell ground states and experimentally established molecular geometries. We will take up benzene, naphthalene, anthracene, phenanthrene and triphenylene as the objects of this purpose and calculate their bond lengths and total π-electron energies. As a special model molecule we choose naphthalene and investigate its ground state and excited state properties rather in detail, since its spectroscopic properties are relatively well known. In order to demonstrate that the method may be useful at least with the same degree of accuracy as some ordinary and consistent methods, the usual SCF-CI calculation is carried out for comparison and the open-shell SCF-CI procedure is applied to the lowest triplet state of naphthalene. The same values for semi-empirical parameters with the zero-differential overlap assumption are used in the MC-LCAO-MO and all the SCF-CI calculations.

We reported previously a brief comment on the diagonal elements in a secular equation from which MO's are determined in the MC-LCAO-MO method [4]. Detailed results and further comments in this respect will be given in subsequent sections.

2. Some Remarks on the Method of Calculation

In this section we give a brief outline of the semi-empirical MC-LCAO-MO method [1] and introduce a new parametrization in order that the method may be applied easily and extensively to various unsaturated hydrocarbons.

The computational procedures in the method are as follows:

Step 1. A set of π-MO's is calculated with appropriate bond lengths as initial data.

Step 2. A CI calculation is carried out; the π-electron energy E_π, the total electronic energy $E(=E_\pi+E_\sigma)$ and the π-bond orders P_{pq} after CI are computed (for the working formulae of E_π, E_σ and P_{pq}, see Ref. [1]).

Step 3. The bond lengths are revised through the relationship

$$r_{pq}=1.523-0.193\,P_{pq}\,. \tag{1}$$

Control is returned to *Step 1*, in which the revised bond lengths are used in place of the initial data. This process is repeated until a self-consistent solution is obtained with respect to bond lengths.

In *Step 1*, in order to construct a secular equation from which MO's are determined, we have used the formula [1, 2]

$$\alpha_p=-I_p-\textstyle\sum_{q\neq p}[(pp|qq)+(q:pp)] \tag{2}$$

for the diagonal elements and the formulae

$$\beta_{pq}=\beta_0\exp[-(r_{pq}-b)/a]\ \text{(Approximation (1))} \tag{3a}$$

and

$$\beta_{pq} = -\tfrac{1}{2} K S_{pq}(I_p + I_q) \text{ (Approximation (2))} \tag{3b}$$

for the off-diagonal elements. Here I_p is an appropriate valence-state ionization potential of atom p, $(pp|qq)$ is the two-center electronic repulsion integral and $(q{:}pp)$ is the penetration integral.

To begin with, these formulae are used for the calculation of the ground-state MO's of naphthalene. The constants β_0, a, b, K, and I_p in Eqs. (2) and (3) are set equal to the values -2.38 eV, 0.39380 Å, 1.397 Å, 0.86291, and 11.290 eV, respectively. The two-center electronic repulsion integrals $(pp|qq)$ are evaluated by the formulae [5, 6]

$$Z^{-1}(pp|qq) = 0.1227 - 0.005093\varrho + 0.000070\varrho^2 \quad \text{for} \quad r_{pq} \leqq 4.8\ \text{Å} \tag{4a}$$

and

$$Z^{-1}(pp|qq) = \varrho^{-1}[1 - (12/\varrho^2) + (324/\varrho^4)] \quad \text{for} \quad r_{pq} > 4.8\ \text{Å} \tag{4b}$$

(in a.u.) with $\varrho = Zr_{pq}/a_0$, the one-center integral being $(pp|pp) = 0.1227\,Z$ a.u. Here the effective nuclear charge for carbon $2p\pi$ AO's in neutral alternant hydrocarbons, $Z = 3.250$, is assumed to be constant throughout the calculations. The penetration integral due to the hydrogen atoms is included for only nearest neighbours, being given a constant value 0.627 eV [5]. Non-nearest neighbour β_{pq}'s are also included. The bond angles used in computation of non-neighbour carbon-carbon distances are all kept constant, 120°. The other formulae necessary for calculations are exactly the same as those given in Ref. [1].

