BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1878—1881 (1969)

The Dipole Moments of Diphenyl Sulfide, Sulfoxide, Sulfone, and Their Derivatives

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(Received December 27, 1968)

The electric dipole moments of diphenyl sulfide, sulfoxide, and sulfone and their derivatives were determined in benzene solutions at 25°C. The observed moments are used to estimate the mesomeric moments on the assumption of the vector addition of group moments. The mesomeric moments of the phenylmercapto, phenylsulfinyl, and phenylsulfonyl groups are estimated to be −0.12, 0.10, and 0.44 D, respectively. The steric effect of ortho-substituents is also discussed on the basis of the dipole moment data.

Quantum chemical considerations1) and spectral investigations2) both lead to the conclusion that the delocalization of π-electrons from benzene ring to the vacant 3d-π orbitals of a sulfur atom is important for aryl sulfoxides and sulfones. The chemical evidence3) is in conformity with this prediction.

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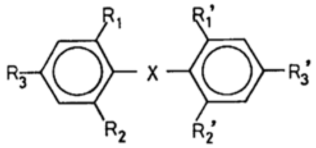
1) W. E. Moffitt, *Proc. Roy. Soc. (London)*, **A200**, 409 (1950); H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

2) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, New York, N. Y. (1963).

3) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962); E. L. Wehry, *J. Am. Chem. Soc.*, **89**, 41 (1967).

Contrary to the cases of sulfoxides and sulfones, the chemical behavior of diphenyl sulfides[4] was interpreted in terms of the electron-donating conjugation of the sulfur atom, just like that of diphenyl ethers. Craig and others,[5] however, concluded that both the sulfur 3p and 3d orbitals are utilized in the sulfur-carbon bonding of aryl sulfides. The electric dipole moments of diphenyl sulfide, sulfoxide, and sulfone, and some of their derivatives were already reported,[6] but the available data are not sufficient to discuss the nature of sulfur-carbon bonding in aryl sulfides, sulfoxides, and sulfones. This paper will describe the observed dipole moments of diphenyl sulfide, sulfoxide, sulfone, and their derivatives, such as:



X: S, SO, SO_2

$R_1=R_1'$, $R_2=R_2'$: H, CH_3

$R_3=R_3'$: H, CH_3, OCH_3

The mesomeric moments of these compounds are estimated by comparing the present data with the observed moments of relevant aliphatic sulfides, sulfoxides, and sulfones. The contribution of the vacant 3d orbitals of sulfur atoms to conjugation will be discussed, together with the steric effect of substituents.

Experimental

The preparation of all the materials used in this work was described elsewhere.[7] Benzene was used as a solvent throughout this work, and purified by fractional distillation through a 100-cm column packed with stainless-steel helices after being shaken with concentrated sulfuric acid.[8]

The measurements of the dielectric constants, ε, the specific volumes, v, and the square of the refractive indices, n^2, were carried out by the same apparatus and method as in a previous work.[9] All the data were obtained at 25±0.02°C. In the present investigation, the weight fraction, w, of solutes covers up to about 0.02.

Results and Discussion

The observed values of ε's, v's, and n^2's are, fairly well within the range of experimental errors, expressed by the linear equations of w's. The results are summarized in Table 1. The molecular polarizations, P's, were obtained from these experimental data according to the Halverstadt-Kumler's method.[10] The molecular refractions, R_D's, for the sodium D line were used to estimate the total distortion polarizations. They were assumed to be

