Conformational Analysis of Some Benzyl *t*-Butyl Sulfoxides by Measurement of Their Dipole Moments

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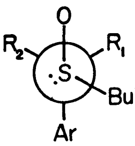
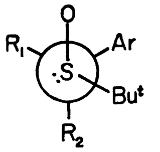
Favored conformations of benzyl *t*-butyl sulfoxides and their α-methyl derivatives in solutions were determined from their dipole moments and compared with those in crystals.

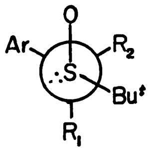
In connection with studies on stereochemistry of the reactions involving α-sulfinyl carbanion, the conformations of the related sulfoxides have been investigated.[1-4] Some of the present authors investigated the methylation and deuteration of benzyl alkyl sulfoxides *via* carbanion intermediates, a highly stereospecific nature of the reaction being revealed.[5-8] Furthermore, the conformations of the above sulfoxides in crystalline states were determined by means of X-ray crystal analysis. The results show that p-bromobenzyl *t*-butyl sulfoxide (1b) takes conformation III (where Ar=p-BrC$_6$H$_4$ and R$_1$=R$_2$=H),[9] and (*RR*/*SS*)-*t*-butyl 1-(p-bromophenyl)ethyl sulfoxide (2b; R$_1$=CH$_3$, R$_2$=H)[10] and its (*RS*/*SR*) isomer (3b; R$_1$=H, R$_2$=CH$_3$)[11] conformations II and I, respectively, in crystalline state. On the other hand, benzyl *t*-butyl sulfoxide (1a) takes conformation II in which the *t*-butyl and phenyl groups are gauche to each other as shown by LIS and ASIS measurements.[12] The stereochemistry of its deuteration was again best rationalized by assuming conformation II.



(I)
ϕ 180°



(II)
300°(−60°)



(III)
60°

Thus, another more decisive evidence on their conformations in solution is necessary to settle this apparent disagreement. Since the dipole moment often offers a very conclusive evidence for the conformation in solution of a molecule carrying two polar substituents at suitable positions, their dipole moments were determined.

Experimental

Materials. The sulfoxides were prepared according to known methods. The new compounds were identified by spectral and elementary analyses. Benzene for the solvent was carrefully purified and dried.

Dielectric Measurement. Dielectric constants of the benzene solution of the sulfoxides were determined at 25 °C with a heterodyne-beat apparatus. The dipole moments were calculated according to the method of Halverstadt and Kumler[13,14] from the observed dielectric constants and densities of the benzene solution at varying concentrations. The molar refraction was calculated from the bond refraction values.[14]

Results and Discussion

The dipole moments of substituted benzyl *t*-butyl sulfoxides are given in Table 1. The substituent effect on the (*RS*/*SR*), or threo, series (3) is apparently anomalous since the dipole moment of p-bromo derivative is lower than that of both unsubstituted and p-nitro derivatives. Since the conformations of the molecules are governed by the steric circumstances around the bond in question and insensitive to the electronic effect of the substituents far from the bond, the sulfoxide molecules appear to take a similar conformation irrespective of the para-substituents when the configuration is the same. Thus, the anomalous substituent effect is reasonable only when the angle between the C–X (X=Br or NO$_2$) and the S–O bond moment vectors are larger than a right angle, which is only possible in confor-

Table 1. Observed dipole moments (μ) of the sulfoxides and related compounds

Compound	R$_1$	R$_2$	Ar	No.	μ/D
(*R*/*S*)Benzyl *t*-butyl sulfoxide	H	H	C$_6$H$_5$	1a	3.90
(*R*/*S*)p-Bromobenzyl *t*-butyl sulfoxide	H	H	p-BrC$_6$H$_4$	1b	4.72
(*R*/*S*)p-Nitrobenzyl *t*-butyl sulfoxide	H	H	p-NO$_2$C$_6$H$_4$	1c	6.44
(*RR*/*SS*) 1-Phenylethyl *t*-butyl sulfoxide	CH$_3$	H	C$_6$H$_5$	2a	3.84
(*RR*/*SS*) 1-(p-Bromophenyl)ethyl *t*-butyl sulfoxide	CH$_3$	H	p-BrC$_6$H$_4$	2b	4.23
(*RR*/*SS*) 1-(p-Nitrophenyl)ethyl *t*-butyl sulfoxide	CH$_3$	H	p-NO$_2$C$_6$H$_4$	2c	5.69
(*RS*/*SR*) 1-Phenylethyl *t*-butyl sulfoxide	H	CH$_3$	C$_6$H$_5$	3a	3.86
(*RS*/*SR*) 1-(p-Bromophenyl)ethyl *t*-butyl sulfoxide	H	CH$_3$	p-BrC$_6$H$_4$	3b	3.42
(*RS*/*SR*) 1-(p-Nitrophenyl)ethyl *t*-butyl sulfoxide	H	CH$_3$	p-NO$_2$C$_6$H$_4$	3c	4.26
Methyl phenyl sulfoxide					3.88
p-Bromobenzyl *t*-butyl sulfone					4.90

