160. *The Magnetic Susceptibility of Certain Organic Compounds. Part I. The Constitution of the* p-*Benzoquinone, Quinol, and Quinhydrone System.*

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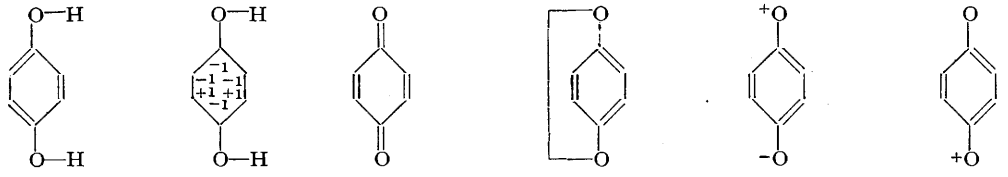
Magnetic susceptibility measurements carried out on quinhydrone and its constituents showed that the law of additivity holds. Three resonance formulæ are suggested for quinone.

Many investigators (cf. Table II) have measured the magnetic susceptibility of quinone, quinol, and quinhydrone with a view to elucidate the type of linkage between the components of the quinhydrone molecule,

but none of these authors has discussed the constitution of the components in the light of their magnetic susceptibility values. The object of the present investigation was to determine these values and apply the results to the elucidation of the structures.

Gray and Cruickshank's method (*Tran. Faraday Soc.*, **1935**, **31**, 1491) was adopted for calculating the theoretical values. The experimental values obtained for quinol (cf. Table II) are in good agreement with the calculated values based on Gray and Cruickshank's suggestion (*loc. cit.*) that the benzene nucleus oscillates in equal times between the Kekulé and the internal-ionic form, (I) and (II).



(I.) (II.) (III.) (IV. (V. (VI.)

Table I shows the method of calculation for formula (III) for benzoquinone, that for (IV) and (V) being similar. In (IV) the bond depression for O—O was obtained by analogy from N→O. As (IV) and (V) gave $\chi \times 10^6 = 40{\cdot}746$ and $43{\cdot}740$, respectively, the mean is $39{\cdot}282$.

TABLE I.

No. of atoms.	Charge on each.	Diamagnetism of each.	Total diamag.	Bond depression.
4C	−0·04	C^{-1} 0·04 × 14·69 = 0·587		2C=C = 19·0
		C^{0} 0·96 × 9·96 = 9·562	40·597	2C=O = 20·56
2C	+0·42	C^{+1} 0·42 × 6·64 = 2·789		4C—C = 7·92
		C^{0} 0·58 × 9·96 = 5·777	17·132	4C—H = 2·12
4H	+0·04	H^{+1} 0·04 × 0·0		
		H^{0} 0·96 × 2·372 = 2·278	9·112	Total 49·60
2O	−0·42	O^{-1} 0·42 × 9·40 = 3·948		
		O^{0} 0·58 × 7·09 = 4·112	16·120	
		Total	82·961	
		Bond depression	49·600	
		Mol. diamagnetism	33·361	

Several experimental values have been reported for *p*-benzoquinone (see Table II); Lonsdale (*Proc. Roy. Soc.*, **1937**, **159**, 153) concluded from magnetic data that the double bonds in the nucleus are indicated by a small anisotropy, and stated that the evidence is definitely against the fixation of the double bonds, at least when the molecule is in a strong magnetic field. Although Palacios and Foz's value (*Anal. Soc. Fis. Quim.*, 1935, **33**, 627) satisfies the simple formula for benzoquinone (III), based on Gray and Cruickshank's method, yet it is lower than that found by other authors. Similar anomalous electric dipole moments in solution were observed by Jenkins *et al.* (*Nature*, 1935, **136**, 990) and were attributed either to a general solvent effect or to an abnormally large atomic polarisation. Coop and Sutton (J., 1938, **1277**) measured the dipole moment of *p*-benzoquinone in the vapour state and concluded that their result was in good agreement with a simple quinone structure (III) in resonance with others of the Kekulé type, (IV) (Pauling and Sherman), (V), and (VI) (Robinson). Our high value is in harmony with the suggestion that the molecule resonates in equal times between structures (III), (IV), and (V).

For quinhydrone several structures based on chemical evidence have been put forward (cf. Pfeiffer, " Organische Molekülverbindungen," 1927). Our experimental values differ slightly from those of Banerjee (*Z. Krist.*, 1938, **100**, 316), but both values indicate that the law of additivity holds well within the range of experimental errors. The bond linking the quinol and the quinone molecule could not be represented other than by the conventional dotted line.

Calculations.—Calculations of magnetic susceptibility values based on Gray and Cruickshank's method give the following results.

For quinol the values obtained for the resonance forms (I) and (II) are 46·513 and 82·595 respectively; the mean is 64·554, in good agreement with our experimental value (cf. Table II).

EXPERIMENTAL.

Gouy's method was used, since Banerjee's (*loc. cit.*) could not be applied to all our compounds. The field strength was of the order of 13,000 gauss produced by a Weiss electromagnet. The container was a stoppered Monax glass tube, 0·6 cm. in diameter and 16 cm. long. The gap between the pole-pieces of the electromagnet was 1·1 cm. The pole-faces were 1·5 cm. in diameter, with an angle of 39° for producing maximum homogeneity. The usual precautions were adopted.

Hoare's formula (*Proc. Roy. Soc.*, 1934, **147**, 88) was used for calculation. The meniscus correction was eliminated by locating the lower flat edge of the tube exactly centrally between the pole-pieces of the electromagnet.

Materials.—The solvents were purified according to Weissberger and Proskauer (" Organic Solvents," 1935). Quinol, repeatedly crystallised from purified benzene, had m. p. 170·3°. *p*-Benzoquinone was freed from quinhydrone by steam

distillation in presence of ferric chloride under reduced pressure at 60°; after extraction by ether and two crystallisations from light petroleum, it had m. p. 115·8° (cf. Zimmerli and Lyon, U.S.P., 1,883,284, 1933). Quinhydrone, prepared from its constituents, had m. p. 171°.

In order to secure uniformity of packing, the substance was finely powdered in an agate mortar, and introduced into the specimen tube in small amounts, being packed after each addition by gentle tapping, followed by pressing down with a flat-ended glass rod just sliding into the tube. Consistency of results after different packings is regarded as proof of random orientation.

Results.—Typical results for $\chi \times 10^6$ are given in Table II.

TABLE II.

	Experimental values.					Calculated values.	
Substance.	(i).	(ii).	(iii).	(iv).	(v).	Pascal.	Gray and Cruickshank.
Benzoquinone	38·20	33·31	41·28	40·0	40·0 [a]	40·80	39·28
Quinol	64·73	64·58	—	—	64·0 [a]	66·82	64·55
Quinhydrone	105·0	84·23	—	—	111·7 [b]	107·62	103·84

(i) Authors' values. (ii) Palacios and Foz's values (*loc. cit.*). (iii) Pascal's value on powder (*Bull. Soc. chim.*, 1911, **9**, 177, 809). (iv) Lonsdale's mean value on a crystal (*loc. cit.*). (v, *a*) Krishnan and Banerjee's mean values on crystals (*Phil. Trans.*, 1935, *A*, **234**, 265). (v, *b*) Banerjee's mean value on a crystal (*loc. cit.*).

We thank Prof. Frank L. Warren for suggesting this research.

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