# THE DIPOLE MOMENTS OF SOME ARYL METHYL SULPHIDES

## EVIDENCE FOR THE EXPANSION OF THE VALENCE SHELL OF SULPHUR

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Abstract—The electric dipole moments of a number of aryl methyl sulphides have been measured in benzene solution at  $30^{\circ}$  and the data discussed. The moments of *p*-aminophenyl methyl and *p*-dimethylaminophenyl methyl sulphide indicate that sulphur enters into d-orbital resonance in these compounds.

THE elements below the first row of the periodic table can in certain circumstances expand their valence shells by utilizing the vacant d-orbitals. In the case of sulphur, there is increasing evidence for the d-orbital utilization.<sup>1</sup> Our interest in d-orbital resonance prompted us to determine the dipole moments of a number of aryl methyl sulphides. Measurement of electric dipole moments is indeed an important method of obtaining information about the electronic distribution in molecules in their ground state.

#### Dipole moments

The dielectric constants  $(\epsilon_{12})$  and densities  $(d_{12})$  of dilute benzene solutions were measured at 30° and the empirical constants  $\alpha$  and  $\beta$  for each compound were calculated from the equations,<sup>2</sup>

$$\epsilon_{12} = \epsilon_1 (1 + \alpha w_2)$$
$$d_{12} = d_1 (1 + \beta w_2)$$

where  $\epsilon_1$  and  $d_1$  are the dielectric constant and density of the solvent, respectively, at 30° and  $w_2$  is the weight fraction of the solute.

The molar polarization  $(P_2)$  of the solute was calculated from the relation,<sup>2</sup>

$$P_2 = M_2 \frac{(\epsilon_1 - 1)(1 - \beta)}{(\epsilon_1 + 2) d_1} + \frac{3M_2 \alpha \epsilon_1}{d_1 (\epsilon_1 + 2)^2}$$

where  $M_2$  is the molecular weight of the solute. The dipole moment  $\mu$  was calculated from:

$$\mu = 0.01281[(P_2 - R_p)T]^{\frac{1}{2}}$$

 $R_{\rm D}$  is the molar refraction of the solute for the sodium D line and T the absolute temperature.

#### RESULTS

The results are given in Tables 1 and 2.

<sup>a</sup> C. W. N. Cumper and S. Walker, Trans. Faraday Soc. 52, 193 (1956).

<sup>&</sup>lt;sup>1</sup> G. Cilento, Chem. Rev. 60, 147 (1960).

100 w <sub>1</sub>	€18	<i>d</i> <sub>11</sub>	100 w <sub>s</sub>	€12	<i>d</i> <sub>12</sub>		
Methyl phenyl sulphide		Methyl m-tolyl sulphide					
1.260	2.3183	0.87351	2.384	2.3039	0.87161		
3.997	2.3316	0.87511	3.553	2.3229	0.87317		
4.808	2.3443	0.87638	4.612	2.3396	0.87464		
Me	thyl p-tolyl si	Iphide	2,3-Dimet	hylphenyl me	thyl sulphide		
2.834	2.3157	0.87169	2.874	2.2505	0.87195		
3.859	2.3348	0.87301	3.684	<b>2·2</b> 981	0.87298		
4.935	2.3561	0.87452	4.628	2.3055	0.87438		
2,4-Dime	thylphenyl me	thyl sulphide	2,5-Dime	thylphenyl m	ethyl sulphid		
2.394	2.3064	0.87102	3.026	2.3007	0.87187		
3.236	2.3231	0.87232	3.734	2.3083	0.87263		
3.573	2.3282	0.87272	4.609	2.3197	0.87375		
2.6-Dimethylphenyl methyl sulphide		3,4-Dimei	3,4-Dimethylphenyl methyl sulphide				
3.450	2.3051	0.87222	2.903	2.2.79	0.87149		
4.145	2.3141	0.87318	3.731	2.3073	0.87258		
5.010	2.3244	0.87410	4.580	2·3170	0.87361		
Methyl 2	2,3,5,6-tetran	uethylphenyl					
•	sulphide		p-Fluorophenyl methyl sulphide				
2.269	2.2.37	0.86978	2-234	2.3092	0.87261		
2.797	2.3007	0.87003	3.940	2.3456	0.87644		
3.282	2.3085	0.87171	4.292	2.3547	0.87775		
m-Chlor	rophenyl meth	yl sulphide	m-Bromophenyl methyl sulphide				
2.914	2.3318	0.87517	2.765	2.3168	0.87906		
3.344	2.3434	0.87641	3-460	2-3317	0.88140		
4.306	2.3680	0.87916	4.481	2.3511	0∙88526		
p-Chlor	ophenyl meth	yl sulphide	p-Brom	ophenyl meth	yl sulphide		
2.397	2.3223	0.87458	2.205	2.3045	0.87651		
4 477	0 1710	0.07000	2.504	3.3393	0.00150		

