990. *Physical Properties and Chemical Constitution. Part XLIV.* The Electric Dipole Moments of Some Dialkyl Sulphides, Disulphides, Sulphoxides, and Sulphones*

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The electric dipole moments of eight dialkyl sulphides, the corresponding sulphoxides and sulphones, and of nine dialkyl disulphides 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 relation to the conformation of the molecules and the nature of the sulphur–oxygen bond.

MANY determinations of the electric dipole moments of dialkyl sulphides, sulphoxides, and sulphones have been reported in the literature, but in very few cases have the dipole moments of the sulphide and of its two oxidised forms been reported by the same authors. It therefore seemed desirable to measure the dipole moments of a series of sulphides, sulphoxides and sulphones in order to obtain a consistent set of values which could be utilised in discussions on molecular conformation and on the nature of the sulphur–oxygen bond.

EXPERIMENTAL AND RESULTS

The apparatus and technique of measurement, the method of calculation, and the mode of presenting the results are as described in previous Parts [1] of this Series. The dielectric constants (ε_{12}), specific volumes (v_{12}), the square of the refractive indices (n_{12}^2), and the specific refractions of the solutions were linear functions of their weight fractions (w_2) over the concentration range investigated. The measured properties of the benzene solutions at 25·00° are presented in Table 1 and the slopes of the graphs of dielectric constant (α) and specific volumes (β) against weight fraction, together with the polarisation data and dipole moments, are collected in Table 2.

Preparation and Purification of Compounds.—The final purification of each compound was performed immediately before its dipole moment was measured. The sulphoxides are hygroscopic compounds, and their solutions were prepared and handled under nitrogen in a dry box. As many compounds as possible were examined for purity by vapour-phase chromatography.

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* Part XLIII, preceding Paper.

[1] C. W. N. Cumper, A. A. Foxton, J. Read, and A. I. Vogel, *J.*, 1964, 430.

The infrared and ultraviolet spectra of all the components were determined, and details will be given in a subsequent Communication.

Dialkyl Sulphides.—These were prepared from the alkyl bromide or iodide, and sodium sulphide.[2]

Dimethyl sulphide. Aqueous sodium sulphide was added slowly to a mixture of methyl iodide and 95% ethanol at the b. p., the resulting mixtures heated under reflux for 2 hr. and then distilled. On addition of water to the distillate dimethyl sulphide separated out as a yellow oil, which was removed, set aside over sodium hydroxide pellets for 24 hr., washed until neutral, and dried. The crude sulphide was fractionated, and the middle fraction washed repeatedly with 15% sodium hydroxide solution, then with water, dried, and finally fractionated twice from sodium. The product had b. p. 38°/760 mm., d_4^{20} 0·8486, n_D^{20} 1·4357.

Diethyl sulphide, prepared as above, could not be freed completely from unreacted ethyl iodide. It was therefore prepared from fuming sulphuric acid, absolute ethanol, and sodium sulphide.[3] The product was dried over potassium hydroxide and fractionated from sodium. The diethyl sulphide had b. p. 92°/760 mm., d_4^{20} 0·8362, n_D^{20} 1·4428.

Higher sulphides were prepared from the corresponding alkyl bromides as described for methyl sulphide. Some of the physical properties of many sulphides and disulphides have been described previously.[4] Di-n-propyl sulphide had b. p. 142°/762 mm., d_4^{20} 0·8394, n_D^{20} 1·4490. Di-isopropyl sulphide had b. p. 119°/760 mm., d_4^{20} 0·8164, n_D^{20} 1·4393. Di-n-butyl sulphide had b. p. 187°/764 mm., d_4^{20} 0·8403, n_D^{20} 1·4529. Di-n-pentyl sulphide had b. p. 86°/3·7 mm., d_4^{20} 0·8407, n_D^{20} 1·4561. Di-t-butyl sulphide was supplied, and purified by gas chromatography, by the British Petroleum Co. Ltd.; it had b. p. 149°/760 mm.

Dibenzyl sulphide. Benzyl chloride in 95% ethanol was heated under reflux, aqueous sodium sulphide added slowly, and heating continued for 4 days. The ethanol was then distilled off, and the residue poured on to crushed ice. The oil that separated was placed in a Towers drying apparatus at 120°/10 mm. to remove water and benzyl chloride. On cooling, the dibenzyl sulphide solidified, and treatment with activated charcoal followed by repeated recrystallisation from aqueous ethanol gave crystals of constant m. p. (49°).

