CCLXII.—*The Parachor of Co-ordinated Hydrogen in the Ortho-substituted Phenols.*

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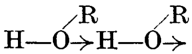
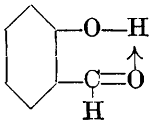
CO-ORDINATED hydrogen is generally assumed to occur in the polymerised molecules of hydroxylic compounds (I) and also as part of a chelate ring in many ortho-substituted phenols (II) (Sidgwick and Callow, J., 1924, **125**, 532), in β-diketones (Sidgwick, J., 1925, **127**, 907), in the monoximes of α-diketones (Taylor and Ewbank, J., 1926, 2818), and elsewhere. Sugden has recently ("The Parachor and Valency," 1930, p. 150) disputed the occurrence of this chelation in β-diketones, on the ground of their parachor values. We do not, however, know what the parachor of co-ordinated hydrogen is. Associated liquids (type I above) are less suitable for the investigation of this property (owing to the impossibility of determining their molecular complexity) than the chelate compounds, where co-ordination takes place within a single molecule. We have therefore determined the parachors of a series of substituted phenols and their derivatives.

(I.)



$$\mathrm{H{-}\overset{R}{O}{\rightarrow}H{-}\overset{R}{O}{\rightarrow}}$$



(II.)

EXPERIMENTAL.

Purification of Materials.—Benzene. Frozen out 4 times, shaken twice with concentrated sulphuric acid, and distilled over sodium; m. p. 5·5°. (All recorded temperatures are corrected.)

p-*Xylene.* Kahlbaum's material was frozen out 4 times, and distilled over sodium; m. p. 13·4° (13·4°, Perkin, J., 1900, **77**, 278).

Phenol. Freed from its homologues by conversion into the hydrate and freezing this out 5 times: then distilled thrice; m. p. 40·6° (41°, "International Critical Tables," 1926; 40°, Tammann, *Z. physikal. Chem.*, 1910, **69**, 571).

o-*Nitrophenol.* Recrystallised from water and then from light petroleum; m. p. 44·5° (44·3°, Mills, *Phil. Mag.*, 1882, **14**, 27; 44·95°, Hulett, *Z. physikal. Chem.*, 1899, **28**, 666). Another sample made from the pure phenol (above) had the same m. p.

o-*Nitroanisole.* Made by methylation of *o*-nitrophenol with methyl sulphate in presence of xylene, by the method used by Robinson and Baker (J., 1929, 156) for the methylation of dinitroguaiacol. Purified by shaking with alkali, and repeated distillation in a vacuum. Pale yellow; b. p. 144°/14 mm.; m. p. 9·3—9·4° (9·4°, Hantzsch, *Ber.*, 1906, **39**, 1097).

m-*Nitrophenol.* Recrystallised from benzene; m. p. 96° (96°, Neumann, *Ber.*, 1886, **29**, 2979; 97°, Holleman, *Rec. trav. chim.*, 1902, **21**, 435).

p-*Nitrophenol.* Recrystallised twice from benzene; m. p. 112° (111·4°, Mills, *loc. cit.*; 111·8°, Garelli and Calzolari, *Gazzetta*, 1899, **29**, ii, 363).

p-*Nitroanisole.* By the methylation of *p*-nitrophenol with methyl sulphate (Ullmann, *Annalen*, 1903, **327**, 115); yield 90%; m. p. 54° (54°, Willgerodt, *Ber.*, 1882, **15**, 1004).

Salicylaldehyde. Owing to the difference of the density and m. p. of our purified product from the recorded values (especially Walden, *Z. physikal. Chem.*, 1906, **55**, 220; 1907, **59**, 395), this was purified in three ways. (1) The aldehyde in benzene solution was shaken with alkali to remove salicylic acid, washed, dried, and distilled. (2) The bisulphite compound was decomposed with dilute sulphuric acid, and the aldehyde steam-distilled, and fractionated in a vacuum. (3) A laboratory sample was frozen out 5 times. All three products were neutral to litmus, and boiled at 195°/760 mm. and 92°/22 mm.; they melted at 0·9—1·0°; $d_{4^\circ}^{25^\circ}$ 1·1612. Walden (*loc. cit.*) gives m. p. — 10°, $d_{4^\circ}^{25^\circ}$ 1·1539. As a further proof of identity the phenylhydrazone was prepared; it melted at 142° (142—143°, Lockemann and Lucius, *Ber.*, 1913, **46**, 1013).

