963. *Energy Levels and Absorption of Some Monosubstituted Benzene Derivatives.*

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In order to obtain further information on the most important electronic structures which contribute to the molecular state in photochemical excitation, the energy levels of molecules such as Ph·X·R (X = O, S; R = Me) have been calculated by the valence-bond (V.B.) method.

The present theoretical results are perfectly consistent with the previous empirical assignment of the bands in thioanisole and diphenyl sulphide: absorption in the 250 mμ region is essentially due to a modified transition of the B_{2u} type, while that in the 275—280 mμ region arises from a transition due to the conjugative interaction of the $3p\pi$ electrons of sulphur with the phenyl ring $(\overbrace{C_6H_5{-}\underset{(\cdot\cdot)}{\ddot{S}}{-}}\text{chromophore})$.

The second phenyl group in diphenyl sulphide is practically ineffective in changing the absorption.

In the analogous oxygenated compounds, anisole and diphenyl ether, the conjugative interaction of *O*-phenyl is significantly weaker than that of *S*-phenyl: the absorption bands in the 220 and the 260—280 mμ region being of B_{1u} and B_{2u} type. Our calculations confirm that in the photo-excited state the mesomeric effect of sulphur is greater than that of oxygen.

THE absorption curves of thioanisole, diphenyl sulphide, anisole, and diphenyl ether in *n*-hexane solution (in ethanol there are negligible modifications) are characterized, in the near ultraviolet region, by two bands as shown below (λ max. in mμ, i = inflection point, f.s. = fine structure; the type of each band is also indicated):

	λ max.	log ε	λ max.	log ε
Thioanisole	254	3·99	280	~ 3·00 (i)
	(B_{2u})		(π_s^8 chromophore)	
Diphenyl sulphide	251	4·09	277	3·76
	(B_{2u})		(π_s^8 chromophore)	
Anisole	219	3·00	265—278	~3·20 (f.s.)
	(E_{2g},* B_{1u})		(B_{2u})	
Diphenyl ether	219	4·00	265—278	~3·20
	(E_{2g},* B_{1u})		(B_{2u})	

* Dunn and Ingold, *Nature*, 1955, **176**, 65.

Mangini and Passerini,[1] investigating the spectroscopic modifications in the near ultraviolet region shown by some alkyl phenyl and diphenyl sulphides, suggested on empirical grounds that such bands arise essentially from the excitation of the six electrons in a benzenoid chromophore, $\overbrace{\text{Ph}\cdot}$, conventionally labelled π^6 (obviously modified by ·SMe or ·SPh acting as side-chain), and from the eight electrons in a chromophore $\text{Ph}\cdot\underset{(\cdot\cdot)}{\ddot{S}}$, arising from interaction of the unshared pair of $3p$ sulphur electrons with the π-shell of the phenyl ring. Such a classification differs from both that of Platt [2] and that of Robertson and Matsen.[3] in the analogous oxygenated systems, anisole and diphenyl ether, the situation is substantially different, and in the longer-wavelength absorption region the sequence of transitions is reversed. This could indicate that in the photoexcited state the mesomeric effect of sulphur is larger than that of oxygen, contrary to what occurs in the ground state [4] or transition state.[5] In previous work, Mangini and Passerini attempted to interpret—although qualitatively—the phenomenon.[6]

The purpose of the present investigation is to study the electronic state of the molecules

[1] Mangini and Passerini, *J.*, 1952, 1168.

[2] Platt, *J. Chem. Phys.*, 1951, **19**, 101.

[3] Robertson and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5243, 5248, 5250.

[4] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

[5] Baker, Barrett, and Tweed, *J.*, 1952, 2831.

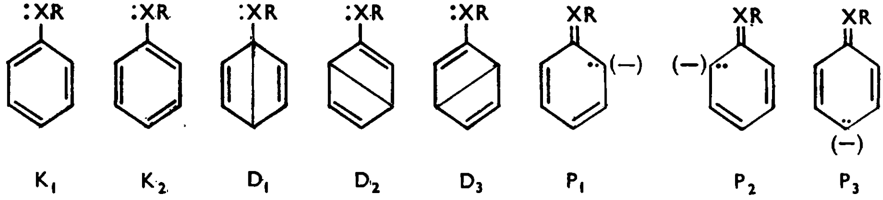
[6] Mangini and Passerini, *Gazzetta*, 1954, **84**, 606.

