

311. *The Lowest Singlet Excited Levels of Naphthalene. Part I.* *A Semi-empirical Calculation.**

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ASMO-CI (Antisymmetrical molecular orbital-configuration interaction) calculations have been carried out on naphthalene, with the approximations suggested by Pariser and Parr for evaluating the molecular integrals. The two lowest configurations in each of the symmetry classes ${}^1B_{1u}$ and ${}^1B_{2u}$ have been used, which make it possible, when using cyclic orbitals, to establish a relation with the functions built to resemble those of benzene. The lowest transition is found to be polarized along the long axis of the molecule (${}^1B_{1u}$), and the second along the short axis (${}^1B_{2u}$). The comparison of calculated f -values with the observed intensities is not entirely satisfactory, and some difficulties in the interpretation of the spectra are discussed.

PARISER and PARR¹ proposed a semi-empirical approximation by which the lowest excited levels of conjugated systems can be calculated with relative ease. Essentially three modifications are introduced into the non-empirical configuration interaction method of Coulson, Craig, and Jacobs² and others, which is derived from the classical treatment of benzene by Goepfert-Mayer and Sklar:³ (1) the two-electron molecular integrals are approximated by linear combinations of only coulomb-type atomic integrals; (2) the values of these atomic integrals are changed from their analytically calculated values to empirical values; and (3) the mono-electronic core integrals between adjacent centres are also given empirical values.

Applied to *trans*-butadiene,⁴ the procedure predicted with rather good accuracy the order, separations, and intensities of the $N \rightarrow V$ transitions. On the contrary, the results obtained by the non-empirical scheme are not so satisfactory.⁵

An investigation of naphthalene is a natural step towards the study of larger molecules of chemical and biological interest. In addition, there will be the opportunity to study the method of calculation for a molecule where the mechanism of electronic excitation is certainly not as simple as in a linear or a pseudo-linear system. In this paper this semi-empirical procedure will be used to investigate the lowest singlet-singlet transitions of naphthalene. A later paper will be concerned with some restrictions that can be made on the present calculation to parallel treatments of the same problem recently proposed by Dewar and Longuet-Higgins⁶ and by Moffitt.⁷

* A summary has been previously published (Moser and Lefebvre, *J. Chem. Phys.*, 1955, **23**, 598).

¹ Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.

² Coulson, Craig, and Jacobs, *Proc. Roy. Soc.*, 1951, *A*, **206**, 297.

³ Goepfert-Mayer and Sklar, *J. Chem. Phys.*, 1938, **6**, 645.

⁴ Moser, *J.*, 1954, 3455.

⁵ Lefebvre, Thesis, London, 1953; Pullman, *J. Chim. phys.*, 1954, **51**, 188.

⁶ Dewar and Longuet-Higgins, *Proc. Phys. Soc.*, 1954, **67**, *A*, 795.

⁷ Moffitt, *J. Chem. Phys.*, 1954, **22**, 320.

The calculation has been restricted to the two symmetry classes which correspond to allowed singlet π - π transitions from the ground state, and to the two lowest configurations within these classes. This choice has been made because : (1) There are reasons to believe that the lowest three singlet transitions of naphthalene are allowed even though the character of the first band has sometimes given rise to the interpretation of a forbidden transition.⁸ But Platt⁹ suggested that the weakness of the transition could be accounted for by a resemblance between naphthalene and a cyclic molecule. (2) The restriction to the lowest configurations of each of these symmetry classes makes it particularly easy to put the emphasis on this resemblance, since the use of cyclic molecular orbitals makes it possible to build from these configurations functions which would be convenient for the truly cyclic molecule. If there is any particular significance to be attached to this configurational interaction when using the cyclic orbitals, it would be also necessary to consider that same interaction when using other molecular orbitals not greatly different from these.

