CCCLXXXV.—*The Parachor and Chemical Constitution. Part VI. Some Cases of Supposed Ring-chain Tautomerism.*

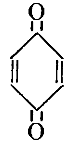
By FREDERICK BASIL GARNER and SAMUEL SUGDEN.

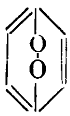
THE strictly additive character of the parachor sets obvious limits to its application to problems of chemical constitution, for a change in position of a radical or of a linkage in the molecule has no effect upon the value of this constant. If, however, two isomeric substances differ in structure by the replacement of a double bond by a ring, they should exhibit differences in parachor which will be greater the greater the number of atoms in the ring. The conversion of a double bond into a four-membered ring should give a decrease in the parachor of 11·6 units, whilst the corresponding figures for five- and six-membered rings are 14·7 and 17·1, respectively (see values for ring constants, Sugden and Wilkins, this vol., p. 142).

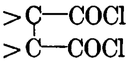
In this paper, the evidence of the parachor as to the structure of quinones, acid chlorides, and benzils is presented. Other substances in which similar structural changes have been postulated will be considered in later papers.

(1) *Quinones.*

Most of the reactions of *p*-quinones are represented by the formula (I), but the peroxide formula (II) has been suggested on chemical grounds by Graebe (*Annalen*, 1868, **146**, 1), whilst Hartley and Leonard (J., 1909, **95**, 34) and Haakh (*J. pr. Chem.*, 1910, **82**, 546), from a study of absorption spectra, and Binder (*Chem.-Ztg.*, 1921, **45**, 1114), from heats of combustion, also prefer formula (II).

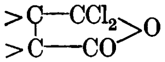
(I.)


(II.)




$$\begin{array}{l} >C—COCl \\ >C—COCl \end{array}$$

(III.)



(IV.)

We have measured the parachors of *p*-benzoquinone and toluquinone with the following results, from which it is evident that the liquid substances contain little or none of the peroxide form.

TABLE I.

	[*P*], obs.	[*P*], calc. (diketone).	[*P*], calc. (peroxide).
p-Benzoquinone......	236·8	236·1	219·0
Toluquinone	272·0	275·1	258·0

(2) *Acid Chlorides.*

The chlorides of dibasic acids would normally be assigned formula (III); in some reactions, however, these substances behave as if they possessed the structure (IV).

Auger (*Ann. Chim.*, 1891, **22**, 36), on chemical evidence, considered that succinyl chloride was a mixture of the two forms, the unsymmetrical chloride being in large excess. This view was criticised by Morrell (J., 1914, **105**, 1733), who maintained that this substance should be represented by the symmetrical formula. Ott (*Annalen*, 1912, **392**, 245) agreed with this, although his determinations of molecular volume seemed to indicate the existence of an equilibrium mixture of the two forms.

Phthalyl chloride offers a still more interesting example, for it has been obtained in two isomeric modifications melting at 15° and 88·5° (Ott, *loc. cit.*; Scheiber, *Ber.*, 1913, **46**, 2368; Csányi, *Monatsh.*, 1919, **40**, 81). Ott (*loc. cit.*) and Pfeiffer (*Ber.*, 1922, **55**, 413) have shown that the less stable high-melting modification has probably the unsymmetrical formula, whilst the low-melting form has the symmetrical structure.

We have prepared and examined succinyl chloride and the two forms of phthalyl chloride, with the results shown in Table II.

TABLE II.

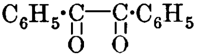
Substance.	[*P*], obs.	[*P*], calc. (symmetrical).	[*P*], calc. (unsymmetrical).
Succinyl chloride	282·6	282·6	267·9
Phthalyl chloride, m. p. 13° ...	373·9	377·5	362·8
Phthalyl chloride, m. p. 88·5°	367·8	377·5	362·8

For succinyl chloride, the parachor shows clearly that the liquid has the symmetrical formula and cannot contain an appreciable amount of the unsymmetrical modification. With phthalyl chloride, a difference in the expected direction is found between the two isomerides, but the parachors are not in very good agreement with the predicted value in either case. This is probably to be explained by interconversion of the isomerides (compare Csányi, *loc. cit.*); the high-melting form is rapidly changed to the low-melting form at temperatures above its m. p. and shows a progressive change of density when kept at 90° for an hour. The figure given for this substance therefore represents a mixture containing a little of the low-melting isomeride (see p. 2881). We were unable to prepare the low-melting form with a m. p. higher than 13° (Csányi gives 15°), and this may also have contained a little of the other isomeride. In general, therefore, the parachor confirms the conclusions of Ott and Pfeiffer as to the structure of the two forms of this substance.

