erty, but since their behavior is not consistent in the several examples he investigated[6] they have not been included. It does not seem very likely that these two solvents should have any specific associations with the solute, especially since Grossmann's[7] data for ether are in line with those for hexane and carbon tetrachloride. However, the values for ΔF obtained in hexane are consistently too high and are usually the same as the gas values[9] although the values in decalin are lower (see Fig. 5).

Conclusions

The changes in the heats of tautomerization of acetylacetone in decalin, tetrachloroethylene and bromoform may be interpreted in terms of the Onsager–Kirkwood model of electrostatic interaction, using the volume of the solvent molecule for the "cavity." The gas value of the heat of tautomerization may be obtained to a fair degree of accuracy from the dilute solution values. The value for acetylacetone arrived at in this way (2.4 kcal./mole) is the same as the experimentally determined gas value. Similar treatment of Grossmann's data for ethyl acetoacetate in hexane, carbon tetrachloride and ether leads to a value of $-\Delta H_{\text{gas}} = 2.0$ kcal./mole for this tautomeric change. Application of the Onsager model as described would appear to account for the behavior of such equilibria in most non-polar or slightly polar solvents, provided no other specific interaction occurs between the solvent and either tautomer. Even where specific associations of the solvent with the tautomeric forms would be expected, namely, in alcohol and methanol–water mixtures, a separate straight line relation between $-\Delta F$ and solvent property $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$ has been obtained. Extrapolation of this line gave also a fair approximation to the gas value of ΔF, but the slope of the line differed from that with non-polar solvents and acidic solvents. The correspondence between the dipole moments of the tautomers (according to Equation 3) and the slope of the line is obviously affected. As far as the data available at present can indicate, acidic solvents will also give a straight line relationship, and so will polar solvents provided no specific associations are visualized. These lines also extrapolate to a reasonably good approximation of the gas value of ΔF.

OTTAWA, CANADA RECEIVED JANUARY 11, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Absorption Spectra of Some Phenyl Sulfides, Sulfoxides and Sulfones Containing Nitro and Amino Groups

BY H. HARRY SZMANT AND J. J. MCINTOSH

The ultraviolet absorption spectra of phenyl sulfides, sulfoxides and sulfones containing amino- and nitro-substituents are reported and discussed in terms of the electronic structures.

In continuation of our studies[1] of the spectroscopic behavior of the sulfur group at its various oxidation states we wish to report in this paper the results obtained with a series of mono- and disubstituted phenyl sulfides, sulfoxides, and sulfones. In order to intensify any spectroscopic results which could be attributed to the electron transmitting capacity of the sulfur-containing group, we have chosen to investigate the *p*-nitro-, *p*-amino- and, finally, the *p*-nitro-*p'*-amino substituents. The latter represent a system in which the electron push and pull, if it is to be coöperative, must be exerted *via* the sulfur group.

Experimental[2]

The physical properties, the spectrophotometric data and other pertinent information concerning the compounds used in this study are summarized in Table I. The absorption spectra reproduced in Figs. 1–4 were obtained by using solutions in 95% ethanol and a Beckman DU spectrophotometer.

Preparation of Compounds.—***p*-Nitrophenyl phenyl sulfoxide** was prepared by the oxidation of the sulfide with 30% hydrogen peroxide in glacial acetic acid.

Anal. Calcd. for $C_{12}H_9O_3NS$: C, 58.29; H, 3.63. Found: C, 58.54; H, 3.79.

Phenyl *p*-aminophenyl sulfoxide was prepared by the hydrolysis of the acetanilide obtained by the Schmidt reaction of *p*-phenylthionylacetophenone. The anilide had a m.p. 137–137.5°.

Anal. Calcd. for $C_{14}H_{13}O_2NS$: C, 64.84; H, 5.05. Found: C, 64.93; H, 5.20.

The identical product was obtained by the oxidation of *p*-phenylmercaptoacetanilide by means of hydrogen peroxide.

