1099. *Physical Properties and Chemical Constitution. Part XLV.*[1] *The Electric Dipole Moments of some Aryl Sulphides, Sulphoxides, and Sulphones.*

By C. W. N. CUMPER, J. F. READ, and A. I. VOGEL

The electric dipole moments of diphenyl sulphide, *oo'*-, *mm'*-, and *pp'*-ditolyl and -dichlorodiphenyl sulphides, together with those of their corresponding sulphoxides and sulphones, have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25·00°. The results are discussed in terms of the conformation of the molecules and the conjugation between the aromatic rings and the remainder of the molecule. Conjugation is thought to occur in the sulphones but only to a small extent in the sulphides and sulphoxides.

THE phenyl rings in diphenyl ether are twisted about the C–O bonds from a planar structure.[2] Diphenyl sulphide is also non-planar and diphenyl sulphides with *ortho-* or *meta*-substituents could have several conformations. One object of the present investigation was to examine this conformational problem by dipole moment studies. Sulphur atoms can act both as electron donors and as electron acceptors; by comparing the results obtained in this communication with those for alkyl sulphides, sulphoxides, and sulphones,[1] it was hoped to obtain further evidence on these properties of the sulphur atom.

EXPERIMENTAL AND RESULTS

The electric dipole moments were measured in benzene solution at 25·00° as described previously.[1] Table 1 contains the measured properties of the solutions and Table 2 the calculated polarisation data and dipole moments.

Preparation and Purification of Compounds.—The dipole moment of each compound was measured immediately after its purification. The infrared and ultraviolet spectra of each compound were determined and compared with published spectra.[3]

---

[1] Part XLIV C. W. N. Cumper, J. F. Read, and A. I. Vogel, *J.*, 1965, 5323.

[2] G. P. Smith and W. S. Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230; K. Higasi and S. Uyeo, *Bull. Chem. Soc. Japan*, 1939, **14**, 87. See also ref. 22, 23.

[3] G. Leandri, A. Mangini, and R. Passerini, *Gazzetta*, 1954, **84**, 3, 73; *J.*, 1957, 1386; E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84, 231; 1950, **72**, 1292.

