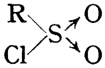
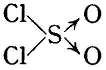
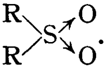
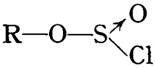
253. *Studies in Dielectric Polarisation. Part XIX. The Dipole Moments of Some Aromatic Sulphonyl Chlorides.*

By George T. O. Martin and James R. Partington.

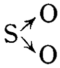
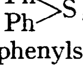
The structure of the sulphonyl chlorides  $\begin{smallmatrix}\mathrm{R}\\ \mathrm{Cl}\end{smallmatrix}\!>\!\mathrm{S}\!\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}$ may be considered as intermediate between those of sulphuryl chloride  $\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\!>\!\mathrm{S}\!\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}$ and of the sulphones  $\begin{smallmatrix}\mathrm{R}\\ \mathrm{R}\end{smallmatrix}\!>\!\mathrm{S}\!\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}$. Their moments resemble those of the sulphones rather than that of sulphuryl chloride, but a consideration of the molecular configuration shows that they are of the order expected.

Trunel (*Compt. rend.*, 1935, **200**, 557, 2186) has recorded the dipole moments of some chlorosulphinates  $\mathrm{R{-}O{-}S}\!\begin{smallmatrix}\nearrow\mathrm{O}\\ \diagdown\mathrm{Cl}\end{smallmatrix}$, which are isomeric with the sulphonyl chlorides. The methyl and ethyl compounds have moments of 2·30 and 2·63 respectively, while the moments of the higher members of the series (R = C_3H_7, C_4H_9, C_6H_{13}) are all about 2·70. The values of the moments of the *iso*propyl and *iso*butyl compounds are 2·83 and 2·66 respectively, while the phenyl compound has the smaller moment of 2·43. All these values are lower than those observed in the present work for the sulphonyl chlorides, which possess two semipolar bonds, in contrast to the single semipolar bond in the chlorosulphinates.

The values found for the compounds investigated are tabulated below, together with those of other similar compounds for comparison (values from "A Table of Dipole Moments," *Trans. Faraday Soc.*, 1934; all in benzene solution):

Sulphuryl chloride	1·86	**p*-Toluenesulphonyl chloride	5·01
*Benzenesulphonyl chloride	4·47	**p*-Bromobenzenesulphonyl chloride	3·23
Diphenylsulphone	5·14	Diphenyl sulphide	1·50

* Present work.

In calculating the moments of the sulphonyl chlorides, the sulphur atom is assumed to occupy the centre of a regular tetrahedron, at the corners of which the chlorine atom, the phenyl group, and the two oxygen atoms are situated. The two S→O moments need not be considered separately since their resultant can be calculated from the moments of diphenyl sulphide and diphenylsulphone. It seems reasonable to assume the tetrahedral angle between the Ph—S and S—Cl bonds, since the latest value calculated for the valency angle of sulphur in aromatic sulphides is close to this, *viz.*, 113° (Hampson and Sutton, *Trans. Faraday Soc.*, 1935, **31**, 945). With this angle in diphenyl sulphide, the moment of the Ph—S link is calculated to be 1·36. That of the  $\mathrm{S}\!\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}$ group can be found from that of diphenyl sulphide and of diphenylsulphone. Since in the latter compound the moment of the SO_2 group acts in the same line as that of the  $\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix}\!>\!\mathrm{S}$ group, it is given by the difference between the moments of diphenyl sulphide and diphenylsulphone, *i.e.*, 5·14 − 1·50 = 3·64. To calculate the moment of the S—Cl link the moment of sulphuryl chloride is used. From this the moment of the  $\mathrm{S}\!<\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}$ group is calculated to be 3·64 − 1·86 = 1·78, and, on the assumption of the tetrahedral angle between the S—Cl bonds, the moment of the S—Cl link is found to be 1·54. The moment of benzenesulphonyl chloride can now be regarded as made up of three components, due severally to the SO_2, Ph—S, and S—Cl moments. All these lie in one plane, the Ph—S and S—Cl moments inclined at an angle of 109½° to each other and the SO_2 moment acting at an angle of 125¼° to each of them. Vector addition of these three moments gives a resultant of 4·26. In view of the uncertainty of the angles involved and the neglect of interaction of the moments, this can be considered to be in good agreement with the observed value of 4·47.

