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The Conjugative Effects of Thia, Sulfinyl and Sulfonyl Groups on the Dissociation of *p*-Substituted Phenols[1]

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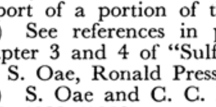
Several di- or tetramethyl substituted derivatives of bis-(4-hydroxyphenyl)sulfides, sulfoxides and sulfones were newly prepared and their acid dissociations, UV and IR spectra were reinvestigated. Essentially no steric inhibition was observed in the 3-d orbital resonance with the sulfinyl and the sulfonyl groups in both the acid dissociations and the UV spectra of the substituted phenols. However, a small but noticeable steric inhibition by ortho methyl groups was observed with the mercaptophenol.

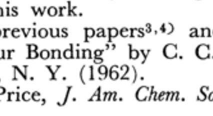
The electron-withdrawing conjugative abilities of sulfinyl and sulfonyl group have been displayed in numerous examples.[2] Evidence for the 3d orbital resonance between the positively charged sulfur group and the double bond has been deduced from dipole moments of various sulfonyl compounds,[2] dissociation constants of sulfinyl and sulfonyl phenols,[5] ultraviolet spectra and others.[2]

Earlier theoretical consideration[6] and the studies of the dissociation constants and ultraviolet spectra of hindered sulfones[3,4,7] have led to the conclusion that the p-d orbital overlap is quite insensitive to the rotation around the C–S bond axis.

In seeking further supporting evidence for the stereo-insensitivity of the 3-d orbital resonance, we have undertaken the syntheses of a number of sterically more hindered sulfoxides and sulfonio compounds of the following structures (1) and (2)



(1)



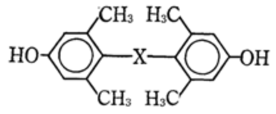
(2)

R, R′ and R′′: H or CH_3

for the determination of their acid-dissociation constants, and concluded that there is little steric inhibition on the electron-accepting type conjugation involving 3-d orbital resonance of the sulfur atom.

However, it was found recently[8] that the reaction between 3, 5-xylenol with thionyl chloride gives bis-(2-hydroxy-4, 6-dimethylphenyl)sulfide instead of the bis-(4-hydroxy) isomer which we originally considered to be the bis-(4-hydroxy)-compound and hence the sulfoxide thus prepared was also the bis-(2-hydroxy) isomer. Meanwhile, Meyers *et al.* has shown that the bis-(4-hydroxy)-sulfide (3a) can be obtained by the reaction between xylenol and sulfur dichloride.[8]

Therefore, we have reinvestigated the whole problem by preparing a new set of sulfides and sulfoxides together with the sulfones, and studied the acid dissociations, UV and IR spectra. Here again, essentially no steric inhibition was observed in the 3-d orbital resonance with the sulfinyl and the sulfonyl group in both the acid dissociations and the UV spectra of the substituted phenols.



(3)

a $X{=}S$
b $X{=}SO$
c $X{=}SO_2$

Experimental

Bis-(4-hydroxyphenyl)sulfide: (General Method for the Preparation of Bis-(4-hydroxyphenyl)-sulfides). Sulfur dichloride, 28 g, was added dropwise under cooling with stirring into 150 m*l* of chloroform solution containing 50 g of phenol. After kept standing the reaction mixture at room temperature overnight, the crude sulfide was obtained in a yield no less than 85%. The crude sulfide was recrystallized from the

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[1] a) Paper XVI on "Sulfoxides"; b) The authors are indebted to the Petroleum Research Fund, administered by the American Chemical Society for the generous support of a portion of this work.

[2] See references in previous papers[3,4] and also Chapter 3 and 4 of "Sulfur Bonding" by C. C. Price and S. Oae, Ronald Press, N. Y. (1962).

[3] S. Oae and C. C. Price, *J. Am. Chem. Soc.*, **80**, 3425, 4938 (1958).

[4] S. Oae and C. Zalut, *ibid.*, **82**, 5359 (1960).

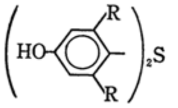
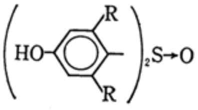
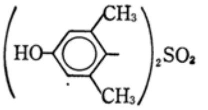
[5] a) F. G. Bordwell and G. D. Cooper, *ibid.*, **84**, 1058 (1962); b) F. G. Bordwell and P. J. Boutan, *ibid.*, **79**, 717 (1957).

[6] a) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); b) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

[7] a) H. Kloosterziel and H. von J. Backer, *Rec. Trav. Chem.*, **72**, 185 (1953); b) W. E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955); c) E. A. Fehnel and M. Carmack, *ibid.*, **72**, 1291 (1950).