TABLE 1

$100w_2$	ε_{12}	v_{12}	n_{12}
Diphenyl sulphide			
0·0951	2·2757	1·14424	1·49777
0·2030	2·2770	1·14403	1·49767
0·3435	2·2798	1·14361	1·49794
0·6643	2·2853	1·14277	1·49828
1·1654	2·2938	1·14155	1·49884
1·5484	2·3009	1·14049	1·49929
1·9385	2·3072	1·13942	1·49979
oo′-Ditolyl sulphide			
0·1700	2·2765	1·14408	1·49762
0·3586	2·2780	1·14366	1·49777
0·7168	2·2816	1·14286	1·49812
1·0512	2·2849	1·14218	1·49854
1·3399	2·2878	1·14149	1·49880
1·6559	2·2908	1·14084	1·49919
2·1053	2·2974	1·13984	1·49955
mm′-Ditolyl sulphide			
0·0126	2·2765	1·14418	1·49783
0·2261	2·2785	1·14378	1·49793
0·4750	2·2828	1·14338	1·49820
0·7268	2·2874	1·14294	1·49844
1·0811	2·2938	1·14209	1·49874
1·3163	2·2985	1·14159	1·49896
1·7056	2·3056	1·14084	1·49938
pp′-Ditolyl sulphide			
0·1103	2·2772	1·14427	1·49775
0·2018	2·2792	1·14403	1·49787
0·3917	2·2836	1·14364	1·49802
0·8154	2·2931	1·14282	1·49832
1·5756	2·3119	1·14133	1·49900
1·7335	2·3187	1·14091	1·49922
oo′-Dichlorodiphenyl sulphide			
0·0834	2·2784	1·14424	1·49753
0·2261	2·2858	1·14402	1·49768
0·4242	2·2957	1·14274	1·49792
0·7210	2·3107	1·14148	1·49827
0·9579	2·3226	1·14040	1·49863
1·1859	2·3342	1·13946	1·49882
1·4181	2·3460	1·13868	1·49902
mm′-Dichlorodiphenyl sulphide			
0·2008	2·2777	1·14373	1·49795
0·3460	2·2805	1·14321	1·49805
0·5576	2·2842	1·14236	1·49826
0·7747	2·2891	1·14152	1·49850
0·9729	2·2927	1·14070	1·49865
1·2194	2·2981	1·13980	1·49896
1·4220	2·3013	1·13894	1·49915
pp′-Dichlorodiphenyl sulphide			
0·1226	2·2746	1·14393	1·49764
0·3731	2·2757	1·14287	1·49784
0·5705	2·2770	1·14211	1·49800
0·9201	2·2781	1·14071	1·49837
2·5552	2·2858	1·13441	1·50023
4·0843	2·2933	1·12823	1·50170
5·6118	2·3005	1·12219	1·50348
Diphenyl sulphoxide			
0·0773	2·2826	1·14421	1·49772
0·1936	2·2923	1·14392	1·49790
0·4028	2·3129	1·14309	1·49810
0·7873	2·3454	1·14196	1·49849
1·2982	2·3898	1·14020	1·49907
1·6271	2·4250	1·13887	1·49932
1·7894	2·4406	1·13825	1·49969
oo′-Ditolyl sulphoxide			
0·0886	2·2821	1·14405	1·49744
0·2268	2·2930	1·14368	1·49764
0·3688	2·3036	1·14322	1·49785
0·5680	2·3189	1·14260	1·49815
0·8149	2·3387	1·14190	1·49851
0·9241	2·3476	1·14158	1·49863
1·0919	2·3608	1·14114	1·49891
mm′-Ditolyl sulphoxide			
0·1651	2·2887	1·14397	1·49791
0·2600	2·2970	1·14371	1·49802
0·4017	2·3098	1·14333	1·49810
0·5988	2·3276	1·14276	1·49828
0·7680	2·3426	1·14226	1·49843
1·0021	2·3629	1·14164	1·49862
1·2148	2·3816	1·14108	1·49878
pp′-Ditolyl sulphoxide			
0·0762	2·2856	1·14422	1·49765
0·1126	2·2857	1·14411	1·49771
0·3196	2·3054	1·14346	1·49789
0·5742	2·3310	1·14279	1·49820
0·9223	2·3706	1·14178	1·49855
1·2881	2·4012	1·14090	1·49884
1·4140	2·4115	1·14049	1·49900
oo′-Dichlorodiphenyl sulphoxide			
0·0836	2·2799	1·14403	1·49756
0·1636	2·2886	1·14366	1·49764
0·3408	2·3026	1·14283	1·49783
0·5054	2·3170	1·14215	1·49798
0·6896	2·3313	1·14131	1·49813
0·8920	2·3473	1·14042	1·49833
1·0135	2·3572	1·13986	1·49843
mm′-Dichlorodiphenyl sulphoxide			
0·0938	2·2792	1·14404	1·49751
0·1842	2·2839	1·14367	1·49760
0·3577	2·2930	1·14287	1·49780
0·5299	2·3025	1·14212	1·49798
0·6951	2·3112	1·14139	1·49816
0·8527	2·3188	1·14077	1·49832
0·9973	2·3270	1·14012	1·49845
pp′-Dichlorodiphenyl sulphoxide			
0·1612	2·2787	1·14385	1·49758
0·2285	2·2807	1·14346	1·49765
0·3668	2·2845	1·14279	1·49780
0·7954	2·2974	1·14103	1·49823
1·0785	2·3061	1·13974	1·49854
1·5450	2·3204	1·13760	1·49898
1·6067	2·3223	1·13730	1·49911
Diphenyl sulphone			
0·0489	2·2817	1·14427	1·49772
0·0622	2·2842	1·14422	1·49776
0·1347	2·2926	1·14394	1·49783
0·3028	2·3137	1·14333	1·49800
0·5261	2·3428	1·14246	1·49817
0·9428	2·3978	1·14092	1·49851
1·2093	2·4315	1·14000	1·49880
oo′-Ditolyl sulphone			
0·1161	2·2877	1·14402	1·49746
0·1769	2·2936	1·14385	1·49764
0·4129	2·3195	1·14297	1·49781
0·5328	2·3327	1·14252	1·49790
0·6733	2·3470	1·14208	1·49801
0·9445	2·3769	1·14112	1·49824
1·1160	2·3959	1·14057	1·49831

TABLE 1 (*Continued*)

$100w_2$	ε_{12}	v_{12}	n_{12}	$100w_2$	ε_{12}	v_{12}	n_{12}
mm'-Ditolyl sulphone				*pp'*-Ditolyl sulphone			
0·0899	2·2875	1·14412	1·49778	0·0401	2·2816	1·14435	1·49763
0·2400	2·3049	1·14367	1·49785	0·0591	2·2851	1·14429	1·49764
0·4885	2·3356	1·14289	1·49803	0·1096	2·2920	1·14417	1·49772
0·6826	2·3636	1·14206	1·49827	0·2287	2·3067	1·14384	1·49783
0·8604	2·3835	1·14160	1·49837	0·4796	2·3438	1·14313	1·49804
0·9992	2·4006	1·14112	1·49847	0·7160	2·3744	1·14245	1·49826
1·2426	2·4328	1·14030	1·49867	0·9817	2·4120	1·14170	1·49847
oo'-Dichlorodiphenyl sulphone				*mm'*-Dichlorodiphenyl sulphone			
0·0520	2·2783	1·14426	1·49751	0·0635	2·2796	1·14410	1·49755
0·0951	2·2815	1·14400	1·49757	0·1281	2·2849	1·14381	1·49761
0·1778	2·2889	1·14359	1·49760	0·2768	2·2966	1·14309	1·49768
0·3738	2·3032	1·14264	1·49778	0·4208	2·3074	1·14241	1·49779
0·5331	2·3170	1·14182	1·49796	0·5848	2·3205	1·14167	1·49793
0·7060	2·3297	1·14101	1·49807	0·7691	2·3352	1·14087	1·49804
0·8149	2·3386	1·14046	1·49816	0·9309	2·3476	1·13995	1·49819
pp'-Dichlorodiphenyl sulphone							
0·1014	2·2790	1·14395	1·49769				
0·1593	2·2816	1·14371	1·49775				
0·3598	2·2903	1·14273	1·49790				
0·6435	2·3028	1·14138	1·49816				
0·8548	2·3119	1·14037	1·49832				
1·2682	2·3299	1·13841	1·49864				
1·5004	2·3400	1·13733	1·49888				

