energy of $-SH$.[8,9] The fact that S_{CO} is the lowest of the three has no effect on the order since $-OH$ has the highest ionization energy. This fact should, however, serve to separate the wave length and intensity of C_6H_5OH from $C_6H_5NH_2$ and C_6H_5SH, which it does (see Fig. 2). This interpretation receives additional support from a consideration of the spectrum of compounds of the type $(C_6H_5)_2X$.[5]

The vapor spectrum of thiophenol is more diffuse than that of phenol or aniline. This is to be expected since there is a non-bonding electron spectrum in the same wave length region for all sulfur compounds.

Summary

The spectrum of thiophenol has been obtained in both the vapor phase and in solution. The spectrum does not occupy the position relative to phenol and aniline that is expected from the ionization energies of the substituent groups. Is is suggested that this may be due to a relatively smaller resonance integral between the ring and substituent for thiophenol.

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[8] The perturbing effect of the substituent level is proportional to the square of this resonance integral.

[9] Wheland and Pauling, ref. 4, suggested that a small value of β_{CS} would account for the anomalous directing power of -SH.

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Molecular Orbital Theory and Spectra of Monosubstituted Benzenes. III. Compounds of the Type $(C_6H_5)_2X$

BY W. W. ROBERTSON AND F. A. MATSEN

Introductory and Experimental

Compounds of the type $(C_6H_5)_2X$ provide an interesting extension of the theory developed for the C_6H_5X compounds.[1] Here, X is a group with an unshared pair of electrons on its central atom, for example, oxygen, nitrogen or sulfur.

The vapor spectra of the $(C_6H_5)_2X$ compounds were obtained at several different pressures on a three-meter grating. The spectra were all quite diffuse. However, the diphenyl ether spectrum (Fig. 1) has enough structure to show a resemblance to the spectra of monosubstituted benzenes. An even greater similarity to the typical monosubstituted benzene spectrum was shown by the spectrum of diphenylmethane which will be considered in a later paper. This greater similarity is to be expected since the methylene group would couple the phenyl groups to a lesser extent than the oxygen atom, which in turn would couple to a lesser extent than the $-NH-$ group. The similarity to the monosubstituted spectra indicates that the excitation produced by this absorption is localized mainly in one phenyl ring and that the excited state is a derivative of the B_{2u} state in benzene.

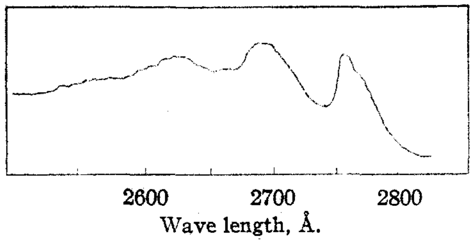

Fig. 1.—Microphotometer tracing of the near ultraviolet absorption spectrum of the vapor of diphenyl ether.

Previous work on the solution spectra of the diphenyl compounds are scattered through the literature[2]; they were retaken in this Laboratory to put all the diphenyl and monophenyl compounds on a comparable basis.

The solution spectra were obtained on predistilled compounds in ethyl alcohol on a Beckman quartz spectrophotometer. These are given in Fig. 2, and may be compared with the spectra of the corresponding C_6H_5X molecules in Fig. 3. From Figs. 2 and 3, it may be seen that the absorption of the $(C_6H_5)_2X$ compounds is at approximately the same wave length, but is more intense than for the corresponding C_6H_5X molecule.

Theoretical

The calculations presented below are based on the planar configuration of the molecule. Although the molecule has its greatest stability in this configuration, the stability is probably not great enough to freeze the molecule, so, consequently, all interplanar angles have a finite probability. Fortunately, this fact does not affect the frequency of absorption in the approximation used here. While the extent of interaction and the position of the electronic energy levels are functions of the interplanar angles, the ground states and excited states are affected in almost equal amounts so that the excitation energy remains relatively constant (see Fig. 4).

