The resulting energies and coefficients are

$$\frac{E^+_e}{E^-_e} = (H_{aa}{}^t + H_{bb}{}^t)/2 \pm {}^1/_2 \sqrt{(H_{aa}{}^t - H_{bb}{}^t)^2 + 4H^t{}_{ab}{}^2}$$

and

$$C_a/C_b = H^t{}_{ab}/(E - H^t{}_{aa})$$

To evaluate $H^t{}_{aa}$, $H^t{}_{bb}$ and $H^t{}_{ab}$ one writes the antisymmetrized functions

$$\psi_a = \frac{1}{\sqrt{8!}} \sum_P (-1)^P \mathrm{P}\chi_1(1)\chi_1(2)\chi_2(3)\chi_2(4)\chi_3(5)\chi_4(6)\chi_7(7)\chi_7(8) \times 2^{-1/2}\alpha(1)\beta(2)\alpha(3)\beta(4)[\alpha(5)\beta(6) - \alpha(6)\beta(5)]\alpha(7)\beta(8)$$

$$\psi_b = \frac{1}{\sqrt{8!}} \sum_P (-1)^P \mathrm{P}\chi_1(1)\ \mathrm{P}\chi_1(1)\chi_1(2)\chi_3(3)\chi_3(4)\chi_2(5)\chi_5(6)\chi_7(7)\chi_7(8) \times 2^{-1/2}\alpha(1)\beta(2)\alpha(3)\beta(4)[\alpha(5)\beta(6) - \alpha(6)\beta(5)]\alpha(7)\beta(8)$$

The total Hamiltonian H^t may be broken up into two parts, $H^t = H + H^1$ where $H^1 = \sum_{\substack{\gamma=1 \\ \mu<\gamma}}^{8} \frac{e^2}{r_{\gamma\mu}}$ and $H = \sum_{\gamma=1}^{8} H\gamma$. $H\gamma$ is the Hamiltonian for the γth electron excluding electron repulsion.

The operator H averaged over each of the antisymmetrized orbitals ψ_a and ψ_b yields the sum of the one electron energies since all exchange integrals vanish by virtue of the orthogonality of the χ's. Then

$$H_{aa} - H_{bb} = \frac{2\beta}{3(\delta^2 - 1)}$$

Further

$$H_{ab} = 0$$

The electron repulsion terms are: $H^1{}_{aa} - H^1{}_{bb} = (\Gamma_{2222} - \Gamma_{3333}) + 2(\Gamma_{1122} - \Gamma_{1133}) + 2(\Gamma_{1144} - \Gamma_{1155}) + 2(\Gamma_{2244} - \Gamma_{3355}) + (\Gamma_{1313} - \Gamma_{1212}) + (\Gamma_{1515} - \Gamma_{1414}) + (\Gamma_{3535} - \Gamma_{2727}) + (\Gamma_{5757} - \Gamma_{4747})$

and

$$H^1{}_{ab} = -\Gamma_{2435}$$

where

$$\Gamma_{i^1j^1k^1l^1} = \int\int \chi_{i^1}(\gamma)\,\chi_{j^1}(\gamma)\,\frac{e^2}{r_{\gamma\mu}}\,\chi_{k^1}(\mu)\,\chi_{l^1}(\mu)\,d\tau_\gamma d\tau_\mu = \sum_{i,j,k,l} \lambda_{i^1i}\lambda_{j^1j}\lambda_{k^1k}\lambda_{l^1l}\gamma_{ijkl}$$

and

$$\gamma_{ijkl} = \int\int \phi_i(\gamma)\phi_j(\gamma)\,\frac{e^2}{r_{\gamma\mu}}\,\phi_k(\mu)\phi_l(\mu)\,d\tau_\gamma d\tau_\mu$$

