

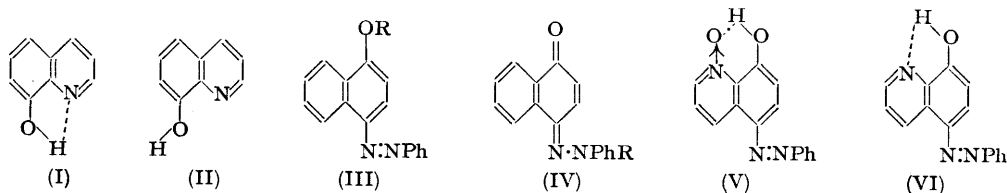
122. Aromatic Azo-compounds. Part VIII.* A Study of Intramolecular Hydrogen Bonding in 8-Hydroxyquinoline.

By G. M. BADGER and R. G. BUTTERY.

4-Phenylazo-1-naphthol exists in solution as an equilibrium mixture of the azo- and the phenylhydrazone tautomer. Similar tautomerism is shown to occur with 8-hydroxy-5-phenylazoquinoline, but this exists predominantly in the azo-form. With 8-hydroxy-5-phenylazoquinoline *N*-oxide, little or none of the phenylhydrazone tautomer is present. It is suggested that the position of the equilibrium is affected by the presence of a weak intramolecular hydrogen bond in 8-hydroxy-5-phenylazoquinoline and a very strong bond of the same type in its *N*-oxide.

THE existence of intramolecular hydrogen bonding in 8-hydroxyquinoline can be inferred from its physical properties. Its m. p. is more than 100° below that of any of the isomeric hydroxyquinolines; it has a small wet m. p. depression (3°); and it is steam-volatile (see also Lutskii¹). The fact² that it forms metallic chelates can also be taken as evidence that the parent compound is chelated. Moreover, although the infrared absorption of phenol shows a single intense band in the first overtone region at 7050 cm.⁻¹, that for 8-hydroxyquinoline shows two peaks of weak intensity around 6600 and 6830 cm.⁻¹ (both values estimated by inspection of the published curve).³ Such twin peaks are typical of *ortho*-substituted phenols in which weak intramolecular hydrogen bonding can occur,⁴ and the absorption can be similarly interpreted in terms of the two structures (I) and (II).

On the other hand, intramolecular hydrogen bonding in 8-hydroxyquinoline would involve the formation of a five-membered ring and it is widely held that for significant



hydrogen bonding the ring must be six-membered (see, for example, Rodebush⁵); certainly the O-H...N distance is abnormally large for hydrogen bonding. Hearn, Morton, and Simpson,⁶ working with the ultraviolet spectra, furthermore could find no evidence for the existence of appreciable intramolecular hydrogen bonding in 8-hydroxyquinoline. In a new approach to this problem the absorption spectrum of 8-hydroxy-5-phenylazoquinoline has been compared with those of its *N*-oxide and of 4-phenylazo-1-naphthol.

4-Phenylazo-1-naphthol is known to exist in solution as an equilibrium mixture of the azo-form (III; R = H) and the quinone phenylhydrazone tautomer (IV; R = H), each of which has a characteristic absorption spectrum.⁷ 4-Phenylazo-1-methoxynaphthalene (III; R = Me), a model for the azo-form, gives a simple absorption curve with a maximum at 3920 Å. In the same way 1:4-naphthaquinone methylphenylhydrazone (IV; R = Me), a model for the phenylhydrazone tautomer, gives a simple absorption curve with a

* Part VII, *J.*, 1955, 2816.

¹ Lutskii, *Zhur. obshechi Khim.*, 1954, **24**, 561; *Chem. Abs.*, 1955, **49**, 6260.

² Perekalin, *J. Gen. Chem. (U.S.S.R.)*, 1951, **21**, 129.

³ Wulf and Liddel, *J. Amer. Chem. Soc.*, 1935, **57**, 1464; Hilbert, Wulf, Hendricks, and Liddel, *Nature*, 1935, **135**, 147.

⁴ Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, New York, 1940, p. 320.

⁵ Rodebush in "Advances in Nuclear Chemistry and Theoretical Organic Chemistry," ed. Burk and Grummitt, Interscience, New York, 1945, p. 151; cf. Wheland, "Advanced Organic Chemistry," Wiley, New York, 1949, p. 52.

⁶ Hearn, Morton, and Simpson, *J.*, 1951, 3318.

⁷ Kuhn and Bar, *Annalen*, 1935, **516**, 143; Burawoy, Salem, and Thompson, *J.*, 1952, 4793; Burawoy and Thompson, *J.*, 1943, 1443.

maximum at 4600 Å (see Fig. 1). The spectrum of 4-phenylazo-1-naphthol, however, consists of two broad bands, with maxima at 4080 Å (associated with the azo-form) and 4620 Å (phenylhydrazone tautomer) (Fig. 2), the relative intensities of the bands indicating that the azo-form occurs to a somewhat greater extent in ethanol solution. On the other hand, the phenylhydrazone tautomer is almost entirely absent from 8-hydroxy-5-phenylazoquinoline *N*-oxide (V) in ethanol. Strong intramolecular hydrogen bonding, involving the formation of a six-membered ring, would certainly be expected with this compound, and it seems that this is sufficient to shift the equilibrium almost entirely towards the azo-form.