o-*Methoxybenzaldehyde.* Salicylaldehyde (50 g.), 50% aqueous potassium hydroxide (30 c.c.), and water (500 c.c.) were shaken together. Redistilled methyl sulphate (100 g.) and potassium hydroxide solution (100 g.) were added alternately in small portions, the mixture being kept alkaline and well-shaken. Finally, the mixture was heated for an hour on the water-bath. *o*-Methoxybenzaldehyde was extracted with ether; it crystallised when the ether was removed, and was fractionated in a vacuum; b. p. 119°/13 mm.; m. p. 35·6° (35°, Voswinckel, *Ber.*, 1882, **15**, 2024; 38°, Katschalowski and von Kostanecki, *ibid.*, 1904, **37**, 2347).

m-*Hydroxybenzaldehyde.* Recrystallised thrice from hot water; m. p. 104° (104°, Rieche, *Ber.*, 1889, **22**, 2348; 108°, Jowett, J., 1900, **77**, 707).

p-*Hydroxybenzaldehyde.* Recrystallised twice from hot water; m. p. 117° (115—116°, Reimer and Tiemann, *Ber.*, 1876, **9**, 834).

p-*Methoxybenzaldehyde.* Purified through the bisulphite compound; b. p. 249° (248°, Perkin, J., 1889, **55**, 551).

p-*Methoxysalicylaldehyde* (*o*-vanillin). A pure laboratory sample; m. p. 41° (41°, Friedländer, *Sitzungsber. Wien Akad.*, 1909, **118**, 660).

Methyl salicylate. Fractionated in a vacuum; b. p. 98°/12 mm.; m. p. − 0·8°; $d_{4^\circ}^{25^\circ}$ 1·1782 (m. p. − 8·3°, Schneider, *Z. physikal. Chem.*, 1897, **22**, 233).

Methyl p-*hydroxybenzoate.* Made from Kahlbaum's acid by the method of von Hoessle (*J. pr. Chem.*, 1894, **49**, 501). Recrystallised from a mixture of alcohol and water, and then from benzene; m. p. 128° (131°, von Hoessle): further recrystallisation did not affect the m. p. The benzoyl derivative melted at 133° (135°, von Hoessle) and the acetyl derivative at 83° (85°, von Hoessle).

Measurement of Surface Tension.—The apparatus used was essentially that of Sugden (J., 1924, **113**, 271) as modified by Hammick and Andrew (J., 1929, 754). It was calibrated with benzene. At higher temperatures a glycerol bath with adjustable thermostat was used, which could be kept constant within 0·1°.

Measurement of density. At 25° this was done in an ordinary pyknometer. For substances with higher melting points, a 5 c.c. pipette with capillary tubes and a tap at the top was used. This was fixed in a test-tube containing the substance and immersed in the bath. When temperature equilibrium was reached, the liquid was sucked into the pipette up to the mark, and the tap closed. The pipette was then removed and weighed. Repeated measurements showed that the results were accurate to less than 1 part in 1000 parts. The errors of the surface tensions are less than 1 in 200 (Sugden, *loc. cit.*), so the error of the parachor should not exceed 1 in 400: this is well within the accuracy of additivity of the parachor.

The thermometers were calibrated against a standard.

Boiling Point Measurements.—In order to discover whether the association of *p*-nitrophenol is affected by temperature, its molecular weight was determined ebullioscopically in *p*-xylene. The apparatus was a modification of that of Washburn and Cottrell, and is described by Sidgwick and Sutton (this vol., p. 1467). A known volume of pure *p*-xylene was run into the apparatus, and successive weighed amounts of solute were added through the side-tube. The ebullioscopic constant was determined with benzil as solute with the following results:

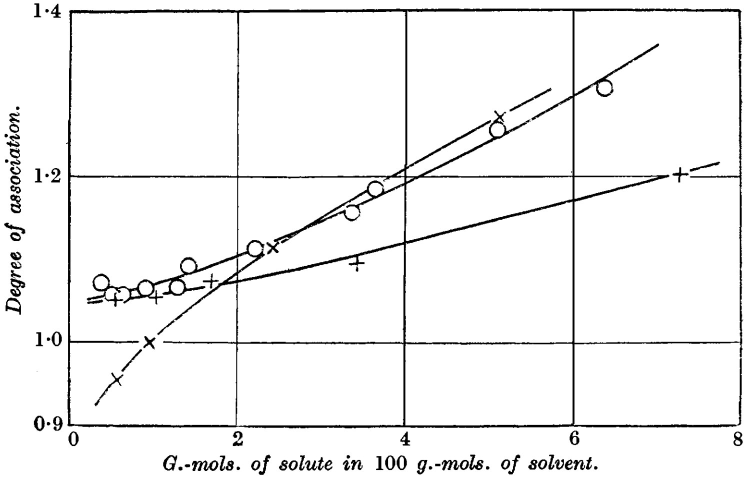
Rise in b. p.	G. of benzil in 100 g. of xylene.	*E.*
0·133°	0·703	3·97
0·360	1·763	4·29
0·557	2·707	4·32
0·819	3·980	4·32
	Mean	4·23

