809. *Energy Levels of Planar Diphenyl.*

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A revision of London's [1] calculations on the lower π-electron energy levels of planar diphenyl gives results which provide a satisfactory quantitative correlation of the absorption spectra of diphenyl and benzene.

IN applying Goeppert-Mayer and Sklar's [2] method of antisymmetrized molecular orbitals to the quantitative interpretation of the absorption spectrum of diphenyl, London [1] formulated the spatial wave functions for the lower excited states not as twelve-factor products of one-electron molecular orbitals extending over the whole molecule, but as two-factor products of the six-electron total wave functions of the individual benzene rings.* He thus provided a means of estimating separately (*a*) the so-called π-electron energy levels of a hypothetical diphenyl molecule with a $C_{(1)}$–$C_{(1')}$ bond of infinite length (*i.e.*, the energy levels of two non-interacting benzene molecules, each in its own appropriate state of excitation); and (*b*) the changes in energy brought about by reducing the length of the $C_{(1)}$–$C_{(1')}$ bond from infinity to the equilibrium internuclear distance.

London rejected Goeppert-Mayer and Sklar's partially corrected values for (*a*) in favour of values related more closely to the absorption spectrum of benzene, and in so doing anticipated in some measure an argument which has become familiar recently as the basis of Moffitt's [3] modification of the method of antisymmetrized molecular orbitals. It is now recognized that, although Goeppert-Mayer and Sklar's technique in its original form (with the original atomic wave functions and the original Hamiltonian operator) may be expected

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* Wave functions of the more conventional type have recently been used by Iguchi (*J. Phys. Soc. Japan*, 1937, **12**, 1250).

[1] A. London, *J. Chem. Phys.*, 1945, **13**, 396.

[2] Goeppert-Mayer and Sklar, *ibid.*, 1938, **6**, 645; Sklar and Lyddane, *ibid.*, 1939, **7**, 374.

[3] Moffitt, *Proc. Roy. Soc.*, 1951, *A*, **210**, 224, 245; 1953, *A*, **218**, 486; *Reports Progr. phys.*, 1954, **17**, 173; Moffitt and Scanlan, *Proc. Roy. Soc.*, 1953, *A*, **218**, 464; 1953, *A*, **220**, 530.

to provide only a very poor approximation to the observed energy levels of an unsaturated hydrocarbon molecule, the same technique can often be employed fairly satisfactorily to calculate the relatively small energies of interaction between the constituent atoms or groups.

It is of interest in this connexion to investigate to what extent Goeppert-Mayer and Sklar's procedure succeeds in correlating the absorption spectrum of diphenyl with that of benzene; we therefore revised London's calculations, which incorporated a number of errors [4] and approximations carried over from earlier work.[2] The amended results are now presented.

For want of crystallographic data, the $C_{(1)}$–$C_{(1')}$ bond length in diphenyl is taken as 1·48 Å, and the other C–C bond lengths as 1·40 Å (cf. benzene [5]). If the central bond is extended indefinitely, the π-electron molecular orbitals of diphenyl degenerate into two identical sets of benzene orbitals, which, for either ring, can be written in the following real form: [6]

$$\begin{aligned}
A &= 0{\cdot}322053\ (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)\\
B &= 0{\cdot}456078\ (\phi_2 + \phi_3 - \phi_5 - \phi_6)\\
C &= 0{\cdot}263317\ (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)\\
D &= 0{\cdot}588307\ (\phi_2 - \phi_3 + \phi_5 - \phi_6)\\
E &= 0{\cdot}339659\ (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)\\
F &= 0{\cdot}553167\ (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)
\end{aligned}$$

$$\left[\int\phi_1\phi_2 d\tau = 0{\cdot}256967;\ \int\phi_1\phi_3 d\tau = 0{\cdot}037898;\ \int\phi_1\phi_4 d\tau = 0{\cdot}017188\right]$$

The numeral subscripts conform with organic chemical usage: the atomic orbital ϕ_i is the $2p$-orbital of the carbon atom $C_{(i)}$ having its principal symmetry axis normal to the plane of the molecule. Where necessary in the following discussion, primes (′) will be used to distinguish the atomic or molecular wave functions of one ring from those of the other.