Ph·X·R (I), where X = O or S; R = alkyl or phenyl, in order to acquire further information, less empirical, on the most important valence-bond structures which take part in the molecular state during the photochemical excitation.

The valence-bond method has been followed, avoiding semi-empirical parameters, but where possible developing the necessary formulæ rigorously.

Molecules Ph·X·R (R = alkyl).—We can assume that, in this case, the influence of R on the electronic states is of lower order, or at least has an almost constant weight on the first few energy levels: this simplifies the problem to discussion of a molecule of type $C_6H_5-\ddot{X}-$ having C_{2v} symmetry. For such molecules we have considered resonance as occurring between the 8 limiting structures (II). If we call Γ_i the reducible representation of the C_{2v} group coming from the above 8 structures, it can be shown that $\Gamma_i = 5A_1 + 3B_1$.

(II)



Wave functions of types A_1 and B_1, respectively, will be of the forms:

$$\Psi'_{A_1} = c_1(K_1 + K_2) + c_2D_1 + c_3(D_2 + D_3) + c_4(P_1 + P_2) + c_5P_3 \quad . \quad (1)$$

$$\Psi'_{B_1} = d_1(K_1 - K_2) + d_3(D_2 - D_3) + d_2(P_1 - P_2) \quad . \; . \; . \; . \; . \; . \quad (2)$$

where the *c*'s and *d*'s are certain coefficients.

From our previous calculations of the energies concerned with structures P_3 and $(D_2 - D_3)$ these can be left aside in the mesomeric system (II) because their energy is too high to exert any effective influence in the first excited levels; analogously, it can be shown that structures D_1 and $(D_2 + D_3)$ differ only very slightly. Functions (1) and (2) can now be written

$$\Psi'_{A_1} = c_1(K_1 + K_2) + c_2(D_1 + D_2 + D_3) + c_4'(P_1 + P_2) \quad . \; . \quad (3)$$

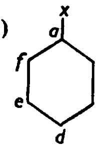
$$\Psi'_{B_1} = d_1(K_1 - K_2) + d_2(P_1 - P_2) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Each structure in equations (3) and (4) has been expressed by a combination of determinantal basic functions (1), with eigenvalues $S_z = 0$: [7]

$$\begin{Bmatrix} a\ b\ c\ d\ e\ f\ x\ y \\ \alpha\ \beta\ .\ .\ .\ .\ \beta\ \alpha \end{Bmatrix}$$

where *a, b, c, d, e, f* represent the atomic eigenfunctions of carbon atoms in the benzene ring (III), *x* that of the hetero-atom, $y = x$, *b*, or *f*, depending on the particular structure considered, and α and β are the spin-functions. Substituting such linear combinations in the matrix elements of the secular equations derived from (3) and (4) and making use of symmetry, one can obtain all H_{ij} and S_{ij}; these can be written as sums of integrals between the basic functions.

(III)



According to the rigorous valence-bond method, the latter have to be developed as a function of the exchange intergrals of all orders. Such an operation is practically impossible for the extremely high number of exchange integrals which occur between two basic functions with eight electrons. The development of the calculation has been accomplished up to triple exchanges inclusive as shown in the Table.

As the values of integrals between two basic functions are independent of the symmetry operations, we have taken advantage of the fact that the basic functions of the problem can be derived from those of benzene by a product of $x(\beta)x(\alpha)$. Now the perturbation due to these orbitals may be considered nearly equal in the integrals between two basic functions

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[7] Eyring, Walter, and Kimball, "Quantum Chemistry," J. Wiley, New York, 1944.

TABLE.

We set

$$\int ab \dots\dots M\ ba \dots\dots d\tau \equiv A^2$$

$$\int ac \dots\dots M\ ca \dots\dots d\tau \equiv B^2$$

$$\int ad \dots\dots M\ da \dots\dots d\tau \equiv C^2$$

$$\int ax \dots\dots M\ xa \dots\dots d\tau \equiv S^2_1$$

$$\int bx \dots\dots M\ xb \dots\dots d\tau \equiv S^2_2$$

$$\int cx \dots\dots M\ xc \dots\dots d\tau \equiv S^2_3$$

$$\int dx \dots\dots M\ xd \dots\dots d\tau \equiv S^2_4$$

with $M = 1, H$ and writing down only the atomic functions which do not correspond in the two members of exchange integrals. With this position we have, for example,