TABLE 2

Compound	α	β	${}_{\infty}P_2$ (cm.^{3})	R_D (cm.^{3})	${}_{o}P$ (cm.^{3})	μ (D)	Previous values for C_6H_6 solution	
			Sulphides					
Diphenyl	$1{\cdot}71_2$	$-0{\cdot}260_9$	109·0	60·21	48·80	1·55	1·48[a] 1·55[c]	1·51[b] 1·57[d]
oo'-Ditolyl	$0{\cdot}98_9$	$-0{\cdot}218_6$	98·99	70·48	28·51	1·18	1·08[e]	
mm'-Ditolyl	$1{\cdot}76_5$	$-0{\cdot}200_4$	131·4	70·59	60·84	1·73	1·64[e]	
pp'-Ditolyl	$2{\cdot}37_0$	$-0{\cdot}198_5$	155·9	69·50	86·43	2·06	1·95[b]	1·97[e]
oo'-Dichlorodiphenyl	$5{\cdot}06_5$	$-0{\cdot}434_7$	296·9	70·21	226·7	3·33	3·29[e]	
mm'-Dichlorodiphenyl	$1{\cdot}93_6$	$-0{\cdot}394_3$	151·8	71·70	80·12	1·98	1·93[e]	
pp'-Dichlorodiphenyl	$0{\cdot}47_4$	$-0{\cdot}395_4$	90·35	80·75	9·60	0·68	0·56[e]	0·58[b]
			Sulphoxides					
Diphenyl	9·23	$-0{\cdot}346_8$	399·1	60·32	338·8	4·07	4·00[f] 4·08[g,h]	4·03[b] 4·11[a]
oo'-Ditolyl	7·84	$-0{\cdot}293_6$	397·8	76·77	321·1	3·96		
mm'-Ditolyl	8·85	$-0{\cdot}277_3$	442·7	69·57	373·1	4·27		
pp'-Ditolyl	9·75	$-0{\cdot}276_1$	481·5	71·63	409·9	4·48	4·41[f]	4·43[b]
oo'-Dichlorodiphenyl	8·09	$-0{\cdot}445_8$	469·0	70·15	398·8	4·42		
mm'-Dichlorodiphenyl	5·30	$-0{\cdot}436_3$	327·4	73·00	254·4	3·53		
pp'-Dichlorodiphenyl	3·02	$-0{\cdot}447_3$	210·3	71·72	138·6	2·60	2·59[b]	2·73[i]
			Sulphones					
Diphenyl	$12{\cdot}9_7$	$-0{\cdot}370_4$	582·5	60·62	521·9	5·05	4·97[h] 5·06[g] 5·08 5·09[d]	5·12[j]
oo'-Ditolyl	$10{\cdot}8_2$	$-0{\cdot}345_7$	559·5	68·07	492·4	4·91		
mm'-Ditolyl	$12{\cdot}7_2$	$-0{\cdot}337_0$	648·1	69·89	578·3	5·32		
pp'-Ditolyl	$13{\cdot}7_5$	$-0{\cdot}282_0$	700·1	74·62	626·1	5·54		
oo'-Dichlorodiphenyl	7·89	$-0{\cdot}494_8$	481·6	68·65	413·0	4·50		
mm'-Dichlorodiphenyl	7·81	$-0{\cdot}477_2$	478·8	68·21	410·6	4·48		
pp'-Dichlorodiphenyl	4·35	$-0{\cdot}474_0$	292·4	70·36	222·1	3·30		

[a] E. Bergmann, L. Engel, and S. Sándor, *Z. phys. Chem.*, 1930, *B*, **10**, 397. [b] G. C. Hampson, R. H. Farmer, and L. E. Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147. [c] M. Gomel, N. Marziano, and R. Passerini, *Bull. Soc. chim. France*, 1959, 1908. [d] J. De Vries and W. H. Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888. [e] M. Rolla, M. Sanesi, and G. Leandri, *Ann. Chim.* (*Italy*), 1952, **42**, 664; 1954, **44**, 424; 1956, **46**, 1127. [f] N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564. [g] E. N. Gur'yanova, *Zhur. fiz. Khim.*, 1950, **24**, 479. [h] M. J. Aroney, L. R. Fisher, and R. J. W. Le Fèvre, *J.*, 1963, 4450. [i] E. Bergmann and M. Tschudnowsky, *Ber.*, 1932, *B*, **65**, 457. [j] V. Baliah and Sp. Shanmuganathan, *Trans. Faraday Soc.*, 1959, **55**, 232.