The lowest-energy molecular states [2] of each of the infinitely separated benzene rings are, in Craig's [7] notation:

$$\begin{aligned}
\Phi_0 &= 6^{-\frac{1}{2}}(|ABC\overline{ABC}|)\\
\Phi_1 &= 24^{-\frac{1}{2}}(|AB\boldsymbol{C}\overline{AB\boldsymbol{D}}| + |A\boldsymbol{B}C\overline{AC\boldsymbol{E}}| \pm |AB\boldsymbol{D}\overline{AB\boldsymbol{C}}| \pm |AC\boldsymbol{E}\overline{A\boldsymbol{B}C}|)\\
\Phi_2 &= 24^{-\frac{1}{2}}(|AB\boldsymbol{C}\overline{AB\boldsymbol{D}}| - |A\boldsymbol{B}C\overline{AC\boldsymbol{E}}| \pm |AB\boldsymbol{D}\overline{AB\boldsymbol{C}}| \mp |AC\boldsymbol{E}\overline{A\boldsymbol{B}C}|)\\
\Phi_3 &= 24^{-\frac{1}{2}}(|AB\boldsymbol{C}\overline{AB\boldsymbol{E}}| + |A\boldsymbol{B}C\overline{AC\boldsymbol{D}}| \pm |AB\boldsymbol{E}\overline{AB\boldsymbol{C}}| \pm |AC\boldsymbol{D}\overline{A\boldsymbol{B}C}|)\\
\Phi_4 &= 24^{-\frac{1}{2}}(|AB\boldsymbol{C}\overline{AB\boldsymbol{E}}| - |A\boldsymbol{B}C\overline{AC\boldsymbol{D}}| \pm |AB\boldsymbol{E}\overline{AB\boldsymbol{C}}| \mp |AC\boldsymbol{D}\overline{A\boldsymbol{B}C}|)
\end{aligned}$$

[Upper signs: singlet states. Lower signs: triplet states ($\sum m_s = 0$)]

Bars are used to differentiate between α and β spin factors; and for clarity the symbols for singly " occupied " orbitals are printed in bold-face type. The states Φ_1 and Φ_4 are degenerate.

The wave functions for the ground state and the lower excited π-electron states of a diphenyl molecule with an infinitely long central bond are, in non-normalized form:

$$\begin{aligned}
&\Psi_0 = \Phi_0\Phi_0';\\
&\Psi_1 = \Phi_0\Phi_1' + \Phi_1\Phi_0';\ \Psi_5 = \Phi_0\Phi_3' + \Phi_3\Phi_0'\\
&\Psi_2 = \Phi_0\Phi_1' - \Phi_1\Phi_0',\ \Psi_6 = \Phi_0\Phi_3' - \Phi_3\Phi_0'\\
&\Psi_3 = \Phi_0\Phi_2' + \Phi_2\Phi_0';\ \Psi_7 = \Phi_0\Phi_4' + \Phi_4\Phi_0'\\
&\Psi_4 = \Phi_0\Phi_2' - \Phi_2\Phi_0';\ \Psi_8 = \Phi_0\Phi_4' - \Phi_4\Phi_0'
\end{aligned}$$

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[4] Parr and Crawford, *J. Chem. Phys.*, 1948, **16**, 1049.

[5] Cox, *Rev. Modern Physics*, 1958, **30**, 159.

[6] Coulson, " Valence," Oxford University Press, 1952, p. 240.

[7] Craig, *Proc. Roy. Soc.*, 1950, *A*, **200**, 474.

Appropriately antisymmetrized (Table 1), these functions can be used as zero-order functions in the calculation of the perturbation of the energy levels of planar diphenyl brought about by the reduction of the central-bond length from infinity to 1·48 Å. The resulting increments (ΔE) in the " vertical " excitation energies are listed in Table 2. It is of course impossible to assess the changes in the individual energy levels explicitly, for there is no obvious way of adapting Goeppert-Mayer and Sklar's approximation to provide a means of estimating the energy of repulsion between the carbon " cores " (nuclei plus σ-electrons).[8] Nor is it clear whether any allowance should be made for the difference between the potential of the $C_{(1)}$ and $C_{(1')}$ cores in diphenyl and the potential of the corresponding cores in benzene.

