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Polar Conjugative Effect of Aryldithia Group on the Dissociation and Ultraviolet Spectra of Substituted Phenols¹⁾

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A few substituted aryldithiaphenols have been synthesized and their acid dissociations, NMR chemical shifts and UV spectra have been determined. The relatively stronger acidic nature of *p*-aryldithiaphenols over that of the meta-isomers is interpreted as being caused by the 3d-orbital resonance effect of the aryldithia group.

Some years ago, small blue shifts of UV spectra of dialkyl disulfides in the following order, *i.e.*, methyl, ethyl, isopropyl and *t*-butyl, were suggested to be due to the decrease of acidity of α -hydrogen in these dialkyl disulfides.²⁾ Meanwhile, the acidic nature of α -hydrogen in dialkyl disulfides has been demonstrated in several cases, where the disulfides have another electron-withdrawing group such as

carboxyl or carboalkoxy group at α -carbon.³⁻⁷⁾ A typical example would be the alkaline cleavage of dithioglycolic acid, in which the initial step is presumed to be the removal of α -proton:

1) Paper on "3d Orbital Resonance in Divalent Sulfides" (XII).

2) N. A. Rosenthal and G. Oster, *J. Am. Chem. Soc.*, **83**, 4445 (1961).

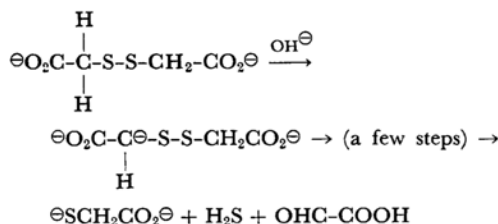
3) A. Schöberl and H. Eck, *Ann.*, **552**, 105 (1936).

4) J. P. Danehy and J. A. Kreuz, *J. Am. Chem. Soc.*, **83**, 1109 (1961).

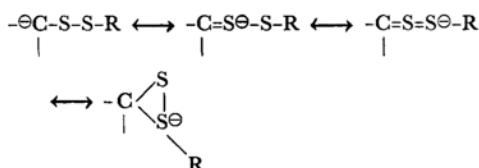
5) E. G. Howard, *J. Org. Chem.*, **27**, 2212 (1962).

6) J. P. Danehy and E. Hunter, *ibid.*, **32**, 2047 (1967).

7) J. P. Danehy, "The Alkaline Decomposition of Aliphatic Disulfides," in "Organic Sulfur Compounds," Vol. II, ed. by N. Kharasch and Cal Y. Meyers, Pergamon Press, New York (1963).



Although this apparent acidity is presumed to be due to the following 3d-orbital resonance of dithia group, there is no unambiguous evidence to support it.



Therefore it is desirable to have a set of quantitative data to illustrate the existence of 3d-orbital resonance of dithia group.

We have synthesized a few dithia-substituted phenols and measured their dissociation constants, chemical shifts and UV spectra. This paper will describe the results and their implications.

Experimental

Bis(4-hydroxyphenyl) Disulfide. Into 2 g of 4-hydroxythiophenol suspended in 30 ml of water was added a solution containing a little over an equivalent amount of ferric chloride. The mixture was warmed for 30 min, the resulting precipitate was collected and recrystallized from benzene-*n*-hexane mixture: 80% yield, mp 149–150°C, colorless needles. (Found: C, 57.87; H, 4.14%)

Bis(3-hydroxyphenyl) Disulfide. The reaction of 3-hydroxythiophenol with ferric chloride solution similarly gave bis(3-hydroxy-phenyl) disulfide in 80% yield: colorless needles, mp 94–95°C. (Found: C, 57.93; H, 4.15%. Calcd for $\text{C}_{12}\text{H}_{10}\text{OS}_2$: C, 57.58; H, 4.03%.)

4-Nitro-4'-hydroxydiphenyl Disulfide. 4-Nitrobenzenesulfonyl chloride prepared from bis(4-nitrophenyl) disulfide (4.9 g) and dry Cl_2 gas was dissolved in 30 ml of absolute ether. This solution was added dropwise into an absolute ether solution of 4-hydroxythiophenol (4 g) with cooling and stirring. After refluxing 10 min, the solvent was evaporated and the remaining product was recrystallized from aqueous ethanol; yellow needles, 8 g (90% yield), mp 118–120°C. (Found: C, 51.69; H, 3.47%. Calcd for $\text{C}_{12}\text{H}_9\text{NO}_3\text{S}_2$: C, 51.60; H, 3.25%.)