Sulphides. Diphenyl sulphide. This was prepared from freshly distilled sulphur monochloride and dry A.R. benzene.[4] The product had b. p. 115°/3 mm., d_4^{20} 1·1133.

pp'-*Ditolyl sulphide* was obtained by reducing [5] the corresponding sulphoxide, (see below), with amalgamated zinc wool and hydrochloric acid. The reaction mixture was filtered, and the sulphide precipitated by the addition of water and washed with aqueous ethanol. Repeated recrystallisation from benzene and then from aqueous ethanol gave the product of constant m. p. (56°).

pp'-*Dichlorodiphenyl sulphide* was obtained by reducing [6] its sulphoxide with zinc dust and glacial acetic acid at 90°. The solution was stirred at this temperature until the evolution of hydrogen ceased, filtered hot, and the sulphide precipitated by the addition of water. Recrystallisations from ethanol and then from benzene gave a product of constant m. p. (95°).

oo'-*and* mm'-*Ditolyl and -dichlorodiphenyl sulphides.* These were prepared by Zeigler's method [7] using the modified procedure of Leandri, Mangini, and Passerini.[8] The appropriately substituted thiophenol was first made by the method Tarbell and Fukushima.[9] This involved diazotising the corresponding aniline, reacting it with an aqueous solution of potassium ethyl xanthate and hydrolysing the product with alkali. A cold solution of the diazotised amine was then added to the phenol at 40°, the resulting red oil was separated, dissolved in ether, washed successively with alkali, acid, and water, dried, and the solvent removed. Disulphide impurities were removed by refluxing the crude sulphide with an ethanolic solution of stannous chloride which had been saturated with hydrogen chloride. The sulphide was precipitated with water, dissolved in ether, washed with alkali to remove thiols, then with acid and finally with water. The solution was dried, the ether removed, and the product fractionated three times. The *ortho*-isomers were recrystallised from aqueous ethanol and light petroleum (b. p. 40—60°) to constant m. p. Thus were obtained: oo'-*ditolyl sulphide*, b. p. 117°/0·4 mm., m. p. 64° (Found: C, 78·7; H, 6·6; S, 14·6. Calc. for $C_{14}H_{14}S$: C, 78·5; H, 6·6; S, 15·0%); oo'-*dichlorodiphenyl sulphide*, b. p. 148°/0·4 mm., m. p. 69° (Found: C, 56·1; H, 2·9; S, 13·1; Cl, 28·4. Calc. for $C_{12}H_8Cl_2S$: C, 56·5; H, 3·2; S, 12·6; Cl, 27·8%); mm'-*ditolyl sulphide*, b. p. 115°/0·4 mm. (Found: C, 78·9; H, 6·8; S, 14·8%); mm'-*dichlorodiphenyl sulphide*, b. p. 128°/0·1 mm. (Found: C, 56·1; H, 2·8; S, 12·0; Cl, 27·3%).

Sulphoxides. Diphenyl sulphoxide.[10] Thionyl chloride and dry benzene were stirred at 0° and freshly powdered anhydrous aluminium chloride added slowly. The solution was refluxed to remove hydrogen chloride and then poured slowly on to crushed ice. The oil was removed, washed with water, and excess benzene distilled off. The residue, which solidified, was crystallised from light petroleum (b. p. 60—80°), treated with activated charcoal, and recrystallised from ethanol to a constant m. p. (71°).

pp'-*Ditolyl sulphoxide* was prepared from toluene and thionyl chloride as described [5] for diphenyl sulphoxide. The product was recrystallised successively from ligroin and from benzene to a constant m. p. (95°).

pp'-*Dichlorodiphenyl sulphoxide* was prepared as above from chlorobenzene and thionyl chloride, the product being recrystallised from ethanol to a constant m. p. (143°).

oo'- *and* mm'-*Ditolyl and -dichlorodiphenyl sulphoxides.* The corresponding sulphides could not be oxidised to their sulphoxides with hydrogen peroxide in acetone or in glacial acetic acid. If 10% acetic anhydride was added to the latter solvent the corresponding sulphoxide was obtained in about 70% yield. The sulphide dissolved in the acetic acid, acetic anhydride solvent was cooled below 10°, the theoretical quantity of 30% hydrogen peroxide added slowly, and the mixture allowed to stand for two days. For the *ortho*-isomers the sulphoxide was precipitated with water, filtered, washed, and recrystallised from aqueous ethanol and from ligroin to a constant m. p. The *meta*-isomers were fractionated three times. Thus were obtained: oo'-*ditolyl sulphoxide*, m. p. 122° (Found: C, 74·6; H, 6·6; S, 14·3. $C_{14}H_{14}SO$ requires: C, 73·0; H, 6·1; S, 13·9%); oo'-*dichlorodiphenyl sulphoxide*, m. p. 103° (Found: C, 53·8; H, 3·3; S, 11·2; Cl, 24·8. $C_{12}H_8Cl_2SO$ requires: C, 53·2; H, 3·0; S, 11·8; Cl, 26·2%); mm'-*ditolyl*

---

[4] W. W. Hartman, L. A. Smith, and J. B. Dickey, *Org. Synth.*, Coll. Vol. II, 242.

[5] G. C. Hampson, H. Farmer, and L. E. Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 146.