Disulphides. Four dialkyl disulphides were presented by the British Petroleum Co. Ltd. They had been purified by gas chromatography and were redistilled immediately before use. Dimethyl disulphide had b. p. 109°/761 mm., d_4^{20} 1·0642; diethyl disulphide had b. p. 152°/762 mm., d_4^{20} 0·9921; di-n-propyl disulphide had b. p. 194°/754 mm., d_4^{20} 0·9597; and di-t-butyl disulphide had b. p. 640°/755 mm., d_4^{20} 0·9225.

The remaining disulphides were obtained from the corresponding thiols (from alkyl bromides and thiourea) by oxidation with iodine.[5] The purification, including washing with sodium hydroxide solution, was as described for the alkyl sulphides, except that sodium was not added before the final fractionations. Thus were obtained propane-1-thiol, b. p. 67°/763 mm.; di-n-propyl disulphide, b. p. 86°/16 mm., d_4^{20} 0·9595; propane-2-thiol, b. p. 56°/761 mm.; di-isopropyl disulphide, b. p. 95°/56 mm., d_4^{20} 0·9435; butane-1-thiol, b. p. 99°/768 mm.; di-n-butyl disulphide, b. p. 84°/3 mm., d_4^{20} 0·9433; pentane-1-thiol, b. p. 126°/761 mm.; di-n-pentyl disulphide, b. p. 119°/7 mm., d_4^{20} 0·9220.

Dibenzyl disulphide. A pure commercial sample (Hopkin and Williams) was recrystallised from ethanol to constant m. p. (80°).

Diphenyl disulphide was prepared from thiophenol by the method of Kekule and Linnemann;[6] it was recrystallised to constant m. p. (61°) from ethanol and from acetone.

Di-t-butyl trisulphide was supplied, and purified by gas chromatography, by British Petroleum Co. Ltd. d_4^{25} 0·9881, n_D^{25} 1·5203.

Alkyl Sulphoxides.—These were prepared[2] by oxidising the corresponding sulphide with 30% hydrogen peroxide. To impede the formation of sulphone, a slight excess of sulphide was employed, and the temperature maintained below 20°. Alkyl sulphoxides are extremely hygroscopic, and were always handled in a dry box.

The freshly distilled sulphide was dissolved in acetone, and 30% hydrogen peroxide added during 2 hr. at 0°. The mixture was stirred until the sulphide layer disappeared, and then

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[2] D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, 1941, **63**, 2939.

[3] H. L. Gray and G. O. Gutekunst, *J. Amer. Chem. Soc.*, 1920, **42**, 856.

[4] A. I. Vogel and D. M. Cowan, *J.*, 1943, 16; S. Bezzi, *Gazzetta*, 1935, **65**, 693.

[5] A. I. Vogel, " Practical Organic Chemistry," 3rd edn., Longmans, Green and Co., London, 1956, p. 496.

[6] A. Kekule and E. Linnemann, *Annalen*, 1862, **123**, 277.