TABLE 1

3.236	2.3231	0.87232	3.734	2.3083	0.87263		
3.573	2.3282	0.87272	4.609	2.3197	0.87375		
2,6- <i>Dimet</i>	hylphenyl me	thyl sulphide	3,4-Dime	thylphenyl me	thyl sulphide		
3.450	2.3051	0.87222	2.903	2.2379	0.87149		
4.145	2.3141	0.87318	3.731	2.3073	0.87258		
5.010	2.3244	0.87410	4.580	2.3170	0.87361		
Methyl 2	2,3,5,6-tetram	ethylphenyl					
•	sulphide		p-Fluor	ophenyl meth	yl sulphide		
2.269	2.2.37	0.86978	2.234	2.3092	0.87261		
2.797	2.3007	0.87003	3.940	2.3456	0.87644		
3.282	2.3085	0.87171	4.292	2.3547	0.87775		
m-Chlor	ophenyl meth	yl sulphide	m-Brom	ophenyl meth	yl sulphide		
2.914	2·3318	0.87517	2.765	<b>2</b> ·3168	0.87906		
3.344	2-3434	0.87641	3.460	2.3317	0.88140		
4.306	2.3680	0.87916	4.481	2.3511	0.88526		
p-Chlor	ophenvl meth	vl sulphide	p-Brom	ophenyl meth	yl sulphide		
2.397	2.3223	0.87458	2.205	2.3045	0.87651		
4.477	2.3739	0.87988	3.506	2.3282	0.88159		
5.549	2.3993	0.88265	4.468	2.3475	0.88526		
p-Iodophenyl methyl sulphide		p-Dimethylthiobenzene					
2.956	2.3070	0.88141	1.599	2.2.350	0.87146		
3.693	2.3164	0.88475	2.148	2.3108	0.87281		
4.527	2.3297	0.88837	2.930	<b>2</b> ·3310	0.87485		
Methy	p-nitrophen	l sulphide	p-Methylthioacetophenone				
2.085	2.5230	0.87491	2.368	2.4135	0.87295		
3.003	2.6380	0.87770	2.731	2.4391	0 87389		
4.192	2.7899	0.88097	3.641	2.4959	0.87602		
			4-Amino-2-methylphenyl n		enyl methyl		
p-Amin	ophenyl meth	yl sulphide		sulphide	-		
1.200	2.3252	0.87069	0.853	2.2968	0.87011		
2.581	2.4002	0.87375	1.444	2.3202	0.87132		
5.046	2.5282	0.87922	1-717	2.32.75	0.87188		

100 w,	 ۴ <sub>18</sub>		100 w <sub>a</sub>	€1 <b>3</b>	<i>d</i> <sub>13</sub>
	ino 7 6-dimath	vlokanyl	m_M		methyl
+	methyl sulnhi	de	111-2020	sulphide	inciny:
0.649	2.2863	0.86937	3.927	2-3534	0.87597
1.422	2.3156	0.87083	4.357	2.3630	0.87677
2.300	2.3475	0.87215	4.940	2.3781	0.87763
р- <i>М</i>	ethoxyphenyl	methyl	4-Metho	oxy-3,5-dime	thylphenyl
•	sulphide	•	1	methyl sulphi	ide
0.977	2-2-09	0.87004	1.170	2.2873	0.87004
4∙056	2.3768	0.87604	2.167	2.3052	0.87140
4.969	2.4040	0.87793	2.878	2.3234	0.87267
4-Meth	wxy-2,6-dimet	hylphenyl	4-Meth	oxy-2,5-dime	thylphenyl
	methyl sulphi	de	i	methyl sulph	ide
<b>2</b> ·739	2.3358	0.87286	2.030	2.3018	0.87202
2.816	2.3377	0.87330	3.004	2.3182	0.87384
3.839	2.3650	0.87502	3.890	2.3358	0.87530
p-L	Dimethylamino	phenyl			
	methyl sulphi	de	N,N-	Dimethyl-p-o	anisidine
2.932	2.4184	0.87320	2.005	2.3072	0.87080
3.243	2.4362	0.87401	2.564	2.3197	0.87160
3.864	2.4674	0.87508	3.004	2.3305	0.87200
p-	Dimethoxyber	nzene		Anisole	
3-315	2.3371	0.87179	4.561	<b>2</b> ·3331	0.87260
3.968	2.3528	0.87463	5.374	2.3468	0.87344
4.844	2.3697	0.87593	6.223	2.3606	0.87478
	Fluorobenzei	ne		Chlorobenze	ne
2.894	2.3234	0.87141	3.890	2.3547	0.87549
3.796	2.3434	0.87259	4.467	<b>2</b> ·3678	0.87665
4.740	2.3650	0-87376	5.342	<b>2</b> ·3891	0.87807
	Bromobenzei	ne		Iodobenzen	e
5.222	2.3526	0.88782	2.391	2.2906	0.87923
5-934	2.3651	0-89045	3.327	2.2396	0.88325
6.726	2.3790	0-89352	5.059	2.3180	0.89128
	Nitrobenzene	•		Acetopheno	ne
3.378	<b>2</b> ·7167	0.87660	3.339	2.5418	0.87315
4·330	2.8532	0.87889	4.617	2.6101	0.87447
5·364	2-9981	0.88126	5.635	2.6897	0.87615
	Aniline		N,	N-Dimethyla	niline
3-669	2.3695	0.87255	2.729	2.3267	0-86989
4.515	<b>2</b> ·3918	0-87395	4.507	2.3682	0.87103
4.689	2.3972	0.87426	5-367	2.3885	0.87184
	p-Anisidine	2	m-0	Chloroacetop	henone
1.463	2.3055	0.87099	3.043	2.4279	0.87519
2.751	2.3435	0.87361	4.598	<b>2·50</b> 95	0.87888
3.588	2.3708	0.87517	5-584	2.5668	0.88142