[6] M. Gazdar and S. Smiles, *J.*, 1910, **97**, 2248.

[7] J. H. Ziegler, *Ber.*, 1895, **28**, 1674.

[8] G. Leandri, A. Mangini, and R. Passerini, *Gazzetta*, 1954, **84**, 3.

[9] D. S. Tarbell and D. K. Fukushima, *Org. Synth.*, Coll. Vol. III, p. 809.

[10] R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.

sulphoxide, b. p. 134°/0·9 mm. (Found: C, 74·8; H, 6·5; S, 14·4%); mm′-*dichlorodiphenyl sulphoxide*, b. p. 161°/0·4 mm. (Found: C, 53·0; H, 3·1; S, 12·3; Cl, 25·9%).

Sulphones. Diphenyl sulphone was prepared from benzenesulphonyl chloride and dry benzene by the Friedel–Crafts reaction using ethylene dichloride as solvent.[11] The reaction mixture was poured on to ice and dilute hydrochloric acid, steam distilled, and the residual diphenyl sulphone allowed to crystallise. It was recrystallised from ethanol, decolourised with activated carbon, and recrystallised from benzene to a constant m. p. (129°).

pp′-*Ditolyl sulphone* was prepared from *p*-toluidinesulphonyl chloride by the preceding method. It was recrystallised from ethanol to a constant m. p. (159°).

pp′-*Dichlorodiphenyl sulphone.* The corresponding sulphoxide, dissolved in boiling 40% acetic acid solution, was oxidised with potassium permanganate. The solids were filtered off, the sulphone extracted from them with hot ethanol, treated with activated charcoal, and recrystallised from ethanol to a constant m. p. (148°).

oo′- *and* mm′-*Ditolyl and -dichlorodiphenyl sulphones* were prepared by oxidising the corresponding sulphides with peracetic acid.[12] The freshly distilled sulphide was dissolved in a glacial acetic acid, acetic anhyride mixture at 0° and excess 30% hydrogen peroxide added slowly. The solution was allowed to stand for 7 days, the excess peroxide decomposed with manganese dioxide, and the solvent removed at less than 30 mm. pressure. The residue was dissolved in hot ethanol, treated with activated charcoal, and recrystallised from ethanol to a constant m. p. Thus were obtained: oo′-*ditolyl sulphone*, m. p. 104° (Found: C, 69·3; H, 5·8; S, 12·9. Calc. for $C_{14}H_{14}SO_2$: C, 68·3; H, 5·7; S, 13·0%); oo′-*dichlorodiphenyl sulphone*, m. p. 183° (Found: C, 50·5; H, 3·6; S, 10·7; Cl, 23·7. Calc. for $C_{12}H_8Cl_2SO_2$: C, 50·2; H, 2·8; S, 11·2; Cl, 24·7%); mm′-*ditolyl sulphone*, m. p. 96° (Found: C, 68·4; H, 5·6; S, 13·1%); mm′-*dichlorodiphenyl sulphone*, m. p. 110° (Found: C, 50·2; H, 2·9; S, 12·3; Cl, 25·8%).

DISCUSSION

The dipole moments of the compounds studied are collected in Table 2; they have not been corrected for any solvent effect but this is unlikely to affect the general conclusions given below. The moment of *pp*′-dichlorodiphenyl sulphide (0·68 D) is high because of inadequate allowance for its atom polarisation.

Sulphides.—The dipole moment of diphenyl sulphide (1·55 D) is slightly less than that of alkyl sulphides [1] (*ca.* 1·60 D) and this could be attributed to several factors. (1) According to the equation of Buckingham and Le Fèvre [13] the true (vapour phase) moment of diphenyl sulphide should be a little greater than in benzene solution, whereas that of dimethyl sulphide should be smaller. (2) The $\widehat{CSC}$ bond angle may be greater; in *pp*′-ditolyl and *pp*′-dibromodiphenyl sulphides [14] it is 109° compared with 99 or 105° in dimethyl sulphide.[15] (3) There is a mesomeric displacement of electrons from the sulphur atom into the phenyl rings; this displacement has been postulated in divinyl sulphide (1·20 D) and thiophen [16] (0·49 D) which have substantially lower dipole moments than those of their corresponding saturated compounds (1·61 and 1·90 D, respectively [17]). The conjugation would involve the 3 *p*-electrons of the sulphur atom and would be at a maximum for two coplanar phenyl rings. Coplanarity is sterically impossible for diphenyl sulphide; and the small difference between its moment and the moments of alkyl sulphides suggests that any mesomeric interaction between the sulphur atom and the phenyl rings must be small. Phenyl methyl sulphide, however, has a dipole moment [18] (1·31, 1·38 D) significantly smaller than the dipole moments of dimethyl sulphide (1·45 D) and diphenyl sulphide

---

[11] G. Holt and B. Pagdin, *J.*, 1960, 2508.

[12] A. Pomerantz and R. Connor, *J. Amer. Chem. Soc.*, 1939, **61**, 3386.

[13] A. D. Buckingham and R. J. W. Le Fèvre, *J.*, 1952, 1932.

