

## Organic Sulfur Compounds. XII. The Ultraviolet and Infrared Spectra of the Substituted Benzenesulfinic Acids and Their Esters

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(Received January 7, 1966)

The ultraviolet spectra of several substituted benzenesulfinic acids and their ethyl esters have been recorded, and the assignments of the absorption have been discussed briefly.

There have been relatively few studies of the ultraviolet spectra of the sulfinic acids and their esters, although many systematic investigations have been published on the related sulfoxides, sulfones and sulfides.<sup>1-3)</sup> Detoni and her collaborator<sup>4)</sup> measured the ultraviolet spectra of benzenesulfinic acid and *p*-toluenesulfinic acid in ethanol, but no discussion was given. Brederick et al.<sup>5)</sup> studied the ultraviolet spectra of the above two compounds in heptane, methanol and water; they found that the spectra of the dissociated anion was overlapped on those of the free acid in the hydroxylic solvents. They pointed out the close similarity between the spectrum of the undissociated acid and that of the corresponding ester, and also the presence of a similar absorption band in the spectrum of the sulfoxide. Later, Ritchie<sup>6)</sup> estimated the dissociation constants of several benzenesulfinic acid derivatives by the ultraviolet spectroscopic method, but he presented no details of the spectra themselves.

### Results and Discussion

**The ultraviolet Spectra of the Sulfinic Acids in Water.**—The ultraviolet spectrum of the sulfinic acid in water is actually that of the completely dissociated anion, as has been pointed out by Brederick,<sup>5)</sup> since the sulfinic acid has a rather strong acid character. When the solution was increased in acidity by the addition of hydrochloric acid, the absorption spectrum of the undissociated acid

appeared, making it possible to estimate the dissociation constant of the sulfinic acid. For example, the  $pK_a$  of *p*-chlorobenzenesulfinic acid could be estimated as 1.14 from the absorption curves shown in Fig. 1.

Aliphatic sulfinic acid exhibited no absorption maximum in the ordinary ultraviolet region, as may be seen in Fig. 2. This fact indicates that both the  $\pi$ - $\pi^*$  and  $n$ - $d\pi$  transitions in the  $SO_2H$  or the  $SO_2^-$  group need high energies corresponding to absorptions well below 200  $m\mu$ ; This situation may be easily understood by considering that the aliphatic sulfoxides have an  $n$ - $d\pi$  absorption at around 210  $m\mu$ .<sup>16)</sup>

The values of the absorption maxima of the substituted benzenesulfinic acids and their anion are listed in Table I.

The spectra of the anions are very close to those of the parent mono-substituted benzenes in the shape of the absorption curve and also in the wavelength of the band maximum. Only slight red shifts

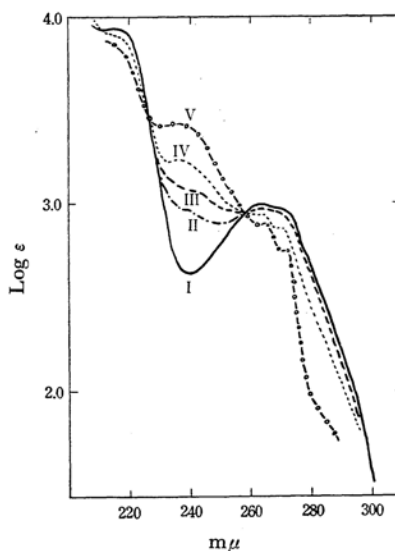


Fig. 1. Ultraviolet spectra of *p*-chlorobenzenesulfinic acid.

