

### 9. *The Parachors of Some Substituted Methanes.*

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THE usefulness of the parachor is due to the fact that Sugden's atomic and structural constants are in general additive as such to within the limits claimed ( $\pm 1-2\%$ ). It is true that a specific constant of  $-3.2$  is necessary to produce agreement between observation and calculation in the case of esters and it has been suggested that the *gem*-dimethyl group is also to be given a specific parachor value (Sugden, "Parachor and Valency," p. 43). Such specific constants are not a serious disadvantage to the system, seeing that they are limited in number and approximately invariant in value. A study of the data, however, shows that there is a certain amount of negative parachor anomaly of a variable kind unassociated with any particular structure. All that can be said about it is that it appears to be connected with the accumulation of certain negative atoms and groups in the molecule. Thus, for *s*-tetrabromoethane,  $P_{\text{obs.}}$  is 310.4,  $P_{\text{calc.}}$  being 315.8; on the other hand, for the *s*-tetrachloro-compound  $P_{\text{obs.}}$  and  $P_{\text{calc.}}$  are 260.5 and 261.0 respectively. Again,  $P_{\text{obs.}}$  for chloropicrin is 236.8, as against  $P_{\text{calc.}} = 241.8$ . On the system of atomic and structural parachor constants adopted by Mumford and Phillips (J., 1929, 2118) this effect of negative substituents is very apparent and these authors have sought to express it in terms of certain "strain constants."

It may be expected that the phenomenon will reveal itself in its simplest form among the substituted methanes, and we have therefore sought to supplement the existing data by determinations of the parachors of tetranitromethane, nitroform, and carbon tetrabromide.

The necessary data for the computation of the parachor of triphenylmethane are given

by Przyluska (*J. Chim. physique*, 1909, **7**, 518). His results yield the mean parachor 578, the extreme values being 580.2 at 108.7° and 577.3 at 278.7°. The value calculated from Sugden's constants is 591.9, the anomaly being -13.9.

Two sets of data are available for the evaluation of the parachor of diphenylmethane. Morgan and Daghlein (*J. Amer. Chem. Soc.*, 1911, **33**, 657) give densities and surface tensions that yield the value  $P_{\text{obs.}} = 419.0$  ( $P_{\text{calc.}} = 419.0$ ). The data of Harkins and Ewing (*ibid.*, 1919, **41**, 1977) give  $P_{\text{obs.}} = 414.5$ , indicating an anomaly of -4.5. In view of this discrepancy between the two sets of results, we have redetermined the parachor of diphenylmethane and have obtained the value  $P_{\text{obs.}} = 419.6$ .

## EXPERIMENTAL.

Surface tensions were determined by the "bubble pressure" method of Sugden, the apparatus being standardised with pure benzene. Densities were found either with a standardised dilatometer or, in the case of solutions, with a 10 c.c. specific gravity bottle.

It was not possible to keep carbon tetrabromide molten for any length of time without decomposition. The method of Hammick and Andrew (*J.*, 1929, 764) for the determination of the parachors of substances in solution was therefore used, the surface tensions and densities of solutions of carbon tetrabromide in carbon tetrachloride being measured at 25°. A value for the parachor of tetranitromethane in benzene solution was also obtained.

The materials used were prepared by standard methods and carefully purified.

In the tables,  $\gamma$  is given in dynes/cm.

*Determinations with molten substances.*

TABLE I.

Tetranitromethane, m. p. 13.5°.				Diphenylmethane, m. p. 26.0°.			
Temp.	$d_4^{25}$ .	$\gamma$ .	$P_{\text{obs.}}$	Temp.	$d_4^{25}$ .	$\gamma$ .	$P_{\text{obs.}}$
20.0°	1.638	30.47	281.1	29.9°	0.997	38.81	420.5
25.0	1.629	29.44	280.2	40.1	0.990	36.95	418.4
30.0	1.620	28.98	280.7	50.0	0.982	36.28	419.8
35.0	1.614	28.74	281.2	60.0	0.976	35.42	419.8
50.0	1.584	26.45	280.6				
Mean $P_{\text{obs.}} = 280.8$ ; $P_{\text{calc.}} = 301.2$ .				Mean $P_{\text{obs.}} = 419.6$ ; $P_{\text{calc.}} = 419.0$ .			
Nitroform, m. p. 15.0°.							
20.0	1.479	33.98	246.5	25.0	1.469	33.6	247.5
Mean $P_{\text{obs.}} = 247.0$ ; $P_{\text{calc.}} = 244.2$ .							

Attempts to maintain liquid nitroform at temperatures above 25° led to decomposition.

*Determinations in solution at 25.0°.* In Table II,  $x$  is the molar fraction of solute,  $M_m$  the mean molecular weight of the solution,  $P_m$  the mean parachor, and  $P_x$  the parachor of the solute (cf. Hammick and Andrew, *loc. cit.*).

TABLE II.