A molecular orbital treatment of the spectra of C_6H_5X compounds was developed in the

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[1] Matsen, THIS JOURNAL, 72, 5243 (1950).

[2] Ley and Specker, *Z. wiss. Phot.*, **38**, 12 (1939); Kato and Someno, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **33**, 209 (1937); **34**, 905 (1938). Recent work on phenyl sulfide: Fehnel and Carmack, THIS JOURNAL, **71**, 85 (1949); American Petroleum Institute Ultraviolet Spectrogram 113. (The intensities in this spectrum are too high by a factor of ten. This is confirmed by a private communication from the laboratory at which spectrum was taken.)

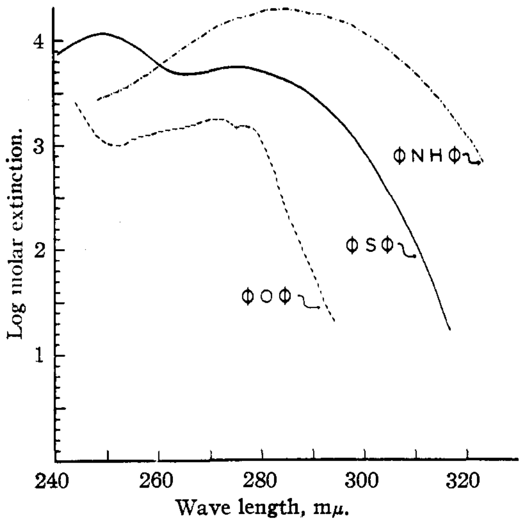

Fig. 2.—Solution absorption spectra of diphenyl ether, diphenyl sulfide and diphenylamine in ethanol.

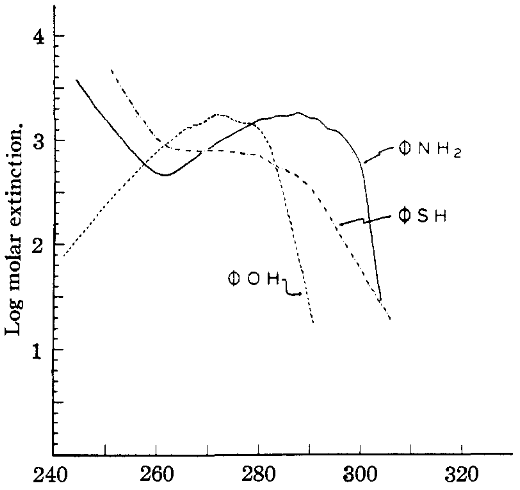

Fig. 3.—Solution absorption spectra of phenol, thiophenol and aniline in ethanol.

first paper of this series.[1] In this treatment, electron repulsion was neglected and the integrals were not evaluated, but expressed in terms of parameters to which approximate values could be empirically assigned. Thus

$$\int\phi_i H\phi_i d\tau = \alpha,\ \int\phi_i H\phi_{i+1} d\tau = \int\phi_X H\phi_1 d\tau = \beta \text{ and}$$
$$\int\phi_X H\phi_X d\tau = \alpha + \delta\beta$$

where ϕ_i are orbitals on the ring carbon atoms, ϕ_X is the orbital on the substituent, X, and H the Hamiltonian for the system. The quantity δ is an electronegativity parameter which is assigned the value of 0.8 for $-NH_2$, 1.1 for $-SH$, and 1.8 for $-OH$ to fit the experimental intensity and frequency.[3]

