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157. Tsutomu Momose, Yo Ueda, and Shujiro Goya : Organic Analysis. XVI.*[1] Ultraviolet Spectral Study of Substituent Effect on Benzenesulfonamide.

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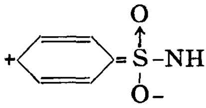
Benzenesulfonamide shows considerably strong absorption in the ultraviolet range due to contributions of the structures , etc., and several isolated papers have reported studies concerning the nature of its numerous derivatives. Kumler, *et al.*[1] discussed the ultraviolet absorption spectra of benzenesulfonamide, and *p*- and *m*-aminobenzenesulfonamide in acid, neutral, and alkaline solutions. Vandenbelt, *et al.*[2] and Robinson, *et al.*[3] reported the effect of pH on the spectra of several sulfonamide compounds. Grammaticakis[4] compared the spectra of *o*-, *m*-, and *p*-substituted benzenesulfonamides, and Iritani[5] and Maschka, *et al.*[6] studied the nature of a number of benzenesulfonamide derivatives. It is surprising that very little is known about substituent effect on a compound. This paper describes the spectral effect of substituents in the *para*-position of benzenesulfonamide and of N¹-substituted benzenesulfonamides, dealing with 47 sulfonamide compounds.

Experimental

Some of the compounds measured were previously prepared in this laboratory,[7] and others were synthesized in accordance with the literature and their purity checked by their melting point.

Absorption spectra were measured with a Beckman Model DK-2 Recording Spectrophotometer in a concentration of 5×10^{-4} to $5\times10^{-5}M$, using 95% EtOH as a solvent, and in a wave-length region of 210~360 mμ.

Results and Discussion

Table I shows the spectral data of *para*-substituted benzenesulfonamides and the shift of wave length of the first primary bands, measured in 95% EtOH. Fig. 1 shows some typical curves. Both electron-donating and electron-attracting groups give a bathochromic effect on benzenesulfonamide. This effect is larger on the first band than on the second, and when the first band shifts to a longer wave-length region, the second band loses its fine structure, or sometimes disappears as seen in amino, acetamido, and nitro compounds.

In electron-donating groups of substituents, bathochromic shift occurs in the order of $CH_3 < NH_2CH_2 = AcNHCH_2 < OCH_3 < OH < AcNH < NH_2$, while in electron-attracting groups, the order is $COOH < CN < CHO < NO_2$.

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*[1] Part XV : Talanta (1959), in press.

*[2] Katakasu, Fukuoka (百瀬 勉, 上田 陽, 合屋周次郎).

1) W. D. Kumler, L. A. Strait : J. Am. Chem. Soc., **65**, 2349(1943).

2) J. M. Vandenbelt, L. Doub : *Ibid.*, **66**, 1633(1944).

3) E. J. Robinson, L. F. Pekrul : *Ibid.*, **67.**, 1186(1945).

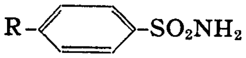
4) P. Grammaticakis : Bull. soc. chim. France, [5], **21**, 92(1954).

5) N. Iritani : Yakugaku Zasshi, **65**, 507(1945).

6) A. Maschka, M. Stein, W. Traner : Monatsh., **84**, 1071(1953); **85**, 168(1954).

7) T. Momose, Y. Ueda : Yakugaku Zasshi, **67**, 23(1947); M. Ishidate, T. Momose : *Ibid.*, **67**, 214 (1947).

TABLE I.



R-⟨ ⟩-SO_2NH_2

R	λ_{max} (mμ)	log ε	λ_{max} (mμ)	log ε	λ_{max} −217.5 (mμ)
H	217.5	3.95	264	2.80	0.0
CH_3	224	4.10	262	2.60	6.5
OH	237	4.23	264	3.19	19.5
CH_3O	235.5	4.27	263	3.11	18.0
Cl	227	4.08	248	4.32	9.5
COOH	234.5	4.21	276	3.14	17.0
CN	236	4.33	276.5	3.20	18.5
CHO	250	4.18	283.5	3.19	32.5
NO_2	261	4.07			43.5
NH_2	262	4.28			44.5
NH_2CH_2	225	4.08	262	2.67	7.5
AcNH	257	4.43			39.5
$AcNHCH_2$	225	4.12	262.5	2.69	7.5
$AcNHC_2H_4$	225	4.15	262	2.66	7.5
$AcNH(CH_3)CH$	225	4.16	261.5	2.67	7.5
$AcN(CH_3)CH_2$	224	4.15	263	2.70	6.5
$AcNH(CH_3)C_3H_5$	225.5	4.17	262	2.68	8.0
$NH_2CONHCH_2$	225	4.11	262	2.69	7.5
$NH_2CONHN{=}CH$	295	4.45			77.5