[14] W. R. Blackmore and S. C. Abrahams, *Acta Cryst.*, 1955, **8**, 329; J. Toussaint, *Helv. Chim. Acta*, 1945, **28**, 1233; *Bull. Soc. chim. belges*, 1944, **13**, 111.

[15] L. Pierce and M. Hayashi, *J. Chem. Phys.*, 1961, **35**, 479; L. O. Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036.

[16] B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, 1946, **68**, 1005.

[17] C. W. N. Cumper and A. I. Vogel, *J.*, 1959, 3521.

[18] V. Baliah and M. Uma, *Tetrahedron*, 1963, **19**, 455; H. Lumbroso and C. Marschalk, *J. Chim. phys.*, 1952, **49**, 385.

(1·55 D); here the mesomeric moment is appreciable because steric interference between the phenyl and methyl groups does not occur.

The dipole moment of *pp'*-ditolyl sulphide can be calculated to be 1·99 D, (assuming a C–CH_3 group moment[19] of 0·37 D, a diphenyl sulphide moment of 1·55 D, and a $\widehat{CSC}$ angle of 107°), and is 0·07 D less than the observed value. Similarly the calculated dipole moment of *pp'*-dichlorodiphenyl sulphide is —0·34 D, (C–Cl group moment of —1·59 D derived from chlorobenzene[20]) compared with the observed value of ±0·68 D. The difference could arise from an enhanced mesomeric shift of electrons from the sulphur atom towards the benzene rings or from an inadequate allowance for atom polarisation. The distortion polarisation was equated to the R_D value (80·75 c.c.) and this would have to be increased by 9% to reduce the dipole moment by 0·34 D. In either case the mesomeric moment would not be large and this is presumably also the case in the *ortho-* and *meta*-isomers.

The dipole moments of *ortho-* and *meta*-substituted diphenyl sulphides depend upon the angle between the plane of the phenyl ring and that of the C–S–C grouping. The molecules cannot be planar but conformations (*a*) in which one phenyl ring is twisted 90° out of the C–S–C plane and (*b*) in which both rings are perpendicular to this plane have been suggested. The calculated moments are shown in the columns headed μ_a and μ_b respectively in Table 3. Neither structure gives acceptable results for all the compounds studied.

TABLE 3

		μ_b		
Sulphide	μ_a	*cis*	*trans*	$\mu_{exp.}$
oo'-Ditolyl	1·12D	1·47	1·33	1·18
mm'-Ditolyl	1·58	1·88	1·77	1·73
oo'-Dichlorodiphenyl	3·86	3·71	2·49	3·33
mm'-Dichlorodiphenyl	2·63	2·82	0·60	1·98

C–CH_3 Bond moment + 0·37D (toluene).
C–Cl Bond moment — 1·59D (chlorobenzene).
C_6H_5–S Group moment — 1·30D (diphenyl sulphide).

In crystalline *pp'*-dibromodiphenyl sulphide[21] each ring is twisted 36° about the C–S bond out of the C–S–C plane and in *pp'*-ditolyl sulphide through 33·8°. The molar Kerr constant of diphenyl sulphide, measured in solution,[22] indicates that the rings are twisted about 42° out of the $\widehat{CSC}$ plane. Similar structures have been suggested for diphenyl ether[23] and *oo*-di-iododiphenyl ether.[24] For the three configurations of *ortho-* and *meta*-disubstituted diphenyl sulphides shown in Figure 1 the calculated dipole moments can be shown by vector addition to be given by the formulæ,

$$\begin{array}{l}\mu\mathrm{I} \\ \ \mathrm{II}\end{array} = 1{\cdot}55 - 2\mu_x(\cos\alpha\cos\gamma \mp \sin\alpha\sin\gamma\cos\beta),$$

$$\mu\mathrm{III} = \{(1{\cdot}55 - 2\mu_x\cos\alpha\cos\gamma)^2 + 4\mu_x{}^2[(\sin\alpha\cos\gamma\cos\beta)^2 + (\sin\alpha\sin\beta)^2]\}^{\frac{1}{2}}.$$

The angle β is the " angle of twist " about the C–S bond (Figure 1), α the angle between the C–CH_3 or C–Cl bond and the S–C direction, (60° for *ortho-* and 120° for *meta*-substituents), and 2γ the $\widehat{CSC}$ angle which is assumed to be 107°. The dipole moments of toluene (+0·37 D) and of chlorobenzene (—1·59 D) were used for the C–CH_3 and C–Cl bond moments μ_x. Conformation (III) is less likely than the others because it is unsymmetrical and *ortho*-substituents would be close together.

---

[19] C. W. N. Cumper, A. I. Vogel, and S. Walker, *J.*, 1957, 3640.
[20] C. W. N. Cumper and A. I. Vogel, *J.*, 1960, 4723.
[21] J. Toussaint, *Bull. Soc. chim. belges*, 1945, **54**, 319.
[22] M. J. Aroney, R. J. W. Le Fèvre, and J. Saxby, *J.*, 1963, 1167.
[23] R. J. W. Le Fèvre, A. Sundaram, and K. M. S. Sundaram, *Bull. Chem. Soc. Japan*, 1962, **35**, 690.
[24] K. Higasi, " Dielectric Relaxation and Molecular Structure," *Res. Inst. App. Elect., Hokkaido Univ. Japan*, No. 9, 1961.