$$\int abcdefxx\ M\ bdcaexfx\ d\tau = ABCS_2$$

Symmetry A_1:

$$\begin{aligned}H_{11} = 4\Bigl\{&5Q + 12A^2 - 24B^2 - 3C^2 - 5S_1^2 - 10S_2^2 - 10S_3^2 - 5S_4^2 + 14B^3 - 30A^2B - 24ABC + \\ &20BS_1S_3 + 10BS_2^2 + 20BS_2S_4 + 10BS_3^2 - 12AS_1S_2 - 12AS_2S_3 - 12AS_3S_4\Bigr\}\end{aligned}$$

$$\begin{aligned}H_{22} = 4\Bigl\{&9Q + 18A^2 - 54B^2 + 9C^2 - 9S_1^2 - 18S_2^2 - 18S_3^2 - 9S_4^2 + 36B^3 - 36A^2B - 72ABC + \\ &36BS_1S_3 + 20BS_3^2 + 36BS_2S_4 + 20BS_2^2 - 16AS_1S_2 - 16AS_2S_3 - 16AS_3S_4 - 16CS_2S_3 - \\ &8CS_1S_4\Bigr\}\end{aligned}$$

* $$\begin{aligned}H_{33} = 4\Bigl\{&4Q + 4A^2 - 8\overline{A}^2 - 8B^2 - 8\overline{B}^2 - 4C^2 - 4\overline{C}^2 - 4S_1^2 - 2S_2^2 - 4\overline{S}_2^2 - 4S_3^2 - 2S_4^2 + \\ &6B^3 - 12A^2B + 6ABC - 12AS_1S_2 - 2AS_3S_4 + 4BS_2^2 + 2BS_3^2 - 8BS_1S_3 + 6BS_2S_4 - \\ &4CS_1S_4 + 6CS_2S_3 + 2\overline{B} - \overline{A}^2 + 2\overline{B}^2 - 8\overline{A}\overline{C} - \overline{S}_2^2 - 16B^3 + 10A^2B + 6ABC + 5BC^2 - \\ &2AS_1S_2 + 3AS_2S_3 + 2BS_1^2 - 2BS_2^2 - 2BS_3^2 - BS_4^2 - BS_2S_3 - 2BS_2S_4 + 30S_2S_3\Bigr\}\end{aligned}$$

$$\begin{aligned}H_{12} = -4\Bigl\{&6Q + 18A^2 - 36B^2 - 6S_1^2 - 12S_2^2 - 12S_3^2 - 6S_4^2 + 24B^3 - 36A^2B - 36ABC + \\ &28BS_1S_3 + 14BS_3^2 + 28BS_2S_4 + 14BS_2^2 - 16AS_1S_2 - 16AS_2S_3 - 16AS_3S_4 - 4CS_2S_3 - \\ &4CS_1S_4\Bigr\}\end{aligned}$$

$$\begin{aligned}H_{13} = 4\Bigl\{&5S_2 - 4CS_3 - 4AS_3 - 10AS_1 - BS_4 + 10ABS_1 + 12ABS_3 + 10BCS_1 + 4BCS_3 - 21BS_2^2 \\ &- 4C^2S_2 + 15A^2S_2 - B^2S_4 + 7ACS_4 - ACS_2 - 7S_2^3 - 3S_2S_4^2 + 3S_1S_2^2 - 2S_2S_3^2 - S_2S_4^2\Bigr\}\end{aligned}$$

$$\begin{aligned}H_{23} = -4\Bigl\{&6S_2 - 6CS_3 - 6AS_3 - 12AS_1 + 12ABS_1 + 18ABS_3 + 12BCS_1 + 4BCS_3 - 31B^2S_2 - \\ &C^2S_2 + 16A^2S_3 - 2B^2S_4 + 6ACS_4 - 9S_2^3 - 4S_2S_4^2 + 3S_1S_2^2 - 2S_2S_4^2\Bigr\}\end{aligned}$$