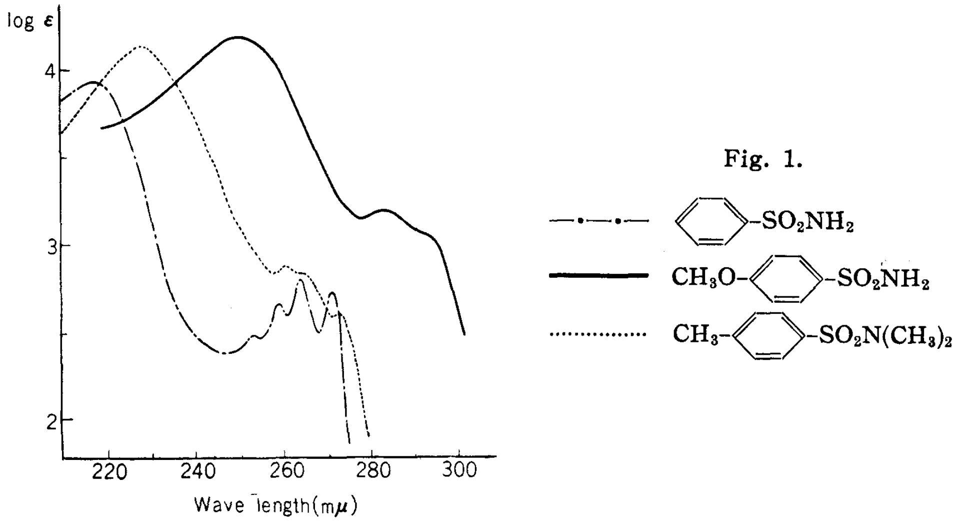


Fig. 1.

It is interesting to compare displacement of the absorption maxima from monosubstituted benzenes with the opposite character of substituents. As examples of electron-donating groups, phenol and aniline absorb respectively at 211 and 230 mμ,[8] while *p*-hydroxybenzenesulfonamide and sulfanilamide absorb respectively at 237 and 262 mμ. In such a case, large displacement can be seen from the isolated monosubstituted benzenes. In electron-attracting groups, *p*-carboxybenzenesulfonamide and *p*-nitrobenzenesulfonamide absorb respectively at 234.5 and 261 mμ, which lie in the neighborhood of the absorption maximum of benzoic acid at 230 mμ and of nitrobenzene at 286.5 mμ.[8]

This difference in displacement suggests that the first band is greatly affected by the electronic interaction of two groups attached to the benzene ring. Electron-donating groups may easily interact with *para*-substituted electron-attracting sulfonamide group across the ring, while electron-attracting groups may be hindered from such interaction. For example, *p*-hydroxybenzenesulfonamide shows a large bathochromic shift

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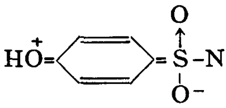
8) L. Doub, J. M. Vandenbelt: J. Am. Chem. Soc., **69**, 2714(1947).

due to contribution of the structures  $\mathrm{H\overset{+}{O}{=}C_6H_4{=}\overset{\overset{O}{\uparrow}}{\underset{O^{-}}{S}}{-}NH_2}$, etc. Such correlation of the displacement of spectra with the electronic nature of a substituent agrees with the results obtained in numerous disubstituted benzenes by Doub, *et al.*[8] and by Rao,[9] and in several *para*-substituted phenyl methyl sulfones by Fehnel, *et al.*[10] Fig. 2 also confirms the above suggestion showing that the magnitude of the shift is approximately linear to Hammett's σ[11] only in the electron-donating groups.

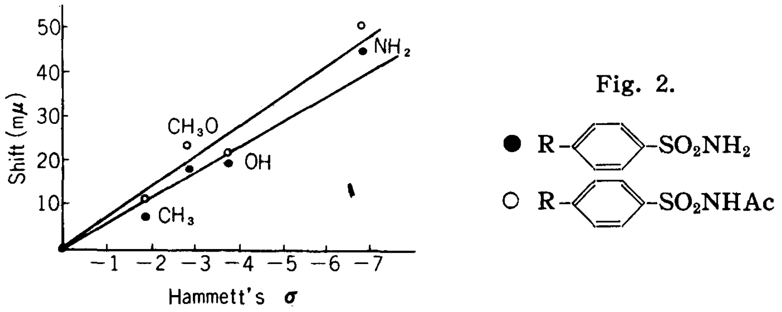
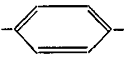


Fig. 2.

