LV.—*The Parachor and Chemical Constitution. Part VIII. Ring-chain Valency Tautomerism in Phorone Derivatives.*

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DURING the course of the investigation described in the preceding paper, Professor Ingold and Dr. Shoppee were good enough to allow the author to determine the parachor of a number of the substances which exhibit this peculiar type of tautomeric change. The present paper records the data obtained for the surface tension and density of these substances together with a brief discussion of the effect of the changes in structure upon the parachor.

The large amount of chemical evidence accumulated by Ingold and Shoppee indicates that substitution in the $\alpha\alpha'$-positions in phorone produces, to a greater or less degree, a change in structure from the open-chain configuration (I) to the dicyclic structure (II).

$$\text{(I.)}\quad O{=}C\!\left\langle\begin{matrix}CX{=}CMe_2\\ CX{=}CMe_2\end{matrix}\right. \;\rightleftarrows\; O{=}C\!\left\langle\begin{matrix}CX{-}CMe_2\\ |\quad\;\; |\\ CX{-}CMe_2\end{matrix}\right.\quad\text{(II.)}$$

This should bring about a considerable diminution in the parachor, since two non-polar double bonds with a parachor of $2 \times 23{\cdot}2$, are replaced by ring structures which have smaller parachors. The constants for the rings concerned have been determined by Sugden and Wilkins (J., 1927, 139) and have the values : 3-ring 16·7, 4-ring 11·6, 5-ring 8·5.

The parachors found for the phorone derivatives are collected in Table I in the column headed " [*P*] obs." The next column gives the parachor calculated on the assumption that the substance is a derivative of phorone and contains two double bonds. It will be seen that, whereas phorone has a nearly normal parachor, the dibromo-derivative has a large negative anomaly which becomes still larger in the oxy- and bromo-oxy-derivatives. The general trend of the parachors is therefore in good agreement with the conclusions as to structure reached by Ingold and Shoppee, since the dibromo-compound exhibits the reactions of both open-chain and cyclic structures, and the oxy- and bromo-oxy-derivatives behave chemically as if they consisted entirely of the isomeride of formula (II).

TABLE I.

Substance.	[P] obs.	[P] calc.	Anomaly.
Phorone	367·9	372·2	− 4·3
Dichlorophorone	427·7	446·6	−18·9
Dibromophorone	463·2	474·0	−10·8
Acetoxyphorone	459·4	476·0	−16·6
Bromoacetoxyphorone	506·4	526·9	−20·5
Bromomethoxyphorone	455·3	482·1	−26·8
Benzoyloxyphorone	583·9	609·9	−26·0
Bromobenzoyloxyphorone	642·4	660·8	−18·4
p-Bromobenzyloxyphorone	630·7	655·0	−24·3
Bromo-*p*-bromobenzyloxyphorone	684·0	705·9	−21·9
Distyryl ketone	564·5	562·0	+ 2·5
Dibromodistyryl ketone	650·7	663·8	−13·1

The largest anomaly found occurs with bromomethoxyphorone (−26·8), and nearly the same value is reached by benzoyloxy- and *p*-bromobenzyloxy-phorone. The last two substances were crystallised to constant melting point, and hence there is little doubt as to their purity. Three specimens of the bromomethoxy-derivative, prepared by different methods, were examined, and all had the same surface tensions and densities; hence it is very improbable that this liquid product contained any appreciable amount of impurity. The mean anomaly for these three substances (−25·7) may therefore be taken to represent the effect of complete conversion into the bicyclic form, from which it follows that the structural constant for the fused-ring structure in (II) has the value 46·4 −25·7 = 20·7.