For the CI calculation, a limited number of singly and doubly excited configurations (28 configuration functions including the ground configuration) are taken into account; the doubly excited configurations taken are composed of 23 configuration functions and they are chosen out of configurations with energies not exceeding about 16.0 eV relative to the energy of the ground configuration. The MO's obtained are assumed to become self-consistent when further iteration processes yield a total energy change less than five in the seventh decimal place (in eV).

The MO levels thus obtained are given in Table 1. The ε_{ii}'s are the eigenvalues of MO's ϕ_i obtained in the present method, which are exactly of the diagonal matrix elements of the one-electron Hamiltonian operator. The F_{ii}'s, which correspond to the eigenvalues of the closed-shell SCF MO's ϕ_i, are computed by the formula

$$F_{ii} = \varepsilon_{ii} + \textstyle\sum_f (2J_{fi} - K_{fi}) \tag{5}$$

where J_{fi} and K_{fi} are the molecular Coulomb and exchange repulsion integrals, respectively. The sequence of the MO levels shown in Table 1 is quite different from that obtained by the SCF method (for the latter results, see Table 2) and appears to be erroneous.

In a previous note [4], it was found that this result comes about by making use of Eq. (2) as diagonal elements; we proposed therein the formula

$$\alpha_p^0 = -I_p - \textstyle\sum_{q \neq p}(q{:}pp) \tag{6}$$

Table 1. MO levels for the ground state of naphthalene obtained by the previous MC-LCAO-MO method (eV)

MO	Approximation (1)[a]				Approximation (2)[a]	
		ε_{ii}	F_{ii}		ε_{ii}	F_{ii}
ϕ_1	b_{1u}	-70.599	-11.200		-70.932	-11.907
ϕ_2	b_{3g}	-66.157	-7.575		-66.103	-7.489
ϕ_3	b_{2g}	-62.340	-13.970		-62.402	-14.161
ϕ_4	b_{1u}	-61.670	-12.117		-61.602	-11.764
ϕ_5	a_u	-60.881	-9.720		-60.519	-9.250
ϕ_6	b_{3g}	-59.773	-1.680		-59.659	-1.381
ϕ_7	b_{2g}	-56.924	-2.811		-56.860	-2.667
ϕ_8	b_{1u}	-56.769	-1.773		-56.802	-1.788
ϕ_9	a_u	-53.837	-1.044	b_{3g}	-53.851	-1.056
ϕ_{10}	b_{3g}	-53.801	-0.773	a_u	-53.845	-1.159

[a] The columns under Approximation (1) and Approximation (2) are the results calculated with Eqs. (3a) and (3b), respectively.

instead of Eq. (2). Then, the matrix elements of the one-electron Hamiltonian operator between MO's ϕ_i and ϕ_j are calculated to be

$$\varepsilon_{ij}=\delta_{ij}U_{ij}-\textstyle\sum_p\sum_{q\neq p}C_{pi}C_{pj}(pp|qq)\,, \tag{7}$$

where U_{ii} and C_{pi} are the eigenvalues and atomic orbital coefficients, respectively, of MO's ϕ_i calculated by means of Eq. (6) as diagonal elements, δ_{ij} being the Kronecker symbol. The MC-LCAO-MO method thus modified was first applied to the triphenylene mono-negative ion [3].

3. Computational Detail

The MC-LCAO-MO method in which Eq. (6) is used instead of Eq. (2) is applied to the calculation of the ground-state MO's of naphthalene. For the purpose of comparison, the usual SCF-CI calculation is also carried out with the same atomic integrals, values of constants and species of configuration functions as in the MC-LCAO-MO calculation (as to the matrix elements of the Hartree-Fock operator used in the SCF calculation, see Appendix). Table 2 lists the MO levels thus calculated. The table shows that the sequences of the MO levels together with their symmetries obtained by the two methods are in complete agreement with each other. Furthermore, the magnitudes of F_{ii} and ε_{ii} obtained by the MC-LCAO-MO method compete with the corresponding values derived from the SCF calculation. This suggests that Eq. (6) may be adequate to be employed for similar calculations in ordinary unsaturated hydrocarbons.