Symmetry B_1:

$$H_{11} = 4\Bigl\{3Q - 9C^2 - 3S_1^2 - 6S_2^2 - 3S_4^2 - 6S_3^2 - 6B^3 - 18A^2B + 12CS_2S_3 - 8CS_1S_4\Bigr\}$$

$$\begin{aligned}H_{22} = 4\Bigl\{&4Q + 4A^2 - 8\overline{A}^2 - 8B^2 - 8\overline{B}^2 - 4C^2 - 4\overline{C}^2 + 4S_1^2 - 2S_2^2 - 4S_3^2 - 2S_4^2 + 6B^3 - \\ &12A^2B + 6ABC - 4S_3^2 - 12AS_1S_2 - 2AS_3S_4 + 4BS_2^2 + 2BS_3^2 - 8BS_1S_3 + 6BS_2S_4 - \\ &4CS_1S_4 - 6CS_2S_3 - 2\overline{B} - \overline{A}^2 + 2\overline{B}^2 - 8\overline{A}\overline{C} - \overline{S}_2^2 - 16B^3 + 10A^2B + 6ABC + 5BC^2 - \\ &2AS_1S_2 + 3AS_2S_3 + 2BS_1^2 - 2BS_2^2 - 2BS_3^2 - BS_4^2 + BS_2S_3 - 2BS_2S_4 + 3CS_2S_3\Bigr\}\end{aligned}$$

$$\begin{aligned}H_{12} = 4\Bigl\{&3S_2 - 6AS_1 - 3BS_2 - 3BS_4 - 6ABS_1 + 4BCS_1 - B^2S_2 - 8C^2S_2 + 3A^2S_2 + 3B^2S_4 + \\ &2ABS_3 + 3ACS_4 + 3ACS_2 - 3S_2^3 + S_2S_4^2 + 3S_1S_2^2 - 6S_2S_3^2 - S_2S_4^2\Bigr\}\end{aligned}$$

* The integrals so marked refer to the polar atom.

having the same spin distribution in the benzenic orbitals or reducible to this by symmetry operations.* This is approximately true only if the integral between two basic functions does not involve a coulombic integral.

The values of the exchange integrals have been considered independently of the atomic functions which do not participate in the exchange,† except for double exchange integrals in polar structures.

The numerical calculation should now be possible. At first we used the values for Z proposed by Zener and Slater,[8] but as these values do not lead to good results,[8a] we have used those proposed by Kohlrausch : [9] unfortunately, with the latter values the matrix elements converge slowly as we increase the order of exchange integrals added. Even exchange integrals of higher order than triple still have noticeable values, and it is necessary to introduce them in the expression for the matrix elements. This, of course, complicates the problem.

We have therefore tried to find a method which could allow the introduction of exchanges of higher order without requiring the complete development of integrals between two basic functions. We have obtained S_{ij} elements as follows: in the integral between two basic functions one can exchange only atomic eigenfunctions having the same spin : now, all the exchanges between atomic eigenfunctions with spin α and then with spin β having been made, all the other exchanges result from their combination. Such a situation is expressed by the following formula : ‡

$$S = (-1)^{R_0} S_{0\alpha}S_{0\beta} + S_{0\beta}\sum_n(-1)^{p_n + R_0}S_{\alpha n} + S_{\alpha 0}\sum_n(-1)^{q_n + R_0}S_{\beta n} +$$
$$+ \sum_n(-1)^{p_n}S_{xn}\sum_n(-1)^{q_n}S_{\beta n}$$

where $S_{0\alpha}$ and $S_{0\beta}$ are the overlap values of exchange between the atomic eigen-functions with spin α and β respectively of the first exchange integral; R_0 is the number of exchanges necessary to have the starting function from the first exchange integral; $S_{\alpha n}$ and $S_{\beta n}$ are the values corresponding to the overlap of the n-th exchange between atomic eigenfunction of α-spin and β-spin among themselves; p_n and q_n are the number of exchanges necessary to obtain distribution α or β respectively from the n-th exchange in the first exchange integral.

When calculating the values of the matrix elements H_{ij}, the method followed by us takes advantage of the regularity shown by H_{ij} with subsequent additions of double, triple, . . . exchange integrals. If one compares the successive values with the corresponding overlap integrals, it is possible to make quite a good extrapolation to the final value with all orders of exchange.

By following this method it is possible to calculate the secular equations for the problem of the electronic states in any molecule of the type $Ph{\cdot}\ddot{X}{\cdot}Alk$.

Molecules $Ph{\cdot}\ddot{X}{\cdot}Ph$.—The problem is now more complicated because of the larger number of π electrons. It is obvious that we must introduce additional approximations : first we shall consider the molecule $Ph{\cdot}\ddot{X}{\cdot}Ph$ as composed of two parts : $Ph{\cdot}\ddot{X}{\cdot}$ and ${\cdot}Ph$.