TABLE 1

100 w_2	ε_{12}	v_{12}	n_{12}
Dimethyl sulphide			
0·1219	2·2800	1·14451	1·49754
0·1657	2·2811	1·14452	1·49751
0·3599	2·2875	1·14460	1·49748
0·7280	2·3002	1·14476	1·49727
1·2743	2·3196	1·14499	1·49702
1·6283	2·3324	1·14514	1·49687
1·7365	2·3362	1·14518	1·49678
*Di-*n*-propyl sulphide*			
0·1430	2·2765	1·14453	1·49750
0·2098	2·2781	1·14459	1·49743
0·3688	2·2816	1·14468	1·49736
0·7832	2·2900	1·14493	1·49711
1·1145	2·2974	1·14513	1·49691
1·4580	2·3048	1·14533	1·49671
1·5628	2·3070	1·14536	1·49664
Di-n-butyl sulphide			
0·1472	2·2764	1·14455	1·49749
0·2062	2·2772	1·14458	1·49747
0·4242	2·2809	1·14468	1·49735
0·8131	2·2872	1·14490	1·49714
1·0662	2·2921	1·14504	1·49701
1·4901	2·2991	1·14527	1·49681
1·6510	2·3020	1·14537	1·49674
Di-n-pentyl sulphide			
0·1380	2·2758	1·14454	1·49747
0·2096	2·2771	1·14459	1·49743
0·5206	2·2815	1·14478	1·49726
0·9975	2·2877	1·14508	1·49701
1·2320	2·2913	1·14524	1·49689
1·6897	2·2979	1·14552	1·49664
1·8723	2·3004	1·14564	1·49656
Dimethyl disulphide			
0·0998	2·2780	1·14426	1·49747
0·2176	2·2838	1·14403	1·49749
0·3669	2·2904	1·14374	1·49752
0·6616	2·3032	1·14314	1·49758
0·8811	2·3125	1·14272	1·49762
1·0613	2·3198	1·14233	1·49766
1·2005	2·3265	1·14206	1·49769
Di-n-propyl disulphide			
0·1706	2·2791	1·14428	1·49747
0·2933	2·2828	1·14418	1·49746
0·5099	2·2896	1·14395	1·49744
0·8343	2·2991	1·14364	1·49741
1·1450	2·3083	1·14331	1·49738
1·4724	2·3180	1·14296	1·49736
1·5978	2·3220	1·14286	1·49734
Di-n-butyl disulphide			
0·0628	2·2765	1·14441	1·49749
0·1601	2·2785	1·14433	1·49748
0·3414	2·2835	1·14423	1·49745
0·6267	2·2906	1·14402	1·49740
1·0724	2·3021	1·14374	1·49736
1·3285	2·3087	1·14358	1·49733
1·7192	2·3190	1·14333	1·49730
Di-n-pentyl disulphide			
0·1376	2·2779	1·14441	1·49737
0·2461	2·2800	1·14433	1·49734
0·4017	2·2840	1·14426	1·49731
0·6752	2·2901	1·14410	1·49729
0·8945	2·2947	1·14401	1·49724
1·1481	2·3005	1·14388	1·49721
1·2939	2·3036	1·14381	1·49718
Diethyl sulphide			
0·0517	2·2754	1·14449	1·49750
0·1374	2·2780	1·14458	1·49745
0·2764	2·2823	1·14474	1·49735
0·5636	2·2908	1·14496	1·49714
0·8276	2·2978	1·14518	1·49699
0·9796	2·3023	1·14532	1·49689
1·3615	2·3132	1·14551	1·49662
Di-isopropyl sulphide			
0·1052	2·2784	1·14450	1·49721
0·1719	2·2795	1·14461	1·49715
0·3455	2·2824	1·14473	1·49703
0·7248	2·2930	1·14512	1·49674
1·0802	2·3001	1·14538	1·49650
1·4190	2·3084	1·14576	1·49628
1·5005	2·3110	1·14583	1·49623
Di-t-butyl sulphide			
0·1326	2·2762	1·14460	1·49749
0·4543	2·2810	1·14485	1·49732
0·9174	2·2888	1·14515	1·49699
1·3803	2·2959	1·14560	1·49668
1·5203	2·2982	1·14561	1·49660
Dibenzyl sulphide			
0·0951	2·2752	1·14422	1·49772
0·1813	2·2763	1·14404	1·49777
0·3756	2·2785	1·14374	1·49790
0·7151	2·2824	1·14275	1·49831
1·0611	2·2866	1·14195	1·49861
1·4560	2·2911	1·14100	1·49899
1·7830	2·2950	1·14024	1·49929
2·0807	2·2981	1·13956	1·49954
Diethyl disulphide			
0·1251	2·2785	1·14426	1·49744
0·2020	2·2814	1·14415	1·49744
0·4132	2·2892	1·14385	1·49744
0·6844	2·2990	1·14344	1·49744
0·8427	2·3057	1·14315	1·49744
1·0613	2·3136	1·14288	1·49744
1·3527	2·3248	1·14244	1·49744
Di-isopropyl disulphide			
0·0742	2·2772	1·14439	1·49735
0·2611	2·2831	1·14421	1·49734
0·4371	2·2884	1·14410	1·49730
0·6422	2·2952	1·14395	1·49730
0·9077	2·3043	1·14372	1·49729
1·0728	2·3095	1·14366	1·49728
1·4013	2·3203	1·14335	1·49725
Di-t-butyl disulphide			
0·1184	2·2769	1·14439	1·49727
0·2331	2·2791	1·14433	1·49725
0·4527	2·2840	1·14420	1·49722
0·6655	2·2881	1·14407	1·49719
0·8891	2·2931	1·14395	1·49717
1·1675	2·2989	1·14383	1·49713
1·3213	2·3021	1·14372	1·49710
Dibenzyl disulphide			
0·0922	2·2760	1·14408	1·49771
0·2136	2·2784	1·14378	1·49781
0·3657	2·2810	1·14345	1·49793
0·7113	2·2871	1·14237	1·49832
1·1111	2·2946	1·14118	1·49874
1·5077	2·3019	1·14014	1·49917
1·6668	2·3047	1·13961	1·49933

TABLE 1 (*continued*)