There is at present little information as to the relation between the constant for fused-ring structures and those for the isolated rings of which they may be supposed to be composed. The *cyclo*propene esters examined by Sugden and Wilkins (*loc. cit.*) gave a constant approximately equal to the sum of the double-bond and 3-ring constants, whilst benzene and many of its derivatives give parachors which can be predicted accurately by using a structural constant equal to the 6-ring constant + three double bonds. It seems probable, therefore, that the fused-ring structure in (II) may be regarded as composed of a five-membered ring upon which is superimposed the effect of a three-membered ring giving a constant of 16·7 + 8·5 = 25·2. This is nearly 5 units higher than the value found for the fully cyclised phorone derivatives, but the difference is probably due to the effect of the two *gem*-dimethyl groups which are known to stabilise ring structures and diminish unsaturation. In the series of *cyclo*propane esters studied by Sugden and Wilkins (*loc. cit.*), the presence of *gem*-carbethoxyl groups produced a marked lowering of the constant for a three-membered ring which, with two such groupings in the molecule, fell to 12·9. In this connexion, it is worthy of note that phorone shows a small negative anomaly although there is no chemical evidence for the presence of the cyclic isomeride, whilst distyryl ketone, in which the *gem*-dimethyl groups are replaced by phenyl, has a parachor slightly higher than the calculated value. The dibromo-derivative of this ketone shows, however, a marked negative anomaly, indicating partial conversion to the bicyclic form.

Acetoxyphorone is found by Ingold and Shoppee to behave as if it were a *cyclo*pentene derivative; this would correspond to an anomaly of $-14{\cdot}7$ which is in good agreement with the value found, *viz.*, $-16{\cdot}6$, when allowance is made for the effect of the *gem*-dimethyl groups.

In general, therefore, the parachors of these substances exhibit changes which confirm the structural conclusions reached by Ingold and Shoppee. Incidentally it may be noted that they supply a further example of the relation between parachor constants and unsaturation which has been discussed in earlier papers of this series.

It is noteworthy that the parachors of substances such as dibromophorone which are presumably equilibrium mixtures of isomerides show no appreciable change with temperature. The composition of the equilibrium mixture must therefore remain nearly constant, from which it follows that the heat evolved or absorbed by the change from the open chain to the bicyclic structure must be small. If this is correct the isomerides are substances which differ in reactivity (unsaturation) but have nearly the same energy content.

EXPERIMENTAL.

The determination of the parachor involves the measurement of the surface tension and density at a series of temperatures; the parachor is then calculated by the formula $[P] = M\gamma^{\frac{1}{4}}(D - d)$, where M is the molecular weight, γ the surface tension in dynes/cm., and D and d the density of the liquid and vapour respectively in g./c.c. For the substances described below, d is very small at the temperature of observation and has been neglected.

Densities were determined with a U-shaped pyknometer, and surface tensions by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). To save space the observed pressures are not recorded but only the surface tensions deduced therefrom.

Phorone, $C_9H_{14}O$, $M = 138{\cdot}2$, m. p. 28°. Densities determined: $D^{30^\circ}_{4^\circ} = 0{\cdot}880$, $D^{50^\circ}_{4^\circ} = 0{\cdot}864$, $D^{69^\circ}_{4^\circ} = 0{\cdot}848$, $D^{89^\circ}_{4^\circ} = 0{\cdot}830$, whence $D^{t^\circ}_{4^\circ} = 0{\cdot}906 - 0{\cdot}00084t$.

t	29·5°	51·5°	71°	99°	
γ	30·22	27·94	25·77	22·88	
D	0·881	0·863	0·846	0·823	
Parachor	367·8	368·3	368·2	367·3	Mean = 367·9

αα'-Dichlorophorone, $C_9H_{12}OCl_2$, M = 207·1, b. p. 119—121°/17 mm. Densities determined: $D_{4°}^{19°}$ = 1·173, $D_{4°}^{57°}$ = 1·136, $D_{4°}^{88°}$ = 1·107, whence $D_{4°}^{t°}$ = 1·191 – 0·00095t.