This assumption implies the disappearance of symmetry in the molecule during our calculations. Certain other effects also have to be regarded as less important, for example :

(i) The splitting of levels due to symmetry (interaction of the two structures $\overbrace{(1)\ C_6H_5\text{–}\ddot{X}}\overbrace{\text{–}C_6H_5\ (2)}$ and $\overbrace{(2)\ C_6H_5}\overbrace{\text{–}\ddot{X}\text{–}C_6H_5\ (1)}$; this interaction is probably not very

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* This is justified by the fact that overlap of the atomic function of the hetero-atom with the atomic function of the carbon atoms of the benzene nucleus decreases rapidly with the increase in distance : the exchange integrals of high order involving the atomic eigenfunction of the hetero-atom, therefore, lead to very little difference.

† This is demonstrable if the atomic integrals having many centres are calculated with Mulliken approximations.

‡ It is noteworthy that analogous formulæ can be derived for the H_{ij} : this way of working—although more rigorous—is very difficult, and the method to be described later has been preferred.

[8] Zener, *Phys. Rev.*, 1930, **36**, 51; Slater, *ibid.*, p. 57.

[8a] See also Scrocco and Salvetti, *Ricerca sci.*, 1953, **23**, 1410.

[9] Kohlrausch, *Acta Phys. Austriaca*, 1950, **3**, 452.

important, since the absorption spectra of compounds $\mathrm{Ph{\cdot}\ddot{X}{\cdot}Ph}$ are very similar to those corresponding to the alkyl-aryl type.

(ii) The interaction of $p\pi$ electrons of the heteroatom X with the $2p\pi$ electrons of the second benzene ring (we have, however, taken some account of this interaction by introducing in the values of the matrix elements in connection with the part Ph·, half of the calculated value of the perturbation of the $p\pi$ electrons of X already found when solving the problem of the structure $\mathrm{Ph{\cdot}\ddot{X}{\cdot}}$).

(iii) The interaction benzene nucleus(1)–benzene nucleus(2) (this can almost certainly be considered very unimportant as it should play almost an identical rôle in the first few energy levels whatever the central atom X).

This procedure, although not absolutely orthodox, could represent a good approximation to the real state of the molecule. It is also known that molecules of the type considered are not coplanar.

We must therefore take into consideration not only the different interaction of the $2p\pi$-orbitals of the benzene nucleus with the $p\pi$-orbitals of the X atom, but also the interaction between the latter and the σ skeleton of the molecule. In practice only the exchange integrals between the p-orbitals of the hetero-atom and the two trigonal orbitals σ_1 and σ_2 of the nearby carbon atom will be of importance, together with the trigonal orbitals of atoms b and f, σ_3 and σ_4, which form a σ-bond with the former.

A priori this σ–π interaction would not appear to be negligible because at first it seems to be different for covalent and polar structures (in the latter there is only one p-atomic orbital on the herero-atom). There are, on the other hand, strong reasons to believe that such interaction should have a constant weight in the first two excited levels with which we are concerned.

These considerations are based on the following points : (iv) The angle which the X orbitals form with the plane of the ring varies over the range 50—60° ; this fact, together with the consideration that the σ-orbitals are sp^2 hybrids, makes the overlap integral and the exchange integral between the σ and X orbitals have not very large values.

(v) The interaction energy σ–π which we call $E_{\sigma-\pi}$ is formed by an addition of exchange integrals of various orders. Owing to the spatial position of the $3p_z$ orbital of sulphur one can *a priori* affirm that the terms having the most weight in this addition are the double exchange integrals (with a *minus* sign for " repulsion ") and only those derived from the latter for the successive exchange between two atomic eigenfunctions : *e.g.*, the triple and quadruple, having a *plus* sign. These to some extent compensate for the value of the double integrals. Such compensation could be approximately considered as 1/3 (maybe more than less) ; because if we have a certain distribution of orbitals, increasing the order of exchange integrals, the number of distinct ways in which they could be built up is also increased. Although it is not possible to give a quantitative value to $E_{\sigma-\pi}$, it is clear that for all these reasons one should expect a very small value when compared with that one of the energy corresponding to structures considered in the problem of the molecule $\mathrm{Ph{\cdot}\ddot{X}{\cdot}}$.