TABLE 1 (contd)

TABLE	2
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Compound	æ	β	P <sub>2</sub> (ml)	<i>R</i> <sub>D</sub> (ml)	μ (D)	Previous values in C <sub>6</sub> H <sub>6</sub> solution
Methyl phenyl sulphide	0.7649	0.2013	74.4	39.7	1.31	1.388
Methyl <i>m</i> -tolyl sulphide	0.7485	0.1544	<b>84</b> ·1	45.1	1.39	
Methyl p-tolyl sulphide	0.8299	0.1396	89·5	<b>45</b> ∙0	1.49	1·52 <sup>8</sup>
2,3-Dimethylphenyl methyl						
sulphide	0.4154	0.1429	71.5	50.2	1.03	
2,4-Dimethylphenyl methyl						
sulphide	0.8120	0.1305	<b>98</b> ∙1	49.8	1.55	
2,5-Dimethylphenyl methyl						
sulphide	0.5457	0.1314	80.5	49.6	1.24	
2,6-Dimethylphenyl methyl						
sulphide	0.5441	0.1298	80.6	49-9	1.24	
3,4-Dimethylphenyl methyl						
sulphide	0.5281	0.1269	79.6	49.6	1.22	
Methyl 2,3,5,6-tetramethylphenyl						
sulphide	0.6052	0.0886	103-0	57.6	1.50	
<i>m</i> -Chlorophenyl methyl						
sulphide	1.0710	0.2768	111.9	44·2	1.83	1.894
<i>m</i> -Bromophenyl methyl sulphide	0.8702	0.4351	114.8	47.6	1.83	1.854
p-Fluorophenyl methyl sulphide	0.9314	0.2332	93.8	39.5	1.64	
p-Chlorophenyl methyl sulphide	1.0910	0.2944	112.3	44.3	1.84	1.83
<i>p</i> -Bromophenyl methyl sulphide	0.8331	0.4297	111-9	47.7	1.79	1.834
<i>p</i> -Iodophenyl methyl sulphide	0.6157	0.5059	111.8	52.0	1.73	1.804
<i>p</i> -Dimethylthiobenzene	1.0060	0.2357	117.4	51.6	1.81	1.854
Methyl <i>p</i> -nitrophenyl sulphide	5.5380	0.3456	439.4	44.7	4.43	4.365
<i>p</i> -Methylthioacetophenone	2.8320	0.2302	245-1	48-5	3.13	
<i>p</i> -Aminophenyl methyl sulphide	2.3250	0.2306	175.1	45.2	2.54	2.584
4-Amino-2-methylphenyl						
methyl sulphide	1.7380	0.2325	154-2	47.1	2.31	
4-Amino-2.6-dimethylphenyl				•• -		
methyl sulphide	1.6230	0.1838	162.8	51.7	2.35	
<i>p</i> -Dimethylaminophenyl methyl	1 0100		1020			
sulphide	2.3520	0.1964	214.4	54.5	2.82	
<i>m</i> -Methoxyphenyl methyl						
sulphide	1.0220	0.2185	108-5	47.3	1.74	
<i>p</i> -Methoxynhenyl methyl	1 0220	0 2100	100 5			
sulphide	1.2550	0.2093	124.4	45.4	1.98	1.974
4-Methoxy-3.5-dimethylphenyl	1 2000	0 2000	12	10 1	.,,,	
methyl sulphide	0.9273	0.1651	124.2	56-5	1.83	
4-Methoxy-2.6-dimethylphenyl	0,210	0 1001	1212	500	1 00	
methyl sulphide	1.1760	0.1946	141.8	57.5	2.05	
4-Methoxy-2.5-dimethylphenyl	/ 00	0 1 / 10		0.0		
methyl sulphide	0.8227	0.2032	133.9	54.8	1.98	
N.N-Dimethyl- <i>p</i> -anisidine	0.9842	0.1397	108.2	46.0	1.76	1.70*
<i>p</i> -Dimethoxybenzene	0.9916	0.1765	97.7	39.3	1.71	1.73.7.8 1.709

<sup>8</sup> H. Lumbroso and C. Marschalk, J. Chim. Phys. 49, 385 (1952).

<sup>4</sup> H. Lumbroso and R. Passerini, Bull. Soc. Chim. Fr. 311 (1957); Chem. Abstr. 51, 12582 (1957).

<sup>5</sup> H. Lumbroso and G. Dumas, Bull. Soc. Chim. Fr. 651 (1955); Chem. Abstr. 49, 11340 (1955).

<sup>6</sup> E. Hertel and E. Dumont, Z. Physik. Chem. B30, 139 (1935).

<sup>7</sup> P. F. Oesper, C. P. Smyth and M. S. Kharasch, J. Amer. Chem. Soc. 64, 937 (1942).

<sup>8</sup> K. B. Everard and L. E. Sutton, J. Chem. Soc. 2313 (1949).

\* H. Baba and S. Nagakura, J. Amer. Chem. Soc. 74, 5693 (1952).

