Magnetochemical Study of Hydroxyazobenzenes

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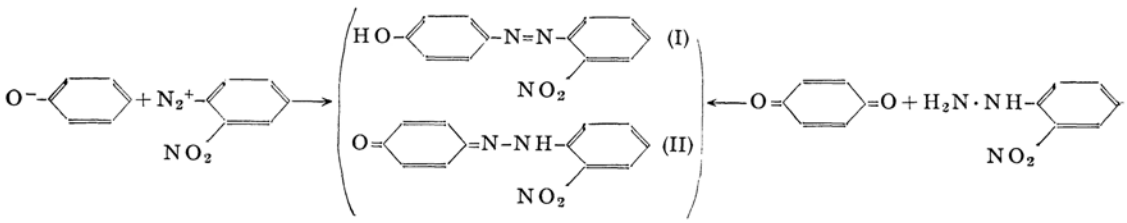
Introduction

Zincke[1] showed in 1884 that the product of the condensation of phenylhydrazine with α-naphthoquinone is identical with 4-benzeneazo-1-naphthol which is prepared by the coupling of diazotized aniline with 1-naphthol, so that the problem of structure immediately presented itself. Although the physical and chemical properties of 4-hydroxyazobenzenes indicate that they exist in the azophenol form, Borsche[2] succeeded to show that "2'-nitro-4-hydroxyazobenzene" (I or II) can be prepared by the following distinct methods similarly.



Furthermore, evidence of the quinonoid character of 2', 4'-dinitro-4-hydroxyazobenzene was provided by its ability to undergo the Diels-Alder reaction[3]. In spite of many researches, the investigators came to the different conclusions in regard to the structure of 2-hydroxyazobenzene; e. g. Kuhn and Bär[4] believed that the spectroscopic evidence favors the benzenoid structure, but on the other hand, Burawoy and Markowitsch[5] suggested that the same evidence favors the quinonoid structure.

These studies are merely concerned with the dissolved state of hydroxyazobenzenes. We can not decide conclusively the structure in the solid state. Diamagnetic susceptibility measurements seem to be of great service in deciding the forms of these compounds, as the azophenol form is made of the benzenoid structures, while the quinonehydrazone form contains the quinonoid structure. In such a case, a large difference between the susceptibilities of these two forms is expected. From this point of view, Pascal[6] examined the molar susceptibilities of some compounds, and compared them with the ones calculated from his own empirical constants. But his results quoted in Table I seem to be unplausible, as they are not consistent with the other evidences, and allowed the equilibrium between two forms in the solid state, and the migration of alkyl groups. Namely he concluded that 4-hydroxyazobenzene is quinonehydrazone form, and 4-methoxyazobenzene and 1-benzeneazo-2-naphthol are mixture of tautomers.

TABLE I

MOLAR SUSCEPTIBILITIES OF HYDROXYAZOBENZENES AND THEIR RELATED COMPOUNDS GIVEN BY PASCAL

Substance	Molar Suscept. $(-\chi_M)$*		
	obs.	calcd. (a)**	calcd. (b)**
4-Hydroxyazobenzene	99.6	117.3	95.0
4-Methoxyazobenzene	118.8	129.1	107.6
1-Benzeneazo-2-naphthol	140.7	153.7	124.8
4, 4'-Dimethoxyazobenzene	147.5	146.9	117.8
4, 4'-Diethoxyazobenzene	171.4	170.6	141.3
4-Aminoazobenzene	118.4	118.8	103.7

* Susceptibility values have been multiplied by 10^6 throughout this paper.

** (a) Azophenol form, (b) Quinonehydrazone form.

For the determination of the structures of hydroxyazobenzenes from the susceptibility measurement, it is necessary to reexamine the molar susceptibilities of azobenzene and its derivatives which have no tautomeric forms, and establish the empirical method to estimate them correctly.

1) T. Zincke and H. Bindewald, *Ber.*, **17**, 3026 (1884).
2) W. Borsche, *Ann.*, **357**, 171 (1907).
3) W.M. Lauer and S.E. Miller, *J. Am. Chem. Soc.*, **57**, 180 (1933).
4) R. Kuhn and F. Bär, *Ann.*, **516**, 143 (1935).
5) A. Burawoy and I. Markowitsch, ibid., **503**, 180 (1933).
6) P. Pascal, *Compt. rend.*, **150**, 1167 (1910), *Bull. soc. chim. France*, **9**, 868 (1911), *Ann. chim. phys.*, **25**, 289 (1912).

Experimental

Materials.—No. 1–10, 19 and 30 were kindly provided by Drs. F. Iimura and M. Kobayashi. No. 11–18 and 20–27 were prepared by the coupling of diazotized aniline or its substituted derivatives with phenol or *p*-cresol, and purified by recrystallization from aqueous ethanol or benzene, and finally by distillation or sublimation in vacuo. No. 28 and 29 were synthesized by the alkali fusion of nitrophenol[7] and recrystallized from aqueous ethanol. No. 28 was sublimed finally in vacuo. Their melting points are presented in Tables II and III.