For further test of adequacy of this parametrization, we take up benzene, anthracene, phenanthrene and triphenylene as well as naphthalene, and calculate their ground-state properties. For simplicity, only the ground configuration is taken into account for anthracene, phenanthrene and triphenylene;

Table 2. MO levels for the ground state of naphthalene (eV)

MO		Approximation (1)					Approximation (2)				
		MC-LCAO-MO			SCF		MC-LCAO-MO			SCF	
		U_{ii}	F_{ii}	ε_{ii}	F_{ii}	ε_{ii}	U_{ii}	F_{ii}	ε_{ii}	F_{ii}	ε_{ii}
ϕ_1	b_{1u}	−19.348	−18.147	−68.122	−18.119	−68.016	−19.976	−18.812	−68.746	−18.767	−68.667
ϕ_2	b_{2g}	−17.479	−15.947	−62.172	−15.945	−62.189	−17.588	−16.063	−62.271	−16.059	−62.283
ϕ_3	b_{3g}	−16.322	−14.521	−64.331	−14.477	−64.077	−16.193	−14.432	−64.281	−14.370	−64.058
ϕ_4	b_{1u}	−15.400	−13.050	−63.193	−13.070	−63.595	−15.136	−12.787	−62.744	−12.799	−63.143
ϕ_5	a_u	−14.790	−12.392	−60.830	−12.448	−60.819	−14.419	−12.010	−60.482	−12.052	−60.481
ϕ_6	b_{2g}	−11.611	− 3.225	−57.659	− 3.138	−57.642	−11.489	− 3.171	−57.562	− 3.070	−57.550
ϕ_7	b_{3g}	−11.042	− 2.578	−58.647	− 2.540	−59.189	−10.891	− 2.449	−58.167	− 2.409	−58.819
ϕ_8	b_{1u}	−10.416	− 1.449	−58.565	− 1.455	−58.268	−10.375	− 1.439	−58.724	− 1.428	−58.403
ϕ_9	a_u	− 9.697	− 0.400	−54.397	− 0.394	−54.408	− 9.778	− 0.493	−54.471	− 0.482	−54.472
ϕ_{10}	b_{3g}	− 8.545	1.010	−57.645	1.028	−57.358	− 8.797	0.711	−58.159	0.756	−57.730

Table 3. Bond lengths (Å)

molecule	bond	Approx. (1)	Approx. (2)	exptl.
benzene		1.398	1.398	1.397[a]
naphthalene	1– 2	1.375	1.378	1.368[b]
	2– 3	1.420	1.416	1.414
	1– 9	1.427	1.424	1.422
	9–10	1.408	1.413	1.419
anthracene	1– 2	1.373	1.376	1.375[c]
	2– 3	1.427	1.423	1.444
	3– 4	1.403	1.404	1.405
	3–12	1.428	1.430	1.433
	1–14	1.421	1.417	1.418
phenanthrene	1– 2	1.433	1.430	1.390[d]
	2– 3	1.413	1.412	1.457
	3– 4	1.384	1.385	1.381
	4– 5	1.407	1.406	1.398
	5– 6	1.384	1.385	1.383
	6– 7	1.411	1.410	1.405
	7– 8	1.439	1.437	1.448
	2– 7	1.413	1.416	1.404
	1–14	1.367	1.370	1.372
triphenylene	1– 2	1.387	1.388	1.377[e]
	2– 3	1.407	1.407	1.416
	3– 4	1.447	1.444	1.447
	3–16	1.410	1.412	1.415
	1–18	1.403	1.403	1.402

[a] Ref. [7]. – [b] The average values of the X-ray [8] and electron-diffraction [9] data.
[c] Ref. [10]. – [d] Ref. [11]. – [e] Ref. [12].

that is, a CI calculation is not carried out for these molecules. For benzene, all the singly and doubly excited configurations having a g representation, namely the A_{1g}, A_{2g} and E_{2g} irreducible representations, of the point group D_{6h} (30 configuration functions including the ground configuration) are taken in the CI calculation. The reason for this is as follows. Benzene has two pairs of degenerate MO's and if these MO's are expressed by real functions as in the present case, they may not so correctly and neatly transform according to an irreducible representation E of complex MO's. All configurations labelled as g then have a possibility to mix with each other. Therefore, all the necessary configurations mentioned above are tentatively taken into account in order to examine the CI effect in benzene.