Compound	α	β	P <sub>2</sub> (ml)	R <sub>D</sub> (ml)	μ( D)	Previous Values in $C_8H_8$ solution
Anisole	0.6887	0.1101	<del>64</del> ·6	33.0	1.25	1.28,8 1.20,10 1.3011
Fluorobenzene	0.9374	0.1250	67·2	<b>26</b> ·0	1.43	1.46,12 1.3918
Chlorobenzene	1.0420	0.2094	<b>80</b> ∙5	31-1	1.57	1.52, <sup>14</sup> 1.50, <sup>15</sup> 1.57, <sup>16</sup> 1.60 <sup>19</sup>
Bromobenzene	0.7612	0·4267	<b>81</b> ·9	33.6	1.55	1.51, <sup>17</sup> 1.52, <sup>16</sup> 1.56 <sup>18</sup> 1.55 <sup>19</sup>
Iodobenzene	0.4934	0.5142	<b>76</b> ·7	39-3	1.36	1.4018
Nitrobenzene	6.0040	<b>0</b> •2770	346.8	32.5	3-95	3.95, <sup>20</sup> 3.90, <sup>14,51</sup> 3.94 <sup>28</sup>
Acetophenone	3.3200	0.1214	205.6	36.4	2.90	2.8911
Aniline	1.2620	0.1379	77.3	30.5	1.53	1.59,28 1.51 **
N,N-Dimethylaniline	1.0340	0.0680	92·3	<b>40</b> ∙6	1.60	1.5824,25,34
<i>p</i> -Anisidine	1.3050	0.2115	102.3	36.3	1.81	1.80*7
m-Chioroacetophenone	2-3920	0.7364	197-3	<b>41</b> ·6	2.78	

TABLE 2 (contd)

### DISCUSSION

In the electronically excited state of methyl phenyl sulphide, sulphur acts as an electron-donor.<sup>28</sup> Sulphur may also function as an electron-acceptor when a powerful electron-releasing substituent is present *para* to methylthio group.<sup>29</sup> The mode of electronic transmission in such *para*-substituted aryl methyl sulphides can be established from dipole moment measurements. When there is electronic interaction between the 1,4-substituents, the observed dipole moment should be greater than the moment calculated by the vector addition of group moments. The dipole moment of a compound like I can be calculated from the equation,<sup>30</sup>

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

- <sup>10</sup> F. L. Warren, J. Chem. Soc. 1858 (1937).
- <sup>11</sup> C. G. Le Fevre and R. J. W. Le Fevre, J. Chem. Soc. 1829 (1950).
- <sup>12</sup> F. Brown, J. M. A. De Bruyne and P. Gross, J. Amer. Chem. Soc. 56, 1292 (1934).
- <sup>13</sup> P. Walden and O. Werner, Z. Physik. Chem. B2, 10 (1929).
- 14 J. W. Williams, Physik. Z. 29, 174 (1928).
- <sup>15</sup> Idem, J. Amer. Chem. Soc. 52, 1838 (1930).
- <sup>16</sup> H. Muller and H. Sack, *Physik. Z.* 31, 815 (1930).
- <sup>17</sup> J. W. Williams, Physik. Z. 29, 271, 683 (1928); J. Amer. Chem. Soc. 50, 2350 (1928).
- <sup>18</sup> A. C. Littlejohn and J. W. Smith, J. Chem. Soc. 2456 (1953).
- <sup>19</sup> P. E. Brown and T. De Vries, J. Amer. Chem. Soc. 73, 1811 (1951).
- <sup>20</sup> C. G. Le Fevre, R. J. W. Le Fevre and K. W. Robertson, J. Chem. Soc. 480 (1935).
- <sup>21</sup> J. W. Williams and C. H. Schwingel, J. Amer. Chem. Soc. 50, 362 (1928).
- <sup>22</sup> H. O. Jenkins, Nature, Lond. 133, 106 (1934).
- 23 I. Fischer, Acta. Chem. Scand. 4, 1197 (1956); Chem. Abstr. 45, 2278 (1951).
- <sup>24</sup> A. V. Few and J. W. Smith, J. Chem. Soc. 753 (1949).
- <sup>25</sup> R. J. B. Marsden and L. E. Sutton, J. Chem. Soc. 599 (1936).
- <sup>16</sup> J. M. Fogelberg and J. W. Williams, Physik. Z. 32, 27 (1931).
- <sup>27</sup> Idem, J. Amer. Chem. 52, 1356 (1930).
- <sup>38</sup> T. S. Govindarajan, Ph.D. Thesis, Annamalai University, 1957. See also A. Mangini and R. Passerini, J. Chem. Soc. 1168 (1952).
- <sup>19</sup> E. A. Fehnel and M. Carmack, J. Amer. Chem. Soc. 71, 2889 (1949).
- <sup>80</sup> Cf. O. Fuchs, Z. Physik. Chem. 14B, 339 (1931).

where  $\mu_1$  is the moment of the group X,  $\mu_2$  is the moment of -SCH<sub>3</sub>,



 $\theta$  is the angle between the axes of rotation of the groups and  $\alpha$  and  $\beta$  are the angles which the moments make with their respective axes of rotation. The axes of rotation are assumed to be directed to the ring.

Since all the compounds under consideration are aryl methyl sulphides, the dipole moment of methyl phenyl sulphide was taken as the moment of the methylthio group. Using the dipole moments of methyl phenyl sulphide (1.31 D) and *p*-dimethylthiobenzene (1.81 D), the angle which the moment of  $-SCH_3$  makes with its axis of rotation was found to be 78° or 102°. The higher value is close to the angles 112° and 99° calculated from the moments of methyl *p*-tolyl sulphide (1.49 D) and methyl *m*-tolyl sulphide (1.39 D), respectively, the moment of toluene being taken as 0.37 D.<sup>31</sup> Therefore the angle was assumed to be 102°.

