

XXXVIII.—*The Parachor and Chemical Constitution.*
Part VII. Further Examples of Semipolar Double
Bonds.

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(1) *Sulphones.*

THE work described in this paper was designed, in the first place, to determine more accurately the effect upon the parachor of the semipolar double bond. It has been shown in Part I (Sugden, Reed, and Wilkins, J., 1925, 127, 1525) that the constant for this structure is about -1.6 units. Some of the substances there studied are, however, difficult to purify, and this value of the constant is of the same order of magnitude as the experimental

error. We have therefore studied a number of sulphones and related substances of the type $RR'S \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$ which contain this structure, since these substances can readily be purified by crystallisation and have convenient melting points. The parachors calculated from the surface tension and density of the fused substances are collected in Table I in the column headed "[P] obs." The next column gives the sum of all the atomic and structural constants except that for the semipolar double bond; by subtracting this sum from [P] obs., one obtains the figures given in the last column, which represent the effect of this structure upon the parachor. It will be seen that the data for these five carefully purified substances lead to a value for the constant sought of -1.6 units, which is identical with the figure obtained in the earlier investigation (*loc. cit.*).

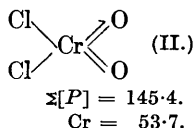
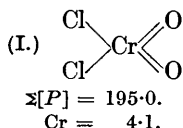
TABLE I.

Substance.	[P] obs.	$\Sigma[P]$.	Semipolar double bond.
<i>p</i> -Toluenesulphonyl chloride	367.8	371.6	-1.9×2
Ethyl <i>p</i> -toluenesulphonate	431.8	432.4	-0.3×2
Benzylmethylsulphone	369.8	373.4	-1.8×2
Diphenylsulphone	465.7	468.3	-1.3×2
Phenylbenzylsulphone	503.5	507.3	-1.9×2
		Mean	-1.6

It is therefore concluded that the semipolar double bond has a small but real negative effect upon the parachor. This may be explained, as suggested in the earlier investigation, by a small contraction in volume due to the electrostatic attraction between the oppositely charged atoms which are joined by this linkage.

(2) Chromium Compounds.

Measurements have also been made of the surface tension and density of chromyl chloride, from which the parachor of this substance is found to be 199.1. From this observation the parachor for chromium can be calculated on the assumption that the oxygen atoms are held (*a*) by non-polar double bonds (I), or (*b*) by semipolar double bonds (II). The first hypothesis leads to an inadmissible

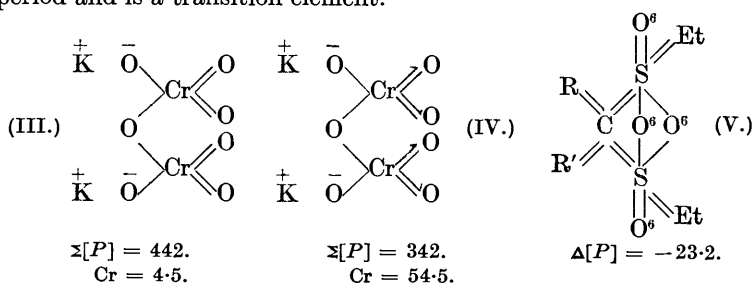


value (4.1) for the parachor for chromium (the smallest atomic parachor yet found is $C = 4.8$), whilst the second hypothesis gives the more reasonable figure of 53.7, which is compatible with the

values found for neighbouring elements in the periodic table, *e.g.*, S = 48.2, Se = 58.*

Further evidence in support of this value can be obtained from the measurements of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1) of the surface tension and density of fused potassium dichromate, from which $[P]$ obs. = 451. This figure can only be regarded as a rough value, since the parachor shows a decided drift with temperature (see Experimental). From Jaeger's data for the alkali halides and sulphates, which will be discussed more fully in a later paper, the parachor of potassium is found to be 106. By the use of this figure, the parachor for chromium in potassium dichromate becomes 4.5 if the oxygen atoms are held by non-polar double bonds (III), and 5.4 if these linkages are of the semipolar type (IV). In these calculations the polar bond between potassium and oxygen has been assigned a value of -1.6 units. Indirect evidence for this figure has been advanced in Part V of this series (Sugden, J., 1927, 1173), and direct evidence from measurements on fused salts has now been obtained and will be discussed in a later paper.

