7. *The Parachor, Surface Tension, and Density of Substituted Phenols and Phenolic Ethers.*

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In continuation of previous work on the constitution of the so-called *o*-hydroxyazobenzenes (*o*-benzoquinonephenylhydrazones; Burawoy and Markowitsch, *Annalen*, 1933, **503**, 180; **504**, 71; 1934, **509**, 60; 1935, in the press), the parachors, surface tensions, and densities of the hydroxyazobenzenes and hydroxybenzaldehydes and their methyl ethers have been investigated, and are discussed in relation to the same properties of the nitrophenols and -anisoles (given by, or calculated from, Jaeger, *Z. anorg. Chem.*, 1917, **101**, 1).

The theoretical parachors were calculated from Sugden's atomic values (" The Parachor and Valency "). The outstanding feature of the results (Table I) is the low value of the parachor of *o*-hydroxy-compounds in comparison, not only with theoretical values, but also with those of corresponding *m*- or *p*-hydroxy-compounds, whereas the methyl ethers in each series do not show these differences. That this negative anomaly cannot be attributed to association due to hydroxyl or amino-groups (Sugden, *op. cit.*) follows from the normal values afforded by (7) and (17) (cf. also Sidgwick and Bayliss, J., 1930, 2027).

The calculated parachors of *o*-hydroxyazo-compounds are identical with those of the corresponding quinonephenylhydrazones, and so determinations cannot decide between the two structures.

Table I.

		Parachor.					
	Substance.	Obs.	Calc.	Diff.	γ	D.	
1	Benzeneazo-β-naphthol methyl ether	594·4	593·1	+ 1·3	40·6	1·113	At 100°
2	β-Naphthaquinone-α-phenylhydrazone	545·8	554·1	− 8·3	40·7*	1·154*	
3	*o*-Methoxyazobenzene	486·9	487·2	− 0·3	36·7	1·073	
4	*m*- ,,	486·9	487·2	− 0·3	35·6	1·062	
5	*p*- ,,	485·0	487·2	− 2·2	36·2	1·071	
6	*o*-Benzoquinonephenylhydrazone	443·3	448·2	− 4·9	35·8	1·094	
7	*m*-Hydroxyazobenzene	449·8	448·2	+ 1·6	42·5*	1·123*	
8†	*p*- ,,	—	—	—	41·6*	—	
9	*o*-Nitroanisole	320·5	323·1	− 2·6	39·5	1·197	At 75°
10‡	*p*- ,,	322·0	323·1	− 1·1	39·9	1·201	
11‡	*o*-Nitrophenol	270·3	284·1	− 13·8	36·1	1·258	
	,,	—	—	—	31·1	1·205	At 125°
12‡	*m*- ,,	278·1	284·1	− 6·0	39·5	1·259	
13‡	*p*- ,,	280·9	284·1	− 3·2	42·5	1·266	
14‡	*o*-Methoxybenzaldehyde	309·9	314·1	− 4·2	37·1	1·083	At 75°
15	*p*- ,, ,,	310·2	314·1	− 3·9	36·4	1·077	
16‡	*o*-Hydroxybenzaldehyde	271·3	275·1	− 3·8	36·7	1·104	
17	*p*- ,, ,,	276·5	275·1	+ 1·4	47·8*	1·173*	

† See p. 39. ‡ Values of γ and D are due to Jaeger (*loc. cit.*).

The density, and much more so, the surface tension, is even more significant than the parachor. The values for any one series are always compared at the same temperature; although this is arbitrarily chosen, the same conclusions could be derived by adoption of any other temperature. For convenience the values of some substances (denoted by *) are extrapolated and given for a temperature at which they are in fact solid.

According to Table I, the surface tensions and the densities of the three sets of isomeric methyl ethers agree among themselves within 2%, but in the corresponding hydroxy-compounds the *o*- has a lower surface tension (by 20—35%) and density (by 3—6%) than its isomerides. This anomaly is also apparent in that, in the *m*- and *p*-series, the methyl ethers always have much smaller surface tensions (by 20—30%) than their phenols, as normally all hydroxylic compounds and their methyl ethers behave, whereas in the *o*-series the difference is slightly in the other direction.