Using the above angle, the dipole moments of a number of sulphides were calculated (Table 3). The group moments of -F, -Cl, -Br, -I,  $-OCH_3$ ,  $-NO_2$ ,  $-COCH_3$ ,  $-NH_2$  and  $-N(CH_3)_2$  were taken as those of fluorobenzene (1.43 D), chlorobenzene (1.57 D), bromobenzene (1.55 D), iodobenzene (1.36 D), nitrobenzene (3.95 D), acetophenone (2.90 D), anisole (1.25 D), aniline (1.53 D) and N,N-dimethylaniline (1.60 D), respectively. All the values given in parentheses were obtained in

	μ <sub>οb</sub> (D)	$\mu_{calc}(D)$	Δμ(D)
Methyl <i>m</i> -tolyl sulphide	1.39	1.40	- <b>0</b> · <b>0</b> 1
Methyl p-tolyl sulphide	1.49	• 1.43	+0.06
2.6-Dimethylphenyl methyl sulphide	1.24	1.29	-0.02
m-Chlorophenyl methyl sulphide	1.83	1·94	-0.11
<i>m</i> -Bromophenyl methyl sulphide	1.83	1.92	-0.09
p-Fluorophenyl methyl sulphide	1.64	1.73	-0.09
<i>p</i> -Chlorophenyl methyl sulphide	1.84	1-82	+0·02
<i>p</i> -Bromophenyl methyl sulphide	1.79	1.81	- <b>0</b> ·02
<i>p</i> -Iodophenyl methyl sulphide	1.72	1.68	+0.04
Methyl p-nitrophenyl sulphide	4.43	3.90	+0.23
p-Methylthioacetophenone	3.13	3.00	+0.13
p-Aminophenyl methyl sulphide	2.54	2.15	+· 0·39
4-Amino-2,6-dimethylphenyl methyl sulphide	<b>2</b> ·35	1.75	+0.60
p-Dimethylaminophenyl methyl sulphide	2.82	2.24	+0.28
<i>m</i> -Methoxyphenyl methyl sulphide	1.74	1.84	-0·10
<i>p</i> -Methoxyphenyl methyl sulphide	1.98	1-86	+0.12
4-Methoxy-3,5-dimethylphenyl methyl sulphide	1.83	2.00	0.12
4-Methoxy-2,6-dimethylphenyl methyl sulphide	2.05	1.77	+ 0-28

TABLE 3. OBSERVED AND CALCULATED DIPOLE MOMENTS OF SOME ARYL METHYL SULPHIDES

<sup>11</sup> J. W. Baker and L. G. Groves, J. Chem. Soc. 1144 (1939).

benzene solution at 30° in the present investigation.<sup>32</sup> In aniline the angle of inclination of the dipole axis to the 1-4 axis of the ring was taken as 48° (calculated from the moments of aniline, 1.53 D, and *p*-phenylenediamine, 1.60 D<sup>33</sup>). J. W. Smith<sup>34</sup> took it as 48½°. Similar angle in anisole was taken as 75° (calculated from the moments of anisole, 1.25 D, and *p*-dimethoxybenzene, 1.71 D). This is in good agreement with the angle of 72° used by Sipos *et al.*<sup>35</sup> The value of  $29\frac{1}{2}°$  was taken for the --N(CH<sub>3</sub>)<sub>2</sub> group.<sup>34</sup> For the --COCH<sub>3</sub> group the angle was assumed to be 134° (calculated from the moments of acetophenone, 2.90 D, and *m*-chloroacetophenone, 2.78 D).

An examination of the data presented in Table 3 reveals that for all sulphides except methyl *p*-nitrophenyl, *p*-aminophenyl methyl, 4-amino-2,6-dimethylphenyl methyl, *p*-dimethylaminophenyl methyl and 4-methoxy-2,6-dimethylphenyl methyl sulphides the calculated moments are in reasonably good agreement with the observed moments. For the *p*-nitro compound the difference is as much as 0.53 D. Here the conjugative interaction of the nitro and methylthio groups through the benzene nucleus is undoubtedly very marked, structure II making an appreciable contribution



to the ground state of the molecule. The difference between the calculated and observed moments of *p*-aminophenyl methyl sulphide is 0.39 D which suggests the possibility of structure III making a significant contribution to the ground state. Such a view is strengthened by the fact that *p*-anisidine, which is the oxygen analogue of the above compound, has a moment of 1.81 D which is almost the same as its calculated moment (1.80 D).

The dipole moment of *p*-dimethylaminophenyl methyl sulphide also lends strong support to the view that the  $-SCH_3$  group acts as an electron-acceptor when powerful electron-releasing groups are present para to it. The observed moment (2.82 D) is very much higher than the calculated value (2.24 D). Such a large difference (0.58 D) cannot be explained unless we assume conjugative interaction of the *para* groups as shown in structure IV. The conclusion thus drawn is again supported by the fact that N,N-dimethyl-*p*-anisidine, the oxygen analogue of the above compound, has a moment of 1.76 D which is in good agreement with the calculated value (1.81 D).