For both of these substances the octet theory predicts that the double bonds holding the oxygen atoms must be semipolar; hence the data discussed above give experimental support to the view that in these compounds of chromium the octet is not exceeded. This is of particular interest, since chromium belongs to the first long period and is a transition element.



(3) β -Disulphones. An Anomaly.

In addition to the simple sulphones referred to in Table I, two β -disulphones were also examined, *viz.*, sulphonal and trional, and were found to exhibit the large anomaly shown in Table II. These anomalies are not due to impurities, for the specimens examined had sharp melting points which were unchanged by crystallisation from a number of solvents. Nor are they due to errors of observation, for check measurements made by another observer in this

* Deduced from measurements on selenium compounds to be described in a later paper of this series.

laboratory, using different instruments, gave substantially the same values for the surface tension and density of trional.

TABLE II.

Substance.	Formula.	[P] obs.	[P] calc.	Anomaly.
Sulphonal	$\text{CMe}_2(\text{SO}_2\text{Et})_2$	465.5	477.2	-11.7
Trional	$\text{CMeEt}(\text{SO}_2\text{Et})_2$	493.8	516.2	-22.4

The close agreement between the observed and calculated values of the parachor for the simple sulphones (Table I) and for a number of other sulphur compounds described in Part I (*loc. cit.*) of this series is convincing evidence that the constant assigned to sulphur (48.2) is substantially accurate, and that the additive character of the parachor persists in sulphur compounds of this type. It is evident, therefore, that the β -disulphones must contain some special structure which is not expressed by their formula and is not present in the simple sulphones.

It may be noted at once that this new structure cannot be the conversion of the semipolar into non-polar double bonds, for such a change would give a large increase in the parachor, whereas the anomaly found is negative. Moreover, since the only structure which has so far been found to have a large negative parachor is the singlet linkage (Sugden, J., 1927, 1173), it seems probable that there is some interaction between the two SO_2 groups by which singlet linkages are formed. We intend to examine other disulphones and similar compounds to obtain further evidence; meanwhile, we suggest as a tentative explanation that these substances are tautomeric, one individual having the structure represented by the usual formula, and the other having the electronic structure (V). The larger anomaly exhibited by trional may then be accounted for by the well-known effect of bulky substituents in stabilising ring structures. For formula (V) the structural constant would be obtained as follows :

$$\begin{array}{rcl}
 2 \text{ Four-membered rings,} & 2 \times 11.6 & = +23.2 \\
 2 \text{ Semipolar double bonds,} & 2 \times -1.6 & = -3.2 \\
 4 \text{ Semipolar single bonds,} & 4 \times -12.4 & = -49.6 \\
 & & \text{---29.6}
 \end{array}$$

For the disulphone formula, the structural constant is that for 4 semipolar double bonds or $4 \times -1.6 = -6.4$. Complete transformation to the structure represented by (V) would therefore give an anomaly of -23.2 ; hence, on this view trional is largely composed of the cyclic isomeride.

EXPERIMENTAL.

In the course of this investigation measurements have been made of the surface tension and density of *p*-toluenesulphonyl chloride,

ethyl *p*-toluenesulphonate, benzylmethylsulphone, diphenylsulphone, phenylbenzylsulphone, chromyl chloride, sulphonal, and trional. Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The constants for the bubblers used were:—

Apparatus.	4d.	10.	15b.	16a.
r_2 (cm.)	0.139	0.166	0.178	0.179
A	0.007767	0.004311	0.00945	0.008272

Densities were determined by means of the U-shaped pycnometer described previously (J., 1924, **125**, 1171), except in the case of chromyl chloride, for which a sealed bulb was used to avoid exposure to the atmosphere.