In Table 3 are shown the bond lengths computed for the ground states of the series of molecules, together with the corresponding observed values [the relationship (1) is used even when CI is not invoked]. The carbon atoms are numbered as in Fig. 1. The bond lengths calculated for the 1–2 and 2–3 bonds in phenanthrene are in substantial disagreement with experiment; this matter has been discussed by Skancke [13]. However, the over-all agreement with experiment is tolerably good.

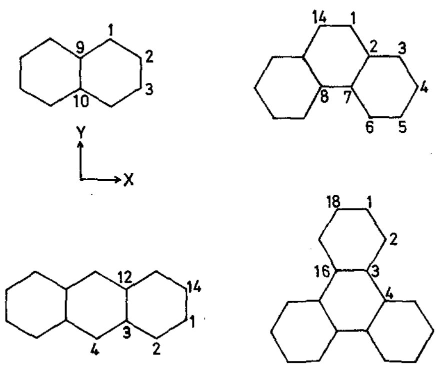

Fig. 1. Numbering of the atoms in naphthalene, anthracene, phenanthrene and triphenylene

Table 4. π-electron energies calculated for the ground states (eV)[a]

	Approximation (1)		Approximation (2)	
molecule	MC-LCAO-MO	SCF	MC-LCAO-MO	SCF
benzene	−183.5790	−183.5790	−183.5324	−183.5324
	(−0.6450)	(−0.6450)	(−0.6548)	(−0.6548)
naphthalene	−393.3682	−393.3745	−393.3182	−393.3268
	(−0.6626)	(−0.6201)	(−0.6915)	(−0.6481)
anthracene	−635.4482	−635.5385	−635.4006	−635.4964
phenanthrene	−642.5153	−642.5950	−642.4724	−642.5646
triphenylene	−935.0038	−935.0982	−935.0555	−935.1732

[a] The values in parentheses are the energy depressions of π-electron energies due to CI.

Table 4 lists the ground state π-electron energies calculated by both methods with the predicted bond lengths shown in Table 3. In benzene, the two methods yield exactly the same values for the π-electron energies and the depression energies due to CI under Approximations (1) and (2). After scrutinizing the coefficients of the ground-state wavefunction, we found that almost all the doubly excited configurations (even those having irreducible representations different from A_{1g}) mix with the ground configuration, the weights of the mixing being different in the two methods. This fact suggests that in such a system as benzene, as mentioned above, if the species of configuration functions taken for CI are unsatisfactory, then the depression energies obtained differ in general in the two methods and the π-electron energies may also be different. Without such allowance for example, it is not always guaranteed that this kind of calculation leads to proper molecular geometry [1].

The π-electron energies of the ground configurations (without CI) differ between the two methods by about 0.05 eV in naphthalene, and by about 0.1 eV in anthracene, phenanthrene and triphenylene, the MC-LCAO-MO method always yielding higher energies. Naturally this difference is lessened when CI is invoked; in the case of naphthalene it is found from the results shown in Table 4 that the CI effect reduces the difference to much smaller values 0.0063 eV under Approximation (1) and 0.0086 eV under Approximation (2). It should be added that even when CI is not invoked at all, the present method yields the bond lengths of conjugated molecules, which can predict fairly well experimental results, and gives the π-electron energies comparable with those obtained by the SCF method.

For all the molecules under consideration, the sequences of MO levels, the MO symmetries, and the magnitudes of F_{ii} obtained by the present method are the same as those by the SCF method. It was found for benzene that the use of Eq. (2) and Eq. (6) in the MC-LCAO-MO calculation results in the same bond lengths, sequence of MO levels, and π-electron energy. This suggests that Eq. (2) is good for calculations of cyclic polyenes C_nH_n having D_{nh} symmetries as well as Eq. (6).