(vi) The values of energy for the structures which we have considered in our problem are obtained from equation (5).

$$E_L = \frac{\int \Psi_L H \Psi_L \mathrm{d}\tau}{\int \Psi_L \Psi_L \mathrm{d}\tau} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

If we neglect the contribution of the term $S_{\sigma-\pi}$ which represents the overlap of σ–π we can write

$$E_L = E_{L\pi} + \frac{\sum\limits_{\sigma-\pi} (\text{Exchange integral})}{S_\pi} \quad . \; . \; . \; . \; . \quad (6)$$

where $E_{L\pi}$ is the π-energy of the L structure, S_π the corresponding overlap, and $\sum\limits_{\sigma-\pi}$ (Exchange integral) is the sum of the exchange integrals between the $3p_z$ orbital of sulphur and the trigonal orbitals of carbon aroms. Now, in the polar structures the term

S_π is about one-half of the corresponding term for the covalent structures; the sum $\sum_{\sigma-\pi}$ (Exchange integral) for the covalent structures is about twice that for the polar structures.

The value $E_{\sigma-\pi}$ is now a constant for the covalent and polar structures. Also the interaction between the two types of structures has approximately the same value.

For this reason we can consider the difference of energy between two levels as independent of the interaction σ–π. In no case is the assignment of transitions affected. The problem is therefore related both to the previous one and to that of finding the matrix elements when the perturbation of the electrons of the hetero-atom have been added to the original phenyl.

When dealing with the lower energies of Ph•, which are principally due to structures of covalent type, we have followed the same procedure as indicated in the previous paragraph, and expressed the matrix elements as functions of integrals between two basic functions; these, which result from six atomic eigenfunctions, are easily written as functions of exchange integrals of all orders, without its being necessary to use any approximation such as the interpolation scheme previously described.

Calculation and Results.—We proceeded as just indicated in the case of anisole (I; X = O), thioanisole (I; X = S), and diphenyl sulphide (I; R = Ph, X = S) with particular consideration to the last; we have also taken into account the fact that the planes in which the two benzene rings lie form an angle of 72°. The atomic eigenfunctions are those of Slater's type without nodes. The exchange integrals have been expressed as a function of integrals between atomic eigenfunctions, following the usual method.

The calculations have been accomplished, when possible, by following the interpolation formulæ of Scrocco and Salvetti [10] or of other authors,[11,12] the following parameters being used: distance C–C 2·63 a.u., distance C–O 2·59 a.u., and Z values, $Z_C = 2{\cdot}088$,[9] $Z_C = 2{\cdot}90$.[9]

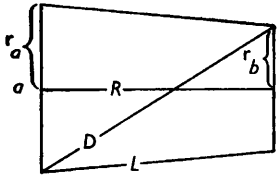
The integrals where the $3p$ sulphur electrons were involved have been calculated as follows: Kohlrausch's paper [9] indicates the procedure to obtain the orbital radii from the screening constants. If we express these values in atomic units, the values of atomic repulsions are

$$(aa/bb) = 1/L + 1/D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

obtained * from (7), where L and D are as indicated in (IV) and R is the internuclear distance between the atoms a and b. This is equivalent to considering the electronic cloud as " concentrated " in two half-charges set over the extremities of the radii of the orbitals.

The distance carbon–sulphur has been taken equal to 3·33 a.u., and the charge $Z_S = 2{\cdot}64$.[9]

The calculation of integrals of type $(xx\overset{+}{V}y)$ has been made by Sklar's method,[13] and the values of $\bar{\bar{Z}}$ necessary for the calculation are: $\bar{\bar{Z}}_C = 3{\cdot}66$, $\bar{\bar{Z}}_O = 4{\cdot}94$, $\bar{\bar{Z}}_S = 4{\cdot}08$. For integrals with more than two centres we adopted Mulliken's approximation. For the electroaffinity of carbon we used the value 0·069 Å proposed by the same author.[14] The ionization potentials are the following: $I_O = 11{\cdot}27$ e.v.,[15] I_O† $= 12{\cdot}6$ e.v., $I_S = 10{\cdot}36$ e.v.[15]



(IV)

On the basis of values obtained by the above method, we calculated all necessary exchange integrals. Also we grouped together the invariable terms such as nuclear repulsion and ionization potentials, so that every integral could be expressed in the form $SQ - A$, S being the overlap of such an integral, Q the coulombic term from which arises the particular exchange integral, and A is expressed in atomic units.

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* A better formula is $(aa/bb) = (1 - S_{ab}{}^4)/L + 1/D$, where $S_{ab} = \int \psi_a \psi_b \, d\tau$.