The hydrolysis of the acetanilide yielded the desired amine of m.p. 151°.[3]

***p,p'*-Dinitrophenyl sulfoxide** was prepared by Mr. Howard Corey of this Laboratory. The corresponding sulfide was dissolved in a large volume of warm glacial acetic acid and to the stirred solution there was added dropwise an equimolar amount of hydrogen peroxide dissolved in acetic acid. The product was crystallized from isopropyl alcohol to remove traces of sulfone and unreacted sulfide.

Anal. Calcd. for $C_{12}H_8N_2O_5S$: C, 49.31; H, 2.76. Found: C, 49.42; H, 2.76.

***p,p'*-Dinitrophenyl sulfone** has been reported in the literature to melt at 282°,[4] 254°[5] and 245°.[6] Our sample was prepared by a vigorous chromic acid oxidation of the corresponding sulfide, and repeated oxidations and crystallizations did not raise the melting point above 250–251°.

Anal. Calcd. for $C_{12}H_8N_2O_6S$: C, 46.75; H, 2.62. Found: C, 47.03; H, 2.91.

***p*-Nitro-*p'*-aminophenyl Sulfide.**—The reduction of *p,p'*-dinitrophenyl sulfide[7] was improved in the following way. The dinitro compound, 0.2 mole, was dissolved in approxi-

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(1) H. H. Szmant and H. J. Planinsek (a) THIS JOURNAL, **72**, 4042 (1950); (b) **72**, 4981 (1950).

(2) All melting points are uncorrected. Microanalyses by the Microanalytical Laboratory, University of Pittsburgh.

(3) E. H. Northey, "Sulfonamides and Allied Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, pp. 364, 381, 385.

(4) E. Fromm and J. Wittmann, *Ber.*, **41**, 2267 (1908).

(5) A. A. M. Witte, *Rec. trav. chim.*, **51**, 299 (1932).

(6) B. Ciocca and L. Canonica, *Gazz. chim. ital.*, **76**, 113 (1946).

(7) R. C. Fuson and S. Melamed, *J. Org. Chem.*, **13**, 690 (1948).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED PHENYL SULFIDES, SULFOXIDES AND SULFONES

No.	Compound	Source[a]	M.p., °C.	Lit.	Maxima[b] λ(mμ)	$\epsilon \times 10^{-4}$	λ'(mμ)	$\epsilon' \times 10^{-4}$
1	*p*-Nitrophenyl phenyl sulfide	1	55	54–55	338–339	1.28	255	0.51
2	*p*-Nitrophenyl phenyl sulfoxide	2	107–107.5	.....	265–267	1.20	...	..
3	*p*-Nitrophenyl phenyl sulfone	3	140–141	143	261–262	1.46	...	..
4	*p*-Nitrophenyl phenyl ether	4	57–58	56–58	300–301	1.20		
5	*p*-Aminophenyl phenyl sulfide	5	96	93–96	255	2.02	...	..
6	*p*-Aminophenyl phenyl sulfoxide	2	151	151	278	1.03	...	..
7	*p*-Aminophenyl phenyl sulfone	5	172–174	176	291–292	1.89	...	..
8	*p*-Aminophenyl phenyl ether	5	84	84–85	243	0.75		
9	*p,p'*-Dinitro phenyl sulfide	6	157–158	160–161	341	1.50	250 235	1.20 1.23
10	*p,p'*-Dinitro phenyl sulfoxide	2	178–180	.....	268	1.82		
11	*p,p'*-Dinitro phenyl sulfone	2	250–251	?	265	2.03	...	..
12	*p*-Nitro-*p'*-amino phenyl sulfide	2	144–145	137–143	342–343	1.33	266	1.65
13	*p*-Nitro-*p'*-amino phenyl sulfoxide	7	130–131	132–134	276	2.02	...	..
14	*p*-Nitro-*p'*-amino phenyl sulfone	7	167–169	167–169	267	2.00	336	0.68
15	*p*-Nitro-*p'*-amino phenyl ether	2	130–132	.....	300	0.85	230	0.90