[8] Through the attention of Professor Cal Y. Meyers; also see Cal Y. Meyers and G. Picciola, *Tetrahedron Letters*, **1962**, 971.

TABLE 1

R	Mp, °C	Analyses %					
		Calcd.			Found		
		C	H	S	C	H	S
Bis-(4-hydroxyphenyl)sulfide							
H, H	150	66.03	4.16	14.68	65.89	4.64	15.01
2-CH_3, H	147	68.26	5.72		68.21	5.79	
2,6-di CH_3	263	70.07	6.65	11.69	69.70	6.85	11.66
Bis-(4-hydroxyphenyl)sulfoxide							
H	195	61.52	4.30	13.68	61.39	4.34	13.65
2-CH_3	201	64.09	5.37	12.23	63.90	5.40	11.76
2,6-di CH_3	172	64.19	6.40	10.71	64.23	6.33	11.12
	for $C_{16}H_{18}O_3S\cdot 1/2H_2O$						
Bis-(4-hydroxyphenyl)sulfone							
H	245	57.72	4.00		57.68	4.31	
2-CH_3	207	60.43	5.07		60.57	5.06	
2,6-di CH_3	156	62.72	5.92		62.34	6.28	

mixture of benzene and *n*-hexane to give colorless plates of mp 149—150°C.

Bis-(4-hydroxy-2-methylphenyl) and bis-(4-hydroxy-2, 6-dimethylphenyl)sulfide were prepared similarly using *m*-cresol and 3, 5-xylenol, respectively, as the starting materials.

Unsubstituted bis-(4-hydroxyphenyl)sulfide was obtained also by another reaction, namely, that between phenol and thionyl chloride, described in our early paper.[4] The product, obtained by this method showed its mp 149—150°C which was undepressed by admixing with the sulfide prepared by the general method.

The results of the preparation are given in Table 1.

Bis-(4-nitrobenzoyloxyphenyl)sulfide. A solution of 10 g of bis-(4-hydroxyphenyl)sulfide and 16 g of freshly prepared *p*-nitrobenzoyl chloride in 50 m*l* of dry pyridine was refluxed for one hour, cooled and then poured into 100 m*l* of ice-water. The precipitate formed was collected, washed with 10% sodium carbonate solution, then with dilute hydrochloric acid and finally with water. When the crude precipitate was recrystallized from benzene, 18 g of the product, mp 141—142°C, was obtained (yield, 76%).

Similarly, the esters of 2-methyl and 2, 6-dimethyl derivatives were also prepared: Bis-(4-nitrobenzoyloxy-2-methylphenyl)sulfide, mp 176.5—177°C.

Found: C, 61.98, H, 3.85; S, 5.88%. Calcd for $C_{28}H_{20}O_8N_2S$: C, 61.76; H, 3.70; S, 5.14%.

Bis-(4-nitrobenzoyloxy-2, 6-dimethylphenyl)sulfide, mp 244—246°C.

Found: N, 4.89; S, 5.48%. Calcd for $C_{30}H_{24}O_8N_2S$: N, 4.77; S, 5.60%.

Bis-(4-acetoxy-2, 6-dimethylphenyl)sulfide, mp 164—165°C.

Found: C, 66.67; H, 6.37%. Calcd for $C_{20}H_{22}O_4S$: C, 67.02; H, 6.19%.

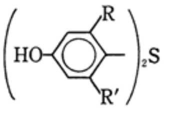
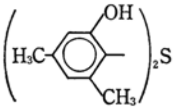
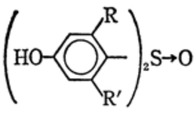
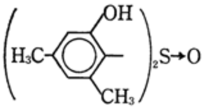
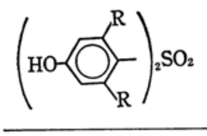
Oxidation of the *p*-Nitrobenzoates of the Sulfides by Perbenzoic Acid. The oxidation of the sulfides by perbenzoic acid has always resulted in the formation of a mixture of the sulfoxides and the corresponding sulfones. However, the reaction could be controlled so as to favor the predominant formation of one component over the other, by changing the temperature, time, the amount of the oxidizing reagent, *etc.*