100 w_2	ε_{12}	v_{12}	n_{12}
Diphenyl disulphide			
0·0907	2·2761	1·14416	1·49775
0·2245	2·2788	1·14373	1·49798
0·4525	2·2837	1·14296	1·49826
0·6573	2·2875	1·14224	1·49853
0·9351	2·2938	1·14139	1·49853
1·1218	2·2977	1·14075	1·49887
1·4746	2·3042	1·13958	1·49907
Dimethyl sulphoxide			
0·1120	2·2996	1·14413	1·49764
0·2037	2·3220	1·14394	1·49763
0·3555	2·3499	1·14346	1·49761
0·6880	2·4192	1·14265	1·49756
0·9235	2·4690	1·14201	1·49750
1·1170	2·5111	1·14151	1·49747
1·4332	2·5765	1·14068	1·49743
1·7064	2·6330	1·13996	1·49740
Di-n-propyl sulphoxide			
0·1423	2·2931	1·14427	1·49769
0·2567	2·3074	1·14411	1·49768
0·4081	2·3289	1·14388	1·49764
0·6821	2·3611	1·14358	1·49760
0·8900	2·3877	1·14329	1·49757
1·1203	2·4174	1·14297	1·49754
1·2820	2·4374	1·14279	1·49751
Di-n-butyl sulphoxide			
0·0907	2·2849	1·14438	1·49756
0·1460	2·2912	1·14433	1·49755
0·1952	2·2959	1·14428	1·49753
0·4169	2·3196	1·14407	1·49747
0·6977	2·3503	1·14381	1·49740
1·1103	2·3952	1·14351	1·49730
1·1961	2·4050	1·14343	1·49728
Dibenzyl sulphoxide			
0·0984	2·2819	1·14418	1·49782
0·1748	2·2865	1·14394	1·49795
0·3165	2·2965	1·14344	1·49801
0·6534	2·3069	1·14234	1·49837
0·9501	2·3396	1·14143	1·49861
1·2684	2·3622	1·14044	1·49897
1·6139	2·3865	1·13946	1·49918
Diethyl sulphone			
0·0403	2·4021	1·14437	1·49763
0·0817	2·2903	1·14427	1·49762
0·1578	2·3038	1·14414	1·49758
0·2889	2·3278	1·14386	1·49755
0·4298	2·3527	1·14357	1·49749
0·5733	2·3777	1·14328	1·49744
0·6939	2·5188	1·14306	1·49739
0·7809	2·4157	1·14284	1·49736
Di-isopropyl sulphone			
0·0280	2·2788	1·14439	1·49752
0·1393	2·2963	1·14424	1·49751
0·2347	2·3090	1·14382	1·49747
0·4344	2·3381	1·14341	1·49743
0·5754	2·3597	1·14309	1·49740
0·9574	2·4162	1·14228	1·49735
1·0750	2·4338	1·14187	1·49731

100 w_2	ε_{12}	v_{12}	n_{12}
Di-t-butyl trisulphide			
0·1940	2·2757	1·14417	1·49716
0·3831	2·2770	1·14395	1·49719
0·6165	2·2789	1·14371	1·49723
1·0245	2·2820	1·14328	1·49733
1·2359	2·2837	1·14282	1·49739
1·6079	2·2861	1·14239	1·49748
1·9010	2·2895	1·14213	1·49754
Diethyl sulphoxide			
0·0897	2·2896	1·14423	1·49758
0·1581	2·3002	1·14407	1·49757
0·2593	2·3160	1·14389	1·49756
0·3659	2·3341	1·14369	1·49754
0·6126	2·3735	1·14317	1·49752
0·7627	2·3997	1·14287	1·49750
0·8984	2·4219	1·14259	1·49748
1·0163	2·4414	1·14239	1·49747
Di-isopropyl sulphoxide			
0·0343	2·2797	1·14441	1·49750
0·1243	2·2902	1·14429	1·49748
0·2138	2·3022	1·14417	1·49747
0·5586	2·3465	1·14376	1·49743
0·7682	2·3745	1·14351	1·49740
0·9693	2·4010	1·14327	1·49736
1·2926	2·4432	1·14289	1·49731
Di-n-pentyl sulphoxide			
0·0846	2·2800	1·14442	1·49748
0·1590	2·2865	1·14433	1·49744
0·3604	2·3039	1·14420	1·49739
0·6486	2·3320	1·14400	1·49729
0·8336	2·3522	1·14389	1·49723
1·0592	2·3668	1·14374	1·49716
1·2233	2·3814	1·14363	1·49712
Dimethyl sulphone			
0·0675	2·2913	1·14416	1·49750
0·1042	2·3008	1·14409	1·49748
0·2715	2·3351	1·14345	1·49745
0·5525	2·3952	1·14234	1·49737
0·6918	2·4232	1·14181	1·49733
0·8348	2·4526	1·14129	1·49730
0·9014	2·4676	1·14103	1·49728
Di-n-propyl sulphone			
0·0499	2·2829	1·14434	1·49758
0·0929	2·2881	1·14422	1·49756
0·2474	2·3101	1·14389	1·49752
0·3881	2·3324	1·14357	1·49746
0·5976	2·3610	1·14313	1·49739
0·8304	2·3940	1·14265	1·49734
1·0450	2·4252	1·14219	1·49725
1·1648	2·4433	1·14190	1·49723
Di-n-butyl sulphone			
0·0521	2·2804	1·14436	1·49758
0·1548	2·2933	1·14418	1·49754
0·2203	2·3025	1·14406	1·49751
0·4479	2·3293	1·14366	1·49743
0·7200	2·3629	1·14319	1·49734
1·0049	2·3987	1·14272	1·49724
1·0504	2·4050	1·14260	1·49722
1·2866	2·4337	1·14220	1·49716