It is advisable that the refluxing should not be kept too long, since prolonged heating leads to a disproportionation to bis(4-nitro-phenyl) disulfide.

2-Nitro-4'-hydroxydiphenyl Disulfide. This compound was prepared in the same manner as in the case of 4-nitro-4'-hydroxy-diphenyl disulfide, from 4.9 g of bis(2-nitrophenyl) disulfide and 4 g of 4-hydroxythiophenol. Recrystallization from aqueous methanol gave yellow needles of mp 118–119°C, 70% yield. (Found: C, 51.60; H, 3.41%. Calcd for $\text{C}_{12}\text{H}_9\text{NO}_3\text{S}_2$: C, 51.60; H, 3.25%.)

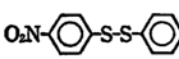
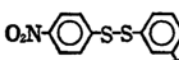
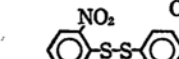
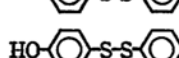
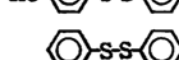
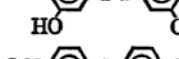
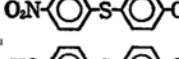
4-Nitro-3'-hydroxydiphenyl Disulfide. Into 50 ml of absolute ether solution containing 2 g of 3-hydroxythiophenol was added dropwise 4-nitrobenzenesulfonyl chloride dissolved in 50 ml of absolute ether under cooling and stirring. After stirring and cooling for 30 min, the solvent was removed *in vacuo*. The resulting oil was recrystallized from benzene-*n*-hexane mixture (without warming); 70% yield, mp 98–100°C. Found: C, 51.59; H, 3.41%. Calcd for $\text{C}_{12}\text{H}_9\text{NO}_3\text{S}_2$: C, 51.60; H, 3.25%.

Results and Discussion

Syntheses and Stabilities of Aryldithiaphenols. Symmetrical disulfides are relatively easy to prepare and quite stable. The unsymmetrical diaryl disulfides not bearing hydroxyl group are also quite stable even under refluxing in chloroform or carbon tetrachloride. However, unsymmetrical phenolic diaryl disulfides are rather unstable and disproportionate readily. Hence, the preparation and the recrystallization of unsymmetrical disulfides bearing a hydroxyl group have to be carried out rather quickly under the condition in which temperature is always kept below 40–50°C. Prolonged heating in ethanol, benzene, and chloroform always leads to the disproportionation. Many attempts to prepare 3- or 4-hydroxydiphenyl disulfide were all unsuccessful, though various conditions were applied changing the temperature, the reaction time, *etc.*

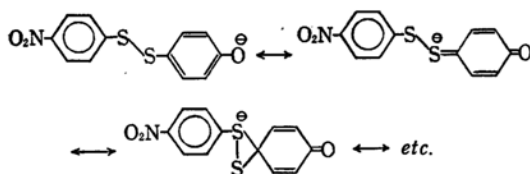
Acid Dissociations. The acid dissociation constants of all the aryldithiaphenols and the related compounds measured in 50 vol% aqueous ethanol solution are summarized in Table 1.

TABLE 1. DISSOCIATION CONSTANTS OF SEVERAL DITHIA-SUBSTITUTED PHENOLS AND THE RELATED COMPOUNDS (25°C, 0.001 M solns. in 50 vol% aqueous ethanol)^{a)}

| Compound | p <i>K</i> _{a1} | p <i>K</i> _{a2} | Δp <i>K</i> _a |
|---|--------------------------|--------------------------|--------------------------|
|  (I) | 9.91 | | |
|  (II) | 10.30 | | |
|  (III) | 9.98 | | |
|  (IV) | 10.08 | 10.68 | 0.60 |
|  (V) | 10.38 | 10.78 | 0.40 |
|  (VI) | 9.86 | | |
|  (VII) | 10.35 | 11.0 | 0.65 |

a) p*K*_a values were estimated using 0.01 N KOH by a standard calculation (A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co. (1962), p. 45).