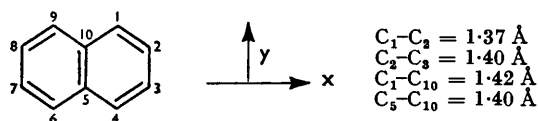
It was hoped that with this limited choice of configurations the qualitative nature of the various transitions would be characterized. Three parallel calculations have been carried out, with three different sets of orbitals : (a) the Hückel orbitals (cf. Coulson¹⁰ for the definition of these orbitals); (b) the cyclic real orbitals, *i.e.*, the orbitals which result from the usual LCAO-MO (linear combination of atomic orbitals-molecular-orbital) theory applied to the molecule without its cross-bond (cf. Lefebvre⁵ for the form of these orbitals); (c) the orbitals found from an investigation of the ground state by the SCF (self-consistent field) method.¹¹ These orbitals are those which are pertinent to the procedure adopted for the evaluation of the molecular integrals. These have been chosen because : (i) orbitals which are specific for the excited states are unknown; (ii) the cyclic orbitals have a particular meaning in relation with the "pseudo-cyclic" character of the molecule; (iii) the Hückel and the cyclic orbitals will be useful when comparing the results with those obtained in some recent investigations.

There will be a brief description of the calculations and in the Discussion section the results will be compared with the experimental observations on the ultraviolet spectrum of naphthalene, and the wave functions and levels proposed by Dewar and Longuet-Higgins⁶ and Moffitt⁷ for this molecule.

CALCULATIONS

The general procedure for the use of Pariser and Parr's method follows that of the usual configuration-interaction method, and so only a very brief outline of the calculations will be necessary here.

Naphthalene is assumed to have the following geometry :¹²



This numbering of the carbon atoms will be useful when using cyclic orbitals. The assumption of unequal bond lengths does not introduce unmanageable complications in the calculation.

From the ten $2p\pi$ atomic orbitals, ten independent real molecular orbitals can be obtained, $\phi_1 \dots \phi_5$ being bonding, $\phi_6 \dots \phi_{10}$ antibonding. From the results of the simple LCAO-MO theory¹³ we infer that the two lowest singlet configurations of the class B_{2u} result from the monoexcitations $5 \rightarrow 6$ and $4 \rightarrow 7$, and the two lowest singlet configurations of the class B_{1u} from the monoexcitations $5 \rightarrow 7$ and $4 \rightarrow 6$. Functions belonging to B_{2u} transform as

⁸ See, *e.g.*, Spomer and Nordheim, *Discuss. Faraday Soc.*, 1950, **9**, 19.

⁹ Platt, *J. Chem. Phys.*, 1949, **17**, 484.

¹⁰ Coulson, *Proc. Phys. Soc.*, 1948, **60**, A, 251.

¹¹ Moser, *J. Chim. phys.*, 1955, **52**, 24.

¹² Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 233; Ahmed and Cruickshank, *ibid.*, 1952, **5**, 852.

¹³ Coulson, *Proc. Phys. Soc.*, 1948, **60**, A, 257.

does y and those belonging to B_{1u} as does x . The following wave function corresponds to the singlet excitation $i \rightarrow j$:

$${}^1\psi_1^{i,j} = (1/\sqrt{2})\{|\dots\phi_i\bar{\phi}_j| - |\dots\bar{\phi}_i\phi_j|\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the orbitals not mentioned in the formula are all doubly occupied.

With the total Hamiltonian in the form used by Goepfert-Mayer and Sklar, the corresponding energy is:¹⁴

$${}^1E_1^{i,j} = E_0 + \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where E_0 is the ground-state energy and ϵ_k the quantity:

$$\int \phi_k^* [H^c + \sum_{l=1}^5 (2J_l - K_l)] \phi_k d\tau = \epsilon_k^c + \sum_{l=1}^5 (2J_{kl} - K_{kl}) \quad . \quad . \quad . \quad . \quad (3)$$

In equation (3), H^c is the Hamiltonian of a π -electron in the absence of all other π -electrons. The energy expression (2) can then be reduced to a linear combination of two sorts of molecular integrals;¹⁵ the one-electron core integral:

$$\epsilon_{kl}^c = \int \phi_k^* H^c \phi_l d\tau \quad (\text{with the notation } \epsilon_k^c \text{ for } \epsilon_{kk}^c) \quad . \quad . \quad . \quad . \quad (4)$$

and the two-electron repulsion integral:

$$\zeta_{pq}^{mn} = \int \phi_m(1) \phi_n(1) (e^2/r_{12}) \phi_p(2) \phi_q(2) d\tau_{12} \quad . \quad . \quad . \quad . \quad (5)$$

of which the Coulomb and exchange molecular integrals J_{ij} and K_{ij} are special cases. For the off-diagonal matrix elements there is the formula:

$$\int {}^1\psi_1^{m,n*} H {}^1\psi_1^{p,q} d\tau = 2\zeta_{pq}^{mn} - \zeta_{nq}^{mp} \quad (m \neq p, n \neq q) \quad . \quad . \quad . \quad . \quad (6)$$