TABLE 1. DIELECTRIC CONSTANTS, SPECIFIC VOLUMES, AND REFRACTIVE INDICES

	R_1,	R_2,	R_3			
X=S						
AI	H	H	H	$\varepsilon=2.2725+1.65w$	$v=1.1445-0.255w$	$n_D^2=2.244+0.326w$
AII	H	H	OCH_3	$\varepsilon=2.2725+3.38w$	$v=1.1442-0.306w$	$n_D^2=2.245+0.281w$
AIII	CH_3	CH_3	OCH_3	$\varepsilon=2.2725+1.96w$	$v=1.1444-0.244w$	$n_D^2=2.245+0.242w$
AIV	CH_3	CH_3	CH_3	$\varepsilon=2.2725+1.01w$	$v=1.1441-0.197w$	
X=SO						
BI	H	H	H	$\varepsilon=2.2725+9.36w$	$v=1.1444-0.325w$	$n_D^2=2.243+0.316w$
BII	H	H	OCH_3	$\varepsilon=2.2725+9.63w$	$v=1.1442-0.348w$	$n_D^2=2.245+0.253w$
BIII	CH_3	CH_3	OCH_3	$\varepsilon=2.2725+6.71w$	$v=1.1442-0.321w$	$n_D^2=2.244+0.302w$
BIV	CH_3	CH_3	CH_3	$\varepsilon=2.2725+6.45w$	$v=1.1442-0.246w$	
$X=SO_2$						
CI	H	H	H	$\varepsilon=2.2725+13.1w$	$v=1.1443-0.362w$	$n_D^2=2.243+0.232w$
CII	H	H	OCH_3	$\varepsilon=2.2725+13.7w$	$v=1.1441-0.383w$	$n_D^2=2.244+0.260w$
CIII	CH_3	CH_3	OCH_3	$\varepsilon=2.2725+9.26w$	$v=1.1441-0.334w$	$n_D^2=2.244+0.174w$
CIV	CH_3	CH_3	CH_3	$\varepsilon=2.2725+9.10w$	$v=1.1441-0.278w$	

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4) A. Mangini and R. Passerini, *J. Chem. Soc.*, **1956**, 4954; G. Bergson, *Arkiv. Kemi.*, **19**, 181, 265 (1962).

5) D. P. Craig and C. Zauli, *Gazz. Chim. Ital.*, **90**, 1700 (1960); L. Goodman and R. W. Taft, *J. Am. Chem. Soc.*, **87**, 4386 (1965).

6) C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956); M. J. Aroney, L. R. Fischer and R. J. W. LeFevre, *J. Chem. Soc.*, **1963**, 4450; C. W. N. Cumper, J. F. Read and A. I. Vogel, *ibid.*, **1965**, 5323, 5860.

7) S. Oae, M. Yoshihara and W. Tagaki, This Bulletin, **40**, 951 (1967).

8) A. Weissberger *et al.*, "Organic Solvents," Interscience Publishers, New York (1955).

9) K. Kimura, Y. Toshiyasu and R. Fujishiro, This Bulletin, **39**, 1681 (1966).

10) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

Table 2. Polarization data and dipole moments

	P (cc)	R_D (cc)	μ (D)
AI	107.2	63.8	1.46
AII	217.9	77.5	2.62
AIII	195.8	98.4	2.18
AIV	138.0	93.1	1.48
BI	405.5	63.8	4.09
BII	537.3	77.7	4.79
BIII	480.0	100.0	4.31
BIV	423.9	93.1	4.02
CI	587.4	62.7	5.07
CII	782.2	79.7	5.87
CIII	662.9	94.9	5.27
CIV	595.5	92.0	4.96
R	SR_2*	OSR_2*	O_2SR_2*
Methyl	(1.45D)	(3.89D)	(4.26D)
Ethyl	1.61	4.02	4.50
n-Propyl	1.60	3.97	4.48
n-Butyl	1.60	4.04	4.53
n-Amyl	1.60	3.98	4.53
Average	1.60	4.00	4.50

* These data were taken from Ref. 6.

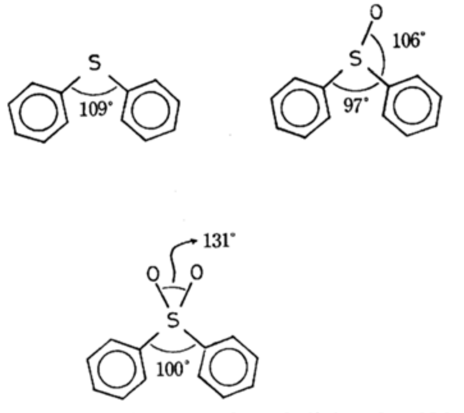

Fig. 1. The valence angles of diphenyl sulfide, sulfoxide, and sulfone.