The above equations for the dipole moments of conformations (I) and (III) cannot be solved for the angle β with any of the compounds studied. If the molecules exist in a single conformation, then (II) remains the only real possibility. The angles β calculated for this conformation are, *oo'*-ditolyl sulphide 73°, *oo'*-dichlorodiphenyl sulphide 68°, *mm'*-ditolyl sulphide 86°, and *mm'*-dichlorodiphenyl sulphide 54°. These results can only provide a general indication of the angle of twist in benzene solution and there must be some torsional oscillation occurring, but whereas the calculated values of the angle β are similar in the two *ortho*-substituted compounds, they differ considerably in the two *meta*-compounds. The reason is probably that the molecules of the *ortho*-compounds exist almost exclusively as conformation (II) but the steric requirements are not so stringent in *meta*-compounds which consequently have some molecules with other conformations. A distribution of the molecules between (II) and (III) would reduce the calculated value of β for *mm'*-ditolyl sulphide and increase it for *mm'*-dichloridiphenyl sulphide.

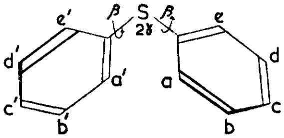

FIGURE 1. Position of substituents

Conformation	(I)	(II)	(III)
ortho-	aa'	ee'	ae'
meta-	bb'	dd'	bd'

Sulphoxides and Sulphones.—Diphenyl sulphoxide has a dipole moment (4·07 D) less than 0·1 D greater than those of alkyl sulphoxides [1] but that of diphenyl sulphone (5·05 D) is over 0·5 D greater than those of alkyl sulphones.[1] Kock and Moffitt [25] suggested that the unoccupied 3 *d*-orbitals of the sulphur atom in sulphones can conjugate with the π-electrons of the phenyl rings, thereby increasing the net dipole moment. Craig and his co-workers [26] have pointed out that highly diffuse 3 *d*-orbitals are normally unlikely to enter into effective conjugation with the π-electrons formed by the carbon atoms. In sulphones, however, the presence of the two electronegative oxygen atoms could so reduce the size of these 3 *d*-orbitals that this interaction would be possible; in sulphoxides the orbital contraction and conjugation would be less.[27] This seems to be substantiated by the dipole moments given above. (The inductive effect would exert a similar influence but it is difficult to see how it could explain the magnitude of the difference between sulphoxides and sulphones.) It is worth pointing out that conjugation in sulphides, involving the occupied 3 *p*-orbitals of the sulphur atom, is subject to strict steric requirements but that involving unoccupied 3 *d*-orbitals in sulphones is not restricted. Thus phenyl methyl sulphone and duryl methyl sulphone have the same dipole moment [28] (4·73 D).

The apparent increment Δμ in the moment along the S–O bond direction when diphenyl, *pp'*-ditolyl, and *pp'*-dichlorodiphenyl sulphides are oxidised to their sulphoxides and sulphones are shown in Table 4. They are only *apparent* S–O bond moments since they include the effect of changes in the mesomeric and inductive contributions from the remainder of the molecule. (The relevant formulæ and values of the angles were given in a previous Paper.[1])

TABLE 4

	Δμ			Δμ	
Substituent	Sulphone	Sulphoxide	Substituent	Sulphone	Sulphoxide
Phenyl-	3·65D	3·03	*p*-Chlorophenyl-	4·27	2·85
p-Tolyl-	3·60	3·00	Alkyl- [2]	3·00	2·90

---

[25] H. P. Koch and W. E. Moffit, *Trans. Faraday Soc.*, 1951, **47**, 7.

[26] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J.*, 1954, 332; D. P. Craig and E. A. Magnusson, *J.*, 1956, 4895. See also D. W. J. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, 1964, **40**, 3733.

[27] G. Cilento, *Chem. Rev.*, 1960, **60**, 147.

[28] P. Cohen-Fernandes, Thesis, Leiden, 1957.

The results for the diphenyl and ditolyl compounds are very similar. When the *para*-position is substituted by a chlorine atom however the mesomeric shift of electrons towards the sulphone group is considerably enhanced. Even if the calculated dipole moment of *pp'*-dichloridiphenyl sulphide (—0·34 D) is employed the $\Delta\mu$ value is still large (3·90 D). The corresponding sulphoxide has a $\Delta\mu$ value (2·85 D) rather less than for diphenyl and ditolyl sulphoxides. This confirms the view that a large mesomeric effect is not involved in the sulphoxides; the lower $\Delta\mu$ value probably arises from an inductive interaction of the C–Cl groups with the remainder of the molecule.