The values of the atomic integrals are those used in the calculation of the SCF MO's.¹¹ The data for the molecular integrals are collected in Table 1. The calculated excitation energies, the calculated intensities (for which the calculated transition energies have been used), and the coefficients of the configurations in the wave-functions are collected in Table 2. C_{ke} is the coefficient which multiplies ${}^1\psi_1^{k,l}$ in a given wave-function.

A number of features of this calculation follow from the results given in Table 2. The order of levels before configurational interaction varies from one set to another, and is not as expected on the basis of the simple LCAO-MO method except when Hückel orbitals are used. The mixing of the configurations of the same symmetry class is considerable in all cases, and has the effect of reducing considerably the intensity of the two lowest transitions. As far as the two lowest levels are concerned, the final order is the same in all three calculations.

DISCUSSION

It is generally accepted that there are in the near-ultraviolet spectrum three singlet-singlet transitions:¹⁶ (1) 3.97 eV ($f = 0.002$), (2) 4.29 eV ($f = 0.18$), and (3) 5.6 eV ($f = 1.70$). These transitions have received various assignments. As mentioned above, the first band is generally regarded as representing an allowed transition, but there is disagreement as to whether this transition is polarized along the short (y) axis¹⁷ or the long (x) axis of the molecule. Recent experimental work¹⁸ indicates that the transition is polarized along the long axis of the molecule, and the second (also allowed) along the y axis.

From the point of view of symmetry assignments, the present results are in satisfactory agreement with McClure's recent assignments.¹⁸ The first transition is $A_{1g} \rightarrow B_{2u}$.

¹⁴ Cf. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

¹⁵ Cf. Parr, Craig, and Ross, *J. Chem. Phys.*, 1950, **18**, 1561.

¹⁶ Klevens and Platt, *ibid.*, 1949, **17**, 470.

¹⁷ *E.g.*, Passerini and Ross, *ibid.*, 1954, **22**, 1012.

¹⁸ McClure, *ibid.*, p. 1668.

TABLE 1.

Molecular integrals		$\delta_{ij} = \zeta_{ij}^H$ (the molecular orbitals are real functions)		S.C.F.		Wave-functions		
$\gamma_{ij} = \zeta_{ij}^H$		$\delta_{ij} = \zeta_{ij}^H$		S.C.F.		For all orbitals		
Cyclic		Hückel		Cyclic		Cyclic		
S.C.F.		Hückel		S.C.F.		Hückel		
γ_{11}	6-330	5-710	6-213	γ_{55}	5-787	5-688	0-269	0-382
γ_{12}	5-452	5-472	5-491	γ_{56}	5-787	5-704	0-338	0-421
γ_{13}	6-171	5-949	6-004	γ_{57}	5-706	5-976	1-458	1-189
γ_{14}	5-910	5-804	6-128	γ_{44}	5-934	6-191	0-757	0-819
γ_{15}	5-769	5-617	5-704	γ_{45}	5-502	5-584	0-410	0-441
γ_{16}	5-769	5-617	5-718	γ_{46}	5-502	5-584	0-381	0-429
γ_{17}	5-804	5-804	6-285	γ_{47}	5-934	6-319	0-152	0-178
γ_{22}	5-544	5-544	5-526	γ_{55}	5-651	5-653	1-186	0-919
γ_{23}	5-384	5-399	5-432	γ_{56}	5-651	5-604	0-393	0-341
γ_{24}	5-601	5-551	5-569	γ_{57}	5-502	5-650	0-353	0-513
γ_{25}	5-392	5-392	5-431	δ_{15}	0-979	1-107	0-145	0-173
γ_{26}	5-392	5-392	5-428	δ_{16}	1-007	0-925	0-145	0-400
γ_{27}	5-601	5-551	5-565	δ_{17}	0-633	0-731	0-688	0-755
γ_{31}	6-111	6-498	5-907	δ_{18}	0-400	0-398	0-798	0-681
γ_{32}	5-706	6-054	5-855	δ_{19}	0-232	0-214	0-556	0-406
γ_{37}	-0-308	-0-223*	0-314	δ_{26}^6	0-556	0-402	0-145	0-142
$\epsilon^1 - 10W_{2p}$	-55-8482	-53-5040	-55-6239	δ_{27}^6	-50-8585	-51-3943	-45-4082	-45-4082
$\epsilon^2 - 10W_{5p}$	-49-9516	-49-9516	-50-0890	$\epsilon^5 - 10W_{2p}$	-49-2199	-49-2199	-46-3869	-48-7543
$\epsilon^3 - 10W_{2p}$	-52-6126	-53-6265	-52-0206	$\epsilon^6 - 10W_{2p}$	-49-2199	-49-2199	-46-3869	-48-7543

* For the cyclic orbitals, ϕ_j as defined analytically here, corresponds to minus the Hückel or SCF ϕ_j orbital.

TABLE 2.

	Transition energies (ev)			f values			Wave-functions			
	Hückel		S.C.F.	Cyclic		S.C.F.	For all orbitals		Cyclic	S.C.F.
	Cyclic	Hückel	Cyclic	Cyclic	S.C.F.	Cyclic	S.C.F.			
$\Delta E_{1,6}^{5,6} (B_{2u})$	5-507	5-107	5-814	(a) Before C.I.	0-66	0-61	0-54	$C_{66} = 1$	$C_{47} = 0$	
$\Delta E_{1,7}^{4,7} (B_{2u})$	5-984	4-525	5-719		0-52	0-23	0-47	$C_{56} = 0$	$C_{47} = 1$	
$\Delta E_{1,7}^{6,7} (B_{1u})$	5-434	5-024	5-032		1-02	1-28	0-68	$C_{57} = 1$	$C_{46} = 1$	
$\Delta E_{1,6}^{4,6} (B_{1u})$	5-889	5-594	5-996		1-11	1-42	0-78	$C_{57} = 0$	$C_{46} = 1$	
				(b) After C.I.	0-02	0-02	0-13	Hückel	Cyclic	S.C.F.
$4-668 (B_{1u})$	3-819 (B_{1u})	4-696 (B_{1u})	4-995 (B_{2u})		0-02	0-02	0-13	$C_{57} = 0-784$	$C_{46} = 0-772$	$C_{57} = 0-892$
$4-984 (B_{2u})$	4-180 (B_{2u})	4-995 (B_{2u})	4-995 (B_{2u})		0-05	0-00	0-00	$C_{46} = -0-621$	$C_{46} = 0-636$	$C_{46} = -0-454$
$6-542 (B_{2u})$	5-939 (B_{2u})	6-333 (B_{1u})	6-333 (B_{1u})		1-28	1-01	1-51	$C_{56} = 0-806$	$C_{56} = 0-520$	$C_{56} = 0-685$
$6-655 (B_{1u})$	6-799 (B_{1u})	6-538 (B_{2u})	6-538 (B_{2u})		2-47	3-43	1-15	$C_{47} = 0-592$	$C_{47} = -0-853$	$C_{47} = 0-728$
								$C_{56} = 0-592$	$C_{56} = 0-853$	$C_{56} = 0-454$
								$C_{17} = -0-806$	$C_{17} = 0-520$	$C_{17} = -0-892$
								$C_{57} = 0-621$	$C_{57} = 0-636$	$C_{57} = 0-728$
								$C_{46} = 0-784$	$C_{46} = -0-772$	$C_{46} = 0-685$

The relative separations of levels is reasonably reproduced: 0.31 eV (Hückel), 0.36 eV (cyclic), 0.30 eV (SCF) compared with the 0.31 eV observed experimentally. Further, in all cases the first transition is very weak [respectively $f = 0.02$ (Hückel), 0.02 (cyclic), 0.13 (SCF) compared with the experimental value 0.002]. Keeping in mind the difficulty of obtaining precise f values, one should not expect better agreement from an approximate calculation.

From the point of view of relative intensities, the results are not as satisfactory, as the hundred-fold difference in observed f values between the first and the second band is not reproduced. In two of the three calculations (cyclic and SCF orbitals), the relative order is even reversed. In general, the intensities are more sensitive than the energies to the form of the wave-functions. But in view of the fact that in the present calculation the intensities of the two lowest transitions are in all cases very weak, regardless of the set of orbitals used, and that the two lowest levels are not widely separated, it might be possible that, if the calculation were improved, the order of the levels would be B_{2u} and then B_{1u} , again with very weak transition moments.