TABLE 1 (*continued*)

100 w_2	ε_{12}	v_{12}	n_{12}	100 w_2	ε_{12}	v_{12}	n_{12}
Di-n-pentyl sulphone				*Dibenzyl sulphone*			
0·0660	2·2815	1·14424	1·49750	0·0659	2·2801	1·14420	1·49766
0·1430	2·2905	1·14415	1·49745	0·1131	2·2846	1·14404	1·49769
0·3719	2·3147	1·14386	1·49738	0·2245	2·2937	1·14361	1·49776
0·6188	2·3403	1·14349	1·49729	0·4521	2·3132	1·14276	1·49800
0·9177	2·3726	1·14309	1·49717	0·6643	2·3289	1·14211	1·49821
1·1099	2·3876	1·14284	1·49708	0·9540	2·3527	1·14103	1·49851
1·2168	2·4049	1·14272	1·49704	1·1570	2·3706	1·14041	1·49862
				1·1763	2·3722	1·14029	1·49865

TABLE 2

Compound	α	β	$_\infty P_2$ (cm.^{3})	R_D (cm.^{3})	$_0P$ (cm.^{3})	μ (D)	Previous values for C_6H_6 soln.
			Sulphides				
Dimethyl ...	3·51$_8$	0·042$_0$	63·06	20·04	43·02	1·45	1·45,[a] 1·46[b]
Diethyl	2·87$_7$	0·087$_3$	81·89	29·14	52·75	1·61	1·61,[c] 1·58,[d] 1·62[e]
Di-n-propyl...	2·13$_5$	0·058$_8$	89·86	37·68	52·18	1·60	1·56[f]
Di-isopropyl	2·32$_9$	0·094$_3$	95·43	38·20	57·23	1·67	
Di-n-butyl ...	1·71$_5$	0·054$_8$	99·45	47·20	52·25	1·60	1·57,[g] 1·58,[f] 1·61[h]
Di-t-butyl ...	1·58$_3$	0·072$_3$	96·57	46·82	49·76	1·57	1·67[b]
Di-n-pentyl...	1·41$_0$	0·063$_0$	109·0	56·40	52·58	1·60	1·59[c]
Dibenzyl	1·16$_6$	−0·235$_8$	105·0	68·40	36·64	1·34	1·38[i]
			Disulphides				
Dimethyl ...	4·33$_9$	−0·200$_4$	103·3	27·14	76·18	1·93	1·93,[b] 1·97[j]
Diethyl	3·76$_6$	−0·149$_2$	122·8	35·70	87·14	2·07	1·96,[j] 1·99,[k] 2·07
Di-n-propyl...	2·99$_4$	−0·101	131·3	45·20	86·11	2·05	1·98[j, l]
Di-isopropyl	3·25$_3$	−0·077$_6$	139·7	46·36	93·35	2·14	
Di-n-butyl ...	2·59$_1$	−0·064$_8$	144·2	55·24	88·99	2·09	1·99,[l] 2·06[m]
Di-t-butyl ...	2·10$_1$	−0·054$_7$	128·4	55·60	72·76	1·89	1·86,[m] 1·93[b]
Di-n-pentyl...	2·22$_0$	−0·051$_2$	153·4	64·32	89·35	2·09	
Dibenzyl	1·82$_9$	−0·283$_6$	147·7	76·52	71·22	1·87	1·90[l]
Diphenyl......	2·09$_5$	−0·330$_5$	138·9	63·35	75·58	1·92	1·92[n]
			Trisulphide				
Di-t-butyl ...	0·76$_8$	−0·122$_8$	94·44	65·79	28·65	1·18	1·13[b]
			Sulphoxides				
Dimethyl ...	20·9$_5$	−0·262	328·2	19·50	308·7	3·89	3·90[o]
Diethyl	16·4$_4$	−0·200$_6$	358·1	28·66	329·4	4·02	3·88[n]
Di-n-propyl...	12·6$_9$	−0·130$_7$	360·7	38·67	322·0	3·97	
Di-isopropyl	13·0$_9$	−0·120$_3$	371·2	39·18	332·0	4·03	
Di-n-butyl ...	10·8$_3$	−0·085$_2$	381·7	48·02	333·7	4·04	
Di-n-pentyl	8·9$_2$	−0·065$_2$	380·2	56·81	323·4	3·98	
Dibenzyl	6·9$_2$	−0·319$_9$	356·0	67·41	288·6	3·76	3·88[i]
			Sulphones				
Dimethyl ...	20·8$_8$	−0·380$_0$	391·0	19·71	371·3	4·26	4·25,[p] 4·26[q]
Diethyl	17·0$_0$	−0·204$_4$	445·2	31·11	414·1	4·50	4·44,[e] 4·50[n]
Di-n-propyl...	14·4$_0$	−0·215$_6$	448·2	38·20	410·0	4·48	4·47[p]
Di-isopropyl	14·8$_1$	−0·237$_7$	458·9	38·24	420·7	4·54	
Di-n-butyl ...	12·4$_1$	−0·174$_4$	467·4	47·25	420·1	4·53	4·46[p]
Di-n-pentyl...	10·6$_4$	−0·134$_4$	474·9	56·38	418·5	4·53	
Dibenzyl	8·2$_3$	−0·349$_3$	439·6	70·14	369·5	4·25	5·00[r]