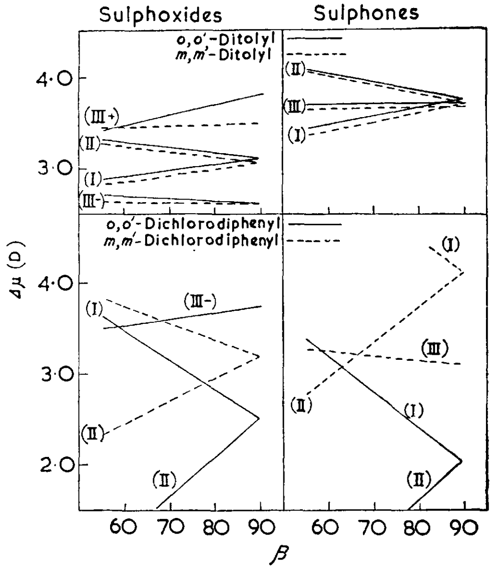

FIGURE 2. Values of $\Delta\mu_3$ which are not shown lie outside the range displayed in this diagram

The possible conformations of the *ortho*- and *meta*-substituted phenyl sulphoxides and sulphones are similar to those of the sulphides. In crystalline *pp'*-dibromodiphenyl sulphone [21] the angle is approximately 90° and in diphenyl sulphoxide [29] it is 82°. The steric repulsion between *ortho*-substituents in conformations (I) and (III) (Figure 1) will be slightly greater than in the sulphides because the $\widehat{\mathrm{CSC}}$ angle is a few degrees less; there will also be an interaction in (II) and (III) between *ortho*-substituents and the oxygen atom(s). The dipole moments of conformations (I), (II), and (III) derived by vector analysis are given by the formulæ,

Sulphones

$$\mu\begin{smallmatrix}\mathrm{I}\\ \mathrm{II}\end{smallmatrix} = 2\mu_{\mathrm{PhS}}\cos\gamma - 2\mu_{\mathrm{X}}(\cos\alpha\cos\gamma \mp \sin\alpha\sin\gamma\cos\beta) + 2\Delta\mu\cos\theta$$

$$\mu\mathrm{III} = [(2\mu_{\mathrm{PhS}}\cos\gamma - 2\mu_{\mathrm{X}}\cos\alpha\cos\gamma + 2\Delta\mu\cos\theta)^2 + 4\mu^2_{\mathrm{X}}((\sin\alpha\cos\gamma\cos\beta)^2 + (\sin\alpha\sin\beta)^2)]^{\frac{1}{2}}$$

Sulphoxides

$$\mu\begin{smallmatrix}\mathrm{I}\\ \mathrm{II}\end{smallmatrix} = [(2\mu_{\mathrm{PhS}}\cos\gamma - 2\mu_{\mathrm{X}}(\cos\alpha\cos\gamma \mp \sin\alpha\sin\gamma\cos\beta) + \Delta\mu\cos\theta)^2 + (\Delta\mu\sin\theta)^2]^{\frac{1}{2}}$$

$$\mu\mathrm{III}^{\pm} = [(2\mu_{\mathrm{PhS}}\cos\gamma - 2\mu_{\mathrm{X}}\cos\alpha\cos\gamma + \Delta\mu\cos\theta)^2 + (2\mu_{\mathrm{X}}\sin\alpha\cos\gamma\cos\beta)^2 + 2\mu_{\mathrm{X}}(\sin\alpha\sin\beta \mp \Delta\mu\sin\theta)^2]^{\frac{1}{2}}$$

In the last equation the plus sign refers to the substituent X and oxygen atom being on either side of the C–S–C plane, with the minus sign X and the oxygen atom on the same

---

[29] S. C. Abrahams, *Acta Cryst.*, 1957, **10**, 417.

side. The C_6H_5–S group moment μ_{PhS} is 1·30 D and θ the angle between the S–O bond and the bisector of the $\widehat{\mathrm{CSC}}$ angle. The values of the angles α, γ, and θ chosen for alkyl sulphones and sulphoxides will be used.[1] Figure 2 shows the calculated $\Delta\mu$ values as a function of the angle of twist β.

The $\Delta\mu$ value for *oo'*- dichlorodiphenyl sulphone, and possibly to a lesser extent for the sulphoxide, is low in comparison with the other results in Figure 2 and Table 4. It would seem that this results from an interaction between the chlorine and oxygen atoms; models show that they can be close together in all the conformations considered, particularly in (II). Solutions of acetone derivatives with various degrees of chlorination also have a tendency for the chlorine and oxygen atoms to be close together in space.[30] The other results confirm that the $\Delta\mu$ values are greater in the sulphones than in the sulphoxides. If the $\Delta\mu$ values are as in Table 4 then with β about 70°, conformation (I) would seem to be more important than (II) for the ditolyl sulphones and sulphoxides, though it is possible that the other conformations also exist. This is to be contrasted with the sulphides where conformation (II) is of greater importance. In *mm'*-dichlorodiphenyl sulphone the chlorine atoms are unlikely to enhance the mesomeric moment between the sulphur atom and the benzene rings to any great extent so that conformation (II) would appear to be of greater importance and this may also be the situation in the corresponding sulphoxide.

The authors thank Imperial Chemical Industries Limited for a grant.

WOOLWICH POLYTECHNIC, LONDON S.E.18. [*Received, April 1st,* 1965.]

[30] L. J. Bellamy and R. L. Williams, *J.*, 1957, 4294.