[a] Source references: (1) H. H. Hodgson and E. W. Smith, *J. Chem. Soc.*, 1634 (1937); (2) see section on "Preparation of Compounds"; (3) E. Bourgeois and P. Huber, *Rec. trav. chim.*, **32**, 37 (1913); (4) R. Q. Brewster and T. Groening, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 445; (5) H. H. Szmant and J. J. McIntosh, THIS JOURNAL, **72**, 4835 (1950); (6) C. C. Price and G. W. Stacey, *Org. Syntheses*, **28**, 82 (1948); (7) Oxidation of *p*-(*p'*-nitrophenyl)-acetanilide and subsequent hydrolysis gave the products reported in ref. 3, pp. 364, 381. [b] The wave lengths in parentheses refer to inflection points.

mately 150 ml. of dioxane, and 0.4 mole of hydrogen sulfide was introduced while the reaction flask was mounted on a trip balance. The reduction was catalyzed by the addition of approximately 0.5 ml. of concentrated ammonia. Upon acidification with hydrochloric acid and steam distillation, the residue was filtered and the filtrate was made basic with ammonia. The yellow product on crystallization from ethanol had a m.p. 144–145° and was obtained in 30–36% yields.

_p_-Nitro-_p'_-aminophenyl ether could not be found in the literature. It was prepared by the reaction of hydrazoic acid with either *p*-(*p'*-nitrophenoxy)-acetophenone or *p*-(*p'*-nitrophenoxy)-benzoic acid. From the reaction of the acetophenone there was obtained first the corresponding acetanilide of m.p. 145°.

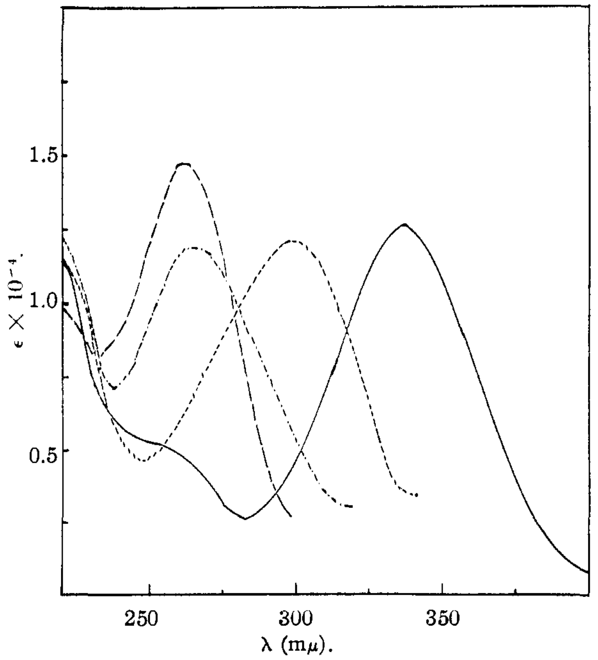


Fig. 1.—Absorption spectra of: ——, *p*-nitrophenyl phenyl sulfide; – – – – –, *p*-nitrophenyl phenyl ether; —·—·—, *p*-nitrophenyl phenyl sulfoxide; — —, *p*-nitrophenyl phenyl sulfone.