These results of the preliminary calculation encourage us to apply the method further to calculations of excited states. We take up naphthalene as an example and apply both the present method and the SCF-CI method to the calculation of its excited states. We take account of the three kinds of transitions, that is *SS* (ground state to higher singlet states), *ST* (ground state to triplet states) and *TT* (lowest triplet state to higher triplet states) transitions. The species of configuration functions taken for the CI calculation consist of all the singly excited and a limited number of doubly excited configurations. They are 29 and 26 functions for the singlet B_{2u} and B_{3u} states, and 29, 30, 26, and 28 functions for the triplet B_{2u}, B_{3u}, A_g, and B_{1g} states, respectively. In order that a similar effect due to CI is expected on the correlation of energy for each electronic state, roughly the same amounts of doubly excited configurations as in the ground state must be invoked in the calculation of each excited state; we choose 22, 20, 22, 24, 20, and 22 functions for the ${}^1B_{2u}$, ${}^1B_{3u}$, ${}^3B_{2u}$, ${}^3B_{3u}$, ${}^3A_g$, and ${}^3B_{1g}$ states, respectively (the wording "singly" and "doubly" is used with regard to the ground configuration).

4. Results and Discussion

Table 5 shows the results for the *SS*, *ST* and *TT* transitions together with the available experimental values. The MO's used are those obtained from the ground state calculation; the predicted bond lengths are employed in the MC-LCAO-MO method, while in the SCF-CI method the experimental values are used as in the usual calculation for excited states. The calculated lower *SS* and *ST* transition energies are a little higher than the experimental values except for the 6.51 eV transition. The calculated oscillator strengths, however, are generally in good agreement with experiment. For the *TT* transitions, the theoretical results appear to agree well with experiments, though some of the experimental assignments are not definite.

As for the *TT* spectra, there are some problems of theoretical interest: One is a question how the lowest triplet state energy and the calculated *TT* spectra vary when the optimum MO's for the lowest triplet configuration are

Table 5. Transition energies (eV) and oscillator strengths for naphthalene

	Approximation (1)				Approximation (2)					
	MC-LCAO-MO		SCF-CI		MC-LCAO-MO		SCF-CI			
state	energy	f	energy	f	energy	f	energy	f	exptl.	
^1A_g	0.000	ref.	0.000	ref.	0.000	ref.	0.000	ref.		
$^1B_{2u}$	4.633	0.064	4.659	0.059	4.388	0.076	4.444	0.069	4.29	0.18[a]
	6.063	0.328	6.089	0.369	5.902	0.299	5.926	0.333	6.51	0.21
	7.814	0.121	7.784	0.070	7.428	0.037	7.369	0.035		
	8.122	0.646	8.187	0.654	7.998	0.737	8.045	0.706	7.40	0.6
$^1B_{3u}$	4.165	0.000	4.179	0.000	3.945	0.000	3.987	0.000	3.97	0.002[a]
	6.284	1.613	6.285	1.579	6.145	1.628	6.151	1.580	5.62	1.70
	7.059	0.009	7.189	0.017	6.553	0.001	6.687	0.014		
	8.302	0.057	8.416	0.079	8.163	0.005	8.299	0.009		
$^3B_{2u}$	3.162		3.228		2.906		3.001		2.64	[b]
	4.337		4.290		4.237		4.194			
	6.878		7.001		6.643		6.715			
$^3B_{3u}$	4.020		4.033		3.822		3.848		3.71	[b]
	4.635		4.639		4.445		4.466			
	6.436		6.458		6.145		6.172			
$^3B_{2u}$	0.000	ref.	0.000	ref.	0.000	ref.	0.000	ref.		
^3A_g	1.849	0.001	1.808	0.001	1.959	0.004	1.864	0.003	1.97	0.002[c]
	2.784	0.007	2.762	0.008	2.755	0.008	2.704	0.009		
	3.125	0.001	3.151	0.000	3.365	0.000	3.342	0.000	3.10	~0.01
	4.694	0.094	4.758	0.091	4.856	0.083	4.896	0.077	4.50	0.13
	5.889	0.000	5.898	0.000	5.827	0.001	5.801	0.000		
$^3B_{1g}$	0.980	0.000	1.010	0.000	1.051	0.001	1.039	0.001		
	2.979	0.000	3.023	0.000	3.014	0.002	3.012	0.000	2.54	0.002[c]
	3.099	0.129	3.110	0.130	3.129	0.118	3.116	0.121	3.00	0.12
	4.803	0.031	4.874	0.035	4.616	0.023	4.690	0.017		
	5.000	0.178	5.032	0.156	5.166	0.334	5.172	0.307	5.25	0.5
	6.299	0.793	6.340	0.762	6.237	0.714	6.261	0.677		