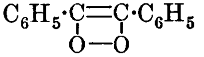
(3) *Benzils.*

Benzil and its derivatives may be formulated either as diketones (V) or as peroxides (VI). From its reactions and colour, benzil itself is usually assumed to have the ketonic structure. Certain alkyloxy-derivatives of benzil are white, or very pale yellow in colour (Irvine, J., 1907, **91**, 536), and the view has been expressed, notably by Schönberg and his collaborators (Schönberg and Kraemer, *Ber.*, 1922, **55**, 1174; Schönberg and Malchow, *ibid.*, p. 3746; Schönberg and Bleyberg, *ibid.*, p. 3753), that these derivatives should be represented by the peroxide formula (VI). It should be noted, however, that on fusion these substances give yellow liquids which are supposed by Schönberg to contain an equilibrium mixture of the two forms.

(V.)



$C_6H_5\cdot\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}\cdot C_6H_5$



$C_6H_5\cdot\underset{O}{\underset{|}{C}}=\underset{O}{\underset{|}{C}}\cdot C_6H_5$

(VI.)

We have prepared and measured 2 : 2′-dimethoxybenzil (Irvine's white benzil) with the results shown in Table III. It will be seen that the parachors found are in good agreement with the values calculated for the diketone formula in both cases, and show no indication of the presence of even a small proportion of the isomeride having the peroxide structure.

TABLE III.

Substance.	[*P*], obs.	[*P*], calc. (diketone).	[*P*], calc. (peroxide).
Benzil	480·8	476·0	464·4
2 : 2′-Dimethoxybenzil	596·8	594·0	582·4

EXPERIMENTAL.

In the course of this work new measurements have been made of the surface tension and density of *p*-benzoquinone, toluquinone, succinyl chloride, phthalyl chloride, benzil, and 2 : 2′-dimethoxybenzil. Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The constants for the bubbler used are: App. 14, $r_2 = 0{\cdot}177$ cm., $A = 0{\cdot}001020$. Densities were determined with the U-shaped pyknometer described previously (J., 1924, **125**, 1171), and are recorded in g. per c.c. All temperatures quoted are corrected by comparison with a standard thermometer with an N.P.L. certificate and are also corrected for exposed stem.

The tables are set out in the same manner as those given in earlier papers of this series and do not need further description. For all the substances studied in the present paper, *d* is very small and has been neglected.

p-*Benzoquinone*, $C_6H_4O_2$, $M = 108\cdot0$. A commercial specimen was purified by sublimation and melted at 115·5° (corr.). Some difficulty was encountered in the density determinations owing to the rapid sublimation of the substance into the cooler parts of the pyknometer; this sublimate was therefore removed and the tube reweighed after each volume determination. Densities determined: $D^{122^\circ}_{4^\circ}$ 1·085, $D^{132^\circ}_{4^\circ}$ 1·074, $D^{141\cdot5}_{4^\circ}$ 1·064, $D^{160\cdot5^\circ}_{4^\circ}$ 1·044, whence $D^{t^\circ}_{4^\circ} = 1\cdot214 - 0\cdot00106t$.

t.	*P.*	*D.*	*φ.**	*γ.*	Parachor.
123·5°	2989	1·083	1·0435	31·81	236·8
139·5	2800	1·066	1·0456	29·86	236·9
154·0	2613	1·051	1·0482	27·94	236·2
167·5	2518	1·036	1·0493	26·96	237·4
				Mean	236·8

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

Toluquinone (2-methyl-1 : 4-benzoquinone), $C_7H_6O_2$, $M = 122\cdot1$, was recrystallised from dilute alcohol and melted sharply at 67° (corr.). In the density measurements, errors due to sublimation were avoided by adopting the procedure described for benzoquinone. Densities determined: $D^{75\cdot5^\circ}_{4^\circ}$ 1·081, $D^{89\cdot5^\circ}_{4^\circ}$ 1·069, $D^{103\cdot5^\circ}_{4^\circ}$ 1·056, $D^{114\cdot5^\circ}_{4^\circ}$ 1·045, $D^{127\cdot5^\circ}_{4^\circ}$ 1·034, whence $D^{t^\circ}_{4^\circ} = 1\cdot152 - 0\cdot000926t$.

t.	*P.*	*D.*	*φ.*	*γ.*	Parachor.
76·5°	3191	1·081	1·0406	33·86	272·3
92·5	3010	1·066	1·0424	32·00	272·4
107·5	2836	1·052	1·0444	30·21	272·0
121·0	2687	1·040	1·0464	28·67	271·7
131·0	2586	1·031	1·0478	27·63	271·6
				Mean	272·0

Succinyl chloride, $C_4H_4O_2Cl_2$, $M = 155\cdot0$, was prepared by the action of phosphorus pentachloride on succinic acid and purified by repeated distillation under diminished pressure and freezing. The final product melted at 18·5° (corr.) and boiled at 95° (corr.)/20 mm. Densities determined: $D^{21^\circ}_{4^\circ}$ 1·371, $D^{49^\circ}_{4^\circ}$ 1·339, $D^{66^\circ}_{4^\circ}$ 1·320, $D^{83\cdot5^\circ}_{4^\circ}$ 1·301, whence $D^{t^\circ}_{4^\circ} = 1\cdot394 - 0\cdot00112t$.

t.	*P.*	*D.*	*φ.*	*γ.*	Parachor.
20·0°	3634	1·372	1·0452	38·75	281·8
49·5	3321	1·339	1·0483	35·50	282·5
65·0	3156	1·321	1·0502	33·81	283·0
79·5	2992	1·305	1·0522	32·21	282·9
				Mean	282·6

as-*Phthalyl chloride*, $C_8H_4O_2Cl_2$, $M = 203{\cdot}0$. Crude phthalyl chloride was prepared by the action of phosphorus pentachloride on phthalic anhydride and converted into the unsymmetrical form by heating with freshly prepared aluminium chloride (Ott, *loc. cit.*). The crude product was purified as described by Scheiber (*loc. cit.*) and Csányi (*loc. cit.*) by slow crystallisation from ligroin and mechanical separation of the prisms of the chloride from the needles of phthalic anhydride. After four crystallisations, a pure product was obtained, m. p. 88·5° (corr.).

This substance is transformed into the symmetrical modification at an appreciable rate even at temperatures just above the melting point. The stable form has a smaller density (1·327 at 90°), so that the transformation can be followed by the change in density. The following results were obtained when the pyknometer containing the unsymmetrical chloride was kept at 90° :

	First series.				Second series.			
Time (mins.) after melting	7	27	47	67	13	22	39	50
$D^{90°}_{4°}$	1·351	1·349	1·347	1·346	1·350	1·348	1·347	1·346

At the end of the experiment the substance was cooled rapidly and its m. p. found to be 81—83°, so that a considerable transformation had taken place. The crystals in the pyknometer (about 2 g.) required about 30 minutes in the bath at 90° to melt completely; it is evident, therefore, that the highest density found (1·351) is still a little lower than that of the pure substance at this temperature; the parachor will therefore be a little too large. The two isomerides have almost the same surface tension at 90°; hence no change in this constant with time was found for the unsymmetrical chloride.

t.	*P.*	*D.*	ϕ.	γ.	Parachor.
90°	3358	1·351	1·0482	35·88	367·8

s-*Phthalyl chloride*, $C_8H_4O_2Cl_2$, $M = 203{\cdot}0$. This substance is difficult to free from phthalic anhydride except by crystallisation from ligroin in a cold room (compare Csányi, *loc. cit.*). As such a room was not available, we converted the purified unsymmetrical form into the symmetrical modification by heating at 150° for 1 hour. The product was fractionated under diminished pressure and the specimen used had b. p. 150° (corr.)/23 mm. and m. p. 13° (corr.). (Csányi gives 15°, but we were unable to obtain a product with this melting point after repeated freezings.) Densities determined: $D^{17·5°}_{4°}$ 1·403, $D^{36·5°}_{4°}$ 1·381, $D^{58°}_{4°}$ 1·360, $D^{68·5°}_{4°}$ 1·349, $D^{90°}_{4°}$ 1·327, whence $D^{t°}_{4°} = 1{\cdot}420 - 0{\cdot}00104t$.

t.	P.	D.	ϕ.	γ.	Parachor.
15°	4169	1·404	1·0403	44·23	372·9
40	3867	1·378	1·0427	41·12	373·0
61	3692	1·357	1·0440	39·31	374·5
90	3390	1·327	1·0469	36·20	375·3
					Mean 373·9

Benzil, $C_{14}H_{10}O_2$, $M = 210{\cdot}1$, was recrystallised from alcohol and melted sharply at 95° (corr.). Densities determined : $D_{4°}^{102°}$ 1·084, $D_{4°}^{118{\cdot}5°}$ 1·071, $D_{4°}^{134°}$ 1·059, $D_{4°}^{151°}$ 1·047, $D_{4°}^{163{\cdot}5°}$ 1·037, whence $D_{4°}^{t°} = 1{\cdot}161 - 0{\cdot}00076t$.

t.	P.	D.	ϕ.	γ.	Parachor.
103°	3573	1·083	1·0363	37·78	481·0
118·5	3415	1·071	1·0376	36·13	481·0
132	3289	1·061	1·0387	34·84	481·1
149	3125	1·048	1·0402	33·16	481·1
162	2984	1·039	1·0417	31·70	480·0
					Mean 480·8

2 : 2′-*Dimethoxybenzil*, $C_{16}H_{14}O_4$, $M = 270{\cdot}2$. *o*-Methoxybenzaldehyde was first prepared by the careful methylation of salicylaldehyde with methyl sulphate : The aldehyde (1 mol.) and methyl sulphate (2 mols.) were mixed and mechanically stirred while caustic soda (5 mols.), dissolved in its own weight of water, was slowly added. The reaction vessel was well cooled and the addition of caustic soda stopped for a time when half of it had been added, the mixture having become a stiff cream; the addition of the remaining caustic soda caused the evolution of considerable heat, and the mixture became thinner. The stirring was continued for some hours after all the alkali had been added, and the mixture allowed to stand over-night. The crude product was separated, washed well with water, dissolved in ether, and the solution dried over calcium chloride. Finally, two distillations in a vacuum gave a pure product, b. p. 122°/20 mm., m. p. 37° (corr.).

The aldehyde was converted into the benzil, as described by Irvine (*loc. cit.*). The specimen used melted sharply at 130° (corr.). Densities determined : $D_{4°}^{130°}$ 1·128, $D_{4°}^{133°}$ 1·126, $D_{4°}^{146°}$ 1·116, $D_{4°}^{147{\cdot}5°}$ 1·115, $D_{4°}^{165°}$ 1·104, $D_{4°}^{168{\cdot}5°}$ 1·101, $D_{4°}^{187°}$ 1·086, whence $D_{4°}^{t°} = 1{\cdot}217 - 0{\cdot}00069t$.

t.	P.	D.	ϕ.	γ.	Parachor.
137·5°	3557	1·122	1·0378	37·64	596·5
155·5	3419	1·110	1·0389	36·22	597·2
178	3207	1·094	1·0409	34·04	596·6
					Mean 596·8

Summary.

(1) Measurements have been made of the surface tension and density of quinone, toluquinone, succinyl chloride, the two forms of phthalyl chloride, benzil, and 2 : 2′-dimethoxybenzil.

(2) The parachors calculated from these observations indicate that, except in the case of phthalyl chloride, these substances have the normal structure, and in the liquid state cannot contain more than a small amount of the isomeride in which a new ring is formed by tautomeric change.

(3) The parachors of the phthalyl chlorides indicate that the lower-melting form has the symmetrical structure, whilst the higher-melting form has the unsymmetrical structure.

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