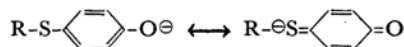
It is interesting to note that the acidity of *p*-nitrophenyldithiaphenol (I) is stronger than that of the meta-isomer (II) by about 0.4 pK_a unit. These observations suggest strongly that the *p*-nitrophenyldithia group does operate an electron-accepting conjugation through benzene ring, involving the expansion of valence shell of the sulfur atoms of the dithia group in the dissociation of the *p*-substituted phenol, as shown below:

TABLE 2. COMPARATIVE σ -CONSTANTS

| Group | | $\Delta(\sigma_p - \sigma_m)$ | Ref. |
|-------|------------|-------------------------------|------|
| | <i>m</i> - | 0.18 | 8 |
| | <i>p</i> - | 0.29 | |
| | <i>m</i> - | 0.16 | 8 |
| | <i>p</i> - | 0.03 | |
| | <i>m</i> - | 0.34 | 8 |
| | <i>p</i> - | 0.44 | |
| | <i>m</i> - | 0.31 | 8 |
| | <i>p</i> - | 0.19 | |
| | <i>m</i> - | 0.26 | This |
| | <i>p</i> - | 0.42 | |
| | <i>m</i> - | 0.52 | 8 |
| | <i>p</i> - | 0.71 | |

These values are calculated from the corresponding pK_a and the ρ -value of 2.50.

Hammett's σ -values of the dithia and the related groups in the dissociations of various substituted phenols are listed in Table 2. While only the inductive or π -inductive effect is transmitted through the benzene ring, the $\Delta(\sigma_p - \sigma_m)$ value becomes negative, as seen in the values of both phenoxy and *p*-nitrophenoxy substituted phenols, the positive values of $\Delta(\sigma_p - \sigma_m)$ for phenylthia and *p*-nitrophenylthia groups⁸⁾ and various other sulfur groups⁹⁾ have been taken to indicate the operation of the 3d-orbital resonance effect of these sulfur groups in the dissociations of the *p*-substituted phenols as shown below:

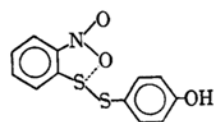


The $\Delta(\sigma_p - \sigma_m)$ value for *p*-nitrophenyldithia group (0.16) is even somewhat larger than that for the corresponding monothia group (0.10) and comes close

to that for phenylsulfenyl group (0.19) which has been known to display 3d-orbital resonance effect both in the dissociation of the substituted phenols and the carbanion forming reactions.¹⁰⁾

Though the *m*-hydroxyphenyl is not identical to *p*-hydroxyphenyl group, it is interesting to compare the acidities of the two isomers, IV and V, because the inductive effects of both groups are presumed not to be much different in view of our previous work on the dissociations of bis(hydroxyphenyl) sulfides, sulfoxides, sulfones and tris(hydroxyphenyl)sulfonium compounds.¹¹⁾ The fact that the compound IV is a stronger acid than the compound V, apparently suggests that the 3d-orbital resonance effect is operating in the former compound.

The less acidic nature of *o*-nitrophenyldithiaphenol (III) as compared to the *p*-nitrophenyl isomer (I) is probably due to the non-bonding interaction of the following type which results in the decrease of



electronegativity of the sulfur atom attached nitrophenyl group, thus decreasing both the 3d-orbital resonance effect and electron-withdrawing inductive effect of the dithia group. A similar non-bonding interaction is already known from the X-ray structural determination of *o*-nitrobenzenesulfenic acid.¹²⁾

TABLE 3. NMR SPECTRA (IN 1,4-DIOXANE, ppm)

| Compound | OH proton | Ring proton |
|----------|-----------|--|
| | 7.87 | 8.10, 7.95, 7.61, 7.46, 7.30, 7.16, 6.61, 6.48 |
| | 7.77 | 8.14, 7.99, 7.62, 7.47, 6.26 (multiplet) |
| | 7.77 | 8.27—8.05, 7.35, 7.19, 6.61, 6.48 |
| | 7.69 | 7.24, 7.10, 6.61, 6.47 |
| | 7.69 | 6.74 (multiplet) |
| | 8.02 | 7.95, 7.80, 7.33, 7.18, 7.02, 6.87, 6.76, 7.61 |
| | 7.71 | 7.27, 7.12, 6.99, 6.69, 6.53 |
| | 7.54 | 7.11, 6.96, 6.60, 6.47 |

10) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York (1965).