mation I (see Figs. 1 and 2). The above qualitative assignment of the conformation agrees with the results of its X-ray crystal analysis and is rationalized by a more quantitative computation on the conformation dependence of dipole moments. From a similar discussion on the (*RR*/*SS*) series (2), the privileged conformation can not be determined uniquely, and both conformers II and III are suspected. However, operation of a considerable repulsive force is expected when methyl and *t*-butyl groups are located gauche to each other, as realized in the conformer III of (2). Conformer II should thus be the more stable of the two.

TABLE 2. BOND AND GROUP MOMENT VALUES[16,17]

Bond or group (+) (−)	*m*/D
H − C	0.0
C − S	0.90
C − C_6H_5	0.35
C − $C_6H_4Br(p)$	1.53
C − $C_6H_4NO_2(p)$	4.00
S − O	3.00

In order to estimate the dipole moments of these molecules quantitatively, they were calculated as the sum of the component bond moments by taking the values in Table 2 and the bond lengths and bond angles reported by Kodama and co-workers.[15] The S–O bond moment was re-evaluated by measuring the dipole moments of some sulfoxides. The observed dipole moment of phenyl methyl sulfoxide gives a larger S–O bond moment (3.2 D) than that reported.[16] The best fit value of S–O bond moment is 3.0 D (Table 2) for this series of sulfoxides, which is employed as the bond moment for the present calculations.

TABLE 3. DIPOLE MOMENTS OF THE SULFOXIDES (1a—3c) CALCULATED BY ASSUMING THE CONFORMATIONS IN CRYSTALS

Ar		Benzyl series (1)	(*RR*/*SS*) series (2)	(*RS*/*SR*) series (3)
	R_1	H	CH_3	H
	R_2	H	H	CH_3
C_6H_5(a)		3.85	3.75(4.03)	3.28(3.53)
p-BrC_6H_4(b)		4.61	4.23(4.87)	2.31(2.68)
p-$NO_2C_6H_4$(c)		6.62	5.91(6.96)	1.70(2.29)
The conformation in crystal		III	II	I

a) The dipole moments calculated by employing the modified bond moments[17] ($m_{S-O}=2.70$ D, $m_{C-S}=1.47$ D) are given in parentheses.

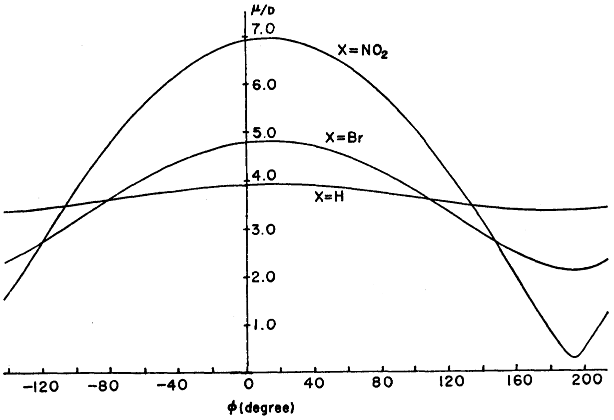


Fig. 1. Dihedral angular dependency of the dipole moments of (*RR*/*SS*)-*t*-butyl 1-phenylethyl sulfoxides.

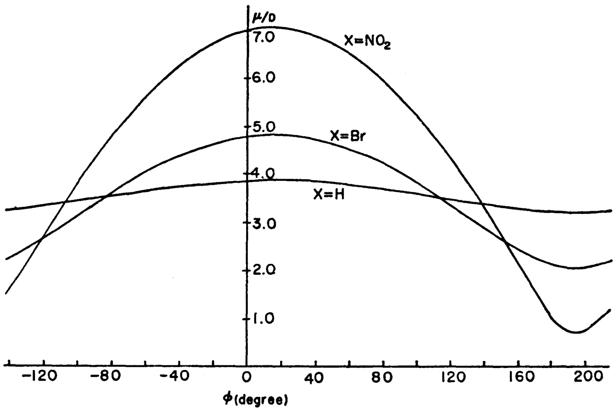


Fig. 2. Dihedral angular dependency of the dipole moments of (*RS*/*SR*)-*t*-butyl 1-phenylethyl sulfoxides.