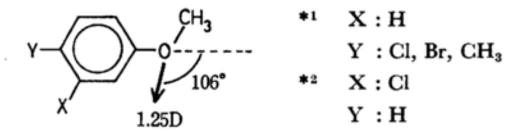

Fig. 2. The group moments of anisole.

*1 Data found in the following tables: A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company, San-Francisco (1963).

*2 Y. Toshiyasu, unpublished work.

Table 3. Mesomeric moments*

AI	−0.12D
AII	−0.03
BI	0.10
BII	0.14
CI	0.44
CII	0.52
Thioanisole**	−0.51
2,4,6-Trimethyl thioanisole**	−0.16

* The sense of moments is directed in such a way as C^+–S^- is positive.

** These moments were calculated by the use of data found in "Tables of Experimental Dipole Moments."

equal to 1.05 R_D. The polarization values and dipole moments, μ's, are tabulated in Table 2, together with the dipole moments of the relevant alkyl sulfur compounds. The mesomeric moments of diphenyl sulfides, sulfoxides, and sulfones were calculated on the basis of the following two assumptions: (1) the difference in dipole moments between diphenyl sulfur compounds and the relevant dialkyl ones is due to delocalization, and the vector subtraction of the latter dipole moments from the former gives the mesomeric moments, and (2) the valence angles[11] of the aryl sulfur compounds depicted in Fig. 1 are used to calculate the mesomeric moments per carbon-sulfur bonding.

It is not a reasonable assumption to divide the conjugation of bis-*p*-methoxyphenyl sulfur compounds in two methoxyphenyl and one diphenyl sulfur part. However, the approximate mesomeric moments of carbon-sulfur bonding are determined by taking the vector subtraction of the group moment of anisole, which is shown in Fig. 2. In order to calculate the mesomeric moment of BI (or BII), it is necessary to estimate the S–O bond moment. This was done by the use of the dipole moment of dialkyl sulfide, that of BI (or BII), and that of dialkyl sulfoxide. The mesomeric moments thus calculated are tabulated in Table 3, together with those of anisole and one of its derivatives.

Table 3 clearly shows that the conjugative effect operative in AI or AII is the same as that of thioanisole, although the mesomeric moment of AI or AII is considerably smaller than that of thioanisole. The conformation[12] of diphenyl sulfide is similar to that of diphenyl ether.[13] It may be inferred that the maximum conjugation of diphenyl sulfide is inhibited by the twisting of two benzene rings. On

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[11] S. C. Abrahams, *Quart. Rev.*, **5**, 407 (1956).

[12] J. Toussaint, *Bull. Soc. Chim. Belges*, **54**, 319 (1945).

[13] K. Higasi, "Dielectric Relaxation and Molecular Structure," Res. Inst. App. Elect., Hokkaido Univ., No. 9, 1961.

the other hand, the mesomeric moments of BI and CI are directed in the opposite sense of those of A's.

As Moffitt[1] and others[2] pointed out, the 3d vacant orbitals of sulfur atoms contribute to the conjugative effect, which is enhanced by methoxy substituents at the para positions. There is a possibility of this type of conjugation in aryl sulfides,[5] also. As far as the ground state is concerned, the increase in the effective positive charge of sulfur atoms[2] is a necessary condition for this type of conjugation. This condition is fulfilled for aryl sulfoxides and sulfones. Any conclusion about the contribution of the vacant 3d orbitals of aryl sulfides to the conjugative effect, however, can not be drawn from the dipole moment measurements alone, but it is evident that the electron-withdrawing conjugation of the sulfur atoms of aryl sulfides is negligible or at least much less than the electron-donating one.

As already stated, the two benzene rings of diphenyl sulfide are twisted about 40° out of the C–S–C plane.[14] This may be due to the steric effect. Hence, the steric hindrance by methyl substituents at the ortho positions may not be observed appreciably. The dipole moment of dimesityl sulfide is not so much different from that of diphenyl sulfide. This is true for aryl sulfoxides and sulfones, although the decrease in the dipole moment of dimesityl sulfone relative to that of diphenyl sulfone amounts to 0.11 D. The change in the valence angle is probably, at least in part, responsible for this decrease in the dipole moment.

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14) M. J. Aroney, R. J. W. LeFevre and J. Saxby, *J. Chem. Soc.*, **1963**, 1167.