- <sup>32</sup> Measurements could be made in the authors' laboratories more conveniently at 30° than at the usual temperature of 25°. For a proper evaluation of data it seemed desirable to have all data taken at 30° and hence the moments of several compounds for which data at 25° were available in the literature have been redetermined.
- <sup>38</sup> K. B. Everard, L. Kumar and L. E. Sutton, J. Chem. Soc. 2807 (1951).
- <sup>84</sup> J. W. Smith, J. Chem. Soc. 81 (1961).
- <sup>25</sup> J. C. Sipos, H. Sawatzky and G. F. Wright, J. Amer. Chem. Soc. 77, 2759 (1955).

It is also significant that 4-amino-2,6-dimethylphenyl methyl sulphide has a moment (2·35 D) which is very much higher than the calculated moment (1·75 D). That this increase is due to the electronic interaction of the *para* substituents and not due to a steric effect caused by the *ortho* methyl groups seems to be indicated by the fact that the observed and calculated moments of methyl 2,6-dimethylphenyl sulphide are very nearly the same. Hence it is not unreasonable to assume that structure V makes some contribution to the normal state of 4-amino-2,6-dimethylphenyl methyl sulphide. Resonance involving such a structure is possible even though methyl groups occupy both positions *ortho* to the —SCH<sub>3</sub> group. The view that resonance in conjugated systems implies coplanar configuration applies only to the first row elements. In the case of elements like sulphur the utilization of d-orbitals permits  $\pi$ -bond formation between the central atom and the nonplanar atoms attached to it. A study of the U.V. absorption spectra of aryl methyl sulphones has indeed revealed<sup>36,37</sup> that conjugation of the sulphonyl group with the benzene nucleus is not inhibited by *ortho* substituents.

#### EXPERIMENTAL

Materials. Methyl m-tolyl sulphide,<sup>38</sup> methyl p-tolyl sulphide,<sup>40</sup> p-fluorophenyl methyl sulphide,<sup>41</sup> m-chlorophenyl methyl sulphide,<sup>39</sup> p-chlorophenyl methyl sulphide,<sup>39</sup> p-iodophenyl methyl sulphide,<sup>44</sup> m-methoxyphenyl methyl sulphide,<sup>48</sup> p-methoxyphenyl methyl sulphide,<sup>44</sup> p-methylthioacetophenone,<sup>45</sup> 4-amino-2-methylphenyl methyl sulphide,<sup>46</sup> methyl 2,3,5,6-tetramethylphenyl sulphide<sup>47</sup> and N,N-dimethyl-p-anisidine<sup>46</sup> were prepared as described in the literature.

m-Bromophenyl methyl sulphide was prepared by methylating *m*-bromothiophenol<sup>49</sup> with dimethyl sulphate; b.p. 248-250°;  $n_D^{30}$  1.6152;  $d_s^{30}$  1.486. Brand *et al.*<sup>50</sup> who prepared it from *m*-aminophenyl methyl sulphide, reported b.p. 110-116°/12 mm.

p-Bromophenyl methyl sulphide was prepared by methylating p-bromothiophenol<sup>49</sup> with dimethyl sulphate; b.p. 248-250°; m.p. 37-38°. Bordwell and Anderson,<sup>49</sup> who prepared it by the bromination of thioanisole, reported m.p.  $34-37^{\circ}$ .

*Methyl* p-nitrophenyl sulphide. p-Nitrothiophenol was prepared by the procedure of Price and Stacy<sup>51</sup> and methylated immediately with dimethyl sulphate without isolating the thiophenol; m.p.  $72-73^{\circ}$  (lit.<sup>52</sup>  $71-72^{\circ}$ ).

p-Aminophenyl methyl sulphide. The foregoing sulphide (15 g), tin (63 g) and conc. hydrochloric acid (209 ml) was refluxed till the solution became clear. The mixture was filtered hot, the solution cooled, neutralized with conc. NaOH solution and extracted with ether. The dried (Na<sub>2</sub>SO<sub>4</sub>) ethereal solution was evaporated, and the residue distilled to give *p*-aminophenyl methyl sulphide, b.p. 139°/15 mm;  $n_{20}^{20}$  1.6337;  $d_{40}^{30}$  1.102. Zincke and Jorg,<sup>58</sup> who prepared it by a different method, reported b.p. 140°/15–16 mm.

- <sup>36</sup> E. A. Fehnel and M. Carmack, J. Amer. Chem. Soc. 72, 1292 (1950).
- <sup>87</sup> V. Baliah and T. Rangarajan, J. Indian Chem. Soc. 38, 33 (1961).
- <sup>88</sup> D. S. Tarbell and D. K. Fukushima, J. Amer. Chem. Soc. 68, 1458 (1946).
- <sup>39</sup> G. Leandri, A. Mangini and R. Passerini, Gazz. Chim. Ital. 84, 3 (1954).
- 40 H. Gilman and N. J. Beaver, J. Amer. Chem. Soc. 47, 1450 (1925).
- <sup>41</sup> H. Zahn and H. Zuber, Chem. Ber. 86, 180 (1953).
- <sup>43</sup> Th. Zincke and P. Jorg, Chem. Ber. 43, 3448 (1910).
- 43 A. Magelli and R. Passerini, Chem. Abstr. 52, 9984 (1958).
- 44 C. M. Suter and H. L. Hansen, J. Amer. Chem. Soc. 54, 4101 (1932).
- <sup>45</sup> H. Burton and P. F. Hu, J. Chem. Soc. 603 (1948).
- 46 P. Pfeiffer and H. Jager, Ber. Dtsch. Chem. Ges. 75, 1889 (1942).
- <sup>47</sup> G. Illuminati, J. Amer. Chem. Soc. 80, 4945 (1958).
- 48 F. G. Bordwell and P. J. Boutan, J. Amer. Chem. Soc. 78, 89 (1956).
- <sup>49</sup> F. G. Bordwell and H. M. Anderson, J. Amer. Chem. Soc. 75, 6021 (1953).
- <sup>50</sup> K. Brand, W. Gabel and E. Rosenkranz, Ber. Dtsch. Chem. Ges. 70, 304 (1937).
- <sup>51</sup> C. C. Price and G. W. Stacy, J. Amer. Chem. Soc. 68, 499 (1946).
- 58 K. Brand and A. Wirsing, Ber. Dtsch. Chem. Ges. 45, 1763 (1912).

