

Dipole moments of aryl *cis*- and *trans*-styryl sulphides and sulphones

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Abstract. The dipole moments of thirteen aryl styryl sulphides and eleven aryl styryl sulphones have been determined. Among them are eight *cis*–*trans* isomeric pairs, four sulphides and four sulphones. The styryl group is found to conjugate with the sulphide function as an electron-withdrawing group. The angles which the styrylthio and styrylsulphonyl groups make with their axes of rotation are calculated. The observed dipole moments of the sulphides and sulphones are compared with the moments calculated by the vector addition of group moments. The dipole moments of *cis* aryl styryl sulphides and sulphones are found to be generally lower than those of their *trans* isomers. An explanation is offered attributing the cause to sterically enhanced styryl–sulphur conjugation in the *cis* isomers.

Keywords. Dipole moments; aryl *cis*- and *trans*-styryl sulphides and sulphones; styryl–sulphur conjugation; styryl–sulphonyl conjugation; steric enhancement of conjugation.

1. Introduction

The non-availability of dipole moment data on the geometrical isomers of α,β -unsaturated sulphides and sulphones prompted us to undertake the present study. Baliah and Shanmuganathan (1959) studied the dipole moments of some α,β - and β,γ -unsaturated sulphones but their study included only a few *trans* α,β -unsaturated sulphones. The scope of the present study includes (i) determining whether the sulphide function conjugates with the styryl group as an electron-donor or as an electron-acceptor, and (ii) estimating the magnitude of the differences between the dipole moments of *cis* and *trans* isomers and determining the steric and polar factors which cause these differences.

2. Experimental

2.1 Materials

Preparation of the sulphides and sulphones used in the present study is described in an earlier paper (Baliah and Rathinasamy 1971).

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Table 1. Polarisation data of aryl styryl sulphides and sulphones.

Aryl	α	$-\beta$	γ	${}_{\infty}P_2$ (ml)	R_D (ml)	μ (D)
<i>Aryl trans-styryl sulphides</i>						
Phenyl	1.29	0.259	—	108.4	72.4	1.34
<i>o</i> -Tolyl	1.14	0.240	—	110.0	77.5	1.27
<i>m</i> -Tolyl	1.41	0.234	—	121.9	78.1	1.48
<i>p</i> -Tolyl	1.66	0.235	0.4035	131.2	78.2	1.62
<i>p</i> -Chlorophenyl	1.20	0.324	0.4184	116.9	79.4	1.37
<i>p</i> -Bromophenyl	1.08	0.464	0.4044	118.9	81.5	1.36
<i>m</i> -Bromophenyl	1.40	0.440	—	138.8	78.8	1.73
<i>p</i> -Methoxyphenyl	2.26	0.279	0.4427	166.6	82.3	2.05
2,6-Dimethylphenyl	1.00	0.229	—	111.3	82.5	1.20
<i>Aryl cis-styryl sulphides</i>						
<i>p</i> -Tolyl	1.63	0.261	0.4241	128.5	77.3	1.60
<i>p</i> -Chlorophenyl	0.855	0.322	0.4478	100.9	81.1	0.99
<i>p</i> -Bromophenyl	0.768	0.430	0.4060	104.8	84.0	1.02
<i>p</i> -Methoxyphenyl	2.30	0.254	0.4318	170.2	83.6	2.04
<i>Aryl trans-styryl sulphones</i>						
Phenyl	11.10	0.345	0.3153	574.2	72.4	4.99
<i>p</i> -Tolyl	11.50	0.316	0.3605	627.0	77.1	5.23
<i>p</i> -Chlorophenyl	7.74	0.406	0.3141	472.5	77.5	4.43
<i>p</i> -Bromophenyl	6.83	0.480	0.3353	483.9	84.2	4.46
<i>m</i> -Bromophenyl	8.00	0.493	0.2867	554.5	78.0	4.87
<i>p</i> -Methoxyphenyl	11.80	0.359	0.2794	679.5	78.1	5.47
2,6-Dimethylphenyl	9.19	0.331	0.3140	541.9	81.6	4.78
<i>Aryl cis-styryl sulphones</i>						
<i>p</i> -Tolyl	10.30	0.322	0.2965	569.7	77.2	4.95
<i>p</i> -Chlorophenyl	6.37	0.395	0.2682	400.8	76.0	4.02
<i>p</i> -Bromophenyl	5.59	0.502	0.3352	405.4	82.1	4.01
<i>p</i> -Methoxyphenyl	10.60	0.363	0.3087	617.0	79.2	5.17