8) S. Oae, "3d Orbital Resonance Involving the Sulfur Atom in Organic Sulfide," in "Organic Sulfur Compounds," Vol. III (in Press); Cal. Y. Meyers, *Gazz. Chim. Ital.*, **93**, 1206 (1963).

9) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962).

11) S. Oae and C. Zault, *J. Am. Chem. Soc.*, **82**, 5359 (1960); S. Oae, M. Yoshihara and W. Tagaki, *This Bulletin*, **40**, 951 (1967).

12) W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964).

NMR Spectra. The proton chemical shifts of OH groups of some aryldithiaphenols and the related compounds in 1,4-dioxane are summarized in Table 3.

Although only a few compounds are available for the study, apparently there are good correlations between the acid strength and the chemical shifts

for both para- and meta- substituted dithiaphenols and monothiaphenols, whose slopes of chemical shifts (ppm) against pK_a values are found to be -1 (Fig. 1). These observations suggest that the chemical shifts are dependent on the molecular structures while the electron densities of hydroxyl

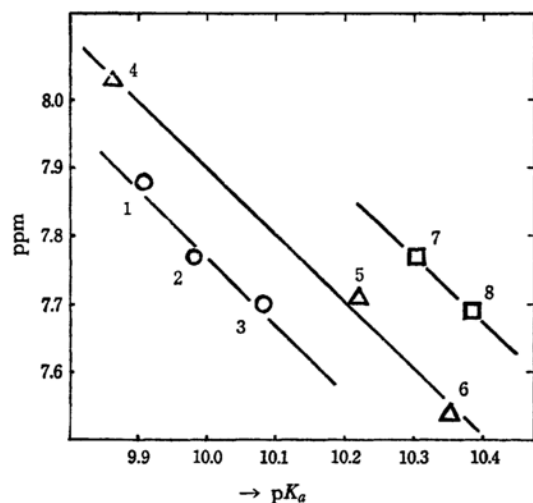


Fig. 1. The relationship between pK_a and the chemical shift of phenolic proton.

- (1) 4-Nitro-4'-hydroxydiphenyl disulfide
- (2) 2-Nitro-4'-hydroxydiphenyl disulfide
- (3) Bis(4-hydroxyphenyl) disulfide
- (4) 4-Nitro-4'-hydroxydiphenyl sulfide
- (5) 4-hydroxydiphenyl sulfide
- (6) Bis(4-hydroxyphenyl) sulfide
- (7) 4-Nitro-3'-hydroxydiphenyl disulfide
- (8) Bis(3-hydroxyphenyl) disulfide

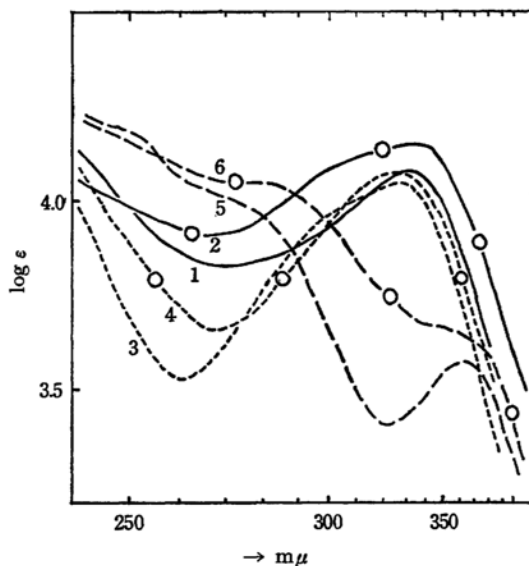


Fig. 2. UV spectra of some nitro-substituted dithiaphenols in 50 vol % ethanol and alkaline solutions.

- 4-Nitro-4'-hydroxydiphenyl disulfide (1, neutral; 2, alkaline)
 4-Nitro-3'-hydroxydiphenyl disulfide (3, neutral; 4, alkaline)
 2-Nitro-4'-hydroxydiphenyl disulfide (5, neutral; 6, alkaline)