The tables below are set out in the same manner as in earlier papers of this series and do not need further description. The parachor is calculated by the usual formula, d , which is very small for all the substances now studied, being neglected.

p-Toluenesulphonyl chloride, $C_7H_7SO_2Cl$, $M = 190.5$, was recrystallised from benzene and melted sharply at 68° (corr.). Densities determined: $D_4^{26^\circ} = 1.261$, $D_4^{37.5^\circ} = 1.237$, $D_4^{133^\circ} = 1.201$, whence $D_4^0 = 1.333 - 0.000961t$.

App.	t .	P .	D .	ϕ .*	γ .	Parachor.
16a	74	4143	1.262	1.0369	35.54	368.6
„	103.5	3697	1.233	1.0404	31.82	367.0
					Mean	367.8

* A correction factor, see J., 1924, **125**, 31.

Ethyl *p*-toluenesulphonate, $C_9H_{12}O_3S$, $M = 200.1$, was recrystallised from ethyl acetate and melted at $33-34^\circ$ (corr.). Densities determined: $D_4^{26^\circ} = 1.166$, $D_4^{56.5^\circ} = 1.157$, $D_4^{69^\circ} = 1.145$, $D_4^{38^\circ} = 1.130$, whence $D_4^0 = 1.206 - 0.000862t$.

App.	t .	P .	D .	ϕ .	γ .	Parachor.
10	40	9290	1.172	1.0142	40.62	430.9
„	53.5	8961	1.160	1.0145	39.18	431.5
„	70	8597	1.146	1.0150	37.62	432.3
„	83	8255	1.134	1.0154	36.14	432.6
					Mean	431.8

Benzylmethylsulphone, $C_8H_{10}O_2S$, $M = 170.1$, was recrystallised from benzene and melted at 124.5° (corr.). Densities determined: $D_4^{26^\circ} = 1.140$, $D_4^{42.5^\circ} = 1.128$, $D_4^{163^\circ} = 1.112$, whence $D_4^0 = 1.246 - 0.000825t$.

App.	t .	P .	D .	ϕ .	γ .	Parachor.
15b	142.5	3665	1.128	1.0371	35.92	369.2
„	164.5	3458	1.110	1.0387	33.93	369.8
„	184	3278	1.094	1.0403	32.22	370.3
					Mean	369.8

Diphenylsulphone, $C_{12}H_{10}O_2S$, $M = 218.1$, was recrystallised from benzene and melted at 125° (corr.). Densities determined: $D_4^{15^\circ} = 1.157$, $D_4^{25^\circ} = 1.142$, $D_4^{72^\circ} = 1.133$, $D_4^{88^\circ} = 1.126$, whence $D_4^0 = 1.267 - 0.000774t$.

App.	<i>t.</i>	<i>P.</i>	<i>D.</i>	$\phi.$	$\gamma.$	Parachor.
15b	137.5	3857	1.161	1.0363	37.77	465.6
„	157	3668	1.145	1.0376	35.97	466.5
„	179.5	3400	1.128	1.0400	33.42	465.0
						Mean 465.7

Phenylbenzylsulphone, $C_{13}H_{12}O_2S$, $M = 232.2$, was recrystallised from alcohol and melted at 146° (corr.). Densities determined: $D_4^{23^\circ} = 1.126$, $D_4^{64^\circ} = 1.116$, $D_4^{73.5^\circ} = 1.108$, $D_4^{86.5^\circ} = 1.098$, whence $D_4^0 = 1.249 - 0.000809t$.