Table II. R_1--$SO_2NR_2R_3$

R_1	R_2	R_3	λ_{max} (mμ)	log ε	λ_{max} (mμ)	log ε	λ_{max} −217.5 (mμ)
H	H	CH_3	219	4.03	264.5	2.93	1.5
CH_3	〃	〃	226.5	4.11	262.5	2.73	9
NH_2	〃	〃	264	4.46			46.5
AcNH	〃	〃	260.5	4.37			43
NH_2CH_2	〃	〃	224.5	4.04	266	2.80	7
CHO	〃	〃	227.5	3.90	253	3.98	10
HON=CH	〃	〃	265	4.31	296.5	3.49	47.5
COOH	〃	C_2H_5	238	4.16	276	3.26	20.5
CHO	〃	〃	228	3.89	253.5	3.99	10.5
HON=CH	〃	〃	265.5	4.32			48
H	CH_3	CH_3	221.5	3.97	264.5	2.98	4
CH_3	〃	〃	229	4.10	262	2.83	11.5
〃	C_2H_5	C_2H_5	231	4.06			13.5

In Table II are shown the spectral data of N^1-mono- and N^1,N^1-di-alkyl-sulfonamide derivatives. Limiting attention to *para*-substituted electron-donating groups, the first primary bands of N^1-alkylsulfonamides have their absorption maxima at a wave lengths longer by 2~3 mμ than corresponding *para*-substituted benzenesulfonamides. This fact suggests that alkylsulfonamide group has a larger electron-attracting character than sulfonamide group. N^1,N^1-Dialkylsulfonamides show more bathochromic shifts of 2~4 mμ than monoalkylsulfonamides in the same bands, and furthermore, ethyl group shows a larger shift than methyl group.

In N^1-acetylsulfonamide group, a larger electron attraction may be expected than sulfonamide group. Table III shows the spectral data of the former derivatives and indicates that the electron-donating groups in the *para*-position effect bathochromic displacement of 3~4 mμ in the first primary bands from the corresponding benzenesulfonamides. Approximate linear correlation of the shift with Hammett's σ, which was mentioned earlier, also holds in this series and the fact is also shown in Fig. 2.

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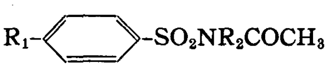
[9] C. N. Ramachandra Rao: Chem. & Ind. (London), **1956**, 667; *ibid.*, **1957**, 1239.

[10] E. A. Fehnel, M. Carmack: J. Am. Chem. Soc., **72**, 1292(1950).

[11] H. H. Jaffé: Chem. Revs., **53**, 191(1953).

TABLE III.



R_1	R_2	λ_{max} (mμ)	log ε	λ_{max} (mμ)	log ε	λ_{max} −217.5 (mμ)
H	H	220	4.02	266	3.04	2.5
CH_3	〃	228	4.11	263	2.83	10.5
OH	〃	239	4.14			21.5
CH_3O	〃	241	4.20	277	2.86	23.5
NH_2	〃	269	4.26			51.5
AcNH	〃	261.5	4.36			44
$AcNHCH_2$	〃	228.5	4.15	264	2.93	11
Ac_2NCH_2	〃	221	4.27	264	2.97	3.5
$AcNH(CH_3)CH$	〃	228.5	4.17	266	2.93	11
$AcN(CH_3)CH_2$	〃	227.5	4.14	267	2.90	10
$Ac_2NC_2H_4$	〃	225	4.34	267	3.00	7.5
COOH	〃	234	4.16	278.5	3.23	16.5
CN	〃	235	4.15	277.5	3.26	17.5
$AcNHCH_2$	CH_3	226	4.10	267	2.80	8.5
COOH	C_2H_5	236.5	4.23	279	3.28	19

Summary

Ultraviolet absorption of 47 benzenesulfonamide derivatives was measured in 95% ethanol. Both electron-donating and -attracting groups in the *para*-position of sulfonamide group effected a shift to longer wave lengths. The correlation of displacement of the absorption maxima with the electronic character of substituents was discussed, and approximately linear relation of the shift with Hammett's σ was found in electron donating groups.

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