† We have used the value which oxygen has in the water molecule following Price and Sugden (*Trans. Faraday Soc.*, 1948, **44**, 116).

[10] Scrocco and Salvetti, *Ricerca sci.*, 1952, **22**, 1766.

[11] Barnett and Coulson, *Phil. Trans.*, 1951, **243**, 221.

[12] Roothaan, *J. Chem. Phys.*, 1951, **19**, 1445.

[13] Sklar and Liddane, *ibid.*, 1939, **7**, 374.

[14] Mulliken, *ibid.*, 1934, **2**, 782.

[15] Landolt–Börnstein, " Zahlenwerte und Functionen," I Band, 1 Teil, 1950.

By substituting the values obtained for the exchange integrals in the expression for the matrix elements and interpolating for the higher-order exchanges as already indicated, it has been possible to write the secular equations for thioanisole and anisole.

Putting $X = Q - E$, where Q is the coulombic integral and E the energy, we obtained the secular equations :

Thioanisole

$$A_1 \quad \begin{vmatrix} (x + 0{\cdot}054) & -0{\cdot}9824(x + 0{\cdot}040) & 0{\cdot}1256(x - 1) \\ -0{\cdot}9824(x + 0{\cdot}040) & (x + 0{\cdot}065) & -0{\cdot}1343(x - 1) \\ 0{\cdot}1256(x - 1) & -0{\cdot}1343(x - 1) & (x + 0{\cdot}210) \end{vmatrix} = 0$$

$$B_1 \quad \begin{vmatrix} (x + 0{\cdot}336) & -0{\cdot}051(x + 1) \\ -0{\cdot}051(x + 1) & (x + 0{\cdot}456) \end{vmatrix} = 0$$

Anisole

$$A_1 \quad \begin{vmatrix} (x + 0{\cdot}126) & -0{\cdot}9830(x + 0{\cdot}123) & 0{\cdot}2083(x - 1) \\ -0{\cdot}9830(x + 0{\cdot}123) & (x + 0{\cdot}131) & -0{\cdot}2176(x - 1) \\ 0{\cdot}2083(x - 1) & -0{\cdot}2176(x - 1) & (x + 0{\cdot}312) \end{vmatrix} = 0$$

$$B_1 \quad \begin{vmatrix} (x + 0{\cdot}365) & 0{\cdot}0123(x - 1) \\ 0{\cdot}0123(x - 1) & (x + 0{\cdot}520) \end{vmatrix} = 0$$

Therefore the lower excitation energies have the following values :

	Calc.	Found
Thioanisole :		
I excited (A_1)	4·55 e.v. ~2730 Å	2750 Å.
II ,, (B_1)	4·73 e.v. ~2630 Å	2540 Å
Anisole :		
I excited (B_1)	4·85 e.v. ~2560 Å	2600—2800 Å
II ,, (A_1)	5·80 e.v. ~2140 Å	2200 Å

There is therefore good agreement between the calculated and experimental values.

Passing to diphenyl sulphide, we have also to consider in our calculation steric hindrance, bearing in mind the fact that exchange integrals are approximately proportional to the corresponding overlap integrals. The secular equations for the $\text{Ph}{\cdot}\ddot{\text{S}}{\cdot}$ group are :

$$A_1 \quad \begin{vmatrix} (x - 0{\cdot}0114) & -0{\cdot}9818(x - 0{\cdot}0242) & 0{\cdot}0992(x - 1) \\ -0{\cdot}9818(x - 0{\cdot}0242) & x & -0{\cdot}1125(x - 1) \\ 0{\cdot}0992(x - 1) & -0{\cdot}1125(x - 1) & (x + 0{\cdot}253) \end{vmatrix} = 0$$

$$B_1 \quad \begin{vmatrix} (x + 0{\cdot}3712) & -0{\cdot}0370(x + 2) \\ -0{\cdot}037(x + 2) & (x + 0{\cdot}363) \end{vmatrix} = 0$$

Solving these, we have the following solutions :

$$\begin{array}{ll} A_1 & E_0 = Q - 0{\cdot}049 \\ A_1 & E_1 = Q + 0{\cdot}298 \\ B_1 & E_2 = Q + 0{\cdot}314 \end{array}$$

which correspond to the following excitation energies

I excited (A_1)	4·72 e.v., 2640 Å
II ,, (B_1)	4·95 e.v., 2500 Å

The weights of the various structures in the various states may be shown to be approximately as follows :

