[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Ultraviolet Spectra of Some Diaryl Sulfones[1]

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The spectra of a series of substituted *p*-phenylsulfonylphenols are presented as well as evidence which suggests a high double-bond character of the sulfur–oxygen bonds in *p*-(4-nitrophenylsulfonyl)-phenol.

During the investigation of the relative acidities of a series of *p*-substituted 4-phenylsulfonylphenols,[1] it was noticed that only one of the phenols, namely, *p*-(4-nitrophenylsulfonyl)-phenol (I), gave a yellow solution in an alkaline medium. Since the unique behavior of this compound is caused by the presence of a nitro substituent far removed from the site of the anion formation, it was of interest to investigate the ultraviolet spectra of a number of phenolic sulfones.

Experimental

The preparation and physical properties of the phenols were reported previously.[1] The ultraviolet spectra were determined by means of a Beckman DU spectrophotometer using solutions in 95% ethanol or in 0.01 molar aqueous sodium hydroxide. The spectral data are summarized in Table I.

TABLE I

ULTRAVIOLET SPECTRA OF *p*-(4-R-$C_6H_4SO_2$)C_6H_4OH

	In 95% Ethanol				In 0.01 *M* NaOH			
R	Max. (mμ)	$\epsilon \times 10^{-4}$	Min. (mμ)	$\epsilon \times 10^{-4}$	Max. (mμ)	$\epsilon \times 10^{-4}$	Min. (mμ)	$\epsilon \times 10^{-4}$
H	256	1.25			290	1.74		
CH_3	256	1.62	234	0.14	290	1.88	250	0.19
F	255	1.88			290	2.65	240	0.32
Cl	262	1.70	240	0.28	293	2.12	246	0.42
Br	262	1.43	244	0.30	295	1.66	254	0.42
					235	1.30		
I	266	1.68			297	2.32	264	1.01
					308[a]	2.03		
					250	1.60		
					263[a]	1.10		
CH_3O	260	2.10	240	1.0	290	2.30	254	0.52
	235	1.25			242	1.37		
H_2N	285	1.81	253	0.39	295	2.36	265	1.32
	242[b]	0.92			256[b]	1.49		
O_2N	285	1.08	265	0.99	345[c]	0.65	305	0.58
	242	1.85			265	2.22		

[a] Inflections. [b] This band is considered due to the absorption of the *p*-hydroxyphenylsulfonyl chromophore since it is relatively unchanged when the spectrum is taken in the presence of 0.1 *M* perchloric acid (244 mμ, ε 9,900). The longer wave length band is hypsochromically displaced in this acid medium to 275 mμ, ε 5,000. [c] Center of broad band.

Discussion

The maxima of *p*-substituted phenols are subject to bathochromic displacements proportional to the magnitude of the electron-withdrawing character of substituents capable of electromeric effects. This is apparent when one examines the data presented in Table II.

TABLE II

MAXIMA OF THE SPECTRA OF *p*-SUBSTITUTED PHENOLS AND PHENOLATE IONS

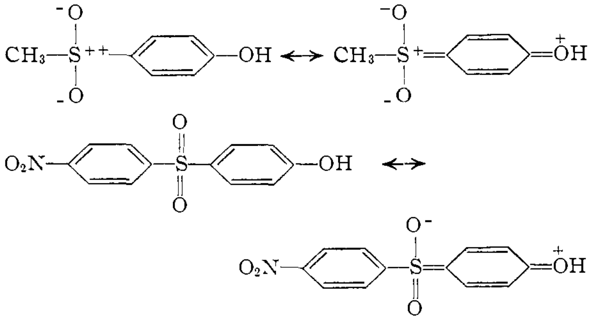
R	Ref.	Phenol[a]	Phenolate[a]	Δλ[b]
H	6	210.5	235	24.5
NH_3^+	6	218.5	...	...
CH_3SO_2[c]	3	223	248	25
Cl	6	225	244	19
$(CH_3)_2S^+$[c]	3	226	218.5	(−7.5)[d]
CH_3SO_2	4	239	269	30
$(CH_3)_2S^+$	3	242	269	27
4-$H_2NC_6H_4SO_2$	[e]	243	256	23
CO_2^-	6	245	280	35
CO_2H	6	255	...	...
4-R′$C_6H_4SO_2$	[e,f]	255–266	290–297	31–35
CH_3CO	6	275	324.5	49.5
HCO	6	283.5	330	46.5
4-$O_2NC_6H_4SO_2$	[e]	285	345[g]	60[g]
O_2N	6	317.5	402.5	85