t	21°	41°	59°	83°	
γ	33·97	32·31	30·15	27·79	
D	1·171	1·152	1·135	1·112	
Parachor	427·0	428·7	427·6	427·3	Mean = 427·7

αα'-Dibromophorone, $C_9H_{12}OBr_2$, M = 296·0, m. p. 32°. Densities determined: $D_{4°}^{33°}$ = 1·556, $D_{4°}^{50·5°}$ = 1·534, $D_{4°}^{73·5°}$ = 1·505, whence $D_{4°}^{t°}$ = 1·598 – 0·00126t.

t	31·5°	49·5°	67·5°	
γ	35·31	33·38	31·46	
D	1·558	1·536	1·513	
Parachor	463·2	463·1	463·2	Mean = 463·2

α-Acetoxyphorone, $C_{11}H_{16}O_3$, M = 196·2, b. p. 109°/3 mm. Densities determined: $D_{4°}^{16°}$ = 1·024, $D_{4°}^{38°}$ = 1·004, $D_{4°}^{58·5°}$ = 0·986, $D_{4°}^{78°}$ = 0·969, whence $D_{4°}^{t°}$ = 1·038 – 0·00088t.

t	16·5°	43·5°	61·5°	84°	
γ	32·64	30·12	28·29	26·08	
D	1·023	1·000	0·984	0·964	
Parachor	458·3	459·6	459·8	459·9	Mean = 459·4

α-Bromo-α'-acetoxyphorone, $C_{11}H_{15}O_3Br$, M = 275·1, m. p. 74°. Densities determined: $D_{4°}^{89°}$ = 1·256, $D_{4°}^{110°}$ = 1·234, $D_{4°}^{133·5°}$ = 1·210, whence $D_{4°}^{t°}$ = 1·348 – 0·00103t.

t	80°	101°	120°	142·5°	
γ	29·45	27·53	25·84	23·80	
D	1·266	1·244	1·244	1·201	
Parachor	506·2	506·6	506·7	506·0	Mean = 506·4

α-Bromo-α'-methoxyphorone, $C_{10}H_{15}BrO_2$, M = 247·1, b. p. 133°/25 mm. Densities determined: $D_{4°}^{23·5°}$ = 1·314, $D_{4°}^{42°}$ = 1·294, $D_{4°}^{60·5°}$ = 1·274, $D_{4°}^{80·5°}$ = 1·253, whence $D_{4°}^{t°}$ = 1·339 – 0·00107t.

t	17·5°	46°	67·5°	89°	
γ	34·86	32·02	29·87	27·73	
D	1·320	1·290	1·267	1·244	
Parachor	454·8	455·6	455·9	455·8	Mean = 455·5

Another specimen prepared from the silver salt and measured with a different pyknometer and bubbler gave the following results: $D_{4°}^{12°}$ = 1·327, $D_{4°}^{40·5°}$ = 1·298, $D_{4°}^{56°}$ = 1·282, $D_{4°}^{73·5°}$ = 1·263, whence $D_{4°}^{t°}$ = 1·339 – 0·00104t.

t	13°	38°	67°	
γ	35·45	32·86	29·81	
D	1·326	1·299	1·269	
Parachor	454·8	455·4	455·0	Mean = 455·1

A third specimen gave the following values for the parachor 11·5°, 454·3; 32°, 455·3; 48°, 454·7; 61·5°, 455·9; 74·5°, 455·8; mean 455·2. It is very improbable, therefore, that this substance contains an appreciable amount of impurities, since modifications in the method of preparation and isolation gave a product with constant physical properties.

α-Bromo-α′-benzoyloxyphorone, $C_{16}H_{17}O_3Br$, $M = 337{\cdot}2$, m. p. 92°. Densities determined: $D_{4^\circ}^{91^\circ} = 1{\cdot}264$, $D_{4^\circ}^{110^\circ} = 1{\cdot}248$, $D_{4^\circ}^{130{\cdot}5^\circ} = 1{\cdot}231$, $D_{4^\circ}^{149^\circ} = 1{\cdot}216$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}344 - 0{\cdot}00086t$.

t	95·5°	117°	136°	162°	
γ	33·22	31·23	29·66	27·35	
D	1·261	1·241	1·224	1·201	
Parachor	642·0	642·6	642·8	642·1	Mean = 642·4

*α-Bromo-α′-*p*-bromobenzyloxyphorone*, $C_{16}H_{18}O_2Br_2$, $M = 402{\cdot}1$, m. p. 63—64°. Densities determined: $D_{4^\circ}^{73^\circ} = 1{\cdot}437$, $D_{4^\circ}^{93{\cdot}5^\circ} = 1{\cdot}418$, $D_{4^\circ}^{113^\circ} = 1{\cdot}397$, $D_{4^\circ}^{135{\cdot}5^\circ} = 1{\cdot}377$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}510 - 0{\cdot}00099t$.

t	73·5°	91°	110°	131°	
γ	35·57	33·93	32·69	30·63	
D	1·437	1·420	1·401	1·380	
Parachor	683·4	683·3	684·1	685·3	Mean = 684·0

α-Benzoyloxyphorone, $C_{16}H_{18}O_3$, $M = 258{\cdot}2$, m. p. 68°. Densities determined: $D_{4^\circ}^{75{\cdot}5^\circ} = 1{\cdot}056$, $D_{4^\circ}^{92^\circ} = 1{\cdot}043$, $D_{4^\circ}^{112{\cdot}5^\circ} = 1{\cdot}026$, $D_{4^\circ}^{133{\cdot}5^\circ} = 1{\cdot}010$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}117 - 0{\cdot}00080t$.

t	75°	93°	117°	131·5°	
γ	32·42	30·82	28·81	27·76	
D	1·057	1·043	1·023	1·012	
Parachor	582·9	582·9	584·4	585·5	Mean = 583·9

*α-*p*-Bromobenzyloxyphorone*, $C_{16}H_{19}O_2Br$, $M = 323{\cdot}2$, m. p. 86—87°. Densities determined: $D_{4^\circ}^{94{\cdot}5^\circ} = 1{\cdot}220$, $D_{4^\circ}^{117{\cdot}5^\circ} = 1{\cdot}119$, $D_{4^\circ}^{133{\cdot}5^\circ} = 1{\cdot}186$, $D_{4^\circ}^{153^\circ} = 1{\cdot}168$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}302 - 0{\cdot}00087t$.

t	96°	101°	115°	128·5°	146°	154·5°
γ	31·86	31·26	29·99	29·18	27·86	27·14
D	1·218	1·214	1·202	1·190	1·175	1·168
Parachor	630·6	629·5	629·2	631·4	631·8	631·6
			Mean = 630·7			

Distyrylketone, $(CHPh{:}CH)_2CO,C_{17}H_{14}O$, $M = 234{\cdot}2$, m. p. 112°. Densities determined: $D_{4^\circ}^{118^\circ} = 1{\cdot}033$, $D_{4^\circ}^{140^\circ} = 1{\cdot}017$, $D_{4^\circ}^{171^\circ} = 0{\cdot}995$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}118 - 0{\cdot}00072t$.

t	120°	130°	144·5°	164°	
γ	38·20	37·14	35·72	33·78	
D	1·032	1·024	1·014	1·000	
Parachor	564·2	564·8	564·6	564·6	Mean = 564·5

$\alpha\alpha'$-*Dibromodistyrylketone*, $C_{17}H_{12}OBr_2$, $M = 392{\cdot}1$, m. p. 98°. This substance decomposed rapidly a few degrees above its m. p. but showed no appreciable change after 1 hour at 100°. Found : γ at $100° = 40{\cdot}07$, $D_{4°}^{100°} = 1{\cdot}516$, whence the parachor $= 650{\cdot}7$.

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