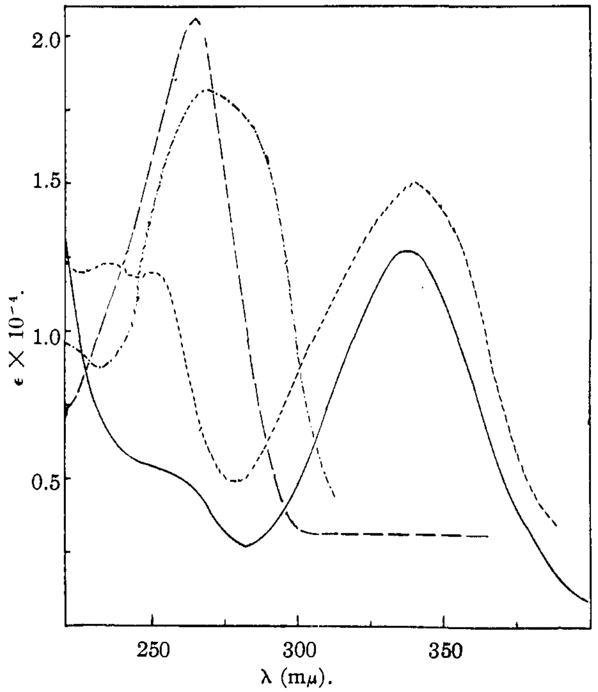


Fig. 2.—Absorption spectra of: ——, *p*-nitrophenyl phenyl sulfide; – – – – –, di-(*p*-nitrophenyl) sulfide; —·—·—, di-(*p*-nitrophenyl) sulfoxide; — —, di-(*p*-nitrophenyl) sulfone.

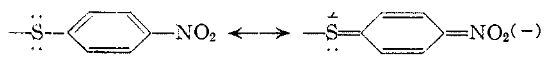
Anal. Calcd. for $C_{14}H_{12}O_4N_2$: C, 61.75; H, 4.44. Found: C, 61.82; H, 4.46.

The acetanilide, on hydrolysis, gave the desired amine which proved to be identical with that obtained by the Schmidt reaction of the benzoic acid.

Anal. Calcd. for $C_{12}H_{10}O_3N_2$: C, 62.60; H, 4.37. Found: C, 62.89; H, 4.23.

Discussion

The maxima of *p*-nitro and *p,p'*-dinitro phenyl sulfide lie in the 338–341 mμ range. These maxima can be attributed to the resonance of the group



since the maximum of *p*-methylmercaptonitrobenzene also lies at 338 mμ.[8,9] Thus, it appears that the resonance of two phenyl groups does not become conjugated through the sulfide function under these conditions. The independent resonance of the nitrophenyl group probably accounts for the secondary maxima observed in the 250–255 mμ range; the hypsochromic shift of the 268 mμ maximum of nitrobenzene is similar to that observed in the case of the *p*-nitroanilinium ion (258 mμ).[10]

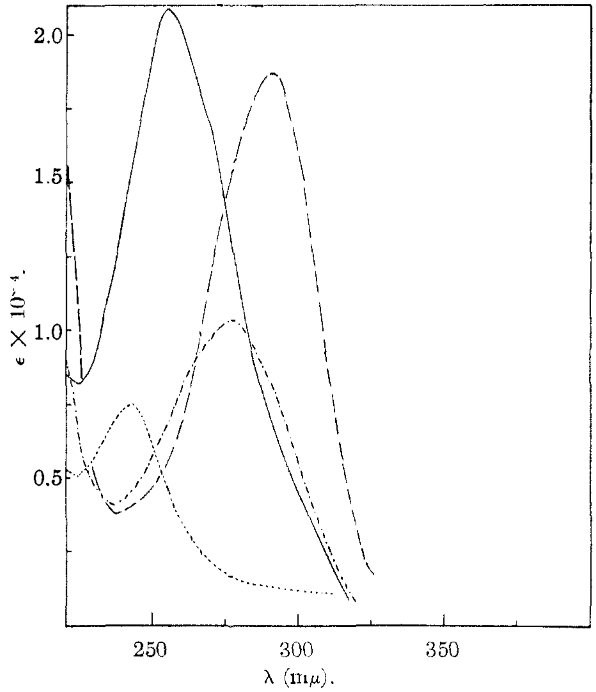
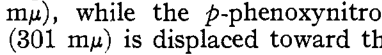


Fig. 3.—Absorption spectra of: ——, *p*-aminophenyl phenyl sulfide; - - - - -, *p*-aminophenyl phenyl ether; —·—·—, *p*-aminophenyl phenyl sulfoxide; — —, *p*-aminophenyl phenyl sulfone.

The spectrum of *p*-nitrophenyl phenyl ether was investigated for comparison with the sulfide. It is noteworthy that both *p*-phenylmercapto- and *p*-methylmercaptonitrobenzene have identical maxima (338 mμ), while the *p*-phenoxynitrobenzene maximum (301 mμ) is displaced toward the ultraviolet when compared to that of *p*-nitrophenol (317.5),[10] for example. These facts indicate that there is practically no contribution of the resonance structure



while the previously observed[1b] resonance contribution of phenoxy groups is significant in the ether.