Brown (J., 1905, **87**, 268) gives the heat of vaporisation of *p*-xylene as 8566 cals./g.-mol., which corresponds to $E = 4{\cdot}14$.

The results obtained with *p*-nitrophenol at 138° are given below. They are calculated on the experimental value 4·23. In Fig. 1 are plotted the values of *A.F.*, the association factor.

Rise in b. p.	G. solute to 100 g. xylene.	Mols. solute to 100 mols. solvent.	Mol. wt.	*A. F.*
0·146°	0·515	0·392	149	1·072
0·191	0·663	0·505	147	1·06
0·247	0·858	0·654	147	1·06
0·344	1·201	0·916	148	1·07
0·485	1·698	1·295	148	1·07
0·522	1·872	1·428	152	1·09
0·785	2·906	2·216	157	1·130
1·162	4·436	3·383	161	1·16
1·222	4·773	3·640	165	1·19
1·615	6·684	5·097	175	1·26
1·947	8·372	6·384	182	1·31

FIG. 1.



—○— p-*Nitrophenol in* p-*xylene at* 138° (*S. & B.*).
—×— p-*Nitrophenol in naphthalene at* 80° (*Auwers*).
—+— *Phenol in naphthalene at* 80° (*Auwers*).

Discussion of Results.

The substances whose parachors are given in Table I are of three kinds : (1) those for which chelation is possible, *i.e.*, ortho-substituted phenols, (2) those phenols which cannot chelate, because the substituent is not in the ortho-position, (3) compounds in which the phenolic hydrogen is replaced by methyl. In Tables II, III, and IV the mean parachors, classified in this way, are tabulated and compared with those calculated on Sugden's values for the open-chain structures (in Table II, " Anomaly I " is this difference : " Anomaly

TABLE I.

Substance.	Temp.	Density.	γ.	[*P*].	[*P*] (mean).
o-Nitrophenol	50°	1·2709	42·3	274·7	274·7*
o-Nitroanisole	25·0	1·2408	45·9	321·0	
	57·4	1·2078	42·3	323·1	322·1
m-Nitrophenol	108·8	1·2698	44·6	282·9	
	118·5	1·2593	43·5	283·6	283·3
p-Nitrophenol	121·0	1·279	46·1	283·2	283·2*
p-Nitroanisole	68·4	1·2083	41·6	321·8	
	94·8	1·1837	39·1	323·3	322·6
o-Hydroxybenzaldehyde	25·0	1·1612	42·0	267·6	
	51·8	1·1310	38·2	268·3	268·0
o-Methoxybenzaldehyde	50·8	1·0992	40·4	312·0	
	79·4	1·0727	39·7	312·7	312·4
m-Hydroxybenzaldehyde	113·6	1·1299	41·7	274·5	274·5
p-Hydroxybenzaldehyde	119·6	1·1364	45·1	278·3	
	136·7	1·1238	42·9	278·0	278·2
p-Methoxybenzaldehyde	25·0	1·1143	43·7	313·9	313·9
o-Vanillin	50·6	1·2065	44·7	325·9	
	90·4	1·1778	39·8	324·2	325·1
Methyl salicylate	25·0	1·1782	38·6	321·5	
	58·0	1·1454	34·9	322·6	322·1
Methyl *p*-hydroxybenzoate	137·2	1·1208	35·8	331·8	331·8
Phenol	49·6	(1·049)†	37·8	222·3	
	51·0	1·0477			
	70·5	1·0297			
	71·4	(1·029)	35·1	222·4	
	90·8	(1·011)	33·4	223·6	
	91·8	1·0106			
	110·5	0·9912			
	110·8	(0·9925)	31·2	224·0	
	130·0	0·9741			
	131·6	(0·9725)	29·1	224·6	
	147·5	(0·9565)	27·3	224·8	
	149·6	0·9538			

* The parachors of these compounds were determined by Bhatnagar and Singh (*J. Chim. physique*, 1928, **25**, 21), who found for *o*-nitrophenol 273·2, and for *p*-nitrophenol 280·8.