Preparations of Bis-(4-nitrobenzoyloxyphenyl)sulfone and Related Sulfones. Chloroform solution, 50 m*l* containing 4.67 g (0.025 mol) of perbenzoic acid was added to 50 m*l* of chloroform solution that contains 7 g (0.01 mol) of bis-(4-nitrobenzoyloxyphenyl)sulfide at 10—15°C. After keeping the mixture at room temperature for 3 days, the solution was washed with 5% sodium carbonate solution, then with water and dried. Evaporation of chloroform followed by recrystallization from chloroform-benzene mixture gave 4.05 g (54.4%) of pale yellow needles of mp 230—232°C. Bis-(4-nitrobenzoyloxy-2-methylphenyl)sulfone was prepared similarly; mp 220—

TABLE 2. pK_a VALUES AND HAMMETT σ-VALUES OF *o*- AND *p*-SUBSTITUTED MERCAPTO, SULFINYL AND SULFONYL PHENOLS IN 50% (BY VOLUME) AQUEOUS ETHANOL AT 25±0.5°C

	pK_a		σ			
			Obs.		Calcd.	
	pK_{a_1}	pK_{a_2}	σ_1	σ_2	σ_1	σ_2
Phenol (I)	11.22±0.02					
Bis-(4-hydroxyphenyl)sulfide (II)	10.28±0.03	11.10±0.07	0.35	0.04		
Bis-(4-hydroxy-2-methylphenyl)sulfide (III)	10.50±0.07	11.42±0.05	0.26	−0.07	0.28	−0.03
Bis-(4-hydroxy-2, 6-dimethylphenyl)sulfide (IV)	10.99±0.05	11.58±0.05	0.08	−0.13	0.21	−0.10
Bis-(2-hydroxy-4, 6-dimethylphenyl)sulfide (V)	9.43±0.04	12.47				
Bis-(4-hydroxyphenyl)sulfoxide (VI)	9.09±0.02	10.06±0.03	0.78	0.43		
Bis-(4-hydroxy-2-methylphenyl)sulfoxide (VII)	9.28±0.03	10.28±0.04	0.71	0.35	0.71	0.36
Bis-(4-hydroxy-2, 6-dimethylphenyl)sulfoxide (VIII)	9.57±0.06	10.74±0.06	0.61	0.18	0.64	0.29
Bis-(2-hydroxy-4, 6-dimethylphenyl)sulfoxide (IX)	9.14±0.01	12.22				
Bis-(4-hydroxyphenyl)sulfone (X)	8.52±0.04	9.42±0.06	0.99	0.66		
Bis-(4-hydroxy-2-methylphenyl)sulfone (XI)	8.77±0.02	9.73±0.02	0.90	0.55	0.92	0.59
Bis-(4-hydroxy-2, 6-dimethylphenyl)sulfone (XII)	9.02±0.03	10.04±0.02	0.81	0.43	0.85	0.52

TABLE 3. ULTRAVIOLET ABSORPTION BANDS OF *p*-SUBSTITUTED PHENOLS IN 6% AQUEOUS ETHANOL SOLUTION

		In neutral mμ (log ε)	In alkaline mμ (log ε)
Phenol (I)		270.5 (3.38) 275.5 (3.38)	288 (3.61)
	R, R'=H (II)	231.2 (4.16) 248.6 (4.16)	265 (4.39)
	R=H $R'=CH_3$ (III)	Nearly 243 (4.25)	263.2 (4.39)
	R, $R'=CH_3$ (IV)	Nearly 258 (shoulder, 4.09) 270.7 (4.13)	277.8 (4.29)
	(V)	262 (4.31)	300 (4.00)
	R, R'=H (VI)	Nearly 237 (shoulder, 4.24) 249 (4.30)	270 (shoulder, 4.35) 285.8 (4.39)
	R=H $R'=CH_3$ (VII)	238—240 (shoulder, 4.25) 249 (4.26)	258.7 (shoulder, 4.18) 297.7 (4.31)
	R, $R'=CH_3$ (VIII)	257.6 (4.37)	264 (shoulder, 4.24) 281 (4.32)
	(IX)	251 (3.90)	286 (4.00)
	R, R'=H (X)	234.8 (4.14) 260.5 (4.28)	258.7 (4.26) 297 (4.48)
	R=H $R'=CH_3$ (XI)	238.7 (4.14) 256.3 (4.30)	261 (4.27) 293 (4.53)
	R, $R'=CH_3$ (XII)	242 (shoulder, 3.61) 256.8 (4.33)	Nearly 262—270 (shoulder, 4.32) 290.5 (4.50)

221°C.

Found: C, 58.26; H, 3.42; N, 4.90%. Calcd for $C_{28}H_{20}O_{10}N_2S$: C, 58.33; H, 3.49; N, 4.86%.