p-Dimethylaminophenyl methyl sulphide<sup>53,54</sup> was prepared by the dimethylation of the above compound. The procedure employed was similar to that used by Bordwell and Boutan<sup>48</sup> for the preparation of N,N-dimethyl-p-anisidine. The sulphide boiled at  $152-154^{\circ}/15$  mm;  $n_D^{30}$  1.6058;  $d_A^{30}$  1.058.

p-Dimethylthiobenzene. Methyl phenyl sulphide was chlorosulphonylated and the resulting p-methylthiobenzenesulphonyl chloride was reduced with zinc dust and sulphuric acid to get p-methylthiothiophenol. This, on methylation with dimethyl sulphate, gave p-dimethylthiobenzene, m.p. 84-85° (lit.<sup>55</sup> 85°).

The following sulphides were obtained by methylating the corresponding thiophenols<sup>36</sup> with dimethyl sulphate and alkali.

2,3-Dimethylphenyl methyl sulphide: b.p. 234-236°;  $n_D^{30}$  1.5751;  $d_4^{30}$  1.003. (Found: C, 70.99; H, 7.96. C<sub>9</sub>H<sub>13</sub>S requires: C, 70.99; H, 7.95%).

2,4-Dimethylphenyl methyl sulphide: b.p. 234-236°;  $n_D^{30}$  1.5706;  $d_4^{30}$  1.006. (Found: C, 71.10; H, 7.88. C<sub>2</sub>H<sub>12</sub>S requires: C, 70.99; H, 7.95%).

2,5-Dimethylphenyl methyl sulphide: b.p. 226-228°;  $n_D^{s0}$  1.5670;  $d_4^{s0}$  1.004. (Found: C, 70.78; H, 7.82. C<sub>9</sub>H<sub>13</sub>S requires: C, 70.99; H, 7.95%).

2,6-Dimethylphenyl methyl sulphide: b.p. 217-218°;  $n_D^{30}$  1.5568;  $d_4^{30}$  0.9828. (Found: C, 70.69; H, 7.65. C<sub>9</sub>H<sub>12</sub>S requires: C, 70.99; H, 7.95%).

3,4-Dimethylphenyl methyl sulphide: b.p. 226-228°;  $n_D^{30}$  1.5674;  $d_4^{30}$  1.003. (Found: C, 71.28; H, 7.65. C<sub>9</sub>H<sub>13</sub>S requires: C, 70.99; H, 7.95%).

4-Amino-2,6-dimethylphenyl methyl sulphide. Methyl 2,6-dimethyl-4-nitrophenyl sulphide<sup>57</sup> (2 g) was refluxed with tin (4 g) and conc. hydrochloric acid (25 ml) till it completely dissolved. The solution was filtered and neutralized with conc. NaOH. The solid obtained was recrystallized from ethanol, m.p. 69°. (Found: C, 64.54; H, 7.89. C<sub>9</sub>H<sub>13</sub>NS requires: C, 64.62; H, 7.83%).

4-Methoxy-2,5-dimethylbenzenesulphonyl chloride. A solution of 2,5-dimethylanisole (20 g) in dry chloroform (100 ml) was kept stirred and treated slowly with freshly-distilled chlorosulphonic acid (100 g), the temp being kept at  $0-5^{\circ}$ . After 1 hr the reaction mixture was poured into crushed ice and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous magnesium sulphate. Evaporation of the solvent gave 4-methoxy-2,5-dimethylbenzenesulphonyl chloride in quantitative yield, m.p. 98-99°.

4-Methoxy-2,5-dimethylbenzenesulphonamide. The foregoing sulphonyl chloride in chloroform was heated with liquor ammonia on a water bath for a few minutes and the chloroform removed. The sulphonamide crystallized from ethanol as needles, m.p. 214-215°. (Found: C, 50.28; H, 6.26. C<sub>9</sub>H<sub>18</sub>O<sub>3</sub>NS requires: C, 50.21; H, 6.09%).

4-Methoxy-2,5-dimethylthiophenol. 4-Methoxy-2,5-dimethylbenzenesulphonyl chloride (30 g) was added to a mixture of conc. sulphuric acid (120 g) and crushed ice (360 g). After adding zinc dust (60 g), the mixture was subjected to steam-distillation. The distillate was extracted with ether, dried over anhydrous magnesium sulphate, the solvent removed and the residue distilled; yield 18 g; b.p. 252-254°. (Found: C, 63.90; H, 6.90. C<sub>9</sub>H<sub>12</sub>OS requires: C, 64.27; H, 7.19%).