Similar calculations can be made for *p*-toluene- and *p*-bromobenzene-sulphonyl chlorides. If the CH_3—Ph moment is taken as 0·4 (the moment of toluene), the three component moments are 1·76, 1·54, and 3·64. The calculated moment for *p*-toluenesulphonyl chloride is thus found to be 4·64, as compared with the observed value of 5·01. If the value 1·53 (the moment of bromobenzene in benzene solution) is assumed for the Ph—Br moment, this cancels the Ph—S moment, leaving a small component in the opposite direction. The moment of *p*-bromobenzenesulphonyl chloride is therefore given by the resultant of the three components 0·17, 1·54, and 3·64, which is calculated to be 2·89, as compared with the observed value of 3·23.

Although the values observed for the moments of all these three compounds are larger than those calculated, they are in the correct order. The moment of *p*-toluenesulphonyl chloride is greater than, and that of the *p*-bromobenzene compound smaller than, the moment of benzenesulphonyl chloride.

EXPERIMENTAL.

Materials.—The benzene used was the same as before. Benzenesulphonyl chloride (Kahlbaum) was fractionated under reduced pressure and fractionally frozen. *p*-Toluenesulphonyl chloride (Kahlbaum) was distilled under reduced pressure and crystallised from *cyclo*hexane, and *p*-bromobenzenesulphonyl chloride (Fraenkel and Landau) was distilled in a vacuum and crystallised from light petroleum.

The physical constants found were :

Sulphonyl chloride.	B. p.	M. p.	$D_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	$[R_L]_D$.
Benzene	117·0°/11 mm.	15·7°	1·3781	1·5521	40·98
p-Toluene	142·6/16	69	—	—	45·57
p-Bromobenzene	150·6/13	77	—	—	48·71

The refractivities of the last two compounds were calculated from that of benzenesulphonyl chloride and those of CH_3 and Br.

Figures for comparison are :

Benzenesulphonyl chloride : b. p. 116·3°/10·7 mm. (Bourgeois, *Rec. trav. chim.*, 1899, **18**, 432); m. p. 14·5° (Krafft and Roos, *Ber.*, 1892, **25**, 2257); $D_{15^\circ}^{15^\circ}$ 1·3842, $D_{25^\circ}^{25^\circ}$ 1·3766 (Perkin, J., 1896, **69**, 1205), from which $D_{4^\circ}^{20^\circ}$ is calculated to be 1·3779. *p*-Toluenesulphonyl chloride : b. p. 145—146°/15 mm. (Krafft and Roos, *loc. cit.*); m. p. 69° (Zincke and Frohneberg, *Ber.*, 1910, **43**, 840). *p*-Bromobenzenesulphonyl chloride : b. p. 153°/15 mm. (Krafft and Roos, *loc. cit.*); m. p. 75—76° (Olivier, *Rec. trav. chim.*, 1914, **33**, 91).

Results.—Solvent, benzene. All measurements at 20°.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	P_2, c.c.	f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
Benzenesulphonyl chloride.					*p*-Toluenesulphonyl chloride.				
0·00000	0·8790	2·281	26·57	—	0·00000	0·8790	2·281	26·57	—
0·00706	0·8844	2·490	29·54	447·6	0·00664	0·8840	2·524	30·03	547·1
0·01427	0·8896	2·704	32·36	431·9	0·01301	0·8855	2·755	33·03	523·2
0·02107	0·8946	2·909	34·83	418·8	0·01886	0·8925	2·967	35·57	503·7
0·02805	0·8996	3·121	37·21	406·0	0·02550	0·8972	3·212	38·27	485·4
$P_{2\infty}$ = 463·4 c.c.; P_E = 40·9 c.c.; μ = 4·47.					$P_{2\infty}$ = 576 c.c.; P_E = 45·6 c.c.; μ = 5·01.				
p-Bromobenzenesulphonyl chloride.									
0·00000	0·8791	2·279	26·56	—	0·03267	0·9258	2·785	33·78	248·1
0·01093	0·8930	2·449	29·11	261·7	0·04367	0·9411	2·954	35·96	242·1
0·02163	0·9103	2·615	31·49	255·1					
$P_{2\infty}$ = 269·0 c.c.; P_E = 48·7 c.c.; μ = 3·23.									

SUMMARY.

The dipole moments of benzene-, *p*-toluene-, and *p*-bromobenzene-sulphonyl chlorides have been measured and shown to be in agreement with the calculated values.

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