Bis-(4-nitrobenzoyloxy-2, 6-dimethylphenyl)sulfone, mp 250—251°C was also obtained by the similar oxidation in 60% yield.

Found: C, 59.33; H, 4.14%. Calcd for $C_{30}H_{24}O_{10}N_2S$: C, 59.60; H, 4.00%.

Preparations of Bis-(4-nitrobenzoyloxy-2-methylphenyl)-sulfoxide and Bis-(4-nitrobenzoyloxy-2, 6-dimethylphenyl)-sulfoxide. a) Bis-(4-nitrobenzoyloxy-2-methylphenyl)sulfoxide: Chloroform solution, 20 m*l* containing 1.23 g (0.0089 mol) of perbenzoic acid was added into an ice-cooled chloroform solution 20 m*l* containing 5 g (0.0089 mol) of bis-(4-benzoyloxy-2-methylphenyl)sulfide at 0°C and the mixture was kept at room temperature for

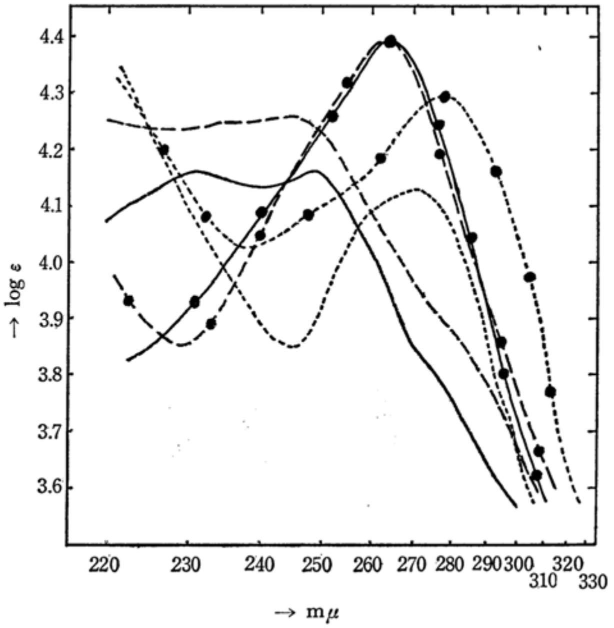


Fig. 1. Ultraviolet spectra of some aryl sulfides in 6% aqueous ethanol and 0.01 N NaOH solution.

Bis-(4-hydroxyphenyl)sulfide	in neutral	———
	in alkali	—●—
Bis-(4-hydroxy-2-methylphenyl)sulfide	in neutral	— — —
	in alkali	--●--
Bis-(4-hydroxy-2, 6-dimethylphenyl)sulfide	in neutral	········
	in alkali	···●···

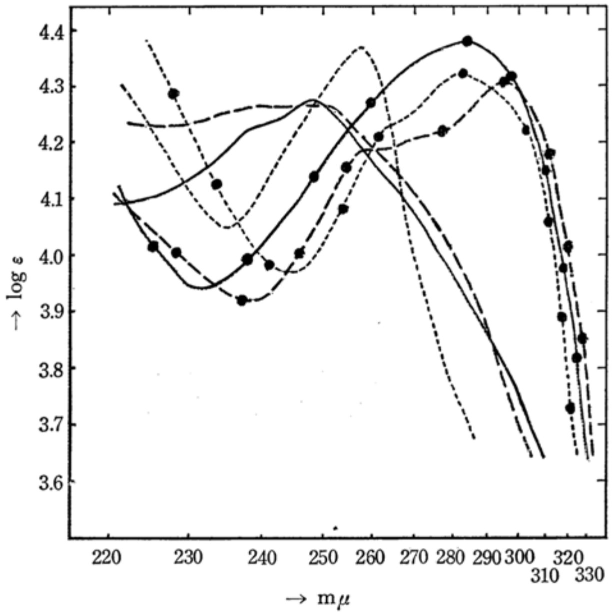


Fig. 2. Ultraviolet spectra of some aryl sulfoxides in 6% aqueous ethanol and 0.01 N NaOH solution.