In other words, if we forget for a moment about the recent experimental symmetry assignment mentioned above, the calculations do not characterize satisfactorily the intensities and it is not possible to differentiate the two transitions, in contrast to the experimental spectrum.

This point will be discussed further, in relation with the semi-empirical procedures proposed by Dewar and Longuet-Higgins⁶ and Moffitt.⁷

The Dewar and Longuet-Higgins Procedure.—The strict degeneracy which exists in the simple LCAO-MO theory between ${}^1E_1^{5,7}$ and ${}^1E_1^{4,6}$ causes an equal mixing of ${}^1\psi_1^{5,7}$ and ${}^1\psi_1^{4,6}$. The two other functions ${}^1\psi_1^{5,6}$ and ${}^1\psi_1^{4,7}$ are assumed not to mix. From the sign of the off-diagonal matrix element:

$$\int {}^1\psi_1^{5,7*} H {}^1\psi_1^{4,6} d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

it results that the function:

$$2^{-1} [{}^1\psi_1^{5,7} - {}^1\psi_1^{4,6}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

is the lower. This produces zero transition moment. In this method the two lowest transitions (the other one being the monoexcitation $5 \rightarrow 6$) are well differentiated by their intensities. The exact order of levels is not calculated but one makes a one-to-one correspondence with the experimental transitions, taking advantage of the fact that they are also well characterized by their transition moments.

As mentioned above, when the calculations are made with the Hückel orbitals, an order of levels that follows that of the simple theory is obtained before configuration interaction. ${}^1E_1^{5,7}$ and ${}^1E_1^{4,6}$ are close together. In consequence there is a nearly equal mixing of the functions ${}^1\psi_1^{5,7}$ and ${}^1\psi_1^{4,6}$ and, as a result, there is nearly a vanishing transition moment, which is characteristic of Dewar and Longuet-Higgins's procedure. However here it is found that the mixing of ${}^1\psi_1^{5,6}$ and ${}^1\psi_1^{4,7}$ is considerably more than that assumed in the above procedure. A large decrease in the f value follows (0.05 instead of 0.66 for the pure $5 \rightarrow 6$ excitation). This is due, in part, to the fact that the levels are rather close to each other.

In the other cases (cyclic and SCF orbitals), the mixing is important in both classes, and in one instance (SCF orbitals) is even more important for the B_{2u} class than for the B_{1u} class. Obviously, in the *a priori* calculation presented here, there is no clear-cut distinction between the two classes, in contrast to the Dewar and Longuet-Higgins scheme.

The effect of mixing of the two configurations in each of the two symmetry classes for both Hückel and cyclic orbitals is presented in Figs. 1 and 2. An arbitrary excitation energy of $30,000 \text{ cm.}^{-1}$ has been used in the calculation of these graphs. Two points may be specifically mentioned: (1) Even a small amount of mixing for the class ${}^1B_{1u}$ has the effect of reducing considerably the intensity calculated from a single configuration. (2) Accidentally, one might calculate zero intensity for either class or perhaps even for both classes.

Moffitt's Procedure.—The cyclic real orbitals used above can be deduced, by the use of symmetry conditions, from the cyclic complex orbitals which have the form :

$$\phi_l = 10^{-3} \sum_k \exp [2\pi i k l / 10] \chi_k \quad (l = 0, \pm 1, \dots \pm 4, 5)$$