App.	<i>t.</i>	<i>P.</i>	<i>D.</i>	$\phi.$	$\gamma.$	Parachor.
15b	153.5	3612	1.125	1.0375	35.40	503.5
„	184	3294	1.100	1.0402	32.38	503.6
						Mean 503.5

Chromyl chloride, CrO_2Cl_2 , $M = 155.0$, was prepared by the action of concentrated sulphuric acid on a mixture of chromic acid and concentrated hydrochloric acid, and purified by distillation: b. p. $115-116^\circ$ (corr.)/758 mm. Densities determined: $D_4^{15^\circ} = 1.937$, $D_4^{24^\circ} = 1.920$, $D_4^{30^\circ} = 1.910$, $D_4^{39^\circ} = 1.893$, $D_4^{49^\circ} = 1.873$, $D_4^{60^\circ} = 1.855$, whence $D_4^0 = 1.965 - 0.00185t$.

App.	<i>t.</i>	<i>P.</i>	<i>D.</i>	$\phi.$	$\gamma.$	Parachor.
4d	19	4532	1.930	1.0401	36.61	197.5
„	41	4271	1.889	1.0416	34.55	198.9
„	64	3966	1.847	1.0438	32.16	199.8
„	78	3754	1.821	1.0456	30.48	200.0
						Mean 199.1

Potassium dichromate, $K_2Cr_2O_7$, $M = 294.2$. The following data are taken from the work of Jaeger (*loc. cit.*).

<i>t.</i>	$\gamma.$	<i>D.</i>	Parachor.
420	140.1	2.271	445.6
454	139.4	2.248	449.7
480	138.4	2.229	452.9
504	137.0	2.213	454.8
			Mean 450.8

Sulphonal, $C_7H_{16}O_4S_2$, $M = 228.2$, was repeatedly crystallised from absolute alcohol and melted at 125.8° (corr.). Densities determined: $D_4^{32^\circ} = 1.183$, $D_4^{41^\circ} = 1.176$, $D_4^{52.5^\circ} = 1.166$, $D_4^{60.5^\circ} = 1.145$, whence $D_4^0 = 1.278 - 0.000725t$.

App.	<i>t.</i>	<i>P.</i>	<i>D.</i>	$\phi.$	$\gamma.$	Parachor.
15b	132.5	3489	1.182	1.0408	34.31	467.1
„	154.5	3268	1.166	1.0430	32.20	466.1
„	169.5	3093	1.155	1.0450	30.54	464.4
„	177.5	3027	1.149	1.0457	29.91	464.4
						Mean 465.5

Trional, $C_8H_{18}O_4S_2$, $M = 242.2$, was recrystallised from absolute alcohol and melted sharply at 75° (corr.). Densities determined: $D_4^{25^\circ} = 1.199$,* $D_4^{36^\circ} = 1.193$, $D_4^{104.3^\circ} = 1.183$,* $D_4^{116.5^\circ} = 1.176$, $D_4^{28^\circ} = 1.163$,* $D_4^{36^\circ} = 1.159$, $D_4^{45^\circ} = 1.150$,* $D_4^{57.5^\circ} = 1.141$, whence $D_4^\circ = 1.272 - 0.00839t$.

App.	<i>t.</i>	<i>P.</i>	<i>D.</i>	$\phi.$	$\gamma.$	Parachor.
14	88.5	3329	1.198	1.0431	35.41	493.2*
14	110	3133	1.180	1.0451	33.39	493.4*
15b	123.5	3268	1.168	1.0431	32.20	494.0
14	136.5	2902	1.157	1.0478	31.01	494.0*
15b	147	3061	1.149	1.0452	30.23	494.3
14	158	2700	1.139	1.0505	28.93	493.3*
15b	164	2899	1.134	1.0471	28.65	494.3
						Mean 493.8

* We are indebted to Mr. F. B. Garner for the observations thus marked.

Summary.

(1) The parachor constant for the semipolar double bond is found to be -1.6 from measurements on five carefully purified sulphones and related compounds. This is in good agreement with the value found in an earlier investigation.

(2) Chromyl chloride is found to contain two semipolar double bonds and potassium dichromate four such linkages. The parachor for chromium is assigned the value 54 units.

(3) Two disulphones, sulphonal and trional, give a large negative anomaly in their parachors. It is suggested that this is due to the production of a cyclic phase by the formation of singlet linkages between oxygen atoms of the SO_2 groups.

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