Magnetic Measurement.—The susceptibilities were measured using a Gouy balance as previously described[8].

Results and Discussion

The results are shown in Table II for azobenzene and its derivatives which have unquestionable form and in Table III for hydroxyazobenzenes. The molar susceptibility of azobenzene has been found to be −111.3 by Pascal[9], while it is −105.0 by Banerjee[10]. Our result supports the latter value, so that Pascal's constitutive correction constant for azo-group 1.8 is not appropriate for the estimation of molar susceptibilities of the other compounds of which the structures will be discussed in this paper. We assumed that the molar susceptibilities are given by the sum of those of constitutional fragments of the molecules. For instance, we assumed that the azophenol form of 4-hydroxyazobenzene is built up from benzene, phenol, and azo-group by the loss of two atoms of hydrogen, and the molar susceptibility is given by the same relation too. Similar computations have been done for the compounds shown in Table II, and the mean value −0.4 has been obtained for the contribution of azo-group. Then the calculated values in Tables II and III have been estimated by the combination of this constant for azo-group and the molar susceptibilities of benzene and its derivatives; the following values were used, benzene −55.2[11], toluene −65.8[12], anisol −72.6[13], dimethylaniline −85.0[13], chlorobenzene −70.0[14], acetophenone −71.6[13], ethyl benzoate −93.3[15], nitrobenzene −61.8[12], phenol −60.8[13], *p*-cresol −71.4[16], resorcinol −67.9[17]. The accordance between the observed and the calculated molar susceptibilities is satisfactorily good within the limit of experimental errors. As the effect of substituents to single benzene nucleus is taken into consideration in our estimations, our calculated values are more compromising for these compounds than the ones obtained by the direct summation of Pascal's constants. For instance, Angus[15] and Trew[18] showed that methyl substitution in the aromatic nucleus gives a diamagnetic increment about one unit lower than the normal CH_2 increment of −11.7; furthermore, French[17] deduced that the isomerides of disubstituted benzenes possess different susceptibilities respectively. Even in our case, the interaction of substituents through an azo-group is not considered, so the results in Table show that the method is not adequate in a few cases.

TABLE II

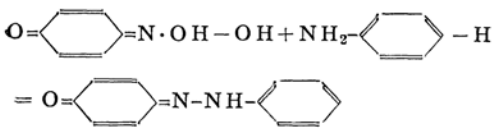
SUSCEPTIBILITIES OF AZOBENZENE AND ITS DERIVATIVES

No.	Substance	M. p.	Suscept. ($-\chi$)	Molar Suscept. ($-\chi_M$) obs.	calcd.
1	Azobenzene	67.5–68.5	0.578	105.3	104.9
2	4-Methyl-	69–69.5	0.590	115.8	115.5
3	2-Methoxy-	39–40	0.574	121.9	122.3
4	4-Methoxy-	55	0.575	122.0	122.3
5	4-Dimethylamino-	115–115.5	0.594	133.8	134.7
6	4-Chloro-	87	0.551	119.4	119.7
7	4-Acetyl-	113–114	0.535	122.1	121.3
8	4-Carboethoxy-	86	0.568	144.4	143.0
9	4-Nitro-	133–134	0.492	111.7	111.5
10	4,4′-Dimethoxy-	162	0.574	139.0	139.7

For the quinonehydrazone form of 4-hydroxyazobenzene, the molar susceptibility

7) R. Willstätter and M. Benz, *Ber.*, 39, 3492 (1906).
8) H. Akamatu and Y. Matsunaga, This Bulletin, 26, 364 (1953).
9) P. Pascal, *Bull. soc. chim. France*, 9, 79 (1911).
10) S. Banerjee, *Z. Krist.*, A 100, 316 (1939).
11) B.C. Eggleston et al., *J. Chem. Soc.*, 1954, 941.
12) F.G. Baddar and S. Sugden, ibid., 1950, 308.
13) "International Critical Tables", Vol. 6, McGraw-Hill Book Co. Inc., New York, 1929, p. 362.
14) C.M. French and V.C.G. Trew, *Trans. Faraday Soc.*, 41, 439 (1945).
15) W.R. Angus, *Bull. soc. chim. France*. 1949, D 483.
16) estimated. = 65.8 (toluene) − 60.8 (phenol) + 55.2 (benzene).
17) C.M. French, *Trans. Faraday Soc.*, 41, 676 (1945).
18) V. C. G. Trew, ibid., 49, 604 (1953). See also, C.M. French, ibid., 50, 1320 (1954).

is estimated as −102.2 by the following schematic chemical equation,



The values used in the above equation are −50.3 for *p*-benzoquinonemonoxime[13], −62.4 for aniline[12], and Pascal's constants for hydrogen and oxygen in alcohol. Consequently the difference of susceptibility between these two forms is expected to be 8.3 in 4-hydroxyazobenzene. Our calculated difference is remarkably smaller than that expected from the calculated molar susceptibilities for two isomeric forms given by Pascal. Although there is no experimental result which can compare with these two expected differences, comparison will be drawn in the later paper on the azo-derivatives of naphthols. For the other compounds, the data on substituted anilines and quinonemonoximes required by the estimation of molar susceptibility for the quinonehydrazone form are not always available, but the susceptibility difference between these two forms may be nearly constant.

