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158. Tsutomu Momose, Yo Ueda, and Shujiro Goya : Organic Analysis. XVII.[*1]
Some Observations on Ultraviolet Spectra of Phenyl Sulfone Derivatives.

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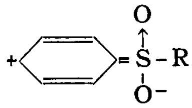
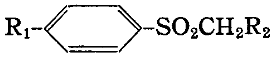
Phenyl sulfone compound absorbs ultraviolet light in strong intensity due to contributions of structures  $^{+}C_6H_5{=}\overset{O}{\overset{\uparrow}{S}}(O^-)-R$, etc., and a few papers have appeared in the literature. Fehnel, *et al.*[1] discussed the nature of absorption spectra of several phenyl methyl sulfone derivatives, and Szmant, *et al.*[2] and Leandri, *et al.*[3] studied bathochromic effect of substituents on the spectra of diphenyl sulfone. This paper describes spectral effect of substituents on phenyl methyl sulfone, comparing with those of sulfonamides described in the preceding paper[*1] of this series.

Experimental

Some compounds were previously[4] prepared in the writers' laboratory and others were prepared in accordance with the literature.

Ultraviolet absorption spectra were measured with a Beckman Model DK-2 Recording Spectrophotometer, using 95% EtOH as a solvent, in a wave-length range of 210~360 mμ. Results are shown in Table I.

Table I. 

R_1	R_2	λ_{max} (mμ)	log ε	λ_{max} (mμ)	log ε
$HCONHCH_2$	H	224	4.13	266	2.87
$AcNHCH_2$	〃	220	4.21	266	2.84
$HCl \cdot NH_2(CH_3)CH$	〃	220.5	4.08	265.5	2.99
$HCl \cdot NH_2C_2H_4$	〃	222.5	4.13	265.5	2.90
AcNH	〃	260	4.36		
COOH	〃	230	4.23	277.5	3.23
CN	〃	229	4.27	276.5	3.22
CHO	〃	223	3.99	273	3.03
HON=CH	〃	265	4.28		
NH_2CH_2	〃	222	4.00	260.5	2.83
$HCl \cdot NH_2CH_2$	CH_3	221	4.08	266	3.02
$HCl \cdot NH_2(CH_3)CH$	〃	221.5	4.11	265.5	3.02
$HCl \cdot NH_2C_2H_4$	〃	222.5	4.14	266	2.88
$(AcO)_2CH$	〃	221	4.18	266.5	3.12
NH_2CH_2	I	230	4.10	274.5	3.16
$HCONHCH_2$	〃	229	4.17	266.5	3.22
CH_3	COOH	226	4.13	261.5	2.86
NH_2CH_2*	〃	221.5	4.13	267	3.05
CN	〃	230	4.19	276	3.19
CHO	〃	226	4.01	274	3.09
HON=CH	〃	266	4.28		
CN	$COOC_2H_5$	231	4.28	278	3.26
$HCl \cdot NH_2CH_2$	$COCH_3$	222.5	4.21	267.5	3.20
$HCONHCH_2$	〃	226	4.19	266.5	3.02
CN	〃	231	4.27	278	3.29

* Measured in H_2O.

[*1] Part XVI : This Bulletin, **7**, 858(1959).

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

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

2) H.H. Szmant, J.M. Dixon : *Ibid.*, **78**, 4384(1956).

3) G. Leandri, A. Mangini, R. Passerini : Gazz. chim. ital., **84**, 73(1954) (C. A., **50**, 223(1956)).

4) T. Momose, T. Shoji : Yakugaku Zasshi, **70**, 22(1950); **71**, 681(1951).

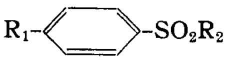
Discussion

When attention is limited to the bathochromic shift of the first primary bands of *para*-substituted phenyl methyl sulfones, they occur in the following order, with reference to some data from the literature,[1] in two different types of substituents.

In electron-donating groups: $CH_3 < AcNHCH_2 < NH_2CH_2 < CH_3O < OH < AcNH < NH_2$.

In electron-attracting groups : $CHO < CN < COOH < NO_2$.

The former almost coincides with the order of bathochromic shift obtained in *para*-substituted benzenesulfonamides, whereas the latter is reversed from the order of electron-attracting groups attached to benzenesulfonamide, except the nitro group. Furthermore, it is interesting to note that the magnitude of the shift of phenyl methyl sulfones is larger than that of benzenesulfonamides in electron-donating groups, and smaller in electron-attracting groups. These data are shown in Table II.

Table II. 

R_2 / R_1	NH_2		CH_3		$\Delta\lambda' - \Delta\lambda$
	λ_{max} (mμ)	$\Delta\lambda$	λ_{max} (mμ)	$\Delta\lambda'$	
H	217.5		217		
CH_3	224	6.5	224.5	7.5	+ 1
CH_3O	235.5	18	238.5	21.5	+ 3.5
OH	237	19.5	239	22	+ 2.5
NH_2	262	44.5	267	50	+ 5.5
AcNH	257	39.5	260	43	+ 3.5
COOH	234.5	17	230	13	− 4
CN	236	18.5	229	12	− 6.5
CHO	250	32.5	223	6	−26.5
NO_2	261	43.5	248	31	−13

This fact reveals that the methyl-sulfone group has a larger electron attraction than the sulfonamide group, which is in agreement with Hammett's σ of 0.728 for p-SO_2CH_3 and 0.621 for p-SO_2NH_2. Consequently, electron-donating groups may easily interact with the methyl-sulfone group across the benzene ring, displacing the spectral maxima to a longer wave length. In electron-attracting groups, on the contrary, the attraction may be decreased by increased electron-attracting power of the methyl-sulfone group, and may give smaller shift of the absorption maxima.

Table I also shows that introduction of an electron-attracting group like I, $COCH_3$, or COOH in the methyl group of methyl-sulfones displaces the first primary band to a longer wave-lengths, but the magnitude of shift is smaller than that of the same substituents on sulfonamide. This difference is particularly evident in *para*-substituted phenyl ethyl sulfone and its corresponding N-methylsulfonamide. The former compound absorbs in almost the same region as the corresponding phenyl methyl sulfone, whereas the latter absorbs in a longer wave-lengths than the corresponding sulfonamide. This fact may prove that electronic interaction of sulfonyl group with the substituents is interrupted by the CH_2 group in sulfone derivatives, but it easily occurs in sulfonamide derivatives by the resonating character of the unshared electron pairs of the nitrogen atom.

Summary

Ultraviolet absorption spectra of phenyl methyl sulfone derivatives were compared with those of benzenesulfonamide derivatives. Introduction of an electron-donating group in the *para*-position of phenyl methyl sulfone causes a larger bathochromic shift of the first primary band than that in the *para*-position of benzenesulfonamide, whereas the introduction of electron-attracting group gives hypsochromic shift from the corresponding benzenesulfonamide. Effect of substituents attached to the methyl group of methyl-sulfones on the spectra was also discussed.

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