[a] Ref. [14]. – [b] Ref. [15]. – [c] Ref. [16].

used instead of those for the ground configuration. The other is a question how molecular geometry of the lowest triplet state differs from that of the ground state and whether the *TT* spectra change when such excited state geometry is used, compared with those calculated using the bond lengths of the ground state.

In order to examine the first question, we carried out the calculation for the lowest triplet state of naphthalene by using the open-shell SCF method of Roothaan [17] (as to the matrix elements of the Hartree-Fock type operator used, see Appendix). As for the lowest triplet B_{2u} state, its π-electron energy calculated by the open-shell SCF MO's, in the absence of CI, is lower than those from the ground state SCF MO's by 0.2349 eV under Approximation (1) and by 0.2446 eV under Approximation (2). When CI is included, the former turns out to be higher than the latter by 0.0033 eV under Approximation (1) and lower by 0.0024 eV under Approximation (2). This shows that the difference in energy due to the MO's used may be reduced to a negligibly small magnitude by the CI effect; an analogous situation has been found in the

Table 6. *TT* transition energies (eV) and oscillator strengths obtained by open-shell SCF-CI method

	Approximation (1)		Approximation (2)	
state	energy	f	energy	f
$^3B_{2u}$	0.000	ref.	0.000	ref.
^3A_g	2.139	0.001	2.213	0.004
	2.953	0.012	2.887	0.014
	3.389	0.001	3.597	0.000
	4.866	0.129	5.043	0.116
	5.933	0.000	5.833	0.000
$^3B_{1g}$	1.074	0.000	1.109	0.001
	3.013	0.000	3.038	0.000
	3.123	0.135	3.135	0.124
	4.913	0.008	4.734	0.015
	5.250	0.406	5.321	0.588
	6.422	0.564	6.403	0.396

Table 7. Bond lengths calculated for the lowest triplet state of naphthalene (Å)

	Approximation (1)		Approximation (2)	
bond	MC-LCAO-MO	SCF[a]	MC-LCAO-MO	SCF[a]
1– 2	1.438	1.449	1.435	1.445
2– 3	1.370	1.357	1.374	1.360
1– 9	1.412	1.404	1.414	1.406
9–10	1.435	1.447	1.431	1.443

[a] Bond lengths listed in this column are the values obtained from the SCF solution not including CI

calculation of the ground state energy described in the preceding section. Table 6 gives the results for the *TT* transition obtained with the open-shell SCF-CI functions optimized for the lowest triplet configuration. All the transition energies listed are slightly higher than those obtained from the ground state MO's, being more apart from experiment (cf. Table 5). On the other hand, the oscillator strengths calculated for the strong transitions (3.00, 4.50, and 5.25 eV) come out to be in good agreement with experiment. Putting together, the results obtained from the two kinds of wavefunctions, the ground state MO's and the triplet state MO's, are not very different from each other.