† Values in brackets were obtained by interpolation.

TABLE II.

Substance.	Parachor.		Anomaly I.	Anomaly II.
	Obs.	Calc. (open).		
o-Nitrophenol	274·7	283·0	−8·3	−14·4
o-Hydroxybenzaldehyde	268·0	275·1	−7·1	−13·2
o-Vanillin	325·1	334·1	−9·0	−15·1
Methyl salicylate	322·1	330·9	−8·8	−14·9
			Mean −8·3	−14·4
Acetylacetone	245·4	247·2	−1·8	− 7·9
Propionylacetone	279·7	286·2	−6·5	−12·6
Benzoylacetone	382·4	381·1	+1·3	−4·8

TABLE III.

Substance.	Parachor. Obs.	Calc.	Anomaly.
m-Nitrophenol	283·3	283·0	+0·3
p-Nitrophenol	283·2	283·0	+0·2
m-Hydroxybenzaldehyde	274·5	275·1	+0·6
p-Hydroxybenzaldehyde	278·2	275·1	+3·1
Methyl *p*-hydroxybenzoate	331·8	330·9	+0·9
Phenol (49·6°)	222·3	227·1	−4·8
„ (147·5°)	224·8	227·1	−2·3

TABLE IV.

Substance.	Parachor. Obs.	Calc.	Anomaly.
o-Nitroanisole	322·1	322·0	+0·1
p-Nitroanisole	322·6	322·0	+0·6
o-Methoxybenzaldehyde	312·4	314·1	−1·7
p-Methoxybenzaldehyde	313·9	314·1	−0·2

II " is explained below). The values given by Sugden (*op. cit.*, p. 150) for the β-diketones are added for comparison in Table II. It will be seen that the parachors of these ortho-phenols are all about 8 units low. This cannot be due to association, since by every test they have been shown not to be associated. It is not likely to be due to any special structural parachor for di-ortho-derivatives of benzene, such as was suggested by Mumford and Phillips (J., 1929, 2112), since the ortho-phenol ethers in Table IV give normal parachors. It must therefore be due to the formation of a chelate ring; and as the anomaly is practically the same in all the four compounds examined, we may assume that the chelation is practically complete in all of them. If this is so, the new 6-ring so formed will cause an increase in the parachor of 6·1 units (Sugden, p. 38): that no modification is introduced by the presence of two 6-rings fused in the ortho-positions may be assumed, since naphthalene is found to give a normal parachor (Bhatnagar and Singh, *loc. cit.*: obs. 312·5, calc. 313·0). The observed defect should therefore be increased by 6·1 to allow for the new ring: values calculated on this basis are given under " Anomaly II " in Table II. It will be seen that of the three β-diketones examined by Sugden, one gives results agreeing with ours (if allowance is made for the presence of some 20% of the ketone form), while the other two, for some unexplained reason, give smaller values.

It therefore appears that the co-ordination of a hydrogen atom to form the group $=\mathrm{O}\rightarrow\mathrm{H}-$ involves a decrease of 14·4 units in the parachor. If we may assume that 1·6 of this are due to the transferred electron, as Sugden finds in such links as $\mathrm{N}\rightarrow\mathrm{O}$ and $\mathrm{S}\rightarrow\mathrm{O}$, the rise in the covalency of the hydrogen from 1 to 2 results in a contraction of 12·8 units. Now Sugden has already shown that when an atom increases its valency in a covalent compound by two beyond the normal (*e.g.*, if we compare quinquevalent with tervalent phosphorus or antimony in their chlorides) a contraction of about 25 units (P 26·1, Sb 24·2, mean 25·2) takes place. For an increase of one in the covalency of hydrogen we might thus expect half of this, or 12·6, and so our result of 12·8 is in agreement with his. The explanation which he gives of this contraction—that it is due to the formation of singlet links—is open to various objections. It implies that a link of one electron can be as stable as a link of two, and in fact is indistinguishable from it in properties. The supposed deduction of singlet links for co-ordinated hydrogen from Pauli's principle is unsound; this principle states that an atom cannot have more than two electrons in the first quantum group, but it does not deny that it may also have two in the second group (see Sidgwick and Callow, *loc. cit.*). Moreover, the application of Sugden's theory to co-ordinated hydrogen in the light of our results leads to the conclusion that the atom has one singlet link, *i.e.*, a valency group of three shared electrons, which is against all analogy. It is more probable that in these atoms, such as phosphorus in the pentachloride, or co-ordinated hydrogen in *o*-nitrophenol, the links are as usual formed of two electrons each, and the observed decrease in the parachor is due to the change in the valency group, in the phosphorus from an octet of two unshared and six shared electrons to a group of ten shared electrons, and in the hydrogen from two shared to four shared. The effect on the parachor is twice as great in the first case as in the second. It is true that while the increase in covalency is also twice as great, the increase in the size of the valency group is the same (*viz.*, 2) in both; but at present we do not know why particular changes of parachor are associated with certain changes in the valency group, and we can only record the facts.