[a] Maxima in mμ. [b] Displacement of maximum in phenolate ion (mμ). [c] *Meta* substituent. [d] See reference 3. [e] This work. [f] R′ groups are methyl, F, Cl, Br, I, Methoxyl. [g] Center of broad band.

Focusing our attention on the spectra of the phenolic sulfones, it is seen that the absorption of the *p*-R-$SO_2C_6H_4OH$ chromophore is sensitive to changes in the R group. It is possible to explain the spectral results by considering the change in electronic character of the sulfone group as a function of the nature of the R substituent. Application of the previously postulated hypothesis[1] permits the prediction that the relative double bond character of the sulfur–oxygen bonds increases in the series

$$CH_3SO_2 < p\text{-}H_2NC_6H_4SO_2 < C_6H_5SO_2 < p\text{-}O_2NC_6H_4SO_2$$

We note that this sequence agrees with the observed locations of the maxima of the respective phenolic sulfones as compared to the other phenols listed in Table II, and parallel conclusions can be drawn when the maxima of the phenolate ions or when the phenol–phenolate displacements are compared. The difference in the extent of conjugation which is suggested by these results can be represented for the two extreme sulfone types by means of the following resonance structures.



Bordwell and Boutan[2] concluded that the resonance of phenols containing the *p*-methylsulfonyl group is restricted to conjugation involving "pri-

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[1] This paper is part of a series of studies dealing with the variable electronic character of the sulfone function. For the preceding paper see H. H. Szmant and G. Suld, THIS JOURNAL, **78**, 3400 (1956).

[2] F. G. Bordwell and P. J. Boutan, *ibid.*, **78**, 87 (1956).

marily the sulfur atom, and that the presence of the sulfur–oxygen bonds is incidental" on the basis of similarities in the behaviors of methylsulfonyl and dimethylsulfonio-substituted phenols. By contrast, the degree of conjugation in I and its anion places the *p*-nitrophenylsulfonyl substituent between the strongly electromeric formyl and nitro groups.

The examination of the spectra of 4-aminophenyl phenyl sulfones tends to corroborate the conclusions concerning the variable electronic nature of the sulfone group in $-SO_2R$. Thus, the maximum of 269 mμ when R is methyl[3] is displaced to 291–292 mμ when R is phenyl[4,5] and to 336–338 mμ when R stands for 4-nitrophenyl.[4,5]

Another approach useful in examining the difference between the electronic character of the sulfur–oxygen bonds in various sulfones employs the relationship shown by Doub and Vandenbelt[6]

$$\delta\lambda'_0 \times \delta\lambda''_0 = 24.05\ (\Delta\lambda_0)$$

to relate the spectral maxima of mono- and *p*-disubstituted benzene derivatives. In this equation $\delta\lambda'_0$ and $\delta\lambda''_0$ are constants characteristic of the substituents (including a value for hydrogen), and $\Delta\lambda_0$ is the displacement of the hypothetical 180 mμ band in benzene. The results of evaluating the $\delta\lambda_0$ constants for the $R-SO_2$ groups by means of the above equation are given in Table III. This treatment demonstrates the gradual differences between the $R-SO_2$ group, and it is of interest to compare the resulting $\delta\lambda_0$ values with those reported[6] for other electron-withdrawing groups

TABLE III

THE $\delta\lambda_0$ VALUES OF $R\text{-}SO_2$ IN *p*-$X\text{-}C_6H_4\text{-}SO_2R$