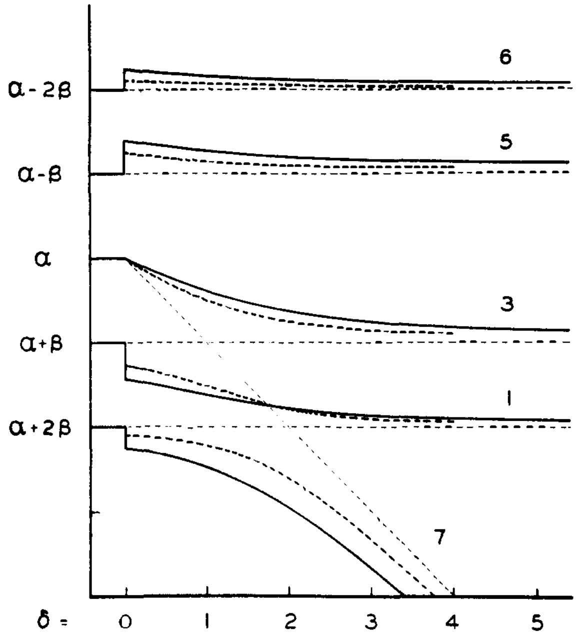

Fig. 4.—Energies of the $(C_6H_5)_2X$ system as functions of δ are plotted as full lines. The heavy dotted lines are the energies of the C_6H_5X system and the light dotted lines, the zero-order levels.

In this treatment it will be assumed that the resonance integrals involving C and X atoms are independent of the C–X–C angle. Then the atomic orbital representation of the system belongs to point group V_h. Since there are thirteen atomic orbitals involved, the representation is 13-dimensional which, however, breaks down into irreducible representations

$$\Gamma(M) = 5A_g + 4B_{1u} + 2B_{2u} + 2B_{3g}$$

The symmetry orbitals will be built from the six orthogonal benzene orbitals, ψ_i and ψ_i', for each benzene nucleus.[1] If polarization, next neighbor interaction, and electron repulsion are neglected, all ψ_i and ψ_i' are mutually orthogonal. Further, since B_{1u}, B_{2u} and B_{3g} do not contain ψ_X, the substituent function, benzene functions belonging to these representations are not perturbed and remain benzene functions. Thus, only zero order functions of class A_g are perturbed. The following symmetry orbitals will be used

$$\chi_1 = (\psi_1 + \psi_1')/\sqrt{2}$$
$$\chi_3 = (\psi_3 + \psi_3')/\sqrt{2}$$
$$\chi_5 = (\psi_5 + \psi_5')/\sqrt{2}$$
$$\chi_6 = (\psi_6 + \psi_6')/\sqrt{2}$$
$$\chi_7 = \psi_X = \phi_X$$

The secular equation for A_g is

$$\begin{vmatrix} \frac{A+\delta}{2} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{6}} \\ 1/\sqrt{6} & A+2 & 0 & 0 & 0 \\ 1/\sqrt{3} & 0 & A+1 & 0 & 0 \\ 1/\sqrt{3} & 0 & 0 & A-1 & 0 \\ 1/\sqrt{6} & 0 & 0 & 0 & A-2 \end{vmatrix} = 0$$

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[3] These values are lower than the δ's given in Paper I where perturbation theory was used. In the $(C_6H_5)_2X$ system the perturbation of the benzene levels is so great that exact solutions of the secular equations must be used. Consequently, the secular equation was also solved for the C_6H_5X problem. With these solutions smaller δ values fit the experimental data.

Here

$$A = (\alpha - E)/\beta$$

The energies as functions of δ are plotted as full lines in Fig. 4. For comparison, the energies of the system C_6H_5X have been plotted as heavy dotted lines in the same figure. The light dotted lines represent the zero order levels. The perturbed levels are indexed on the right by the zero order levels from which they originate.

In the compounds $(C_6H_5)_2X$ the corresponding excited states are

$$\chi_3\psi_4, \chi_3\psi_4', \psi_2\chi_5 \text{ and } \psi_2'\chi_5{}^{4}$$

These states are assumed to mix in the same way as do the states in the corresponding B_{2u} state in benzene. Thus, there are two excited states, one for each ring characterized by $\chi_3\psi_4 + \psi_2\chi_5$ and $\chi_3\psi_4' + \psi_2'\chi_5$. The assumptions that the excitation energy calculated from the molecular orbitals is the excitation energy of the center of gravity of the excited states, and that the lowest of these varies as does the center of gravity, lead to the expression

$$\frac{\nu_B - \nu}{\nu_B} = \frac{2 - [A_5 - A_3]}{4} = \frac{2\beta - [E_3 - E_5]}{4\beta}$$

where ν_B and ν are the frequencies of the 0–0 bands in benzene and the $(C_6H_5)_2X$ compound, respectively.