2.2 Apparatus and measurements

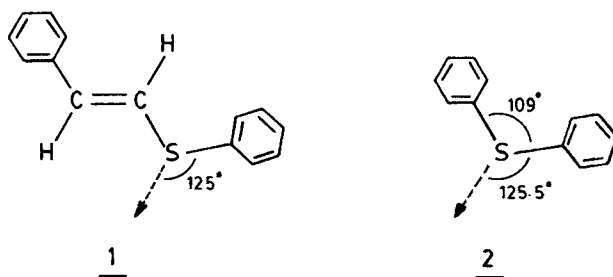
The dielectric constants, densities and refractive indices of the benzene solutions were measured at 30°C with the apparatus described earlier (Baliah and Ganapathy 1963). Definitions of symbols used here and the method of calculating dipole moments are also given therein. The dielectric constant and the specific volume of benzene of 30°C were taken as 2.2628 and 1.1514, respectively. The experimental results are given in table 1.

3. Results and discussion

The angle which the moment of styrylthio group makes with its axis of rotation can be calculated from the moments of *p*-chlorophenyl *trans*-styryl sulphide ($\mu = 1.37$ D), phenyl styryl sulphide ($\mu_1 = 1.34$ D) and chlorobenzene ($\mu_2 = 1.57$ D, Baliah and Uma 1963), making the assumption that the moments of the styrylthio and chloro groups are the same as those of phenyl *trans*-styryl sulphide and chlorobenzene, respectively, and making use of the equation (Fuchs 1931),

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta \cos \alpha \cos \beta,$$

where θ is the angle between the axes of rotation of the phenylthio and chloro groups and, α and β are the angles which the moments μ_1 and μ_2 make with their respective axes. The axes of rotation are assumed to be directed towards the ring. The angle θ was found to be $124^\circ 26'$. When it calculated from the moments of *m*-bromophenyl *trans*-styryl sulphide (1.73 D), phenyl *trans*-styryl sulphide (1.34 D) and bromobenzene (1.55 D, Baliah and Uma 1963), the value was $125^\circ 34'$. Hence the angle θ was taken as $125^\circ(1)$.



The Ph-S-Ph angle in diphenyl sulphide is 109° (Smith 1955; Rolla and Senesi 1961). Therefore the angle which the dipole moment of PhS group makes with its bond axis in 2 is $125.5^\circ (180 - \frac{1}{2} \times 109^\circ)$.

It may be noted that the dipole angle to the styrylthio group in 1 and that of the phenylthio group in 2 are almost the same. This may be expected from the fact that the dipole moment of styrene is 0.12 D (Smith 1955), which is very close to the zero dipole moment of benzene. What is of interest is that though the two dipole angles are almost the same and the groups attached to S in 1 and 2 have zero or very nearly zero moment, the dipole moment of 1 (1.34 D) is considerably lower than that of 2 (1.55 D, Marziano and Passerini 1959). A similar difference is observed between the dipole moments of *p*-chlorophenyl styryl sulphide (1.37 D) and phenyl *p*-chlorophenyl sulphide (1.52 D, McClellan 1963), between the dipole moments of *p*-bromophenyl styryl sulphide (1.39 D) and phenyl *p*-bromophenyl sulphide (1.67 D, McClellan 1963), and between the dipole moments of styryl *p*-tolyl sulphide (1.62 D) and phenyl *p*-tolyl sulphide (1.76 D, McClellan 1963). The lowering observed in the dipole moments of aryl styryl sulphides can be due to any or all of the following causes: (i) change in styryl C-S-C angle, (ii) changes in electron density at the S atom and the β -carbon of the vinyl group, and (iii) change in the extent of C|*p*- π -S|*d*- π overlap if such overlap occurs. The data given in table 2 indicate that both in aryl methyl sulphides (1-7) and diaryl sulphides (8-10), the observed dipole moments are less than the expected dipole moments, when the electron density on S decreases owing to the presence of an electron-withdrawing substituent on the benzene ring attached to the S atom. On the other hand the opposite happens when an electron-donating substituent is present, para to S, in the aryl group; in this case *d*-orbital resonance involving S becomes important (Lumbroso and Passerini 1955; Baliah and Uma 1963; Frost *et al* 1972; Cutress *et al* 1974). Kinetics of H-D exchanges in aromatic sulphides also provide evidence for (*p*-*d*) π -bonding (Schattenstein and Gvozdeva 1969). It may therefore be concluded that the observed lowering of dipole moments in aryl styryl sulphides is due to a decrease in the electron density on S, which can result from electron-release from S to the styryl group.