Bis-(4-hydroxyphenyl)sulfoxide	in neutral	———
	in alkali	—●—
Bis-(4-hydroxy-2-methylphenyl)sulfoxide	in neutral	— — —
	in alkali	--●--
Bis-(4-hydroxy-2, 6-dimethylphenyl)sulfoxide	in neutral	········
	in alkali	···●···

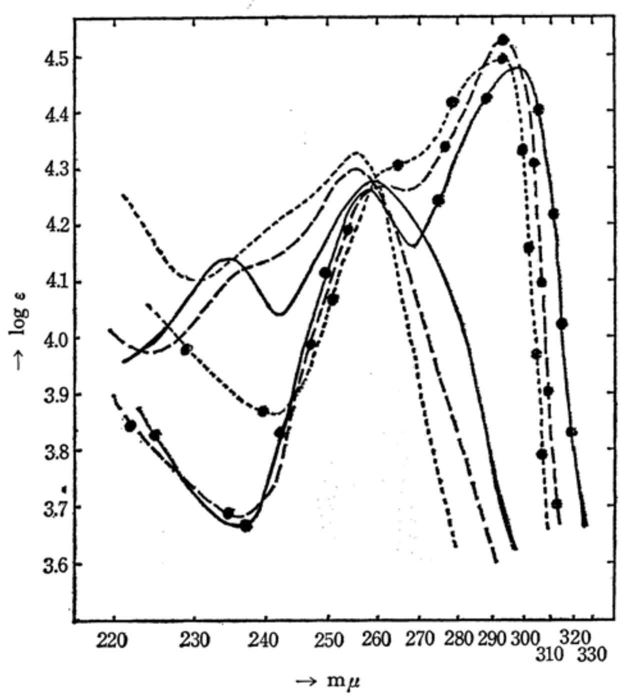


Fig. 3. Ultraviolet spectra of some aryl sulfones in 6% aqueous ethanol and 0.01 N NaOH solution.

Bis-(4-hydroxyphenyl)sulfone	in neutral	———
	in alkali	—●—
Bis-(4-hydroxy-2-methyl)sulfone	in neutral	– – –
	in alkali	--●--
Bis-(4-hydroxy-2, 6-dimethylphenyl)sulfone	in neutral	········
	in alkali	···●···

3 days. After washing with 5% sodium carbonate solution, then with water and drying, evaporation of the solvent followed by the recrystallization from chloroform - *n*-hexane mixture gave 3 g (60%) of pale yellow needles of mp 178—180°C.

Found: C, 60.19; H, 3.33; N, 4.82%. Calcd for $C_{28}H_{20}O_9N_2S$: C, 59.99; H, 3.59; N, 5.00%.

b) Bis-(4-acetoxy-2, 6-dimethylphenyl)sulfoxide: To an ice-cooled chloroform solution, 10 m*l* containing 1 g (0.0028 mol) of bis-(4-acetoxy-2, 6-dimethylphenyl)-sulfide, 0.385 g (0.0028 mol) of perbenzoic acid dissolved in 10 m*l* of chloroform was added under cooling and stirring. After kept standing at 0°C for 3 days, the reaction mixture was washed with 5% sodium carbonate solution, then with water and dried. Removal of the solvent followed by the recrystallization of the residue from benzene-*n*-hexane mixture gave colorless crystals of mp 156—158°C.

Found: C, 64.53; H, 6.33%. Calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.92%.

Hydrolyses of the Esters of Sulfones and Sulfoxides. These esters were hydrolyzed using 30% alcoholic potassium hydroxide solution and the resulting phenols were recrystallized from aqueous ethanol. Their melting points and analytical data are tabulated in Table 1.

The reactions of phenol and *m*-cresol with thionyl chloride in the presence of aluminum chloride[4] also gave bis-(4-hydroxyphenyl)sulfoxide and bis-(4-hydroxy-2-methylphenyl)sulfoxide, respectively, while the same reaction of 3, 5-xylenol resulted in the formation of bis-(2-hydroxy-4, 6-dimethylphenyl)sulfoxide as reported by Meyers and Picciola.[8]

Measurements of Acidity Constants. The acidity constants of the substituted phenols, thus prepared, were determined potentiometrically, using a Hitachi-Horiba model pH meter. The cell was placed in a constant temperature bath and the sample solutions were titrated under nitrogen atmosphere. Since most of the phenols were sparingly soluble in water, 50% (by volume) aqueous ethanol was used as the solvent. The first and the second dissociation constants of most of the bis-substituted phenols were found to be so close to each other that they were estimated by a standard calculation.[9] The results are shown in Table 2.

Ultraviolet Absorption Spectra. The ultraviolet spectra of the substituted phenols were measured using Hitachi Model EPS-2 spectrophotometer. The spectra were taken both in 6% ethanol-water solution and in alkaline solutions. The results are shown in Figs. 1, 2, 3 and in Table 3.

Results and Discussion

The Syntheses of the Compounds. The structural assignments for all the sulfides and the

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9) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen & Co., (1962), p. 45.