From an inspection of Fig. 4, it can be seen that the frequency shift is approximately the same for C_6H_5X and $(C_6H_5)_2X$. The results of the actual calculations are given in Table I. These appear to be in reasonably good agreement with experiment as well as can be judged by the diffuse spectra.

TABLE I

Compound	δ	$(\nu_B - \nu)/\nu_B$
C_6H_5OH	1.8	0.05
$C_6H_5OC_6H_5$	1.8	.05
C_6H_5SH	1.1	.08
$C_6H_5SC_6H_5$	1.1	.08
$C_6H_5NH_2$	0.8	.10
$C_6H_5NHC_6H_5$	0.8	.10

The intensity cannot be calculated by the methods used for C_6H_5X because the perturbation of the benzene levels is too great. However, if one accepts the general observation that the greater the perturbation of the benzene levels the higher is the intensity of absorption, there is qualitative agreement with experiment: namely, that the absorption of the $(C_6H_5)_2X$ is more intense than for the C_6H_5X and that the order of intensity is the same in both series.

Summary

The spectra of compounds of the type $(C_6H_5)_2X$ are presented and compared with the corresponding C_6H_5 spectra. The former are more intense, but lie at approximately the same wave length as do the latter. Conclusions drawn from crude molecular orbital theory are shown to be in qualitative agreement with experiment.

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(4) There are also one-electron states belonging to representation B_{1u}, $1/\sqrt{2}\,(\psi_3 - \psi_3')$ and $1/\sqrt{2}\,(\psi_6 - \psi_6')$, from and to which excitation can occur, producing the excited molecular states $1/\sqrt{2}\,(\psi_3 - \psi_3')\psi_4$, $1/\sqrt{2}\,(\psi_3 - \psi_3')\psi_4'$, $\psi_2\,1/\sqrt{2}\,(\psi_6 - \psi_6')$ and $\psi_2'\,1/\sqrt{2}\,(\psi_6 - \psi_6')$. Since none of these one-electron states interact with the substituent, they are not perturbed and the benzene type transition discussed above is forbidden. It has yet to be established that these states do not interact in any way with the states to which the benzene type transition is allowed.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, THE UNIVERSITY OF TEXAS]

Molecular Orbital Theory and the Near Ultraviolet Absorption Spectrum of Monosubstituted Benzenes. IV. The Phenyl Halides and the Inductive Effect

BY W. W. ROBERTSON AND F. A. MATSEN

Introduction

The intensities and wave lengths of the near ultraviolet absorption of monosubstituted benzenes with an unshared pair of electrons on the substituent are quite well described by molecular orbital theory.[1] For most of the compounds considered, the resonance interaction between the substituent and the ring is the important effect and others, such as the inductive effect, can be neglected. On this basis the spectral properties can in general be correlated with the difference in the ionization energies of the substituent and benzene. The smaller the difference in the ionization energies, the greater is the perturbation of the benzene levels, the longer the wave length and the higher the intensity of the near ultraviolet absorption. For the phenyl halide series the wave lengths lie in the order predicted by this generalization. However, it appears that the intensities lie in the reverse order. Consequently, a further study of the problem is indicated.

Wheland and Pauling[2] have discussed the directing properties of the substituent from the standpoint of molecular orbital theory.

Experimental

The vapor spectra were obtained on a three-meter grating with Eastman Kodak Co. 103-0 plates and were scanned with a Leeds and North-

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(1) Matsen, THIS JOURNAL, **72**, 5243 (1950).

(2) Wheland and Pauling, *ibid.*, **57**, 2086 (1935).