A_1 : fundamental	$0{\cdot}48(K_1 + K_2)$	$0{\cdot}40(D_1 + D_2 + D_3)$	$0{\cdot}12(\text{P}_1 + \text{P}_2)$
I excited	$0{\cdot}15(\text{K}_1 + \text{K}_2)$	$0{\cdot}85(\text{P}_1 + \text{P}_2)$	
B_1 : II ,, ...	$0{\cdot}55(\text{K}_1 - \text{K}_2)$	$0{\cdot}45(\text{P}_1 - \text{P}_2)$	

For the phenyl group, operating as already described, we have the following secular equations :

$$A_{1g} \quad \begin{vmatrix} (x - 0{\cdot}0721) & -0{\cdot}9829(x - 0{\cdot}0844) \\ -0{\cdot}9829(x - 0{\cdot}0844) & (x - 0{\cdot}0594) \end{vmatrix} = 0$$

$$B_{2u} \quad \begin{vmatrix} x + 0{\cdot}2885 \end{vmatrix} = 0$$

These give, for the fundamental and the first excited states, the following energies : $\overline{E}_0 = Q - 0{\cdot}0761$, $\overline{E}_1 = Q - 0{\cdot}2885$, corresponding to an excitation energy of 4·95 e.v. (2500 Å).

The weights of the structures in the two levels considered are as follows :

A_{1g}	$0{\cdot}67\ (K_1 + K_2)$	$0{\cdot}33\ (\mathrm{D}_1 + \mathrm{D}_2 + \mathrm{D}_3)$
B_{2u}	$(K_1 - K_2)$	

Following the approximations, discussed on p. 4963, the molecular functions for diphenyl sulphide come from the product of the molecular functions of groups $\mathrm{Ph{\cdot}\ddot{X}{\cdot}}$ and $\mathrm{C_6H_5{\cdot}}$; the energy levels result from the addition of the energy levels of the two parts.

Let us call the sum of the coulombic integrals relative to the two partial problems W. Then the first four energy levels, to which correspond the first three transitions, are the following (where $\bar{E}_0$ and $\bar{E}_1$ are the energies relative to phenyl; E_0, E_1, E_2, those relative to $\mathrm{Ph{\cdot}S{\cdot}}$) :

$$E_0 + \bar{E}_0 = W - 0{\cdot}125 \qquad E_2 + \bar{E}_0 = W + 0{\cdot}238$$
$$E_1 + \bar{E}_0 = W + 0{\cdot}222 \qquad E_0 + \bar{E}_1 = W + 0{\cdot}238$$

The fact that the third and the fourth level have the same energy, together with the fact that the spectrum of diphenyl sulphide shows a single band in the region corresponding to the particular transition, seems to justify our mode of calculating the perturbations for the second benzene ring.

From the previous values we obtain for the corresponding transitions the following values :

	Calc.	Found
I	4·72 e.v. (2640 Å)	2700 Å
II and III	4·95 e.v. (2500 Å)	2500 Å

As for the weights of the various structures in the various excited levels, they are obtained by multiplication of the relative weights corresponding to the two partial problems.

The first transition is therefore essentially due to a structure of conjugated type, while the second and the third transition, which coincide, form a single band which can be considered a modified benzene band.

Conclusions.—The fundamental fact emerging from our calculation is the following: the band towards the longer wavelength in anisole is essentially due to a transition of type B_{2u} in benzene, although modified, while the band in the 220 mμ region is essentially a transition of type B_{1u} modified. On the other hand, in thioanisole the band in the 250 mμ region is still of the type B_{2u} modified, while the absorption in the 280 mμ region is a new transition due to the interaction of the 3*p* electrons of sulphur with the phenyl ring; *i.e.*, the interaction $\overset{\frown}{\ddot{\mathrm{S}}\text{–}\mathrm{Ph}}$ in thioanisole is much stronger than that of $\overset{\frown}{\ddot{\mathrm{O}}\text{–}\mathrm{Ph}}$ in anisole.

A similar situation to that in thioanisole occurs in diphenyl sulphide, where the maximum in the 275 mμ region is essentially due to the π_S[8] chromophore, as empirically assigned by one of us from an ultraviolet spectral study; it also follows from our previous calculation that the second phenyl group of diphenyl sulphide, compared with that in thioanisole, does not significantly affect the excitation energy.

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