[a] H. Lumbroso and G. Dumas, *Bull. Soc. chim. France*, 1955, 651. [b] P. T. White, "The Dipole Moments of Alkyl Polysulphides," British Petroleum Co. Ltd., unpublished report. [c] W. S. Walls and C. P. Smyth, *J. Chem. Phys.*, 1933, **1**, 337. [d] E. C. E. Hunter and J. R. Partington, *J.*, 1931, 2062. [e] L. E. Sutton, R. G. A. New, and J. B. Bentley, *J.*, 1933, 652. [f] E. C. E. Hunter and J. R. Partington, *J.*, 1932, 2812. [g] K. A. Jensen, *Z. anorg. Chem.*, 1935, **225**, 97. [h] A. H. Bond and J. W. Smith, *J.*, 1956, 4507. [i] E. Bergmann, L. Engel, and S. Sandor, *Ber.*, 1930, **63**, 397. [j] L. M. Kushner, G. Gorin, and C. P. Smyth, *J. Amer. Chem. Soc.*, 1950, **72**, 477. [k] H. E. Westlake, H. L. Laquer, and C. P. Smyth, *J. Amer. Chem. Soc.*, 1950, **72**, 436. [l] V. N. Vasil'eva and E. N. Gur'yanova, *Zhur. fiz. Khim.*, 1959, **33**, 1976. [m] M. T. Rogers and T. W. Campbell, *J. Amer. Chem. Soc.*, 1952, **74**, 4742. [n] E. N. Guv'yanova, *Zhur. fiz. Khim.*, 1950, **24**, 479. [o] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986. [p] H. Lumbroso and R. Passerini, *Bull. Soc. chim. France*, 1955, 1179. [q] M. J. Aroney, L. R. Fisher, and R. J. W. Le Fèvre, *J.*, 1963, 4450. [r] V. Baliah and Sp. Shanmuganathan, *Trans. Faraday Soc.*, 1959, **55**, 232.

set aside for 3 days, the temperature gradually being increased to 15°. The solvents were distilled off and the sulphoxides fractionated under reduced pressure. Some were solids of low m. p., and these were recrystallised from light petroleum (b. p. 40—60°) to constant m. p.

Dimethyl sulphoxide had b. p. 80°/19 mm. Diethyl sulphoxide had b. p. 84°/12 mm. Di-n-propyl sulphoxide had b. p. 72°/1 mm., m. p. 22°. Di-iso-propyl sulphoxide had b. p. 59°/0·9 mm. (Found: C, 54·0, H, 10·4; S, 23·5. $C_6H_{14}OS$ requires: C, 53·7; H, 10·5; S, 23·9%). Di-n-butyl sulphoxide had b. p. 92°/0·9 mm., m. p. 34° (Found: C, 59·5; H, 11·2; S, 19·6. $C_8H_{18}OS$ requires: C, 59·2; H, 11·2; S, 19·8%). Di-n-pentyl sulphoxide had b. p. 120°/1 mm., m. p. 56° (Found: C, 62·4; H, 11·9; S, 16·8. $C_{10}H_{22}OS$ requires: C, 62·9; H, 12·0; S, 16·5%). Dibenzyl sulphoxide was prepared[4] as above except that it was purified by recrystallisation from light petroleum (b. p. 100—120°) to constant m. p. (133°).