If this decrease of $12{\cdot}8 + 1{\cdot}6 = 14{\cdot}4$ represents the effect of the conversion of $>\mathrm{O} + \mathrm{H}-$ into $>\mathrm{O}\rightarrow\mathrm{H}-$, it should occur also in associated hydroxylic compounds in general. The recorded values (Sugden, *op. cit.*, p. 167; Jones, J., 1928, 1196) on the whole support this conclusion. The defect (calculated on the simple molecule) should be $1/2 \times 14{\cdot}4 = 7{\cdot}2$ for a double, and $2/3 \times 14{\cdot}4 = 9{\cdot}6$ for a triple polymeride. Further, since the association normally diminishes with a rise of temperature, the defect should do the same. The results for water (Sugden, *op. cit.*, p. 169) are anomalous on any theory yet advanced: the defect is very small, and increases with rise of temperature (— 1·1 at 0°, — 2·1 at 100°); but methyl alcohol shows the expected anomaly (— 6·5 at — 65°, — 5·3 at 0°, — 1·3 at 190°) and ethyl alcohol almost the same (— 8·0 at — 57°, — 5·8 at 0°, — 1·2 at 200°). The carboxylic acids, which readily form double molecules, but appear not to polymerise any further, give at the ordinary temperature the following anomalies (assuming for the O_2 group the value of 60 found by Sugden in the esters): acetic −6·7, propionic − 6·5, *n*-butyric − 7·4, *n*-valeric − 6·3. Nitric acid (− 6·8 at 11·6°, − 5·5 at 78°) and sulphuric acid (−14·4 at 10°, −6·9 at 133°) also agree. The anomalies are on the whole rather smaller than we should anticipate, but they are in the right direction, and have the expected change with temperature.

When, however, we come to the *m*- and *p*-substituted phenols (Table III), the results are most surprising. The whole behaviour of these compounds points to their being associated. Auwers and his pupils (*Z. physikal. Chem.*, 1895, **18**, 595; 1897, **21**, 337; 1899, **30**, 300) have shown that in solution the *m*- and *p*-nitro- and -aldehydo-phenols are more associated than phenol itself; and this is natural, since the same donor power of the oxygen which makes it co-ordinate in the ortho-position with the hydroxyl of the same molecule would lead to its co-ordination in the meta- and para-positions with that of another molecule, *i.e.*, to association. These compounds should therefore show a negative anomaly like that of the alcohols and acids. But in fact, as can be seen from Table III, they show no negative anomaly at all: the observed values are slightly above the calculated, but within the limits of experimental error. That this is not due to some unexplained term in compounds of this type is shown by the methyl ethers of these phenols (Table IV), which also give normal values, and by the behaviour of phenol itself, which gives the expected defect.

It seemed possible that the association of these phenols might diminish rapidly with temperature, and might practically have disappeared at the temperatures (110—140°) at which the parachors were measured. To test this point, the molecular weight of *p*-nitrophenol was measured ebullioscopically in *p*-xylene solution (at 138°). The results are plotted in Fig. 1, along with those obtained cryoscopically in naphthalene at 80° by Auwers (*Z. physikal. Chem.*, 1895, **18**, 595) for *p*-nitrophenol and for phenol itself. It will be seen that *p*-nitrophenol is almost as much associated at 138° as at 80°, and much more so than phenol at 80°; yet phenol at 80° gives a parachor anomaly of − 4·1, and *p*-nitrophenol none at all (+ 0·2). This explanation therefore will not serve; and at present we can give no reason for the absence in these compounds of the parachor defect which usually accompanies association.

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