The maxima of the mono- and dinitro-phenyl sulfoxides and sulfones all lie between 262–269 mμ. These maxima may be interpreted to result from the absorption of the *p*-nitrophenyl group. The hypsochromic shift (with respect to the 268 mμ maximum of nitrobenzene) observed in the diphenyl sulfoxides and sulfones studied by us is smaller than that observed in the case of *p*-nitrophenyl methyl sulfone (248 mμ).[11] Thus, the electron-withdrawing effect of the sulfone group appears to be smaller in the diphenyl series, and a possible explanation of this may be found in the contribution of resonance structures in which one of the aromatic groups donates electrons to the sulfone group.

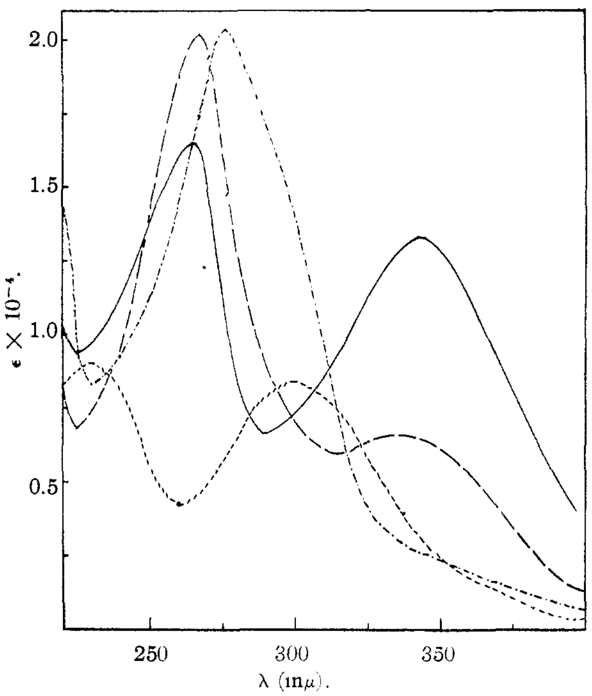


Fig. 4.—Absorption spectra of: ——, *p*-amino, *p*'-nitro phenyl sulfide; - - - - - -, *p*-amino, *p*'-nitro phenyl ether; —·—·—, *p*-amino, *p*'-nitro phenyl sulfoxide; — —, *p*-amino, *p*'-nitrophenyl sulfone.

The maximum of *p*-phenylmercaptoaniline (255 mμ) is similar to those of *p*-methylmercaptoaniline (264 mμ),[8] the *p*-methylmercaptoanilinium ion (254 mμ)[8] or methylmercaptobenzene (254 mμ).[12] We conclude from these comparisons that the 255 mμ maximum results from the resonance of the phenylmercapto group, and that the presence of the amino or of another phenyl group is without much effect.

The greater electron-withdrawing capacity of a sulfone group when compared to the sulfoxide group is illustrated by the difference in the absorption spectra of *p*-phenylthionylaniline and *p*-phenylsulfonylaniline. Whereas, in the corresponding nitro compounds the sulfone had its maximum 3 mμ nearer the ultraviolet, in the amine series the maximum of the sulfone is displaced by 12 mμ toward the visible range as compared to the sulfoxide. An interesting difference is observed between the spectra of *p*-phenylsulfonylaniline (λ_{max} 291 mμ) and *p*-methylsulfonylaniline (λ_{max} 269 mμ).[11] The bathochromic shift may be due to the lowering of the excitation energy in the diphenyl system because of the contribution of the following resonance structures

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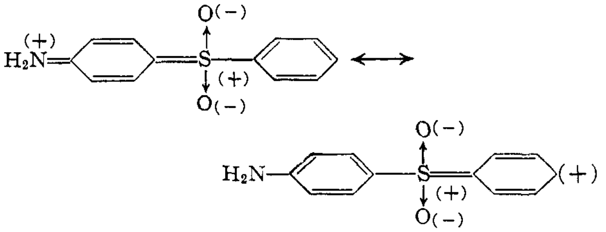
[8] E. A. Fehnel and M. Carmack, This Journal, **71**, 2889 (1949).