Solvent: I)  $H_2O$ , II) 0.01  $N$  HCl, III) 0.02  $N$  HCl, IV) 0.05  $N$  HCl, V) 1.00  $N$  HCl

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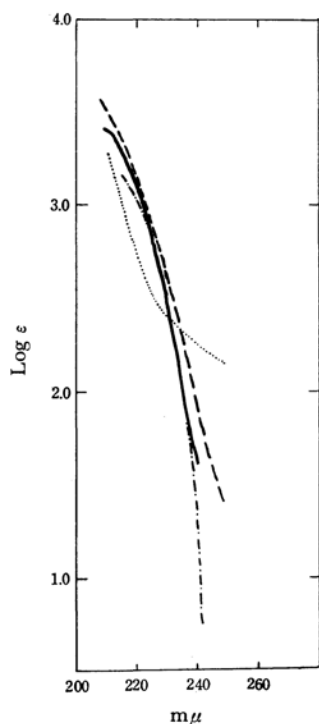
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TABLE I. ULTRAVIOLET SPECTRA OF SUBSTITUTED BENZENESULFINIC ACIDS IN WATER  
 $\lambda_{max}$  in  $m\mu$  and  $\log \epsilon$  (in parenthesis)

| Substituent         | Acid        |            |             | Anion       |           |
|---------------------|-------------|------------|-------------|-------------|-----------|
|                     | $^1L_a$     | W          | $^1L_b$     | $^1L_a$     | $^1L_b$   |
| H                   | 215** (3.8) | 237 (3.4)  | 265 (2.8)   | 215 (3.9)   | 265 (2.9) |
| <i>p</i> -Methyl    | 223 (3.8)   | 240 (3.5)  | 265 (2.8)   | 223 (3.9)   | 265 (3.0) |
| <i>p</i> -Chloro    | 225 (4.3)   | 245 (4.0)  | 270 (3.2)   | 225 (4.2)   | 270 (3.2) |
| <i>p</i> -Bromo     | 230 (4.2)   | ~250 (3.8) | 275** (2.9) | 230 (4.2)   | 275 (3.2) |
| <i>p</i> -Methoxy   | 235* (4.1)  |            | 275 (3.1)   | 232 (4.1)   | 275 (3.3) |
| <i>p</i> -Acetamido | 255* (4.2)  |            |             | 248 (4.2)   | 280* (~3) |
| <i>o</i> -Nitro     |             | 265* (4.0) |             | 270* (4.0)  |           |
| <i>o</i> -Methyl    | 220 (3.8)   | 240 (3.5)  | 265 (3.0)   | 225 (3.9)   | 265 (3.5) |
| <i>o</i> -Methoxy   | 222 (3.8)   | 245 (3.3)  | 282 (3.5)   | 225 (3.9)   | 280 (3.5) |
| <i>o</i> -Nitro     |             | 265* (3.7) |             | 265 (3.7)   |           |
| <i>o</i> -Carboxy   | 232 (3.7)   |            | 280 (3.2)   | 240 (3.5)** | 278 (3.0) |

\* Superposition of several bands. See text.

\*\* Shoulder.

Fig. 2. Ultraviolet spectra of *n*-butanesulfonic acid and its ethyl ester.

— Acid in  $H_2O$   
 --- Acid in  $10^{-3} N NaOH$   
 ..... Acid in  $1 N HCl$   
 - · - Ethyl ester in 95% ethanol

are observed in the maximum of the  $^1L_a$  band compared to those of the corresponding mono-substituted benzenes, suggesting the weakness of the interaction between the sulfinate anion group and the  $\pi$ -electron orbitals of the benzene ring.

The Stuart model of the molecule suggested the presence of a large steric interference between the sulfinate group and a bulky *o*-substituent. Al-

though *o*-nitrobenzenesulfonic acid has almost the same absorption maximum as that of the *p*-isomer, its extinction coefficient is smaller by 0.3 unit in  $\log \epsilon$ , suggesting that the nitro group is rotated out of the benzene plane to some degree.