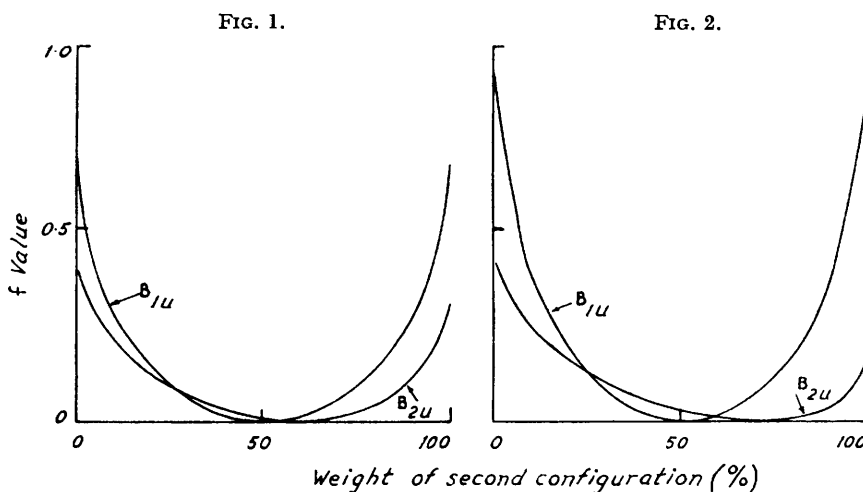
In the ground state, the orbitals up to $l \pm 2$ are doubly occupied. From the four lowest singlet monoexcited wave-functions :

$${}^1\psi_1^{-2,-3}, {}^1\psi_1^{2,3}, {}^1\psi_1^{-2,3}, {}^1\psi_1^{2,-3}$$

Moffitt forms the following combinations :

$$\left. \begin{aligned} \Theta_X &= (1/\sqrt{2}) ({}^1\psi_1^{-2,-3} + {}^1\psi_1^{2,3}) & \Theta_U &= (1/\sqrt{2}) ({}^1\psi_1^{-2,3} + {}^1\psi_1^{2,-3}) \\ \Theta_Y &= (1/i\sqrt{2}) ({}^1\psi_1^{-2,-3} - {}^1\psi_1^{2,3}) & \Theta_V &= (1/i\sqrt{2}) ({}^1\psi_1^{-2,3} - {}^1\psi_1^{2,-3}) \end{aligned} \right\} \quad (9)$$

which satisfy the symmetry requirements for naphthalene, and also correspond to the lowest singlet functions of the truly cyclic molecule. The notation is the same as that used



The effect of mixing of configurations on the *f* value : FIG. 1, Hückel orbitals; FIG. 2, cyclic orbitals

by Moffitt. After allowance for the mixing of the functions belonging to the same symmetry class, the final functions are, in order of increasing energy :

$$\Theta_V, \cos \rho \Theta_U + \sin \rho \Theta_X, \Theta_Y, \cos \rho \Theta_X - \sin \rho \Theta_U$$

A comparison with the wave-functions in Table 2, built from real cyclic orbitals, is possible because of the following identities, which result from the relations between complex and real cyclic orbitals :⁵

$$\left. \begin{aligned} {}^1\psi_1^{5,6} &= (1/\sqrt{2}) (\Theta_X - \Theta_U) & {}^1\psi_1^{4,6} &= (1/\sqrt{2}) (\Theta_V - \Theta_Y) \\ {}^1\psi_1^{5,7} &= (1/\sqrt{2}) (\Theta_V + \Theta_Y) & {}^1\psi_1^{4,7} &= (1/\sqrt{2}) (\Theta_X + \Theta_U) \end{aligned} \right\} \quad (10)$$

Thus the lowest excited wave-function, that is, Θ_V , is seen to result in Moffitt's procedure when equal weights are given to the functions ${}^1\psi_1^{5,7}$ and ${}^1\psi_1^{4,6}$. In the present calculation the lowest level corresponds to the wave-function :

$$0.636 {}^1\psi_1^{4,6} + 0.772 {}^1\psi_1^{5,7}$$

which does not depart notably from equal mixing. From the identities (10), one sees that the large mixing which exists in Table 2, between the singlet monoexcited wave-functions built on real cyclic orbitals, has as a counterpart a small mixing of the functions built to

resemble those of a truly cyclic molecule. The present calculation agrees qualitatively with that of Moffitt, in the sense that in both cases emphasis is put on the functions (9) rather on the functions ${}^1\psi_1^{k,l}$. However it must be noticed that the mixing between Θ_U and Θ_X is somewhat larger in Moffitt's procedure than that resulting from the data of Table 2. Another circumstance is worth mentioning: in both empirical procedures (Dewar and Longuet-Higgins's and Moffitt's) the lowest level is described by an equal mixing of ${}^1\psi_1^{5,7}$ and ${}^1\psi_1^{4,6}$ although the orbitals are not the same. This will be the object of detailed analysis in a later paper.

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