Diamagnetic Susceptibilities of Azo-derivatives of 2-Naphthol

By Yoshio MATSUNAGA

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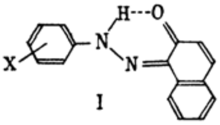
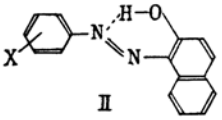
In the previous paper[1], the procedure to estimate the molar susceptibilities of the azophenol and the quinonehydrazone forms of hydroxyazobenzene was presented. We applied it to twenty compounds and concluded that they are all in the azophenol form in the solid state. Continuing this study, we measured the diamagnetic susceptibilities of eight azo-derivatives of 2-naphthol. All specimens were purified finally by sublimation in vacuo. As shown in the Table, we found that the structure of these compounds depends on the nature and the position of the substituents.

It must be noted that our calculated values for the azophenol and the quinonehydrazone forms given by the procedure similar to that described in the previous paper, are in serious disagreement with those given by Pascal[4] and Pacault[5]. As an example, our value for the azophenol form of 1-phenylazo-2-naphthol -146.7×10^{-6} is appreciably smaller than -154×10^{-6} given by the French workers, and the value for the quinonehydrazone form -135.8×10^{-6} estimated by use of the observed value for quinone monoxime is remarkably larger than -124.8×10^{-6} given by Pascal and -130.8×10^{-6} by Pacault. However, the experimental results seem to support our estimations. The observed values of the molar susceptibility of 1-phenylazo-2-naphthol and its *o*-methyl-, *m*-nitro- and *p*-nitro-derivatives are in accordance with the calculated values for the quinonehyrazone form (I), but *p*-methyl-, *o*-methoxy-, *o*-chloro- and *p*-chloroderivatives are found to exist in the azophenol form (II) in the solid state.



I



II

The effect of substituents on the equilibria between these two tautomeric forms in various solutions was examined by Burawoy and his collaborators[6]. According to their conclusion, the concentration of the quinonehydrazone tautomers increases in the order of substituents, $p\text{-Me} < \text{H} \sim p\text{-Cl} < o\text{-Me} < o\text{-Cl} < m\text{-NO}_2 < o\text{-MeO} < p\text{-NO}_2$. In contrast to the above series, our results suggest that MeO, Me and Cl substituted both in the ortho- and para-positions favor the azophenol form, and methyl group in the ortho-position is not so effective as that in the para-position.

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[1] Y. Matsunaga, This Bulletin, **29**, 308 (1956).

[2] Y. Matsunaga, ibid., **29**, 969 (1956).

[3] P. Pascal, *Bull. soc. chim. France*, **9**, 177 (1911).

[4] P. Pascal, *Ann. chim. phys.* **25**, 289 (1912).

[5] A. Pacault and J. Chauvelier, *Bull. soc. chim. France*, **17**, 367 (1950).

[6] A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, **1952**, 4793.

TABLE

DIAMAGNETIC SUSCEPTIBILITIES OF AZO-DERIVATIVES OF 2-NAPHTHOL

Substance	Suscept. ($-\chi \cdot 10^6$)	Molar Suscept. ($-\chi_M \cdot 10^6$)			
		Obs.	Calc. (I)	Calc. (II)	Lit.
β-Naphthoquinone-1-oxime	—	—	—	—	83.9[2]
2-Naphthol	—	—	—	—	97.0[3]
1-Phenylazo-2-naphthol	0.554	137.6	135.8	146.7	140.7[4], 135.5[5]
1-*o*-Tolylazo-2-naphthol	0.567	148.7	146.4	157.3	—
1-*p*-Tolylazo-2-naphthol	0.601	157.6	146.4	157.3	—
1-*o*-Methoxyphenylazo-2-naphthol	0.588	163.6	152.2	164.1	—
1-*o*-Chlorophenylazo-2-naphthol	0.570	161.0	150.6	161.5	—
1-*p*-Chlorophenylazo-2-naphthol	0.571	161.4	150.6	161.5	—
1-*m*-Nitrophenylazo-2-naphthol	0.484	142.0	142.4	153.3	—
1-*p*-Nitrophenylazo-2-naphthol	0.483	141.7	142.4	153.3	—

In the solid state, the effect of substituents appears to be not necessarily similar to that observed by Burawoy on the tautomeric equilibria in the dissolved state.

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Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo