97. *The Parachor and Chemical Constitution. Part XVII. Fluorine Compounds.*

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DURING the last few years aromatic fluorine compounds have become readily accessible owing to the work of Schiemann and his collaborators (Balz and Schiemann, *Ber.*, 1927, **60**, 1186, and later papers). We have used Schiemann's method to prepare a number of these substances and have measured their surface tension and density with the object of obtaining a more accurate value of the atomic parachor of fluorine.

The data obtained are summarised in Table I. Here $\Sigma[P]$ indicates the sum of the appropriate atomic and structural constants other than that of fluorine; the latter is then obtained by subtracting $\Sigma[P]$ from $[P]$ obs. Excluding the last substance, the mean value found is F = 25·0; this should replace the value 25·7 given in an earlier paper (Sugden, J., 1924, **125**, 1180).

The abnormal value given by methoxyboron difluoride is in marked contrast with the regularity shown by the other fluorine compounds. The constant for boron used in calculating $\Sigma[P]$ is 16·4 (Etridge and Sugden, J., 1928, 990). Gasselin (*Ann. Chim. Phys.*, 1894, **3**, 14), who first prepared this substance, found a

No.	Substance.	$[P]$ obs.	$\Sigma[P]$.	F.	*k*.
1	Fluorobenzene	214·3	190·0	24·3	2·32
2	*p*-Fluorochlorobenzene	252·8	227·2	25·6	2·19
3	*p*-Fluorobromobenzene	265·3	240·9	24·4	2·47
4	*p*-Fluorotoluene	255·1	229·0	26·1	2·35
5	*a*-Fluoronaphthalene	322·0	295·9	26·1	2·35
6	*pp'*-Difluorodiphenyl	394·0	345·8	24·1 × 2	2·59
7	Methoxyboron difluoride	128·6	92·5	(18·0 × 2)	1·65
		Mean, excluding no. 7, 25·0.			

normal molecular weight for the vapour, but this does not exclude association in the liquid state. In fact the Ramsay–Shields constant given in the last column of the table indicates that methoxyboron difluoride is an associated liquid and the other fluorine compounds are normal. An attempt was made to determine the molecular weight in solution, but the substance was either insoluble in, or reacted with, all the solvents tried.

$$\text{(I.)}\qquad \begin{matrix}\mathrm{Me{=}O^4}\\ \mathrm{F^6}\end{matrix}\!\gg\!\mathrm{B}\!<\!\begin{matrix}\mathrm{F^6}\\ \mathrm{F^6}\end{matrix}\!>\!\mathrm{B}\!\ll\!\begin{matrix}\mathrm{O^4{=}Me}\\ \mathrm{F^6}\end{matrix}$$

A formula (I) with singlet linkages is readily written for the double molecule and resembles that suggested by one of us for aluminium bromide, Al_2Br_6 (J., 1929, 321). The parachor calculated for this structure is 250·8, whereas the observed value is 2 × 128·6 = 257·2. This indicates 80% of double molecules, which seems a reasonable value.

Experimental.

The tables below are set out in the same manner as in earlier papers of this series and need no further description. All temperatures recorded are corrected for thermometer error and exposed stem.

Substances 2—6 were prepared by the method of Balz and Schiemann (*loc. cit.*) and, except 6, which was recrystallised from alcohol, were purified by fractional distillation. The crude products boiled within a range of 5°, so that two distillations were usually sufficient to obtain a pure fraction.

Fluorobenzene, C_6H_5F, $M = 96{\cdot}07$. The following data are taken from the work of Morgan and Daghlien (*J. Amer. Chem. Soc.*, 1911, **33**, 657); the drop-weights have been recalculated to surface tensions by means of the correction tables of Harkins and Brown (*ibid.*, 1919, **41**, 499).

t.	γ.	D.	$[P]$.	$\gamma(M/D)^{\frac{2}{3}}$.
9·3°	28·56	1·0354	214·5	585·2
34·5	25·20	1·0049	214·2	526·8
			Mean 214·3	$k = 2{\cdot}32$

p-*Fluorochlorobenzene*, C_6H_4FCl, $M = 130{\cdot}5$; b. p. 130°/756 mm. Densities determined: $D_{4°}^{20{\cdot}5°}$ 1·226, $D_{4°}^{37°}$ 1·210, $D_{4°}^{57{\cdot}5°}$ 1·183, $D_{4°}^{65{\cdot}5°}$ 1·168, whence $D_{4°}^{t°} = 1{\cdot}256 - 0{\cdot}00130t$.

t	15°	36·5°	52°	66°	
γ	32·7	30·0	28·1	26·7	
D	1·236	1·209	1·188	1·170	
$[P]$	252·4	252·6	252·8	253·4	Mean 252·8
$\gamma(M/D)^{\frac{2}{3}}$	730·3	680·1	644·3	620·4	$k = 2{\cdot}19$

p-*Fluorobromobenzene*, C_6H_4FBr, $M = 175{\cdot}0$; b. p. 153·5°/756 mm. Densities determined: $D_{4°}^{20°}$ 1·597, $D_{4°}^{45°}$ 1·557, $D_{4°}^{58{\cdot}5°}$ 1·539, $D_{4°}^{79{\cdot}5°}$ 1·511, whence $D_{4°}^{t°} = 1{\cdot}623 - 0{\cdot}00142t$.

t	21°	44°	61°	76°	90°	
γ	34·4	31·6	29·8	27·5	26·0	
D	1·593	1·561	1·536	1·515	1·495	
$[P]$	266·0	265·8	266·1	264·4	264·3	Mean 265·3
$\gamma(M/D)^{\frac{2}{3}}$	789·0	734·6	700·3	652·3	622·1	$k = 2{\cdot}47$

p-*Fluorotoluene*, C_7H_7F, $M = 110{\cdot}1$; b. p. 115·5°/756 mm. Densities determined: $D_{4°}^{16°}$ 1·0007, $D_{4°}^{31{\cdot}5°}$ 0·9857, $D_{4°}^{44{\cdot}5°}$ 0·9709, $D_{4°}^{55{\cdot}5°}$ 0·9595, whence $D_{4°}^{t°} = 1{\cdot}0187 - 0{\cdot}00107t$.

t	12°	31·5°	46·5°	59·5°	
γ	29·6	27·2	25·6	23·7	
D	1·0059	0·9850	0·9689	0·9551	
$[P]$	255·3	255·3	255·6	254·4	Mean 255·1
$\gamma(M/D)^{\frac{2}{3}}$	677·3	631·3	600·4	561·2	$k = 2{\cdot}35$

α-*Fluoronaphthalene*, $C_{10}H_7F$, $M = 146{\cdot}1$; b. p. 215°/756 mm. Densities determined: $D_{4°}^{16°}$ 1·141, $D_{4°}^{36{\cdot}5°}$ 1·122, $D_{4°}^{52°}$ 1·110, $D_{4°}^{76{\cdot}5°}$ 1·088, whence $D_{4°}^{t°} = 1{\cdot}154 - 0{\cdot}000875t$.

t	15°	35·5°	48°	77°	
γ	39·7	37·6	36·2	32·9	
D	1·141	1·123	1·112	1·087	
$[P]$	321·5	322·3	322·3	321·9	Mean 322·0
$\gamma(M/D)^{\frac{2}{3}}$	1008·5	965·5	935·5	863·2	$k = 2{\cdot}35$

pp′-*Difluorodiphenyl*, $C_{12}H_8F_2$, $M = 190\cdot1$; m. p. 87°. Densities determined: $D_{4^\circ}^{118^\circ}$ 1·1116, $D_{4^\circ}^{128\cdot5^\circ}$ 1·1027, $D_{4^\circ}^{139\cdot5^\circ}$ 1·0930, $D_{4^\circ}^{149^\circ}$ 1·0848, whence $D_{4^\circ}^{t^\circ} = 1\cdot1274—0\cdot000869\ (t—100)$.

t	107°	124°	140°	158·5°	
γ	29·3	27·9	26·1	24·5	
D	1·1212	1·1064	1·0925	1·0765	
$[P]$	394·5	394·9	393·6	392·8	Mean 394·0
$\gamma(M/D)^{\frac{2}{3}}$	897·6	862·4	814·0	771·0	$k = 2\cdot59$

Methoxyboron difluoride, $CH_3\cdot O\cdot BF_2$, $M = 79\cdot9$. We are indebted to Prof. G. T. Morgan for a specimen of this substance. It was redistilled immediately before measurement and boiled sharply at 86°. Densities determined: $D_{4^\circ}^{35\cdot5^\circ}$ 1·417, $D_{4^\circ}^{43^\circ}$ 1·406, $D_{4^\circ}^{51^\circ}$ 1·393, $D_{4^\circ}^{64^\circ}$ 1·372, $D_{4^\circ}^{76\cdot5^\circ}$ 1·354, whence $D_{4^\circ}^{t^\circ} = 1\cdot473—0\cdot00156t$.

t	45°	52°	60°	65°	74°	
γ	26·0	25·7	24·1	23·7	22·6	
D	1·403	1·392	1·379	1·372	1·358	
$[P]$	128·6	129·1	128·3	128·5	128·3	Mean 128·6
$\gamma(M/D)^{\frac{2}{3}}$	384·9	382·3	360·8	356·0	341·9	$k = 1\cdot65$

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