4-Methoxy-2,5-dimethylphenyl methyl sulphide was prepared from the foregoing thiophenol by methylation. It crystallized from ethanol as flakes, m.p. 65-66°. (Found: C, 66.20; H, 7.50.  $C_{14}H_{14}OS$  requires: C, 65.88; H, 7.74%).

4-Methoxy-2,6-dimethylbenzenesulphonamide. Chlorosulphonylation of 3,5-dimethylanisole gave 4-methoxy-2,6-dimethylbenzenesulphonyl chloride which was then treated with liquor ammonia. The sulphonamide, thus obtained, crystallized from dil. ethanol as lustrous flakes, m.p. 140–141°. (Found: C, 50·46; H, 6·10. C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>NS requires: C, 50·21; H, 6·09%).

4-Methoxy-2,6-dimethylthiophenol was obtained by reducing 4-methoxy-2,6-dimethylbenzenesulphonyl chloride with zinc dust and sulphuric acid; b.p. 270-272°. (Found: C, 63.90; H, 6.90.  $C_0H_{12}OS$  requires: C, 64.27; H, 7.19%).

4-Methoxy-2,6-dimethylphenyl methyl sulphide was prepared by methylating the above thiophenol.

- 53 Th. Zincke and P. Jorg, Ber. Dtsch. Chem. Ges. 42, 3368, 3374 (1909).
- <sup>54</sup> H. Gilman and F. J. Webb, J. Amer. Chem. Soc. 71, 4065 (1949).
- <sup>55</sup> Th. Zincke and W. Frohneberg, Ber. Dtsch. Chem. Ges. 42, 2728 (1909).
- <sup>56</sup> E. A. Bartkus, E. B. Hotelling and M. B. Neuworth, J. Org. Chem. 22, 1185 (1957).
- <sup>57</sup> B. M. Wepster, Rec. Trav. Chim. 73, 835 (1959).

The sulphide boiled at 114–116°/9 mm;  $n_D^{30}$  1.5670;  $d_4^{30}$  1.036. Kloosterziel and Backer<sup>58</sup> gave b.p. 102–103°/2 mm.

4-Methoxy-3,5-dimethylbenzenesulphonamide. 2,6-Dimethylanisole was chlorosulphonylated and the resulting sulphonyl chloride was treated with liquor ammonia. The sulphonamide, after recrystallizing from dil. ethanol, melted at 108–110°. (Found: C, 50.06; H, 6.32. C<sub>8</sub>H<sub>18</sub>O<sub>8</sub>NS requires: C, 50.21; H, 6.03%).

4-Methoxy-3,5-dimethylthiophenol was obtained by the reduction of 4-methoxy-3,5-dimethylbenzenesulphonyl chloride with zinc dust and sulphuric acid; b.p. 246-248°. (Found: C, 64.00; H, 6.90. C<sub>9</sub>H<sub>13</sub>OS requires: C, 64.27; H, 7.19%).

4-Methoxy-3,5-dimethylphenyl methyl sulphide. Methylation of the foregoing thiophenol gave this compound: b.p.  $106^{\circ}/7$  mm;  $n_D^{so}$  1.5594;  $d_4^{so}$  1.041. (Found: C, 65.43; H, 7.46.  $C_{10}H_{14}OS$  requires: C, 65.88; H, 7.74%).

*Purification of the solvents.* "AnalaR" benzene was frozen three times, dried over sodium wire and distilled over phosphorus pentoxide.

"AnalaR" cyclohexane was washed several times in the cold with a mixture of conc. nitric and sulphuric acids. After repeated washings with distilled water it was dried over sodium wire, distilled, the fraction boiling at  $80.5-81^{\circ}$  collected, passed through a column of silica gel and finally distilled; the fraction boiling at  $80.6^{\circ}$  was used.

n-Butyl ether was freed from any peroxide by shaking with an acidified solution of ferrous sulphate. After repeated washings with water, it was dried over anhydrous calcium chloride and distilled over sodium wire using a fractionating column. The fraction boiling at 141° was collected.

*Physical measurements.* All the dipole moment measurements were made in benzene solution at  $30 \pm 0.05^{\circ}$ . The dielectric constants were measured with Dipolemeter DM 01, manufactured by Wissenschaftlich-Technische, Werkstatten, Weilheim (Obb), Germany. The measuring cell (supplied by the manufacturers) of suitable capacitance formed part of one of two oscillators, frequency approx.  $2 \times 10^{6}$  cps, which were tuned to each other. The instrument was calibrated with purified cyclohexane, benzene and n-butyl ether. Assuming the dielectric constants of these liquids at 30°, the scale value of the measuring condensers was estimated through linear interpolation.

The refractive indices were measured at  $30^{\circ} \pm 0.1^{\circ}$ . The density measurements for all solutions were made at  $30 \pm 0.05^{\circ}$ . In the case of liquids the molar refraction was calculated from the density and refractive index measurements. In the case of solids  $R_{\rm D}$  was estimated from bond refractions.<sup>59</sup>

The dielectric constant and density of benzene at  $30^\circ$  were taken as 2.2628 and 0.86840, respectively.

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<sup>88</sup> H. Kloosterziel and H. J. Backer, Rec. Trav. Chim. 72, 192 (1953).

\* A. I. Vogel, W. T. Cresswell, G. H. Jeffrey and J. Leicester, J. Chem. Soc. 514 (1952).