Evaluation of these expressions is a formidable task and will not be attempted here. Since all the terms in $H^1{}_{aa} - H^1{}_{bb}$ appear as differences between closely related integrals, it will be assumed that $H^1{}_{aa} - H^1{}_{bb}$ is only a small part of the total difference $H^t{}_{aa} - H^t{}_{bb}$. Then

$$C_a/C_b = 1/(1 - K)$$

where

$$K = \delta\beta/3H^1{}_{ab}\,(\delta^2 - 1)$$

With the normalization condition $C^2{}_a + C^2{}_b = 1$

$$C_a = \frac{1}{\sqrt{2}\sqrt{1 - K + \frac{K^2}{2}}}$$

The expression for the dipole strength becomes

$$Q = \sqrt{2}\,(C_a \textstyle\int \chi_3 \times \chi_4 d\tau + C_b \int \chi_2\,(x\chi_5\,d\tau)$$
$$\cong \sqrt{2}\,(C_a\lambda_{33} - C_b\lambda_{55})r/2$$
$$= \frac{1}{\sqrt{1 - K + \frac{K^2}{2}}} \left(\frac{-2\delta}{3(\delta^2 - 1)^2} + K\lambda_{55}\right) r/2$$

When K can be neglected the expression reduces to that used in equation (21). Since K is a positive quantity it decreases the magnitude of the term in the bracket but increases its coefficient. The former effect will probably predominate which indicates that the assumption of equal mixing gives intensities which are too high. This will be most noticeable at low δ values.

Summary

A molecular orbital calculation of the resonance energy, intensity and frequency of absorption and resonance moment of monosubstituted benzenes has been made and the results compared with experiment.

Expressions for extent of migration and frequency of absorption first obtained by Sklar and Herzfeld, respectively, are obtained by a perturbation treatment.

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

Molecular Orbital Theory and Spectra of Monosubstituted Benzenes. II. Thiophenol

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

It has been shown[1,2,3] that the intensity and wave length of the near ultraviolet absorption of a monosubstituted benzene are strongly dependent upon the ionization energy of the substituent. For substituents with an ionization energy greater than that of benzene, the lower the ionization energy of the substituent, the higher is the intensity and the longer is the wave length of the substituted benzene. In Table II of Paper I[1] is given a list of ionization energies from which it can be concluded that the ionization energy of the –SH group is lower than that of the $-NH_2$ and –OH groups. It is, therefore, to be expected that the intensity and wave length of absorption would be in the order $C_6H_5SH > C_6H_5NH_2 > C_6H_5OH$. Sklar[2] predicted a "large intensification" of the spectrum of thiophenol.

The vapor spectrum of thiophenol has not been reported previously. The solution spectrum of thiophenol has been published by Böhme and Wagner.[3a]

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

[2] Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

[3] Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

[3a] Böhme and Wagner, *Ber.*, **75**, 606 (1942).

Experimental

The near ultraviolet absorption spectrum of the vapor of thiophenol was taken in the second order of a three-meter concave grating having a theoretical resolving power of 120,000. The tracing of the spectrogram of thiophenol in Fig. 1 was made on a Leeds and Northrup microphotometer. A Beckman quartz prism spectrophotometer was used to obtain the solution spectrum of thiophenol. This is plotted, together with the spectra of phenol and aniline, in Fig. 2. Ethanol was used as the solvent. The thiophenol was Eastman Kodak Co. "white label" and was subjected to a vacuum distillation immediately before use.

The microphotometer tracing of a spectrogram of the vapor of thiophenol presented in Fig. 1 indicates the lack of discreteness characterizing the spectrum. The dotted lines in the figure locate the positions of peak absorption. The band marked A is choosen as the 0 − 0 band on the basis of relative intensity and position. The positions of the bands, accurate to ±5 cm.$^{-1}$, and their tentative vibrational assignments are listed in Table I.

TABLE I

Band	Wave length, Å.	Wave number	Assignment
A	2857.9	34,980	0 − 0
B	2827	35,360	0 + 380
C	2798	35,730	0 + 750
D	2780	35,950	0 + 970
E	2773	36,050	0 + 1070
F	2753	36,300	0 + 970 + 380
G	2744	36,420	0 + 1070 + 380
H	2725	36,680	0 + 970 + 750
I	2708	36,920	0 + 2 × 970
J	2700	37,030	0 + 970 + 1070

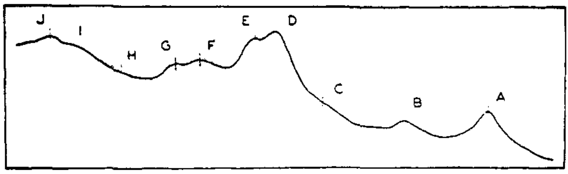

Fig. 1.—Microphotometer tracing of the near ultraviolet absorption spectrum of the vapor of thiophenol. The wave lengths and assignments of the marked bands are given in Table I.