For comparison, the observed and calculated dipole moments of aryl *trans*-styryl sulphides are given in table 3. The dipole angle of the methoxy group was taken as

Table 2. Observed and calculated dipole moments* of some aryl methyl and diaryl sulphides.

Compound	No.	μ_{obs} (D)	μ_{calc} (D)	$\Delta\mu$ (D)
$\text{CH}_3\text{SC}_6\text{H}_4\text{Cl-}m$	1	1.83	1.94	-0.11
$\text{CH}_3\text{SC}_6\text{H}_4\text{Br-}m$	2	1.83	1.92	-0.09
$\text{CH}_3\text{SC}_6\text{H}_4\text{F-}p$	3	1.64	1.73	-0.09
$\text{CH}_3\text{SC}_6\text{H}_4\text{OCH}_3\text{-}m$	4	1.74	1.84	-0.10
$\text{CH}_3\text{SC}_6\text{H}_4\text{OCH}_3\text{-}p$	5	1.98	1.86	+0.12
$\text{CH}_3\text{SC}_6\text{H}_4\text{NH}_2\text{-}p$	6	2.54	2.15	+0.39
$\text{CH}_3\text{SC}_6\text{H}_4\text{NMe}_2\text{-}p$	7	2.82	2.24	+0.58
$\text{C}_6\text{H}_5\text{SC}_6\text{H}_4\text{F-}p$	8	1.38 ^a	1.53	-0.15
$\text{C}_6\text{H}_5\text{SC}_6\text{H}_4\text{NH}_2\text{-}p$	9	2.98 ^b	2.56 ^b	+0.42
$\text{C}_6\text{H}_5\text{SC}_6\text{H}_4\text{NMe}_2\text{-}p$	10	3.33 ^b	2.73 ^b	+0.60

* Data for compounds 1-7 are from Baliah and Uma (1963);
^aMcClellan (1963); ^bBaliah and Kanagasabapathy (1978)

Table 3. Observed and calculated dipole moments of aryl *trans*-styryl sulphides and sulphones

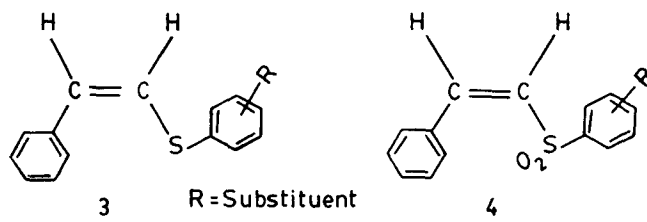
Aryl	μ_{obs} (D)	μ_{calc} (D)
<i>Sulphides</i>		
<i>o</i> -Tolyl	1.27	1.29
<i>m</i> -Tolyl	1.48	1.49
<i>p</i> -Tolyl	1.62	1.60
<i>p</i> -Bromophenyl	1.36	1.35
<i>p</i> -Methoxyphenyl	2.05	1.97
2,6-Dimethylphenyl	1.20	1.17
<i>Sulphones</i>		
<i>p</i> -Tolyl	5.23	5.17
<i>p</i> -Bromophenyl	4.46	4.44
<i>m</i> -Bromophenyl	4.87	4.85
<i>p</i> -Methoxyphenyl	5.47	5.29
2,6-Dimethylphenyl	4.78	4.81

75° (Baliah and Uma 1963) for calculations. It may be seen that only the *p*-methoxy compound has a slightly but significantly higher dipole moment than the calculated one. The methoxy group is an electron-donor and causes *d*-orbital utilisation by sulphur. Even in aryl methyl sulphides, perceptible sulphur-aryl conjugation with *d*-orbital utilisation by sulphur has been observed only when the substituent *para* to S is a strong electron-releasing group (Baliah and Uma 1963).

The dipole angle of the *trans*-styryl sulphonyl group, when calculated from the moments of *p*-chlorophenyl *trans*-styryl sulphone (4.43 D), phenyl *trans*-styryl sulphone (4.98 D) and chlorobenzene (1.57 D), is found to be 119°. A comparison of the observed dipole moments of aryl *trans*-styryl sulphones with the calculated ones (table 3) shows that the agreement is good except again in the case of the methoxy compound.