[9] The same interpretation was postulated by H. P. Koch (*J. Chem. Soc.*, 387 (1949)).

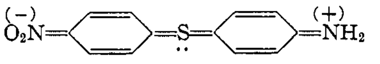
[10] Doub and Vandenbelt, This Journal, **69**, 2714 (1947).

[11] E. A. Fehnel and Marvin Carmack, *ibid.*, **72**, 1292 (1950).

[12] E. A. Fehnel and M. Carmack, *ibid.*, **71**, 84 (1949).

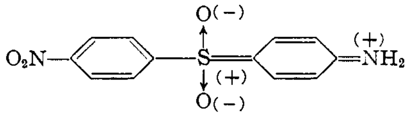


The most significant result of this study was obtained with the amino-nitro compounds. The introduction of a *p*-amino group into *p*-phenylmercaptonitrobenzene caused a bathochromic displacement of about 5 mμ whereas the same structural change in the phenyl ether series gave no displacement of the maximum. This result represents, in our opinion, a definite indication of the greater electron-transmitting capacity of the sulfur atom bridge between two potential conjugated systems, and it is believed that resonance structures such as

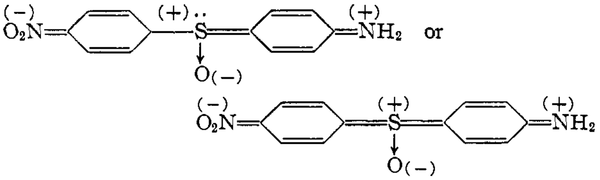


contribute to the spectrum of *p*-nitro-*p*'-aminophenyl sulfide. Additional evidence to this effect was obtained in the very weak basic character of the above nitroaniline.[13]

The introduction of the *p*-amino group into *p*-nitrophenyl sulfoxide and sulfone also causes bathochromic effects. In the case of the sulfoxide the shift of the maximum amounts to 10 mμ while in the case of the sulfone the shift is only 5 mμ. It would seem that in the case of the sulfone the amino group by resonance of the type

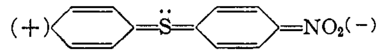


decreases the usual –I effect of the sulfone group and thus the nitrophenyl resonance is restored to the extent present in nitrobenzene itself (268.5 mμ). On the other hand, in the case of the sulfoxide the maximum is displaced *beyond* the wave length characteristic of nitrobenzene. This may be interpreted in terms of contributions by resonance structures

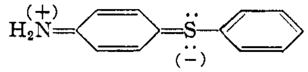


This is the first case in the course of our studies where we encounter a significant difference in the spectroscopic behavior of analogous sulfoxides and sulfones, and it appears that the sulfone group is a better electronic insulator than the sulfoxide group.

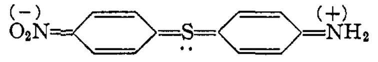
In conclusion the following comments are offered with respect to the spectroscopic evidence of the expansion of the octet in a sulfide group. The sulfur atom readily contributes electrons into resonance with a conjugated system but in doing so the expansion of the octet seems to take place only under special conditions. Thus, there is no evidence of the contribution of structures such as



to the excited states of *p*-nitrophenyl phenyl sulfide, nor is there any evidence of the contribution of structures such as



to the resonance of *p*-phenylmercaptoaniline. However, as pointed out above, upon introduction of both electron-donating and electron-withdrawing groups into a conjugated system involving a sulfur atom, the latter does expand the octet as evidenced by the contribution of structures such as



to the resonance of *p*-nitro-*p*'-amino-phenyl sulfide.

Acknowledgment.—We wish to thank the Research Corporation for the financial aid which made this work possible.

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[13] The hydrochloride was hydrolyzed in water to the nitroaniline and was stable only in concentrated hydrochloric acid. The determination of the basicities of this and related compounds is in progress.