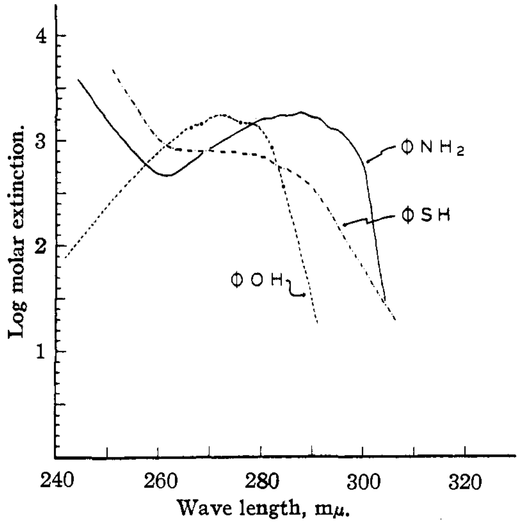

Fig. 2.—Solution absorption spectra of phenol, thiophenol and aniline in ethanol.

Discussion

From Fig. 2 it will be observed that the order of intensity is $C_6H_5NH_2 > C_6H_5SH > C_6H_5OH$. The wave lengths for the 0–0 bands are $C_6H_5NH_2$ = 2937.6 Å. > C_6H_5SH = 2857.9 Å. > C_6H_5OH = 2750.3 Å. It is apparent that a consideration of ionization energies alone will not produce the correct order in the absorption intensities and wave lengths. This type of anomaly has also been noted in the directing power of these groups.[4]

Two refinements may be suggested: (1) It has been assumed that only the lowest level of the substituent interacts appreciably with the benzene ring. In the sulfur atom the interacting orbital is 3p. It is possible that here the 3d orbitals may lie low enough to interact. Recently, Longuet-Higgins[5] has made use of 3d orbitals in his discussion of the aromatic character of thiophene. However, the normal relation between the spectra of thiophenol and diphenyl sulfide[6] suggests that a specific interaction with high substituent level is not the explanation; (2) It has been assumed that the resonance integral between ring and substituent is, for all substituents, equal to the resonance integral between two adjacent carbon atoms in the ring. It is almost certain that there is no equality among these resonance integrals because of differences in distances and electronic structure. It has been suggested by Mulliken[7] and others that the resonance integral varies as does the corresponding overlap integral and there may exist in certain instances an actual proportionality between the two. Mulliken[7] has recently published a series of tables from which overlap integrals of Slater functions may be obtained. In Table II are listed the overlap integrals $(p\pi, p\pi)$ for C–C, C–N, C–O, and C–S bonds together with the parameters used in evaluation. The fact that S_{CS} is smaller than S_{CN} suggests that the resonance integral, β_{CS}, is smaller than β_{CN} which would reduce the effect of the low ionization

TABLE II

	C–C	C–N	C–O	C–S
$t = (\mu_a - \mu_b)/(\mu_a + \mu_b)^a$	0	0.091	0.167	−0.056
R	1.39	1.47	1.42	1.82
	$[C_6H_6]$	$[(CH_3)_3N]$	$[(CH_3)_2O]$	$[(CH_3)_2S]$
$p = [(\mu_a + \mu_b)/2](R/ao)$	4.28	4.96	5.22	5.89
S	0.250	0.163	0.146	0.153

[a] $\mu = (Z - s)/N$; $\mu_C = 1.625$, $\mu_N = 1.950$, $\mu_O = 2.275$, $\mu_S = 1.817$.

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[4] Wheland and Pauling, THIS JOURNAL, **57**, 2093 (1935).

[5] Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949). See also Mulliken, *J. Chem. Phys.*, **7**, 346, 373 (1939).

[6] Robertson and Matsen, THIS JOURNAL, **72**, 5250 (1950).

[7] Milliken, Rieke, Orloff and Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

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.

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

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.

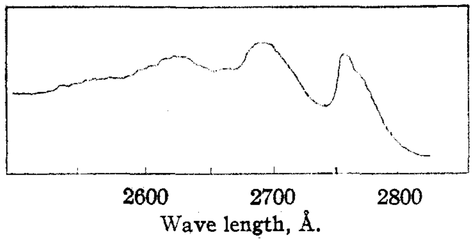

Fig. 1.—Microphotometer tracing of the near ultraviolet absorption spectrum of the vapor of diphenyl ether.

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.

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.)