It is known (v. Auwers and co-workers, *Z. physikal. Chem.*, 1895, **18**, 595; 1897, **21**, 335; 1899, **30**, 300; 1903, **42**, 513) that *m*- and *p*-hydroxybenzaldehydes, -nitrophenols, and -hydroxyazobenzenes are extensively associated in several solvents, but the *o*-derivatives are only slightly associated. Evidence for the behaviour in the homogeneous fused state could be derived from the Ramsay–Shields constant *K* (J., 1893, **63**, 1089), which is usually 2·12 for non-associated compounds. In Table II are given the calculated values, together with the derived association factor *x*, although these are now known to have only qualitative, and not quantitative, significance. The values of the nitroanisoles and of *o*-nitrophenol indicate no association, but those of *p*- and still more so of *m*-nitrophenol indicate considerable association (compare Hewitt and Winmill, J., 1907, **91**, 441). Similarly, *o*- and *p*-methoxy- and *o*-hydroxy-benzaldehyde are normal, but *p*-hydroxybenzaldehyde is associated. On the other hand, all methyl ethers of the hydroxyazobenzenes have $x < 1$, implying that in this case the normal value of *K* is not 2·12, so the lower *K* values of the two phenylhydrazones may indicate a small association; however, *m*-hydroxyazobenzene gives a similar value for *K*, although a higher association would be expected. (Possibly comparison of the last two types of compound is invalidated by structural differences.) Hence, von Auwers's results appear to be confirmed for the fused nitrophenols and hydroxybenzaldehydes, but the behaviour of the hydroxyazobenzenes is not clear.

TABLE II.

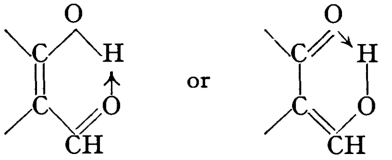
Substance.	Temp. range.	*K*.	*x*.	Substance.	Temp. range.	*K*.	*x*.
Benzeneazo-β-naphthol methyl ether	83—114°	3·1	0·57	*o*-Nitroanisole	55—95°	2·2	0·95
o-Methoxyazobenzene	56·5—88·5	2·8	0·66	*p*- „	115—167·5	2·2	0·95
m- „ „	53—81·5	2·9	0·63	*o*-Nitrophenol............	124·3—170	2·5	0·77
p- „ „	67—98	2·9	0·63	*m*- „	125—170	1·0	3·08
o-Benzoquinonephenylhydrazone	100—130	2·4	0·83	*p*- „	130·5—176·5	1·7	1·39
m-Hydroxyazobenzene	120—148	2·5	0·77	*o*-Methoxybenzaldehyde	52—91	2·3	0·89
β-Naphthaquinone-α-phenylhydrazone ...	150·5—188	2·6	0·74	*p*- „ „	46·5—90·3	2·2	0·95
				o-Hydroxybenzaldehyde	116·2—160	2·0	1·09
				p- „ „	117—145	1·6	1·53

Steric hindrance cannot be the cause of the anomalies in the *o*-hydroxy-compounds, for the densities, surface tensions, and parachors of the methoxy-compounds are normal, although they might be expected to exhibit equal or greater steric hindrance (compare also Sidgwick and Callow, J., 1924, **125**, 527 and previous papers). Moreover, the anomaly cannot be attributed to difference in atomic structure, for the absorption spectra (200—800 mμ) of the *o*-hydroxy- and -methoxy-benzaldehydes are very similar (Tuck, J., 1909, **95**, 1813; Waliaschko, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 754, 785); the spectra of *o*-nitrophenol and its methyl ether show larger differences, but their type is not changed (Baly, Edwards, and Stewart, J., 1906, **89**, 518; Waliaschko, *loc. cit.*, p. 1008). *o*-Nitrophenol and *o*-hydroxybenzaldehyde are therefore undoubtedly phenolic in structure; but the spectra of *o*-hydroxyazobenzenes show that they are actually quinonehydrazones (compare Burawoy and Markowitsch, *loc. cit.*).