Alkyl Sulphones.—The sulphones were prepared by oxidising the corresponding sulphide with excess of peracetic acid.[7] Freshly distilled alkyl sulphide was dissolved in glacial acetic acid–acetic anhydride (1 : 1, v/v), an excess of 30% hydrogen peroxide was added slowly to this solution at 0°, and the mixture set aside for at least 7 days. It was finally kept at 40° for a short period. Excess of peroxide was decomposed by the careful addition of manganese dioxide, the mixture was filtered, and the solvent removed by distillation at <30 mm. The solid residue was dissolved in ethanol, decolourised with charcoal, and recrystallised from ethanol to constant m. p.

Dimethyl sulphone had m. p. 109°; diethyl sulphone, 74°; and di-n-propyl sulphone, 29°. Di-isopropyl sulphone had b. p. 78°/0·5 mm. (Found: C, 48·6; H, 9·6; S, 21·0. $C_6H_{14}O_2S$ requires: C, 48·0; H, 9·4; S, 21·3%). Di-n-butyl sulphone had m. p. 46°. Di-n-pentyl sulphone had m. p. 74° (Found: C, 58·2; H, 10·7; S, 15·5. $C_{10}H_{22}O_2S$ requires: C, 58·0; H, 10·6; S, 15·7%). Dibenzyl sulphone, prepared as above, had a constant m. p. of 151°.

DISCUSSION

The dipole moments of the compounds studied have not been corrected for any solvent effect but, although an allowance for this would alter their values slightly, it would not affect the following discussion. Experimental values for the bond angles in sulphides, sulphoxides, and sulphones have been collected by Abrahams.[8]

(*a*) *Monosulphides.* The monosulphides differ from the other series studied by having a virtually constant dipole moment as the length of the alkyl chains increase from ethyl to pentyl. This constancy suggests that the mean orientation of the $C_{(2)}$–$C_{(3)}$, $C_{(3)}$–$C_{(4)}$, and $C_{(4)}$–$C_{(5)}$ bonds are in directions approximately perpendicular to that of the molecular dipole. From their studies of dipole moments and molar Kerr constants, Aroney, Le Fèvre, and Saxby[9] suggested non-planar conformations for diethyl and di-n-propyl ethers and sulphides, in which corresponding carbon atoms in the two alkyl groups tend to be as far apart as possible. The dipole moments of diethyl, di-n-propyl, and di-n-butyl ethers[10] are also virtually constant in the gas phase, although they decrease along this series in benzene solution.[11]

The dipole moment of di-isopropyl sulphide is 0·07 D greater than that of the straight-chain sulphides, owing to a contribution from the moment induced in the alkyl groups, but di-t-butyl sulphide has a smaller moment. This is probably a result of the repulsion between the bulky t-butyl groups increasing the $\widehat{CSC}$ angle; a 5° increase in the angle would reduce its dipole moment by about 0·1 D even if its component group-moments were unchanged.

If the $\widehat{CSC}$ angle is assumed to be 107° in each alkyl sulphide[8] (R_2S), the apparent R–S group moments (μ_{R-S}) are as in Table 3; they include contributions from the lone-pair electrons of the sulphur atom. The $\widehat{CSC}$ angle in dimethyl sulphide has recently been

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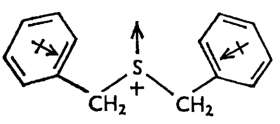
[7] A. Pomerantz and R. Connor, *J. Amer. Chem. Soc.*, 1939, **61**, 3386.

[8] S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 407.

[9] M. J. Aroney, R. J. W. Le Fèvre, and J. Saxby, *J.*, 1962, 2886; 1963, 1167.

[10] L. G. Groves and S. Sugden, *J.*, 1937, 1779.

[11] G. A. Barclay and R. J. W. Le Fèvre, *J.*, 1952, 1643.



reported[12] as 99°, in which case its calculated CH_3–S group moment would be decreased to 1·11 D. The smaller dipole moment of dibenzyl sulphide (1·34 D) is most likely due to the rather larger moments induced in the phenyl groups, as indicated.