To find an answer to the second question, we applied two methods to the lowest triplet state of naphthalene; one is the present MC-LCAO-MO method and the other is the open-shell SCF method combined with the so-called variable bond length technique [18, 19] in which bond lengths are allowed to vary with π-bond orders at each iteration process of an SCF routine. Table 7 shows the bond lengths thus calculated for the lowest triplet B_{2u} state. It is seen that the predicted values of the bond lengths in this excited state are quite different from the experimental and/or theoretical values for the ground

Table 8. *TT* transition energies (eV) and oscillator strengths calculated with the lowest triplet-state bond lengths and wavefunctions

	Approximation (1)				Approximation (2)			
	MC-LCAO-MO		SCF-CI		MC-LCAO-MO		SCF-CI	
state	energy	f	energy	f	energy	f	energy	f
$^3B_{2u}$	0.000	ref.	0.000	ref.	0.000	ref.	0.000	ref.
^3A_g	2.696	0.004	3.490	0.014	2.442	0.009	3.127	0.022
	3.666	0.007	4.125	0.009	3.359	0.009	3.776	0.011
	3.957	0.023	4.483	0.044	3.859	0.006	4.346	0.013
	5.203	0.124	5.612	0.155	5.158	0.109	5.564	0.160
	6.371	0.001	6.680	0.001	6.131	0.000	6.406	0.005
$^3B_{1g}$	1.413	0.001	1.766	0.001	1.297	0.002	1.613	0.003
	3.271	0.120	3.321	0.087	3.228	0.110	3.229	0.076
	3.679	0.000	4.085	0.002	3.481	0.000	3.830	0.000
	4.761	0.041	5.046	0.068	4.587	0.063	4.843	0.096
	5.518	0.832	5.705	1.055	5.465	0.740	5.659	1.005
	6.624	0.291	6.949	0.013	6.438	0.342	6.730	0.035

state; for example, the 1–2 bond is remarkably lengthened while the 2–3 bond contracted. It should be noted that the two methods yield the same tendency toward bond lengthening and shortening in the respective bond compared with the ground state data. The bond lengths obtained by the SCF method are quite similar to those obtained by Cho and Kurihara [20] who used semi-empirical parameters for atomic integrals somewhat different from those employed in the present study.

Listed in Table 8 are the results of the *TT* transitions calculated with the bond lengths and wavefunctions most appropriate to the lowest triplet state. The whole spectrum in each treatment, in particular in SCF-CI, is exceedingly raised compared to those computed with the ground state geometry. Moreover, it is seen from the calculated oscillator strengths that the order of energy levels is reversed in part between allowed and forbidden (or nearly forbidden) transitions, e.g. between the second and the third lowest levels of the $^3B_{1g}$ states. Thus the calculation with the use of the lowest excited triplet geometry does not yield *TT* transition energies successfully.

In short, in so far as the low-lying excited triplet states of naphthalene are concerned, the use of the lowest triplet state geometry leads to rather unsatisfactory results.

5. Concluding Remarks

We have shown that the MC-LCAO-MO method is workable to reproduce bond lengths of unsaturated hydrocarbons in their ground states and yield total π-electron energies which are comparable to those obtained by the conventional closed-shell SCF-CI method. In the calculation of transition energies and their intensities of naphthalene, it is found that the results obtained are in good agreement with those derived from the SCF-CI calculation, explaining well the corresponding observed data available at present. Originally the MC-LCAO-MO method has been designed so as to be easily applied to open-shell systems having degenerate MO's (e.g., the benzene ions, the triphenylene ions and so on), which are usually subject to the Jahn-Teller effect. The present paper demonstrates that the method can also be applied, with the same degree of accuracy as the ordinary semi-empirical SCF-CI method, to calculations of both molecular geometries and electronic spectra of cyclic polyenes having closed-shell ground states.

Several years ago, Julg [21] demonstrated theoretically by using the semi-empirical SCF method that the same bond order-bond length linear relationship as in closed-shell ground states approximately holds also in open-shell ground states and even in excited states of conjugated molecules. If this is the case, it is considered that the MC-LCAO-MO method may be employed to predict molecular geometries (bond lengths) of excited states as well as those of open-shell systems like radicals and ions of unsaturated hydrocarbons. The present results indicate that the method may be employed as a consistent calculation scheme which is applied easily and extensively to unsaturated hydrocarbons independently whether they are closed-shell or open-shell systems.