In the absorption spectra of the undissociated acids, the presence in 240–260  $m\mu$  of a new absorption should be noticed, an absorption which is not observed in the anion. Since similar absorptions are observed in the alkyl aryl sulfoxides, this band will here be designated as the W-band, according to the Jaffé's notation.<sup>3c)</sup> A similar band exists in the spectrum of the corresponding ethyl sulfonates, as is shown in Table II. This W-band may be attributed to an excitation of the lone pair electrons of the sulfur atom into an anti-bonding orbital of the S–O bond or into a vacant 3d orbital of the sulfur atom (this difference depends only on the amount of the double bond character of the sulfoxide S–O bond; the exact estimation is still open to debate); the band appears in a longer wavelength region than the bands of the aliphatic sulfoxides, as a result of the conjugation to the benzene ring. Another postulation involving the excitation of a lone pair of the sulfur atom to an unoccupied orbitals of the aromatic electron system rather than to the sulfinyl group is also possible. With *p*-toluenesulfonic acid, this W-band shifts its maximum from 255  $m\mu$  in heptane,<sup>5)</sup> over 245  $m\mu$  in ethanol to 240  $m\mu$  in diluted hydrochloric acid, and thus reveals its  $n$ -electron donating character. In the sulfinate anions, this W-band shifts to a much lower wavelength, under 200  $m\mu$ , as a result of the contribution of the negatively charged oxygen atom; this situation is the same as in the case of the carboxylic acid and its anion. Since *o*-toluenesulfonic acid, in which the sulfinoxy group is considered to rotate out of the benzene plane due to interaction with a bulky *o*-methyl group, shows its W-band at nearly the same wavelength as in the *p*-isomer, the coplanarity seems

not to be an important requirement in the conjugation between the sulfinyl group and the aromatic  $\pi$ -electron system, as is the case in the aromatic sulfones.<sup>3a,3c,7,8</sup> The existence of the W-band in nitro or carboxyl substituted benzenesulfinic acids is not clear due to the superposition of a strong charge transfer band in these compounds.

### The Ultraviolet Absorption of the Ethyl Ester of the Substituted Benzenesulfinic Acids.

—These are shown in Table II. Aliphatic sulfinate ester exhibited only an end absorption in the ultraviolet region, as in the free acid, indicating the high transition energy of the  $n\text{-}d\pi$  excitation in the sulfinate ester group (Fig. 2).

TABLE II. ULTRAVIOLET SPECTRA OF ETHYL BENZENESULFINATES

| $\lambda_{max}$ (m $\mu$ ) and log $\epsilon$ (in parenthesis) |                  |              |               |
|----------------------------------------------------------------|------------------|--------------|---------------|
| Substituent                                                    | Solvent          | $^1L_a$      | W + $^1L_b$   |
| H                                                              | Methanol         | 216 (3.89)   | 246 (3.52)    |
|                                                                | <i>n</i> -Hexane | 215 (3.96)   | 257 (3.46)    |
| <i>p</i> -Methyl                                               | Methanol         | 224 (3.95)   | 243 (3.70)    |
|                                                                | <i>n</i> -Hexane | 223 (4.00)   | 255 (3.51)    |
| <i>p</i> -Chloro                                               | Methanol         | 228 (4.13)   | 250 (3.73)    |
|                                                                | <i>n</i> -Hexane | 227 (4.14)   | 260 (3.58)    |
| <i>p</i> -Bromo                                                | Methanol         | 233 (4.17)   | 250 (3.80)    |
|                                                                | Ether            | 232 (4.21)   | 258 (3.75)    |
|                                                                | <i>n</i> -Hexane | 232 (4.20)   | 260 (3.71)    |
| <i>p</i> -Methoxy                                              | Methanol         | 249 (4.13)*  |               |
|                                                                | <i>n</i> -Hexane | 235 (4.07)   | 252 (3.94)    |
| <i>p</i> -Cyano                                                | Methanol         | 231 (4.24)   | 270 (3.64)    |
|                                                                | <i>n</i> -Hexane | 230 (4.18)   | 275 (3.50)    |
| <i>p</i> -Nitro                                                | Methanol         | 254 (4.03)** | 280 (3.79)*** |
|                                                                | <i>n</i> -Hexane | 250 (4.07)   | 288 (3.63)    |

\* Broad band, probably superposition of  $^1L_a$  and W +  $^1L_b$ .

\*\* Charge transfer band.

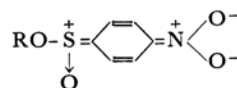
\*\*\* Shoulder.