(*b*) *Disulphides.* In the dialkyl disulphides the planes containing the two R–S–S groupings are inclined[13] at an angle ϕ. Increasing the length of the alkyl chain from methyl to n-butyl alternatively increases and decreases the dipole moment so that the mean conformation of each C–C bond cannot be perpendicular to the direction of the primary dipole. As in the monosulphides, the di-isopropyl compound has a larger moment than the n-alkyl sulphides, due to an enhanced inductive effect, but the t-butyl compound has a substantially lower moment due to an increase in the angle ϕ. The dipole moment of di-t-butyl trisulphide (1·18 D) is also substantially less than those of dimethyl trisulphide (1·66, 1·79 D) and diethyl trisulphide (1·64, 1·70 D).[14]

TABLE 3

Alkyl group	Group moment $\mu_{R\text{-}S}$ (D)	The angle ϕ in disulphides	$\Delta\mu$ Values (D) Sulphoxide	Sulphone
Methyl	1·22	68°	2·92	2·92
Ethyl	1·35	74	2·91	2·99
n-Propyl	1·35	74	2·88	2·99
Isopropyl	1·40	74	2·88	2·96
n-Butyl	1·35	71	2·95	3·05
t-Butyl	1·32	83	—	—
n-Pentyl	1·35	71	2·88	3·04
Benzyl	1·13	60	2·88	3·04
Phenyl	(1·30) *	79	(3·03) *	(3·65) *

* Unpublished results.

If the $\widehat{RSS}$ angle is 107° and the R–S group moment the same as in the monosulphides, an estimate of the azimuthal angle ϕ may be obtained from the equation

$$\mu = 2\mu_{R\text{-}S} \sin 73^\circ \cos(\phi/2),$$

which has been deduced by the vector summation of group moments. The values of ϕ are collected in Table 3. The lower value of ϕ obtained for dibenzyl disulphide results from the orientation and high polarisability of the phenyl rings.

(*c*) *Sulphones.* The sulphones and sulphoxides display small alternations in their dipole moments as the length of the alkyl chain is increased, although the variations may be within experimental error. The average conformation of the chains might differ slightly from that in the parent sulphides.

The dipole moment of the sulphones may be written:

$$\mu_{R_2SO_2} = 2\mu_{R\text{-}S} \cos \tfrac{1}{2}(\widehat{CSC}) + 2\Delta\mu \cos \tfrac{1}{2}(\widehat{OSO}),$$

where $\Delta\mu$ represents the change in dipole moment in the direction of the S–O bond when the sulphide is converted into its sulphone. The R–S bond moment is assumed to be that of the corresponding sulphide. The $\widehat{CSC}$ angle has been taken[8] as 103° and the $\widehat{CSO}$ angle[15] as

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[12] L. Pierce and M. Hayashi, *J. Chem. Phys.*, 1961, **35**, 479.

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[15] J. Toussaint, *Bull. Soc. chim. belges*, 1945, **54**, 319.

107°; these values require an $\widehat{OSO}$ angle of 124°. The calculated values of $\Delta\mu$, Table 3, are reasonably constant, with a mean value of 3·00 D.

The lower moment and $\Delta\mu$ value of dimethyl sulphone (2·92 D) has been attributed to a solvent effect,[16] but it is difficult to see why this should result in a different $\Delta\mu$ value from that of the other alkyl compounds. A change in the conformation of the $C_{(2)}$–$C_{(3)}$ bond between sulphide and sulphone in the other alkyl compounds, together with enhanced induced moments in the alkyl chains, provides a more likely explanation.

(*d*) *Sulphoxides.* For a pyramidal arrangement of the three sulphur valency bonds in sulphoxides it can be shown that,

$$\mu^2_{R_2SO} = [2\mu_{R\text{-}S} \cos \tfrac{1}{2}(\widehat{CSC}) + \Delta\mu \cos \theta]^2 + [\Delta\mu \sin \theta]^2$$

where θ is the angle between the S–O bond and the bisector of the $\widehat{CSC}$ angle. The $\widehat{CSO}$ angle in sulphoxides [8] would appear to be 107° and the $\widehat{CSC}$ angle about 100°, corresponding to 63° for θ. With these angles, the calculated values of $\Delta\mu$ are given in Table 3. (If the $\widehat{CSC}$ angle is taken to be 97°, as in diphenyl sulphoxide,[17] and θ correspondingly greater, the $\Delta\mu$ values are only altered by 0·01 D). The mean value for $\Delta\mu$ is 2·90 D, slightly lower than for sulphones, but the difference may not be significant in view of the uncertainty about the bond angles, and the neglect of solvent effects.

These results demonstrate that the sulphur–oxygen bond is not more polar in sulphoxides than in sulphones, as had been suggested from analysis of infrared spectra,[18] from the strong tendency of sulphoxides to accept hydrogen bonds,[19] and from calculated bond orders.[20] The numerical value for the dipole-moment increment in the direction of the sulphur–oxygen bond when sulphides are oxidised provides a lower limit for the actual moment of this bond. It has been interpreted in terms of a predominantly double-bond character,[21] and this has been confirmed by recent proton magnetic resonance coupling constants.[22]

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