TABLE 4. CHARACTERISTIC SULFOXIDE AND HYDROXY BANDS OF ARYL SULFOXIDES IN KBr DISKS

Sulfoxide	OH, cm^{-1}	S-O, cm^{-1}
Phenol (I)	3360	
Bis-(4-hydroxyphenyl) (VI)	3160	960—975
Bis-(4-hydroxy-2-methylphenyl) (VII)	3140	953
Bis-(4-hydroxy-2, 6-dimethylphenyl) (VIII)	3160	978
Bis-(2-hydroxy-4, 6-dimethylphenyl) (IX)	3120—3160	950

TABLE 5. CHARACTERISTIC SULFONE AND HYDROXY BANDS OF SOME ARYL SULFONES IN KBr DISKS

Sulfone	OH, cm^{-1}	S-O, cm^{-1}
Phenol (I)	3360	
Bis-(4-hydroxyphenyl) (X)	3380—3430	1080 (s) 1103, 1130—1150
Bis-(4-hydroxy-2-methylphenyl) (XI)	3240—3280	1080 (s) 1120, 1150
Bis-(4-hydroxy-2, 6-dimethylphenyl) (XII)	3480—3520	1080 (s) 1130—1145 (doublet)

purities of them are beyond any doubt,10) and we have also confirmed the results of Meyers and Picciola.8) However, a brief comment would be necessary as to the purities of those sulfoxides and sulfones, particularly for bis-(4-hydroxy-2, 6-dimethylphenyl) derivatives, since the same oxidizing reagent, perbenzoic acid, was used for the syntheses of both sulfoxide and sulfone. A trace contamination of the sulfone into the sulfoxide or *vice versa* might not be easily avoided; however, as shown in Tables 4 and 5, there are marked differences in the infrared spectra of both sulfoxides and the corresponding sulfones. Therefore the infrared spectra have been used for the diagnosis of the small contamination of sulfoxides or sulfones. The elemental analyses, the melting point differences, (Table 1), the ultraviolet spectra (Figs. 2, 3 and Table 3) and pK_a values (Table 2) also confirmed the purities of these compounds. It is interesting to note, however, that bis-(4-hydroxy-2-methylphenyl)sulfoxide and -sulfone (mp(s) 201 and 207°C, respectively) showed no depression of mixed melting point upon the admixture of the two compounds and yet their infrared spectra and other properties are widely different to each other. Meanwhile the elemental analysis of bis-(4-hydroxy-2, 6-dimethylphenyl)sulfoxide indicated the presence of a half mole of crystalline water. Since the other properties such as IR, UV, are all consistent with the assigned structure, this is presumably due to the highly crowded structure of the molecule combined with strong basicity of the $S \rightarrow O$ group to form hydrogen bonding that favor the inclusion of water molecule in the crystalline lattice.

Acid Dissociations. The acid dissociation constants of all the phenols measured in aqueous ethanol solution are summarized in Table 2. The observed σ-values in Table 2 were obtained by assuming $\rho=2.72$ which was determined from the pK_a values of *m*-cresol, 3, 5-xylenol, *m*-chloro- and 3, 5-dibromophenols under the present experimental condition, using conventional Hammett σ_m-values.11) The calculated σ-values were obtained simply by adding σ_m-CH_3 value (-0.07) to the observed σ-values of the unsubstituted bis-(4-hydroxyphenyl)sulfide, sulfoxide and sulfone.

Inspection of Table 2 reveals that the acidity increases in the order of sulfide <sulfoxide< sulfone in the same aryl compounds while the substitution of methyl group in the benzene ring reduces the acidity of the phenol. This trend is in well-accord with the increasing electronegetivities of the sulfinyl and sulfonyl groups in this order and also the electron-releasing effect of methyl group.

Sulfides. In the case of bis-(4-hydroxy-2-methylphenyl) sulfide, (III), which has one methyl group in each benzene ring ortho to sulfide group, essentially no steric inhibition of resonance is observed in the acid dissociation; namely the observed and the calculated Hammett σ-values are 0.26 and 0.28, respectively. The introduction of the second methyl group, however, brings about a noticeable difference in the observed and the calculated σ-values, apparently caused by the steric inhibition of resonance.

Our previous work4) and Meyers' recent work12) have shown that there is a substantial electron-accepting type through-conjugation between phenolate oxygen and phenylmercapto sulfur atoms. The electron-accepting conjugative ability of divalent sulfide group has been displayed also in numerous other cases especially when the central sulfur atom bears some electronegative group.13)

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10) A study on the dipole moments of these sulfides, sulfoxides and sulfones are now underway and will be reported soon.