TABLE 1. *Wave functions for the lower excited states of diphenyl (non-normalized).*

Determinant	Coefficient of determinant in wave function Ψ_1	Ψ_2	Ψ_3	Ψ_4	Determinant	Coefficient of determinant in wave function Ψ_5	Ψ_6	Ψ_7	Ψ_8
$\lvert ABC\overline{ABC}A'B'\mathbf{C}'\overline{A'B'\mathbf{D}'}\rvert$	1	1	1	1	$\lvert ABC\overline{ABC}A'B'\mathbf{C}'\overline{A'B'\mathbf{E}'}\rvert$	1	1	1	1
$\lvert ABC\overline{ABC}A'\mathbf{B}'C'\overline{A'C'\mathbf{E}'}\rvert$	1	1	−1	−1	$\lvert ABC\overline{ABC}A'\mathbf{B}'C'\overline{A'C'\mathbf{D}'}\rvert$	1	1	−1	−1
$\lvert AB\mathbf{C}\overline{AB\mathbf{D}}A'B'C'\overline{A'B'C'}\rvert$	1	−1	1	−1	$\lvert AB\mathbf{C}\overline{AB\mathbf{E}}A'B'C'\overline{A'B'C'}\rvert$	1	−1	1	−1
$\lvert A\mathbf{B}C\overline{AC\mathbf{E}}A'B'C'\overline{A'B'C'}\rvert$	1	−1	−1	1	$\lvert A\mathbf{B}C\overline{AC\mathbf{D}}A'B'C'\overline{A'B'C'}\rvert$	1	−1	−1	1
$\lvert ABC\overline{ABC}A'B'\mathbf{D}'\overline{A'B'\mathbf{C}'}\rvert$	±1	±1	±1	±1	$\lvert ABC\overline{ABC}A'B'\mathbf{E}'\overline{A'B'\mathbf{C}'}\rvert$	±1	±1	±1	±1
$\lvert ABC\overline{ABC}A'C'\mathbf{E}'\overline{A'\mathbf{B}'C'}\rvert$	±1	±1	∓1	∓1	$\lvert ABC\overline{ABC}A'C'\mathbf{D}'\overline{A'\mathbf{B}'C'}\rvert$	±1	±1	∓1	∓1
$\lvert AB\mathbf{D}\overline{AB\mathbf{C}}A'B'C'\overline{A'B'C'}\rvert$	±1	∓1	±1	∓1	$\lvert AB\mathbf{E}\overline{AB\mathbf{C}}A'B'C'\overline{A'B'C'}\rvert$	±1	∓1	±1	∓1
$\lvert AC\mathbf{E}\overline{A\mathbf{B}C}A'B'C'\overline{A'B'C'}\rvert$	±1	∓1	∓1	±1	$\lvert AC\mathbf{D}\overline{A\mathbf{B}C}A'B'C'\overline{A'B'C'}\rvert$	±1	∓1	∓1	±1

[Upper signs: singlet states. Lower signs: triplet states]