The spectrum of 8-hydroxy-5-phenylazoquinoline (VI) shows two regions of absorption. The absorption associated with the phenylhydrazone tautomer is of relatively low intensity, and shows only a point of inflexion. Thus weak hydrogen bonding occurs in 8-hydroxy-5-phenylazoquinoline, and shifts the tautomeric equilibrium in favour of the azo-form.

The spectra of 8-hydroxy-5-phenylazoquinoline in a number of other solvents show small differences in the relative intensities of the two absorption bands, the absorption

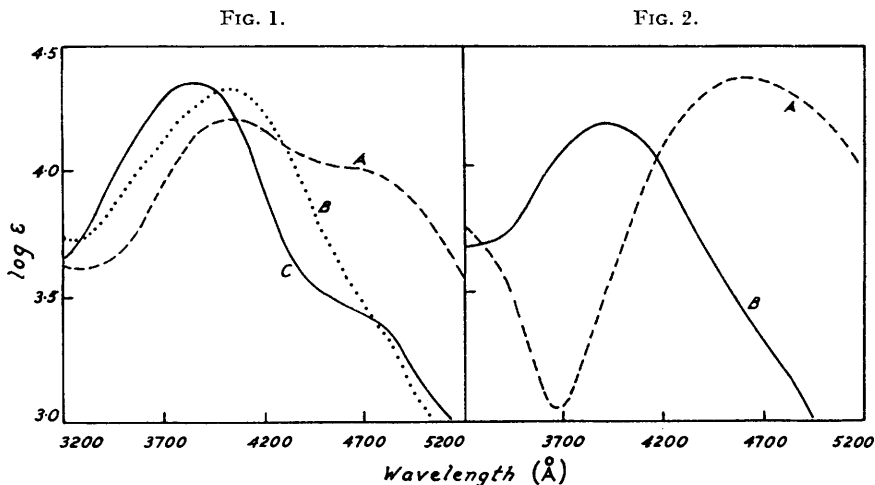


FIG. 1. Absorption spectra of (A) 4-phenylazo-1-naphthol, (C) 8-hydroxy-5-phenylazoquinoline, and (B) 8-hydroxy-5-phenylazoquinoline *N*-oxide, in absolute ethanol.

FIG. 2. Absorption spectra of (A) naphtha-1 : 4-quinone methylphenylhydrazone and (B) 4-phenylazo-1-methoxynaphthalene, in absolute ethanol.

due to the phenylhydrazone tautomer increasing in the order carbon tetrachloride, chloroform, ethanol, and acetic acid. This is not unexpected, for the greater the possibility of intermolecular hydrogen bonding the smaller would be the influence of weak intramolecular hydrogen bonding on the position of the equilibrium. The spectra of 8-hydroxy-5-phenylazoquinoline *N*-oxide in a series of solvents were identical except for slight shifts in the wavelength of the maxima; in this case it seems that the intramolecular hydrogen bond is so strong that intermolecular hydrogen bonding with the solvent is without effect on the equilibrium.

Most of the compounds used in this investigation were prepared essentially by recorded methods. 8-Hydroxy-5-phenylazoquinoline *N*-oxide was prepared by coupling 8-hydroxyquinoline *N*-oxide with benzenediazonium chloride.

EXPERIMENTAL

4-Phenylazo-1-naphthol.—This⁸ was purified by several re-precipitations from alkali. Repeated recrystallisation from benzene gave a product, m. p. 205–206°.

1-Methoxy-4-phenylazonaphthalene.—4-Phenylazo-1-naphthol was methylated with methyl sulphate. After recrystallisation from ethanol the product had m. p. 82–83°.

Naphtha-1 : 4-quinone Methylphenylhydrazone.—Naphtha-1 : 4-quinone was condensed with

⁸ Witt and Dedichen, *Ber.*, 1897, **30**, 2655.

N-methyl-*N*-phenylhydrazine sulphate according to McPherson's method.⁹ After recrystallisation from ethanol the product had m. p. 117—118°.

8-Hydroxy-5-phenylazoquinoline.—A diazotised solution of aniline in dilute hydrochloric acid was added to a cold solution of 8-hydroxyquinoline in acetic acid.¹⁰ The mixture was kept below 5° for 12 hr., after which the azo-compound was precipitated with aqueous ammonia. The crude product had m. p. 182—183°, raised to 185—185.5° by repeated recrystallisation from benzene.

8-Hydroxy-5-phenylazoquinoline N-Oxide.—A solution of benzenediazonium chloride [from aniline (3 g.) in concentrated hydrochloric acid (20 c.c.) and water (100 c.c.) with sodium nitrite (3 g.) in water (20 c.c.) at 0°] was gradually added to a solution of 8-hydroxyquinoline *N*-oxide (5 g.) and sodium hydroxide (30 g.) in water (4 l.) at 0°. After 2 hours' stirring at 0° the solid was collected and acidified with dilute acetic acid. *8-Hydroxy-5-phenylazoquinoline N-oxide* (6 g.), recrystallised from 1 : 1 benzene-light petroleum (b. p. 40—100°), formed orange needles, m. p. 183—184° (Found : C, 67.9; H, 4.1; N, 15.9. $C_{16}H_{11}O_2N_3$ requires C, 67.9; H, 4.2; N, 15.8%).

Absorption Spectra.—The absorption spectra were determined with a Hilger Uvispek Spectrophotometer.

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UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA.

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⁹ McPherson, *Amer. Chem. J.*, 1899, **22**, 364.

¹⁰ Cf. Matsumura, *J. Amer. Chem. Soc.*, 1930, **52**, 4164.