The computation of the dipole moments of the *cis*-isomers of aryl styryl sulphides

and sulphones from the group moments is complicated by the fact that there exists steric hindrance to free rotation of the bulky arylthio or arylsulphanyl group, when the phenyl group is *cis* to them (3 and 4).



Hence, the vector addition of their group moments was not attempted. However, a comparison of the observed dipole moments of the *cis* and *trans* isomers reveals some interesting facts.

Considering the sulphides first, we make the observation that the *cis* and *trans* isomers of *p*-tolyl and *p*-methoxy compounds have almost the same dipole moment, while in other cases the *trans* isomers have higher moments than the *cis* isomers. A possible explanation for the lower dipole moments of the *cis* isomers can be this: Conjugation of S with a styryl group imparts some double bond character to the S-C(styryl) bond. If free rotation of the -S-aryl group gets restricted in the *cis* isomer (3), the S-C π -bond character will also increase. This is a case of steric enhancement of conjugation. Consequently the dipole moment of the molecule decreases.

The fact that the *cis* isomers of *p*-CH₃ and *p*-OCH₃ compounds have almost the same dipole moments as their *trans* isomers indicates that the increased sulphur-styryl conjugation resulting in increased positive charge on S leads to simultaneous increased electron-withdrawal by S from the electron-donating group situated *para* to S in the aryl group. This increases the positive charge on the *p*-group and hence its moment also increases. If the lowering of dipole moment caused by increased S-styryl conjugation is counteracted by the increase in dipole moment caused by electron-withdrawal from the *p*-substituent, there is no apparent change in the dipole moment of the molecule. The two opposing effects being almost equal in the present case may be fortuitous.

Table 4. Dipole moments of *cis* and *trans* isomers of aryl styryl sulphides and sulphones.

Aryl	μ_{cis} (D)	μ_{trans} (D)	$\mu_{trans} - \mu_{cis}$ (D)
<i>Sulphides</i>			
<i>p</i> -Tolyl	1.60	1.62	0.02
<i>p</i> -Chlorophenyl	0.99	1.37	0.38
<i>p</i> -Bromophenyl	1.02	1.36	0.34
<i>p</i> -Methoxyphenyl	2.04	2.05	0.01
<i>Sulphones</i>			
<i>p</i> -Tolyl	4.95	5.23	0.28
<i>p</i> -Chlorophenyl	4.02	4.43	0.41
<i>p</i> -Bromophenyl	4.01	4.46	0.45
<i>p</i> -Methoxyphenyl	5.17	5.47	0.30

In the case of the sulphones also, the *cis* isomer has a lower dipole moment than the corresponding *trans* isomer (table 4), the steric factor again being responsible. The hindered free rotation of the $-\text{SO}_2$ -aryl group (4) has a lowering effect on the dipole moment of the molecule. If the substituent *para* to sulphonyl is electron-releasing, the lowering is less than that observed in the case of *p*-tolyl and *p*-methoxy compounds.

References

- Baliah V and Ganapathy K 1963 *Trans. Faraday Soc.* **59** 1784
Baliah V and Kanagasabapathy V M 1978 *Indian J. Chem.* **B16** 810
Baliah V and Rathinasamy T K 1971 *Indian J. Chem.* **9** 220
Baliah V and Shanmuganathan S P 1959 *Trans. Faraday Soc.* **55** 232
Baliah V and Uma M 1963 *Tetrahedron* **19** 455
Cutress N C, Grindley T B, Katritzsky A R and Topsom R D 1974 *J. Chem. Soc., Perkin II* 263
Frost D C, Herring F G, Katrib A, McDowell C A and McLean R A N 1972 *J. Phys. Chem.* **76** 1030
Fuchs O 1931 *Z. Phys. Chem.* **B14** 339
Lumbroso H and Passerini R 1955 *Bull. Soc. Chim. Fr.* 1179
Marziano N and Passerini R 1959 *Bull. Soc. Chim. Fr.* 1908
McClellan A L 1963 *Tables of experimental dipole moments* (San Francisco: W H Freeman)
Rolla M and Sanesi M 1961 *Ricerca Sci. Rend.* **2 A1** 43; 1962 *Chem. Abstr.* **57** 715
Schattenstein A I and Gvozdeva H A 1969 *Tetrahedron* **25** 2749
Smith J W 1955 *Electric dipole moments* (London: Butterworths)