There are two absorptions of distinctly different characters in the ultraviolet spectra of the substituted benzenesulfinic esters, one at a short wavelength, similar to the  $^1L_a$  band of the corresponding mono-substituted benzenes, and the other in the long wavelength side. The shifts of the  $^1L_a$  band from the position of the parent mono-substituted benzene are slightly larger than those in the sulfinate anion, suggesting a somewhat stronger interaction of the sulfinate ester group with the aromatic  $\pi$ -orbital than that of the sulfinate anion group, although the interaction is still weak compared with those of nitro or carbonyl groups.

The long wavelength band is considered to be an overlapping of the W-band and  $^1L_b$  band. The optical active property of the W-band has been demonstrated clearly by optical rotatory dispersion and circular dichroism measurements of the optically

active *l*-menthyl *p*-toluenesulfinate and *p*-methoxybenzenesulfinate,<sup>7</sup> thus confirming the assignment of this transition to a sulfinyl group origin, although in that earlier paper the long wavelength band has been postulated to be an overlapping of a perturbed  $^1L_a$  benzene transition and the W-band. Discussing the problem of the stereochemistry of the sulfoxides and sulfinate esters, Mislow et al.<sup>8b</sup> assumed the long wavelength band to be arisen from the interaction of the  $^1L_b$  band with the sulfoxide  $(3sp^3)^2 \rightarrow (3sp^3)(3d)$  transition.

The absorption maximum of the long wavelength band does not vary much with the kind of substituent. In the *p*-methoxy derivative, the W-band shows slight blue shift, which is characteristic of  $n\text{-}\pi$  transition. In *p*-nitro and *p*-cyano derivatives, the existence of the W-band again becomes uncertain; probably it is covered by the absorption of the strong charge transfer band. The 250 m $\mu$  absorption of ethyl *p*-nitrobenzenesulfinate shows a red shift in a polar solvent, suggesting that this band is a charge transfer band, similar to that of nitrobenzene.<sup>9</sup> Since the absorption maximum of this compound does not differ much compared with that of nitrobenzene itself (252 m $\mu$  in heptane, 259.5 m $\mu$  in ethanol), the contribution of the lone pair of the sulfur atom could not be ascertained reliably, but the increased extinction coefficient of the long wavelength band suggests the overlapping of the W-band on the 280 m $\mu$  band of nitrobenzene or on the 271 m $\mu$  band of *p*-cyano derivative (both  $^1L_b$  bands). The hypsochromic shift of these long wavelength bands in a polar solvent also supports this interpretation. If this could be true, the W-band may be said to show a large red shift upon coupling with an electron attractive substituent. On the other hand, the nearly-same position of the charge transfer excitation around 250 m $\mu$  seems to indicate the absence of a large contribution of the electrometric polar form in the excited state, as shown below:



In this respect, the sulfinoyl group differs greatly from the sulfide group (for instance, *p*-nitrothioanisole has  $\lambda_{max}$  at 338 m $\mu$ , with log  $\epsilon = 4.12$ ).

In conclusion, the sulfinoyl group and the alkoxy-sulfinyl group may be considered to have only a weak electron attractive conjugation property,

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and at the same time to be very weakly electron donating.

**The Infrared Spectra of the Ethyl Esters of Substituted Benzenesulfinic Acids.**—The spectra were measured in carbon tetrachloride and also in the pure liquid state. The wave numbers of the S—O stretching vibration are shown in Table III. The absorption maximum in the pure liquid is slightly lower in wave number ( $2\text{--}9\text{ cm}^{-1}$ ) than that in a solution, probably because of the association. Ethyl *n*-butanesulfinate absorbs at  $1132\text{ cm}^{-1}$  ( $\text{CCl}_4$ , and neat), which is almost the same as, or even rather lower than, the S—O stretching of ethyl benzenesulfinate. A similar phenomenon has been observed in the sulfoxides<sup>10)</sup> and interpreted as indicating the absence of any strong conjugation between the aromatic ring and the sulfinyl group.