The observed molar susceptibilities of all compounds in Table III are in accordance with the calculated values for the azophenol form, so that there can be no doubt that these hydroxyazobenzenes are in the azophenol form in the solid state. At first glance, the discrepancy in 2, 2′-dihydroxyazobenzene is seriously large, but molar susceptibility of this compound is only 3.3 units higher than that of 4, 4′-dihydroxyazobenzene. In the isomerides of dihydroxybenzene, molar susceptibility of catechol is 2.3 units more diamagnetic than the value for hydroquinone, so the difference between these two dihydroxyazobenzenes may be of probable magnitude, and the calculated values seem to be too small in these cases.

In the *ortho*-compounds, hydrogen bond undoubtedly exists between the nitrogen and oxygen atoms, but the effect of hydrogen bond to the molar susceptibility is not detectable in these compounds either[19]. Furthermore, the position of the proton between the nitrogen and oxygen atoms may not be the same in the tautomeric forms[20], because the observed susceptibility does not deviate so much from the value calculated for azophenol form.

TABLE III

SUSCEPTIBILITIES OF HYDROXYAZOBENZENES

No.	Substance	M. p.	Suscept.	Molar Suscept. ($-\chi_M$)	
			($-\chi$)	obs.	calcd.
11	4-Hydroxy-	152	0.555	110.0	110.5
12	4′-Methyl-4-hydroxy-	150	0.569	120.8	121.1
13	2′-Methoxy-4-hydroxy-	145–146	0.558	127.4	127.9
14	4′-Methoxy-4-hydroxy-	137–139	0.559	127.6	127.9
15	4′-Chloro-4-hydroxy-	153–155	0.537	125.0	125.3
16	2′-Nitro-4-hydroxy-	160–161	0.478	116.2	117.1
17	3′-Nitro-4-hydroxy-	157.5–158.5	0.483	117.4	117.1
18	4′-Nitro-4-hydroxy-	213	0.477	116.0	117.1
19	2-Hydroxy-	81–82	0.559	110.8	110.5
20	5-Methyl-2-hydroxy-	105–107	0.569	120.8	121.1
21	2′, 5-Dimethyl-2-hydroxy-	97–98	0.594	134.4	131.7
22	4′, 5-Dimethyl-2-hydroxy-	111–112	0.582	131.7	131.7
23	2′-Methoxy-5-methyl-2-hydroxy-	119	0.577	139.8	138.5
24	4′-Methoxy-5-methyl-2-hydroxy-	94–95	0.577	139.8	138.5
25	4′-Chloro-5-methyl-2-hydroxy-	152	0.551	135.9	135.9
26	3′-Nitro-5-methyl-2-hydroxy-	162–163	0.496	127.6	127.7
27	4′-Nitro-5-methyl-2-hydroxy-	181–183	0.503	129.4	127.7
28	2. 2′-Dihydroxy-	165–167	0.568	121.7	116.1
29	4, 4′-Dihydroxy-	decomp.	*	118.4**	116.1
30	2, 2′, 4, 4′-Tetrahydroxy-	decomp.	0.537	132.2	130.3

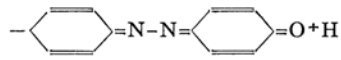
* Monohydrate 0.566.

** 131.4 (Monohydrate) − 13.0 (water).

19) P. Rumpf and M. Séguin, *Bull. soc. chim. France*, 1949, D 366, 1950, 177, 542.

20) G.W. Wheland, "Advanced Organic Chemistry" John Wiley & Sons, Inc., New York, 1949, p. 628.

The observed molar susceptibilities of azo-derivatives of phenol are smaller than the calculated values in many cases. This decrease of diamagnetism will be interpreted by the resonance effect indicated in the structure (III).



(III)

Such an effect will be strengthened by the electron withdrawing substituents, and 2′- and 4′-nitro-derivatives are examples of this. In the azo-derivatives of *p*-cresol, methyl group will perturb such an effect to some extent, so that in some cases the observed values are more diamagnetic than the calculated ones. But we will not discuss in detail these apparent discrepancies on accounts of the complicated influence of substituents and the rather large experimental errors.

Summary

The magnetic susceptibilities of azobenzene and its nine derivatives were measured by the Gouy method. The procedure to estimate the molar susceptibility from the values observed for constitutional fragments of the molecule was applied to these compounds, and the empirical constant for azo-group −0.4 was determined. Twenty hydroxyazobenzenes, mainly derivatives of phenol and *p*-cresol, were also measured, and their molar susceptibilities were compared with the calculated values for the azophenol form and the quinonehydrazone one. The author concluded that they are all in the azophenol form in the solid state.

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