R	X	$\delta\lambda_0$ (mμ)
CH_3	H, CH_3, HO, O^-, H_2N, H_3N^+	38 ± 4[a]
C_6H_5	H, HO, O^-	52 ± 4
$4\text{-}O_2NC_6H_4$	H, HO, O^-, CH_3O, CH_3, Cl, Br, NH_2	76 ± 6

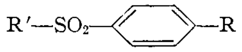
[a] The $\delta\lambda_0$ value for the *p*-$(CH_3)_2S^+$ group (where X is HO, O^-) is 39 ± 2 and thus agrees very well with the value of the methylsulfonyl group.

TABLE IV

Substituent	$\delta\lambda_0$	Substituent	$\delta\lambda_0$
NH_3^+	25.6	$COCH_3$	63.3
SO_2NH_2	37.5	CHO	68.9
CN	43.9	NO_2	91.6
CO_2H	50		

We note that the values of the methylsulfonyl and dimethylsulfonio groups are in agreement with that of the sulfonamide group, while the value of the *p*-nitrophenylsulfonyl group is located among the values of the strongest electron-withdrawing substituents capable of electromeric effects.

Having concluded that the sulfur–oxygen bonds in *p*-nitrophenyl sulfones have a high degree of double-bond character, it is of interest to examine the spectral behavior of the



chromophore in compounds where R′ is methyl, phenyl and *p*-nitrophenyl. In Table V there are listed the displacements of the maxima attributed to the *p*-$RC_6H_4SO_2$ chromophore relative to the parent compounds (R = H) for the three series.

TABLE V

DISPLACEMENTS OF MAXIMA IN *p*-$RC_6H_4SO_2R'$

	Δλ (mμ) for R′ =		
R =	CH_3[a]	C_6H_5[b]	*p*-$O_2NC_6H_4$[c]
Cl	. .	4[d]	3.5[e]
CH_3	8[f]	6[g]	6[e]
HO	22[f,h]	23[d]	23[g]
CH_3O	23[d]	18[d]	25[e]
NH_2	52[f]	56[e]	74[e]
O^-	52[f,h]	56[d]	83[g]

[a] Maximum of parent compound 217 mμ (reference 4). [b] Maximum of parent compound 235 mμ (reference 4). [c] Maximum of parent compound 261 mμ (reference 5). [d] Szmant and Dixon, unpublished work. [e] Reference 5. [f] Reference 4. [g] This work. [h] The displacements (reference 3) in *p*-dimethylsulfoniophenol and phenolate are 22 and 49 mμ, respectively, and thus in good agreement with the above values.

We notice that the displacements in the methyl and phenyl sulfones are of the same magnitude as those observed in the *p*-nitrophenyl sulfones except when the substituents are strongly electron releasing, and then the presumed double-bond character of the sulfone promotes an increase in conjugation.

It is appropriate to point out that while the ultraviolet spectra reveal a considerable difference between the phenols containing either a *p*-methylsulfonyl or *p*-dimethylsulfonio group and the *p*-(4-nitrophenylsulfonyl) substituent, these same substituents cause only slight variations in the ionization constants of the phenols.[1] This apparent discrepancy is understandable if one considers that the position of the equilibrium involving the ionization of a phenol is affected primarily by the degree of resonance stabilization of the phenolate ion, while the displacements in the absorption spectra result from the relative energy levels of the ground and excited states. The increased conjugation in the *p*-nitrophenyl sulfones described in this paper would be expected to decrease the energy of excitation and thus cause the observed bathochromic displacements.

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[3] E. A. Fehnel and M. Carmack, THIS JOURNAL, **72**, 1292 (1950).

[4] A. Mangini and R. Passerini, *Boll. sci. facolta chim. ind. Bologna*, **8**, (1950); *C.A.*, **45**, 3241 (1951).

[5] H. H. Szmant and J. J. McIntosh, THIS JOURNAL, **73**, 4356 (1951).

[6] L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).