Carbon tetrabromide in carbon tetrachloride at 25.0°.						Tetranitromethane in benzene at 25.0°.					
$x$ .	$d_4^{25}$ .	$\gamma$ .	$M_m$ .	$P_m$ .	$P_x$ .	$x$ .	$d_4^{25}$ .	$\gamma$ .	$M_m$ .	$P_m$ .	$P_x$ .
0.0	1.5850	26.00	153.8	219.1	—	0.0	0.8737	28.23	78.05	206.0	—
0.1436	1.834	27.99	179.4	225.0	260.2	0.3377	1.169	27.49	117.95	231.1	280.4
0.2097	1.839	28.32	191.1	227.3	258.0	0.5082	1.302	27.70	138.0	243.2	279.1
0.2945	2.079	29.65	206.2	231.4	260.9	0.6736	1.419	28.19	157.5	255.8	280.0
0.3746	2.208	30.79	220.5	235.3	262.1	0.8561	1.540	28.92	179.0	269.6	280.3
0.4211	2.281	30.86	228.6	236.2	259.5						
Mean $P_x = 260.1$ ; $P_{\text{calc.}} = 276.8$ .						Mean $P_x = 280.0$ ; $P_{\text{calc.}} = 301.2$ .					

## DISCUSSION OF RESULTS.

The results obtained are included in Table III. It will be seen that complete substitution of chlorine into methane produces no appreciable parachor anomaly  $\Delta P$ . Bromine atoms and the nitro-group also have little effect until the fourth hydrogen atom

TABLE III.

	CH <sub>2</sub> R <sub>2</sub> .			CHR <sub>3</sub> .			CR <sub>4</sub> .		
	<i>P</i> <sub>obs.</sub>	<i>P</i> <sub>calc.</sub>	Δ <i>P</i> .	<i>P</i> <sub>obs.</sub>	<i>P</i> <sub>calc.</sub>	Δ <i>P</i> .	<i>P</i> <sub>obs.</sub>	<i>P</i> <sub>calc.</sub>	Δ <i>P</i> .
R = Cl	147·6	147·6	0·0	183·2	184·8	(- 1·6)	219·6	222·0	(- 2·4)
R = Br	—	—	—	221·9	225·9	(- 4·0)	260·1	276·8	-16·7
R = NO <sub>2</sub>	—	—	—	247·0	244·2	(2·8)	280·4	301·2	-20·8
R = C <sub>6</sub> H <sub>5</sub>	419·6	419·0	(0·6)	578·0	591·9	-13·9	—	—	—

is replaced, whereupon a very marked negative anomaly appears ( $-16.7$  and  $-20.8$  respectively). With the phenyl group, however, the considerable anomaly of  $-13.9$  appears when only three of the methane hydrogens have been replaced.

It is not possible at this stage to offer any explanation of these anomalies, though it may be noted that the effect appears to be connected in some way with the size of the substituting atom or group. The existence of the effect in the above cases does, however, raise some doubt as to the correctness of Sugden's formulation of the structures of sulphonal,  $\text{CMe}_2(\text{SO}_2\text{Et})_2$ , and trional,  $\text{CMeEt}(\text{SO}_2\text{Et})_2$ , for which the parachor anomalies are  $-11.7$  and  $-22.4$  respectively (Freiman and Sugden, J., 1928, 263). Until it can be shown that these anomalies are not further examples of the effect of group accumulation a cautious attitude towards cyclic structures involving singlet linkages seems justified.

The system of parachor constants set up by Mumford and Phillips (*loc. cit.*) is no more successful than Sugden's in accounting for the parachors of the substances we have investigated. Using their constants, we should expect  $P_{\text{calc.}} = 271.7$  for carbon tetrabromide. In computing this value we have taken the strain constant for the bromine atom as  $-1.5 \times 9$  (Mumford and Phillips, *loc. cit.*, p. 2118);  $P_{\text{obs.}}$  being 260.1, we have an anomaly of  $-11.6$ . Again, from the observed parachor of nitroform, 247.0, we have computed the strain constant  $\sigma$  as  $-7.1$  for the three nitro-groups. Taking  $\sigma$  for four groups as  $-1.5 \times 7.1$ , we get  $P_{\text{calc.}} = 303.5$ , the anomaly being  $-16.9$ . The calculated values for diphenylmethane, with no strain constant, is 418.4 ( $P_{\text{obs.}} = 419.6$ ). Even if we assume that here we really have a strain constant  $\sigma = -3$  and adopt  $\sigma = -6$  for triphenylmethane, we get  $P_{\text{calc.}}$  for triphenylmethane as 586.4, against 578.0 observed.

## SUMMARY.

Parachors have been determined for nitroform (247.0), tetranitromethane (280.4), carbon tetrabromide (260.1), and diphenylmethane (419.6); that of triphenylmethane has been evaluated from existing data. Negative anomalies have been found for tetranitromethane ( $-20.8$ ), carbon tetrabromide ( $-16.7$ ), and triphenylmethane ( $-13.9$ ).

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