TABLE 4. UV SPECTRA IN 50% ETHANOL AND ALKALINE SOLUTION

| Compound | In neutral $m\mu$ (log ϵ) | In alkaline $m\mu$ (log ϵ) |
|--|--|--|
| <chem>O=[N+]([O-])c1ccc(cc1)SSc2ccc(O)cc2</chem> | 335 (4.07) | sh. 305 (4.10) 336 (4.15) |
| <chem>O=[N+]([O-])c1ccc(cc1)SSc2ccccc2O</chem> | sh. 295 (3.92) 327 (4.05) | 328 (4.07) |
| <chem>[O-][N+]([O-])c1ccc(cc1)SSc2ccc(O)cc2</chem> | sh. 250 (4.19) sh. 280 (3.92) 367 (3.57) | sh. 290 (4.04) sh. 362 (3.62) |
| <chem>Oc1ccc(cc1)SSc2ccc(O)cc2</chem> | 240 (4.15) sh. 280—290 (3.87—3.91) | 253 (4.11) 302 (4.13) sh. 330 (4.07) |
| <chem>Oc1ccc(cc1)SSc2ccccc2O</chem> | 285.5 (4.32) 292 (4.34) | sh. 286 (4.28) 295.5 (4.32) |
| <chem>O=[N+]([O-])c1ccc(cc1)Sc2ccc(O)cc2</chem> | sh. 260 (4.34) 352 (4.69) | 264.5 (4.73) 356 (4.68) |
| <chem>Oc1ccc(cc1)Sc2ccc(O)cc2</chem> | 231.2 (4.16) ^{a)} 248.6 (4.16) | 265 (4.39) ^{a)} |

a) These values are those in 6% ethanol and alkaline solutions in preceding paper (This Bulletin, 40, 951 (1967)).

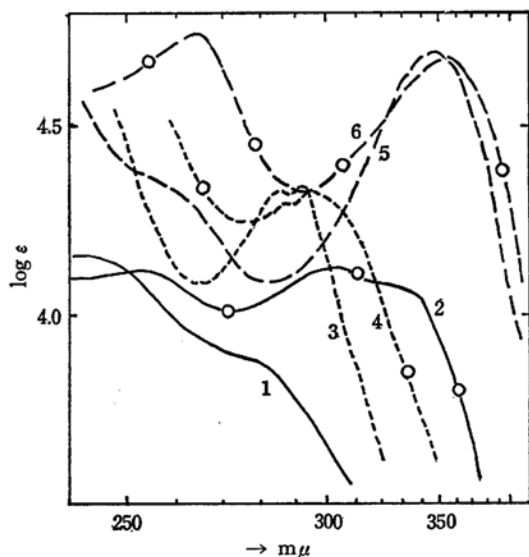


Fig. 3. UV spectra of some hydroxy-substituted dithiaphenols and monothiaphenol in 50 vol % ethanol and alkaline solutions.
 Bis(4-hydroxyphenyl) disulfide (1, neutral; 2, alkaline)
 Bis(3-hydroxyphenyl) disulfide (3, neutral; 4, alkaline)
 4-Nitro-4'-hydroxydiphenyl sulfide (5, neutral; 6, alkaline)

groups are in a direct correlation with the free energies of dissociation.

Ultraviolet Absorption Spectra. The ultraviolet absorption spectra of dithia- and monothiaphenols are taken in 50% ethanol and alkaline solution and summarized in Table 4 and Figs. 2 and 3.

One notices that the λ_{max} for 4-nitro-4'-hydroxydiphenyl disulfide (I), 335 $m\mu$, is at a longer wavelength than that for the meta-isomer (II). Perhaps the chromophore, *p*-nitrophenyldithia group in this case, is perturbed by the *p*-hydroxyphenyl group due to the electron-donation than by the meta group which cannot come in conjugation with the chromophore. It is interesting to note that the λ_{max} (352 $m\mu$) of 4-nitro-4'-hydroxydiphenyl sulfide is at a longer wavelength (17 $m\mu$) than that of the corresponding dithia group (335 $m\mu$), perhaps because of the easy transmission of the electron-withdrawing inductive effect of 4-nitrophenylmercapto group. A question arises as to the possibility through conjugation using 3d-orbitals with the expansion of outer shell of the sulfur atom. However, this possibility does not seem to appear in the ultraviolet absorption spectra. Thus, the λ_{max} of 4-nitro-4'-hydroxydiphenyl sulfide in 50% ethanol solution shifts only slightly to a longer wavelength in alkaline solution (4 $m\mu$), while there are also no red shifts of λ_{max} from neutral to alkaline solutions in the case of the dithia-substituted phenols.