TABLE 2. *Transition energies of diphenyl in relation to those of benzene.*

Benzene			Diphenyl				
Excited state	Symmetry (group D_{6h})	Transition energy (obs.) ev	Excited state	Symmetry (group D_{2h})	Polarization of allowed transition	ΔE ev	Transition energy (calc.) ev
${}^1\Phi_1$	E_{1u}	**6·74** [a]	${}^1\Psi_1$	B_{2u}	long.	0·3638	**7·10**
			${}^1\Psi_2$	B_{1g}		−0·3320	6·41
${}^1\Phi_2$	B_{2u}	4·88 [a]	${}^1\Psi_3$	B_{2u}	long.	−0·0099	**4·87**
			${}^1\Psi_4$	B_{1g}		0·0560	4·94
${}^1\Phi_3$	B_{1u}	6·14 [a, b]	${}^1\Psi_5$	A_g		0·1776	6·32
			${}^1\Psi_6$	B_{3u}	trans.	−0·1750	**5·96**
${}^1\Phi_4$	E_{1u}	**6·74**	${}^1\Psi_7$	A_g		0·8244	7·56
			${}^1\Psi_8$	B_{3u}	trans.	−0·8660	**5·87**
${}^3\Phi_1$	E_{1u}	—	${}^3\Psi_1$	B_{2u}		−0·0079	
			${}^3\Psi_2$	B_{1g}		0·0531	
${}^3\Phi_2$	B_{2u}	—	${}^3\Psi_3$	B_{2u}		−0·0165	
			${}^3\Psi_4$	B_{1g}		0·0497	
${}^3\Phi_3$	B_{1u}	3·8 [c]	${}^3\Psi_5$	A_g		0·0852	3·9
			${}^3\Psi_6$	B_{3u}		−0·0410	3·8
${}^3\Phi_4$	E_{1u}	—	${}^3\Psi_7$	A_g		0·0872	
			${}^3\Psi_8$	B_{3u}		−0·0119	

The symmetry notation is that of Longuet-Higgins and Murrell (ref. 12). The axes of polarization of the allowed transitions from the ground state are in the plane of the molecule: longitudinal = in the direction $C_{(4)}$–$C_{(4')}$; transverse = normal to the direction $C_{(4)}$–$C_{(4')}$. The energies of the allowed transitions are printed in bold-face type.

[a] Solution spectra.[9] [b] Symmetry uncertain (Dunn and Ingold, *Nature*, 1955, **176**, 65). [c] Symmetry uncertain (Shull, *J. Chem. Phys.*, 1949, **17**, 295; McClure, *ibid.*, p. 665; Craig, *ibid.*, 1950, **18**, 236).

Unlike that of benzene, the vapour-phase ultraviolet absorption spectrum of diphenyl has not been resolved into its component electronic transitions, and it is therefore difficult

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[8] Cf. Craig, *Proc. Roy. Soc*., 1950, *A*, **200**, 272 (see foot of p. 280).

[9] Klevens and Platt, Technical Report, Laboratory of Molecular Structure and Spectra, University of Chicago, 1953—54, I, 145.

to decide how closely the allowed transitions at 4·87, 5·87, 5·96, and 7·10 ev suggested by the present calculations correspond with experimental data, especially as the overlapping of some of the transitions makes it impossible to attach very much quantitative significance to the directly observed intensity maxima. A comparison of the spectra of the two molecules measured under comparable conditions in fluorocarbon solutions,[9] however, shows that London's procedure offers a satisfactory interpretation of the grosser features of the spectrum of diphenyl, which are as follows. Covering much the same range as the forbidden 4·88 ev transition in benzene, there is a broad band of high intensity ($\varepsilon_{\text{max.}} \sim 18{,}000$). In the region of the 6·14 ev transition in benzene, but of higher intensity ($\varepsilon_{\text{max.}} \sim 52{,}000$) and rather wider range, there is a band with maxima at 6·0 ev and 6·2 ev, corresponding presumably to the calculated values of 5·87 ev and 5·96 ev. Finally there is a high-intensity transition of energy greater than 7·0 ev, outside the range of the solution spectrum,[10] confirming the quite substantial calculated displacement of the 6·74 ev benzene transition.

So little is known of the nature of the triplet states of diphenyl that it is not possible to comment on the second part of Table 2.

The calculations described here are of course restricted to planar diphenyl, and some disparity between theory and experiment is thus to be expected. In a study based on Pople's [11] extension of Hückel's empirical molecular-orbital method, Longuet-Higgins and Murrell [12,13] have examined the relation between the singlet levels of planar and perpendicular diphenyl and those of benzene, considering not only " locally excited " configurations (as in this paper), but also " charge-transfer " configurations produced by the excitation of an electron from a ground-state orbital of one benzene ring to a higher-energy orbital of the other.