Appendix

The matrix elements of the Hartree-Fock operator used in our SCF calculations, under the zero-differential-overlap assumption, are given as in the following:

1. For a closed-shell configuration

$$F_{pp}=\alpha_p+\tfrac{1}{2}P_{pp}(pp|pp)+\textstyle\sum_{q\neq p}P_{qq}(pp|qq)$$

and

$$F_{pq}=\beta_{pq}-\tfrac{1}{2}P_{pq}(pp|qq)\,.$$

2. For an open-shell configuration

$$F_{pp}=\alpha_p+2\textstyle\sum_q(D_{T,qq}-\zeta D_{O,qq})\,(pp|qq)-(D_{T,pp}-\eta D_{O,pp})\,(pp|pp)+\textstyle\sum_q(D_{T,pq}Q_{qp}+Q_{pq}D_{T,qp})$$

and

$$F_{pq}=\beta_{pq}-(D_{T,pq}-\eta D_{O,pq})\,(pp|qq)+\textstyle\sum_r(D_{T,pr}Q_{rq}+Q_{pr}D_{T,rq})\,,$$

where

$$D_{O,pq}=f\textstyle\sum_m C_{pm}C_{qm} \text{ (the sum is taken over open-shell MO's)}\,,$$

$$D_{T,pq}=\textstyle\sum_k C_{pk}C_{qk}+D_{O,pq} \text{ (the sum over closed-shell MO's)}$$

and

$$Q_{pq}=\delta_{pq}\cdot 2\zeta\textstyle\sum_r D_{O,rr}(pp|rr)-\eta D_{O,pq}(pp|qq)\,.$$

The constants $\zeta=0$, $\eta=-2$ and $f=1/2$ are given for the configuration of the lowest triplet state of naphthalene.

When bond lengths are varied in an open-shell SCF calculation, Eq. (1), in which $P_{pq}=2D_{T,pq}$, is also used.

References

1. Nakayama, M., I'Haya, Y. J.: Intern. J. Quantum Chem. **4**, 21 (1970)
2. Nakayama, M., I'Haya, Y. J.: Intern. J. Quantum Chem. **4**, 43 (1970)
3. I'Haya, Y. J., Nakayama, M., Iwabuchi, T.: Intern. J. Quantum Chem. S**5**, 227 (1971)
4. Nakayama, M., I'Haya, Y. J.: Rept. Univ. Electro-Commun. **29**, 107 (1971)
5. I'Haya, Y.: Advan. Quantum Chem. **1**, 203 (1964)
6. Parr, R. G.: J. Chem. Phys. **33**, 1184 (1960)
7. Langseth, A., Stoicheff, B. P.: Can. J. Phys. **34**, 350 (1956)
8. Cruickshank, D. W. J., Sparks, R. A.: Proc. Roy. Soc. (London) A**258**, 270 (1960)
9. Bastiansen, O., Skancke, P. N.: Advan. Chem. Phys. **3**, 323 (1961)
10. Mason, R.: Acta Cryst. **17**, 547 (1964)
11. Trotter, J.: Acta Cryst. **16**, 605 (1963)
12. Ahmed, F. R., Trotter, J.: Acta Cryst. **16**, 503 (1963)
13. Skancke, P. N.: Acta Chem. Scand. **19**, 401 (1965)
14. Platt, J. R.: Systematics of the electronic spectra of conjugated molecules. New York: Wiley 1964
15. Kasha, M., Nauman, R. V.: J. Chem. Phys. **17**, 516 (1949)
16. Meyer, Y. H., Astier, R., Leclercq, J. M.: J. Chem. Phys. **56**, 801 (1972)
17. Roothaan, C. C. J.: Rev. Modern Phys. **32**, 179 (1960)
18. Dewar, M. J. S., Gleicher, G. J.: Tetrahedron **21**, 3423 (1965)
19. Yamaguchi, H., Nakajima, T., Kunii, T. L.: Theoret. Chim. Acta (Berl.) **12**, 349 (1968)
20. Cho, S., Kurihara, H.: private communication
21. Julg, A.: J. Chim. Phisico Chim. Biol. **65**, 541 (1968)

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