TABLE III. INFRARED SPECTRA OF ETHYL BENZENESULFINATES. S—O STRETCHING VIBRATION IN  $\text{cm}^{-1}$

| Substituent       | H    | <i>p</i> -CH <sub>3</sub> | <i>p</i> -CH <sub>3</sub> O | <i>p</i> -Cl | <i>p</i> -Br | <i>p</i> -NO <sub>2</sub> |
|-------------------|------|---------------------------|-----------------------------|--------------|--------------|---------------------------|
| Neat              | 1132 | 1134                      | 1126                        | 1136         | 1138         | 1138                      |
| in $\text{CCl}_4$ | 1136 | 1136                      | 1135                        | 1142         | 1142         | 1149                      |

The Hammett plot of the wave numbers of the S—O stretching against  $\sigma$  value shows an approximately linear correlation. Since there have been closely related studies of the methyl esters of the substituted benzenesulfinic acids,<sup>11)</sup> further discussion will be omitted here.

### Experimental

**Materials.**—*n*-Butanesulfinic acid was prepared from *n*-butyl bromide by the Grignard method.<sup>12)</sup> Ethyl *n*-butanesulfinate was synthesized from sulfinyl chloride and ethanol, and boiled at  $80^\circ\text{C}/10\text{ mmHg}$ .<sup>13)</sup> *o*-Toluenesulfinic acid, m. p.  $80^\circ\text{C}$ , was prepared from

sulfonyl chloride by reduction with zinc. *p*-Chlorobenzenesulfinic acid, m. p.  $93\text{--}94^\circ\text{C}$ , was obtained by saturating a *p*-chlorobenzenediazonium chloride solution with sulfur dioxide.<sup>14)</sup> *p*-Bromobenzenesulfinic acid, m. p.  $114^\circ\text{C}$ , was prepared by Friedel-Crafts' synthesis from bromobenzene and sulfur dioxide.<sup>15)</sup> *p*-Methoxybenzenesulfinic acid, m. p.  $97\text{--}98^\circ\text{C}$ , was prepared from anisol in a similar way and was purified from water.<sup>15)</sup> *o*-Methoxy derivative, m. p.  $98\text{--}99^\circ\text{C}$ , was prepared from diazotized *p*-anisidine.<sup>16)</sup> *p*-Acetylaminobenzenesulfinic acid, m. p.  $155^\circ\text{C}$  (with decomposition), was prepared by reducing sulfonyl chloride with sodium sulfite.<sup>17)</sup> *p*-Nitrobenzenesulfinic acid, m. p.  $135^\circ\text{C}$ , was obtained in a similar way.<sup>18)</sup> *o*-Nitro-derivative, m. p.  $130^\circ\text{C}$ , was prepared by reducing sulfonyl chloride with stannous chloride and hydrochloric acid in ethanol.<sup>19)</sup> *o*-Carboxybenzenesulfinic acid, m. p.  $125^\circ\text{C}$ , was obtained by the diazonium method and was recrystallized from acetic acid.<sup>16)</sup> Ethyl esters of the benzenesulfinic acids was prepared by treating the sodium salt with ethyl chlorocarbonate in ethanol.<sup>20)</sup>

The ultraviolet spectra were taken on a Beckmann DU quartz spectrophotometer. The concentration of the solution was  $10^{-4}\text{--}10^{-5}\text{ mol/l}$ . The infrared spectra were recorded with a Perkin-Elmer infrared spectrometer Model 21. The dissociation constants were calculated from the variation of the transmission with the change in pH. The  $\text{p}K_a$  values obtained for benzenesulfinic acid, *p*-toluenesulfinic acid and *p*-chlorobenzenesulfinic acid were 1.58, 1.70 and 1.14 respectively. The figures in the literature are 1.29,<sup>21)</sup> 1.46,<sup>22)</sup> 1.84,<sup>23)</sup> 1.21<sup>6)</sup> for the first compound; 1.60,<sup>22)</sup> 1.99,<sup>23)</sup> 1.24<sup>6)</sup> for the second, and 1.09 for *p*-bromobenzenesulfinic acid.<sup>6)</sup>

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