Dipole moments for the conformations in crystals[10,11] were calculated first. Benzyl *t*-butyl sulfoxides are assumed to exist exclusively in conformation III in which the bulky phenyl and *t*-butyl groups are located anti to each other.[9] The results are given in Table 3. The calculated values for the series of (1)[18] and (2) agree very closely with the observed ones (Table 2). However, those for the series of (3) do not agree with the observed ones at all. The dipole moments of the series of (*RR*/*SS*) (2) and (*RS*/*SR*) (3) were then calculated as the function of dihedral angle around C_{benzyl}–S bond. The results are shown in Figs. 1 and 2, where the abscissa represents the dihedral angle (ϕ) between the S–O and C–Ar bonds. The best fit values for the (*RR*/*SS*) series (2) are attained when the dihedral angle ϕ is near 300° (−60°). This is in line with the conclusion from X-ray and other evidences. However, no dihedral angle reasonable for the (*RS*/*SR*) series (3) could be found (Fig. 2). The dipole moment of (*RS*/*SR*) sulfoxides (3) is interpreted by assuming the conformational equilibria between (or among) conformers I and III (or II). Again conformer II should be excluded since the *t*-butyl and methyl groups are gauche to each other (as in conformer III of the (*RR*/*SS*) series). When the mole fraction of conformer I is *X*, the dipole moment of the mixture (μ) is given by the equation,

$$\mu = \{X\mu_{\rm I}^2 + (1-X)\mu_{\rm III}^2\}^{1/2},$$

where $\mu_{\rm I}$ and $\mu_{\rm III}$ refer to the dipole moments of conformer I and III, respectively. The calculated dipole moments for the conformational mixtures are given as the function of *X* in Table 4. Near $X=0.7$, the dipole moments of the (*RS*/*SR*) sulfoxides are reproduced almost quantitatively, and the order of magnitude of dipole moments is in line with the observed values in the range of $X=0.8-0.65$.[17] Thus the (*RS*/*SR*) sulfoxides are concluded to exist as a mixture of confor-

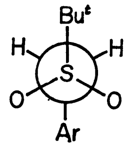
Table 4. Dipole moments of (3)'s calculated by assuming the coexistence of conformers I and III in varying proportions

Ar	X[a]					
	0.85	0.80	0.75	0.70	0.65	0.60
C_6H_5	3.38	3.41	3.44	3.46	3.49	3.51
p-BrC_6H_4	2.91	3.04	3.16	3.28	3.40	3.51
p-$NO_2C_6H_4$	3.28	3.57	3.84	4.10	4.34	4.56

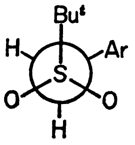
a) Mole fraction of conformer I. Sice the existence of conformer II and other conformers are neglected, the mole fraction of the III should be $1-X$.

mers in which conformer I predominates in benzene solutions.

In conclusion, both the (*RR*/*SS*) and (*RS*/*SR*) isomers of *t*-butyl 1-phenylethyl sulfoxides are shown to take conformations in which bulky *t*-butyl and phenyl groups approach closely. From these observations on dipole moments, the participation of a specific attractive force between the phenyl and the *t*-butyl groups might take place. On the other hand, an alternative explanation in which the repulsive force between the methyl and *t*-butyl groups plays an important role is also possible. In order to decide which of the above effect is more predominant, the conformation of a benzyl *t*-butyl sulfone was determined by measurement of their dipole moments.



(IV)



(V)

The observed dipole moment for *p*-bromobenzyl *t*-butyl sulfone (4) is 4.90 D, while the calculated values for conformers IV and V (where Ar=C_6H_4Br-*p*) are 5.2 and 3.7 D, respectively, and the result favors the anti-conformation in which phenyl and *t*-butyl groups are located farthermost to each other. In view of this, the repulsive force is supposed to play an important role in determining the conformations of these sulfoxides. However, a similar attractive interaction between the alkyl and aromatic groups was reported recently.[12] The conformations of these sulfoxides may also be determined by the cooperation of the repulsive force caused by steric hindrance, the specific attractive force, and other forces in their molecules.

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17) A large C–S bond moment (1.46 D) and a smaller S–O bond moment (2.70 D) are proposed by Saito and coworkers, [S. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 663 (1969) and S. Saito and F. Makino, *ibid.*, **45**, 92 (1972)]. The dipole moments of the (*RR*/*SS*) and (*RS*/*SR*) sulfoxides are also calculated on the basis of these bond moments (see Table 3). The calculated values also explain the observed dipole moments qualitatively. However, the agreements is less satisfactory. Calculation by these bond moments on the (*RS*/*SR*) series also suggests the conformation equilibria, the composistion for the best fit dipole moments containing about 40% of the conformer I. (The order of the dipole moment values agrees in the range X= 0.55—0.30).

18) Conformer II is also compatible with the observed dipole moment.