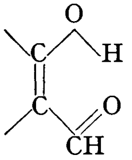
The view that these anomalies are connected with a weakening of the polarity of the *o*-substituted phenols produced by interaction between the two *o*-substituents, similar to the formation of molecular compounds between phenols or anilines and nitrobenzenes, quinones, etc. (Sidgwick, *loc. cit.*), is confirmed by the anomalies of the surface tension, in which replacement of a CH by a CMe group has no appreciable effect on the value of the surface tension, but replacement of an OH by an OMe group generally produces a big decrease of the value. This is, undoubtedly, due to the association of the hydroxyl compounds. Therefore, *o*-substituted phenols, having lost the capacity to associate with other molecules, behave " normally " and have the same surface tension as their methyl ethers.

The anomalies of " *o*-hydroxyazobenzenes " may not necessarily be due to their quinonoid structure; for phenolic *o*-nitrophenol and *o*-hydroxybenzaldehyde show the same behaviour. Effects caused by intramolecular association between the two *o*-substituents would operate also in the alternative quinonehydrazone structure. It is known that the amino-group may replace a hydroxyl group in such compounds (compare Sidgwick, *loc. cit.*).

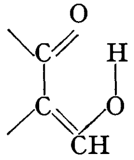
The association may be due to the formation of a new co-ordinate bond of the hydrogen atom (I) (Sidgwick) or to a dipole attraction between the associated groups (Smyth, *J. Amer. Chem. Soc.*, 1929, **51**, 1736; " Dielectric Constant and Molecular Structure," New York, 1931; Martin and co-workers, J., 1932, 2658; 1933, 1413; *Trans. Faraday Soc.*, 1934, **30**, 759). However, strong evidence can be derived from the absorption spectra (λ 200—800 mμ) of the substituted phenols against the assumption that the constitution of the *o*-substituted phenols corresponds to an intermediate state between (II) and (III), possibly representing a very rapid oscillation between these two extreme states (Sidgwick, *Ann. Reports*, 1934, **31**, 37); for the spectra of *o*-hydroxy- and *o*-methoxy-benzaldehyde



(I.)



(II.)



(III.)

are almost identical, and that of β-benzeneazo-α-naphthol is completely different from that of its *O*-methyl ether, but similar to that of its *N*-phenyl ether (β-naphthaquinone-β-diphenylhydrazone). This evidence seems to exclude the assumption of such an intermediate state, which would certainly have an electron configuration (responsible for the absorption between 200 and 800 mμ) different from both the phenolic and the quinonoid structure.

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27); r_2 for the bubbler used was 0·199 cm., and values of *A* are given for each set of determinations. Densities (*D*; g./c.c.) were determined with a U-shaped pyknometer (Sugden, J., 1924, **125**, 1171). For all the substances concerned, *d* is very small and has been neglected.

Benzeneazo-β-naphthol methyl ether (M = 262·1) was prepared according to Charrier and Ferreri (*Gazzetta*, 1912, **42**, 117) and recrystallised from alcohol; m. p. 62°. Densities determined: $D^{84^\circ}_{4^\circ}$ 1·1255; $D^{93\cdot5^\circ}_{4^\circ}$ 1·1185; $D^{104^\circ}_{4^\circ}$ 1·1095; $D^{115^\circ}_{4^\circ}$ 1·1015. A = 0·004.

t.	*P*.	*D*.	*φ*.*	*γ*.	[*P*].	*t*.	*P*.	*D*.	*φ*.*	*γ*.	[*P*].
83·0°	10425	1·126	1·0146	42·30	593·6	104·0°	9909	1·110	1·0151	40·23	594·8
94·0	10148	1·118	1·0148	41·20	594·1	114·0	9645	1·102	1·0154	39·17	595·0
										Mean	594·4

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

β-Naphthaquinone-α-phenylhydrazone (M = 248·1) was recrystallised from alcohol; m. p. 134°. Densities determined: $D^{150\cdot5^\circ}_{4^\circ}$ 1·119; $D^{160\cdot5^\circ}_{4^\circ}$ 1·112; $D^{170\cdot0^\circ}_{4^\circ}$ 1·1055; $D^{188^\circ}_{4^\circ}$ 1·093. A = 0·004.

150·0°	9003	1·119	1·0168	36·60	545·5	172·0°	8527	1·107	1·0175	34·68	545·5
160·5	8843	1·112	1·0169	35·93	546·5	188·0	8208	1·093	1·0179	33·41	545·8
										Mean	545·8

o-Methoxyazobenzene (M = 212·1) (Bamberger, *Ber.*, 1900, **33**, 3190) was recrystallised from ligroin; m. p. 41°. Densities determined: $D^{55\cdot5^\circ}_{4^\circ}$ 1·107; $D^{65\cdot5^\circ}_{4^\circ}$ 1·0985; $D^{75\cdot5^\circ}_{4^\circ}$ 1·0915; $D^{85\cdot5^\circ}_{4^\circ}$ 1·084 (v. Auwers and Hemke, *Ber.*, 1928, **61**, 1030, found $D^{100^\circ}_{4^\circ}$ 1·0728). A = 0·00391.

56·5°	10450	1·106	1·0143	41·43	486·7	75·5°	9937	1·092	1·0148	39·42	486·9
65·0	10248	1·099	1·0145	40·64	487·1	85·5	9657	1·084	10·151	38·32	486·9
										Mean	486·9

m-Methoxyazobenzene was prepared according to Jacobson and Hoenigsberger (*Ber.*, 1903, **36**, 4102) and recrystallised from ligroin; m. p. 33—34°. Densities determined: $D^{53^\circ}_{4^\circ}$ 1·1023; $D^{62^\circ}_{4^\circ}$ 1·0945; $D^{73^\circ}_{4^\circ}$ 1·086; $D^{81\cdot5^\circ}_{4^\circ}$ 1·078. A = 0·005729.

53·0°	6970	1·1023	1·0213	40·78	486·2	73·0°	6595	1·0860	1·0222	38·61	486·8
62·0	6830	1·0945	1·0216	39·96	487·2	81·5	6443	1·0780	1·0225	37·75	487·4
										Mean	486·9

p-Methoxyazobenzene was recrystallised from alcohol; m. p. 56°. Densities determined: $D_{4^\circ}^{69^\circ}$ 1·097; $D_{4^\circ}^{78^\circ}$ 1·089; $D_{4^\circ}^{88^\circ}$ 1·0805; $D_{4^\circ}^{98^\circ}$ 1·073. A = 0·005729.

67·0°	6773	1·099	1·0219	39·65	484·4	88·0°	6352	1·081	1·0229	37·23	484·9
78·0	6568	1·089	1·0223	38·46	485·1	98·0	6210	1·073	1·0236	36·41	485·6
										Mean	485·0

m-Hydroxyazobenzene (M = 198·1) (Jacobson and Hoenigsberger, *Ber.*, 1903, **36**, 4102) was recrystallised from ligroin; m. p. 114—116°. Densities determined: $D_{4^\circ}^{120^\circ}$ 1·107; $D_{4^\circ}^{130^\circ}$ 1·099; $D_{4^\circ}^{139^\circ}$ 1·092; $D_{4^\circ}^{148^\circ}$ 1·084. A = 0·005729.

120·0°	6822	1·107	1·0219	39·93	449·1	139·0°	6436	1·092	1·0229	37·71	449·7
130·0	6592	1·099	1·0225	38·61	449·4	148·0	6346	1·084	1·0230	37·19	451·2
										Mean	449·8

p-Hydroxyazobenzene was recrystallised from alcohol; m. p. 154°. A determination of the density was not possible owing to decomposition above the m. p. The determination of the surface tension was carried out as quickly as possible after melting. The correction factor ϕ is calculated by assuming a density equal to that of *m*-hydroxyazobenzene. A = 0·00391.

176·0°	8552	1·061	1·0167	34·00	—	185·0°	8326	1·052	1·0170	33·10	—

o-Benzoquinonephenylhydrazone (M = 198·1) (Bamberger, *Ber.*, 1900, **33**, 3191) was recrystallised from ligroin; m. p. 83°. Densities determined: $D_{4^\circ}^{100^\circ}$ 1·094; $D_{4^\circ}^{110^\circ}$ 1·087; $D_{4^\circ}^{120^\circ}$ 1·078; $D_{4^\circ}^{130^\circ}$ 1·0705. A = 0·005729.

100·0°	6102	1·094	1·0242	35·79	442·9	120·0°	5814	1·078	1·0250	34·14	444·0
110·0	5923	1·087	1·0247	34·76	442·6	130·0	5625	1·0705	1·0256	33·05	443·7
										Mean	443·3

o-Methoxybenzaldehyde (M = 136·05) was purchased, distilled in a vacuum, and purified according to Katschalowsky and v. Kostanecki (*Ber.*, 1904, **37**, 2347); m. p. 39°. Densities determined: $D_{4^\circ}^{51^\circ}$ 1·104; $D_{4^\circ}^{72^\circ}$ 1·086; $D_{4^\circ}^{81^\circ}$ 1·078; $D_{4^\circ}^{91^\circ}$ 1·069 [v. Auwers (*Annalen*, 1915, **408**, 239) found $D_{4^\circ}^{20\cdot2^\circ}$ 1·1326; Perkin (J., 1896, **69**, 1200) $D_{4^\circ}^{4^\circ}$ 1·1445; and Sidgwick and Bayliss (*loc. cit.*) $D_{4^\circ}^{50\cdot8^\circ}$ 1·0992]. A = 0·005729.

52·0°	6763	1·103	1·0220	39·59	309·4	81·0°	6209	1·078	1·0234	36·39	310·1
72·0	6380	1·086	1·0229	37·38	309·8	91·0	6015	1·069	1·0240	35·28	310·1
										Mean	309·9

p-Hydroxybenzaldehyde (M = 122·05) was recrystallised from water; m. p. 115°. Densities determined: $D_{4^\circ}^{117^\circ}$ 1·143; $D_{4^\circ}^{127^\circ}$ 1·136; $D_{4^\circ}^{135^\circ}$ 1·129; $D_{4^\circ}^{145^\circ}$ 1·120 (Sidgwick and Bayliss found $D_{4^\circ}^{119\cdot6^\circ}$ 1·1364; $D_{4^\circ}^{136\cdot7^\circ}$ 1·1238). A = 0·005729.

117·0°	7600	1·143	1·0203	44·42	275·6	135·0°	7372	1·129	1·0206	43·05	277·1
127·0	7477	1·136	1·0205	43·71	276·3	145·0	7157	1·120	1·0211	41·90	277·2
										Mean	276·6

o-Nitroanisole (M = 153·06), a commercial specimen, after distillation in a vacuum, melted at 9°. Densities determined by Jaeger: $D_{4^\circ}^{25^\circ}$ 1·2472; $D_{4^\circ}^{50^\circ}$ 1·2218; $D_{4^\circ}^{75^\circ}$ 1·1970. The parachors calculated from Jaeger's values of density and surface tension are not concordant (variation 319·5—332·5) and are much too high (Calc.: 323·1). The densities determined by Schmidt (*Z. physikal. Chem.*, 1907, **58**, 525; $D_{4^\circ}^{20^\circ}$ 1·2540) and by Sidgwick and Bayliss ($D_{4^\circ}^{25^\circ}$ 1·2408, $D_{4^\circ}^{57\cdot4^\circ}$ 1·2075) are in agreement with Jaeger's values. Sidgwick and Bayliss found γ^{25° 45·9, $\gamma^{57\cdot4^\circ}$ 42·3 (contrast Jaeger's values); these were confirmed in the present work. A = 0·005729.

26·0°	7809	1·2465	1·0215	45·70	319·4	77·0°	6698	1·195	1·0240	39·28	320·7
55·0	7155	1·217	1·0229	41·93	320·1	95·0	6400	1·177	1·0248	37·58	321·9
										Mean	320·5

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