For the locally excited configurations Longuet-Higgins and Murrell used wave functions of the type $\Phi_n \pm \Phi_n'$ ($n = 1, 2, 3, 4$). In view of this difference, and also the manifold differences in the methods of integral evaluation, it is pleasing to find a notable measure of agreement between the present results and those of the Cambridge authors. In Table 3 are listed the values of ΔE (ev) for the singlet states, (*a*) reproduced *seriatim* from Table 2, (*b*) derived from the final results of Longuet-Higgins and Murrell,[12] and (*c*) recalculated from Longuet-Higgins and Murrell's interaction matrices, the perturbation of the ground state and the locally excited configurations by the charge-transfer configurations being disregarded. [To facilitate comparison, the symbols which Longuet-Higgins and Murrell have adopted for the singlet excited states of benzene (α, p, β, β′) are given along with the orthodox symbols of group theory.]

TABLE 3.

Excited state of benzene	$^1E_{1u}$ (β)		$^1B_{2u}$ (α)		$^1B_{1u}$ (p)		$^1E_{1u}$ (β')	
(*a*)	0·36	−0·33	−0·01	0·06	0·18	−0·18	0·82	−0·87
(*b*)	0·35	−0·37	0·08	0·09	0·32	−0·03	1·17	−1·40
(*c*)	0·38	−0·38	0·00	0·00	0·15	0·00	1·00	−1·15

Only in the last two columns is there a significant difference between (*a*) and (*b*); in each case half the difference is accounted for by charge-transfer effects. The overall agreement between the " empirical " and " non-empirical " results provides some justification for the use of Goeppert-Mayer and Sklar's computational technique in the calculation of relatively small interaction energies.

CALCULATIONS

Very few details need be given of the nature of the calculations, which essentially followed Parr and Crawford's [4,14] revision of Goeppert-Mayer and Sklar's procedure and departed from

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[10] Carr and Stücklen, *J. Chem. Phys.*, 1936, **4**, 760.

[11] Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375; *Proc. Phys. Soc.*, 1955, *A*, **68**, 81.

[12] Longuet-Higgins and Murrell, *ibid.*, p. 601.

[13] Murrell and Longuet-Higgins, *J.*, 1955, 2552.

[14] Parr and Crawford, *J. Chem. Phys.*, 1948, **16**, 526; Crawford and Parr, *ibid.*, 1949, **17**, 726.

established practice only in consequence of the lack of complete orthogonality between the two sets of one-electron benzene orbitals. Arising from this, all multiple exchanges were taken into account which could affect the calculated energies by more than 10^{-6} ev.

The carbon $2s$-wave function was assumed to be of the same form [$r \exp(-1{\cdot}59r)$ in atomic units] as the radial factor of the $2p$-wave functions. The well-known [3, 15] over-estimate of the one-centre Coulomb integral resulting from the use of unmodified atomic wave functions in molecular-orbital calculations, though of little consequence in a perturbation problem of the kind considered here, was avoided by the adoption of Pariser's [16] "empirical" value (10·53 ev) throughout, in the way suggested by Moser.[17] All relevant interactions between the twelve carbon "cores" and the twelve electrons were allowed for, three- and four-centre integrals of all types being evaluated by means of Mulliken's approximation.[18]

In determining the values of ΔE given in Table 2, no allowance was made for interaction between excited configurations of the same symmetry. The justification for applying the variation principle to π-electron wave functions is not immediately obvious,[19] especially when any empirical evaluation of integrals is involved; but if indeed the customary procedure [7] is adopted in the present calculations, the results suggest that the effect of configuration interaction is quite unimportant (ΔE changing by only 0·002—0·02 ev in the singlet states).

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[15] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.

[16] Pariser, *ibid.*, 1953, **21**, 568.

[17] Moser, *ibid.*, p. 2098.

[18] Mulliken, *J. Chim. phys.*, 1949, **46**, 500, 521; Rüdenberg, *J. Chem. Phys.*, 1951, **19**, 1433.

[19] C. A. Coulson, personal communication; cf. Lykos and Parr, *J. Chem. Phys.*, 1956, **24**, 1166; 1956, **25**, 1301.