11) H. H. Jaffé, *Chem. Revs.*, **53**, 222 (1953).

12) C. Y. Meyers, *Gazz. Chim. ital.*, **93**, 1206 (1963).

13) a) N. A. Sheppard, *J. Am. Chem. Soc.*, **83**, 4860 (1966); b) R. R. Beishline, *J. Org. Chem.*, **26**, 2533 (1961); c) V. Baliah and M. Una, *Tetrahedron*, **19**, 455 (1963).

Recently, we have found that phenylmercapto group is much more effective than ethylmercapto group in stabilizing carbanion.14) All these observations suggest strongly that some electron-accepting type through-conjugation is in operation in the dissociated phenolate ion of the above sulfides. Meanwhile, two types of electron-accepting conjugation are conceivable for the divalent sulfide group. One is the conventional electron-accepting conjugation involving the overlap of π-molecular orbitals of benzene ring and 3d orbitals of sulfur atom and the other is the conjugation involving the overlap of 2p-π-orbitals and 3p orbitals of sulfur atom with a pair of electrons in a 3d orbital of the sulfur atom. The former type of conjugation is quite insensitive to angular rotation around C–S axis while the latter requires coplanar arrangement of the atoms attached to the C–S bond for maximum overlapping. The noticeable steric inhibition of resonance in the dissociation of bis-(4-hydroxy-2, 6-dimethylphenyl)sulfide could be interpreted by assuming the latter type conjugation for the resulting phenolate ion, since four ortho methyl groups would force the molecule away from the coplanar arrangement and reduce the overlapping of 2pπ-3p orbitals considerably.

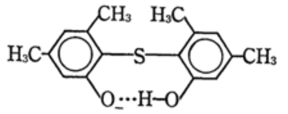
This interpretation, however, has a draw-back for no such steric inhibition of resonance was observed in the dissociation of bis-(4-hydroxy-2, 6-dimethylphenyl)sulfoxide which still retains a lone electron pair on the sulfur atom and is capable of operating the latter type of conjugation in the acid dissociation.

Another possibility is that the conformational change from the unsubstituted bis-(4-hydroxyphenyl)sulfide to bis-(4-hydroxy-2, 6-dimethylphenyl)sulfide may increase the repulsion between two filled orbital of 2pπ of benzene and a 3p of the sulfur atom, and result in the reduction of the electron withdrawing effect in the latter compound.

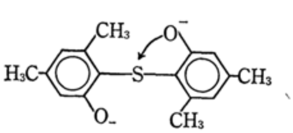
Although there is no evidence to support the idea, the effect of such a conformational change may be readily tested with a few rigid molecules such as 2, 8-dihydroxydibenzothiophene, 2, 7-dihydroxythioxanthene and 2, 8-dihydroxydibenzothiepin and the study on this line is now underway in these laboratories.

It is interesting to note that no such steric inhibition of resonance appears to be in operation in the second ionizations of the sulfides as revealed in the very small differences in σ-values obtained from their pK_{a_2} values.

One notices in Table 2 that pK_{a_1} of bis-(2-hydroxy-4, 6-dimethylphenyl)sulfide (V) is substantially smaller than that of the para-isomer (IV). This is an additional support to Meyers' suggestion in connection with the acid dissociations of bis(4-hydroxyphenyl)sulfide, sulfoxide and sulfone and the corresponding ortho isomers.13,15) Namely, the relatively large first dissociation of the ortho isomers (V) is due to the stabilization of the mono-anion through an intramolecular hydrogen bonding with the vicinal hydroxyl group as shown below (a), while the relatively reduced second dissociation (larger pK_{a_2}) of the ortho isomer is ascribed to the reduced electron-withdrawing power of phenylmercapto group due to the direct field effect of phenolate oxygen, (b).



(a)



(b)

Sulfoxides. The observed σ-value from the pK_{a_1} of bis-(4-hydroxy-2, 6-dimethylphenyl)sulfoxide (VIII) and the calculated value are practically identical, indicating that there is essentially no steric inhibition of resonance by the four bulky ortho methyl groups for the electron-accepting 3-d orbital resonance of the sulfur atom. The σ-values, both observed and calculated, from the second ionization of bis-(4-hydroxy-2-methylphenyl)sulfoxide are also practically identical, though the molecule is crowded around the sulfur atom and little free rotation would be possible. In the second dissociation of more sterically crowded bis-(4-hydroxy-2, 6-dimethylphenyl)sulfoxide, however, the observed σ-value is somewhat smaller (*ca.* 0.1 unit) than the calculated value. Quite often this much of a small difference has been regarded as negligible3) and taken as a reasonable agreement instead. In this case, however, the difference may be real, in view of the fact that a similar discrepancy of the calculated and the observed σ-values was observed in the second dissociation of another sterically crowded bis-(4-hydroxy-2, 6-dimethylphenyl)sulfone. One possible explanation would be that in the second dissociation of these compounds, 2nd 3-d orbital (probably d_{xy}) of the sulfur atom, perpendicular to the 1st 3-d orbital (probably d_{xz}), ought to be mobilized for the overlapping with the second phenolic π-orbitals and this would require a little more specific angular arrangement than a simple 3-d orbital resonance, while two crowded aryl groups may cause a small but noticeable steric problem for such orbital arrangement.

Sulfones. As has been known,2) the sulfone group has larger electron-accepting conjugative

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14) S. Oae, W. Tagaki and K. Uneyama, unpublished work.

15) C. Y. Meyers, *J. Am. Chem. Soc.*, **84**, 4603 (1962).

effect than the sulfoxide group. Thus, bis-(4-hydroxyphenyl)-, bis-(4-hydroxy-2-methylphenyl) and bis-(4-hydroxy-2, 6-dimethylphenyl)-sulfones are stronger acids than the corresponding sulfoxides, (VI), (VII) and (VIII) respectively. Here again, the σ-value observed from pK_{a_1} of bis-(4-hydroxy-2, 6-dimethylphenyl)sulfone is in good agreement with the calculated σ-value, clearly supporting the idea that the electron-accepting conjugation of the sulfone with the first benzene ring does not require any special angular arrangement. Incidentally, this molecule is so rigid that the Stuart model indicates that no free rotation is possible.

However, as has been mentioned earlier, the observed σ-value from the 2nd dissociation of the particular compound is slightly smaller than the calculated value, although there is an good agreement in the σ-values from the second dissociation of less hindered bis-(4-hydroxy-2-methylphenyl)-sulfone. If this difference is real, a similar consideration, discussed earlier, may be also applied here.

Ultraviolet Spectra. The ultraviolet spectra of the sulfides, sulfoxides and sulfones are shown in Figs. 1, 2 and 3, respectively and their absorption maxima and intensities are summerized in Table 3. These spectra are by no means simple, since a spectrum of any of these compounds in neutral solution is considered to be composed of three components, namely, undissociated phenol, monoanion and dianion of dissociated phenol and the separation of them is sometimes rather difficult.

The spectra of the sulfides seem to be consistent with the pK_a data. The shifts of λ_{max} by changing the solvent from neutral to alkaline solution were more remarkable than that of the reference phenol, but smaller than the shifts of the corresponding sulfoxides and sulfones. An exceptionally small shift was observed in the case of bis-(4-hydroxy-2, 6-dimethylphenyl)sulfide (IV), suggesting again a similar steric inhibition of resonance by four ortho methyl groups, operating in the photoexcitation, as in the acid dissociation of the sulfide.

In the case of sulfoxides, the red shifts going from the neutral solutions to the alkaline solutions are larger than those of the corresponding sulfides. The red shifts become more pronounced in the case of the sulfones. This again indicates greater 3-d-orbital resonance in the sulfoxides and sulfones than in the sulfides. It is interesting to note that there is no indication of steric inhibition of resonance in the ultraviolet spectra of the sulfoxides and the sulfones in alkaline media, unlike the small noticeable discrepancies observed in the pK_{a_2} values of bis-(4-hydroxy-2, 6-dimethylphenyl)sulfoxide and sulfone.

Infrared Spectra. It is known[16] that the sulfoxide group forms a strong hydrogen bonding with hydroxyl group because of the semipolar nature of the S-O linkage and hence the characteristic bands of both S-O and H-O bands shifts toward longer wavelengths. In fact, inspection of Table 4 reveals that the characteristic band of 1030—1060 cm^{-1} of sulfoxide group is missing in any of the sulfoxide compounds and a new band of 950—980 cm^{-1} appears in the spectra. A strong and broad band characteristic for hydrogen bonded hydroxyl group is also observed in the region of 3060—3160 cm^{-1} in the spectra of these sulfoxides.

Ability of hydrogen bonding formation of sulfone group is quite small as compared to that of sulfoxide group. Thus, nearly normal absorption bands of hydroxy and sulfone groups are found around 3360 cm^{-1} (for hydroxyl group) and 1120—1170 cm^{-1} (for sulfone group) respectively.

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[16] E. D. Amstutz, J. M. Hunsberger and J. J. Chessick, *J. Am. Chem. Soc.*, **73**, 1220 (1951).