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NMR SPECTRA OF AZOPHENOLS AND QUINONE HYDRAZONES*

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Since Zincke showed in 1884 that the product of the action of phenylhydrazine on α-naphthaquinone is identical with the product of coupling α-naphthol with diazotized aniline, extensive work has been carried out[1,2] on azophenol-quinone hydrazone tautomerism. Chemical reactions, such as methylation and Diels-Alder addition, and physical methods, such as acid dissociation constants, UV and IR spectroscopy, have been employed. As Zollinger has stated[2], physico-chemical methods can in principle show which side of the azo-hydrazone equilibrium is favoured under given conditions, 'but to date no exact determination of the position of such an equilibrium has been possible.' The broad conclusions of UV spectroscopy are that the tautomeric equilibrium, which is solvent-dependent, is increasingly in favour of the hydrazone form in passing from phenols to naphthols and to anthrols[3]. From IR spectra, Hadži[4] concluded that the azophenols are true azo compounds and the azonaphthols are mixtures of tautomeric forms or pure hydrazones.

We have now examined the NMR spectra of azo compounds, and have used the deshielding effect of the azo group on the *ortho* and/or *peri* protons for the identification of the two

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forms; further, the lack of aromatic character in one of the rings of the hydrazone form results in diamagnetic shifts of its protons as compared with those of the azophenol form.

In the region 2.0 to 2.3 (chemical shifts on the τ scale; CCl_4 as solvent unless otherwise stated), where the ortho protons of trans-azobenzene absorb[5], aniline does not show any absorption. The appearance of multiplet absorptions in the region 1.9 to 2.4 representing three protons in the spectra of 2-hydroxy-5-methylazobenzene and its 4'-methoxy and 4'-nitro derivatives show that all three compounds exist in the hydroxyazo form. The spectra of 4-hydroxy-3-methyl- and 2-hydroxy-5-methylazobenzene are similar to those of their methyl ethers in the aromatic region. On the basis that 4-hydroxy-2',4'-dinitroazobenzene undergoes Diels-Alder addition with cyclopentadiene, it has been suggested that the compound exists in the quinonoid form.[6] We find that both 4-hydroxy-3-methyl-2',4'-dinitro- and 2-hydroxy-5-methyl-2',4'-dinitroazobenzene exist only in the azophenol form in dimethylacetamide. However, in $CDCl_3$ solution, while the latter exists exclusively as the azophenol, the former compound displays both forms. The azophenol form is indicated by Me as a sharp singlet at 7.64; and the quinone hydrazone by Me as two doublets at 7.79 and 7.88 (J=1.4 cps), probably representing two stereoisomers. The quinone hydrazone form is confirmed by a single proton absorption at -2.23 (NH chelated with o-NO_2).

In dimethyl sulphoxide, dimethylacetamide, and acetone solutions 4-phenylazo-1-naphthol seems to exist only in the azophenol form; the chemical shift difference for the C_2 and

and C_3 protons is too large for them to be part of a quinone hydrazone system. Also, the spectrum of the methyl ether is very similar to that of the parent dye. Because of low solubility or other difficulties, the behaviour of 4-phenylazo-1-naphthol could not be studied in the solvents in which both tautomeric forms have been reported on the basis of UV data. 4-(*o*-Carbomethoxyphenylazo)-1-naphthol (in $CDCl_3$) exists only as the quinone hydrazone. However, the spectrum of 5-(*o*-carbomethoxyphenylazo)-8-hydroxyquinoline (I) (in $CDCl_3$), which has been found from UV data to display two forms,[7] shows clearly that both tautomers are present and that the ratio of azophenol to quinone hydrazone is approximately 34:66. Fig. 1 gives the spectrum of the C_4 and C_2 protons. The latter shows its characteristic quartet absorption at 1.12; the C_4 proton gives rise to two quartets, the low and high field quartets

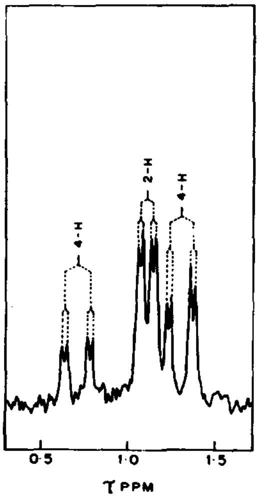
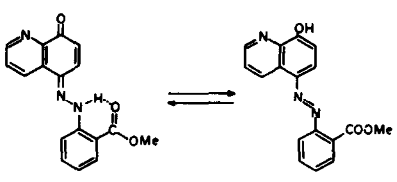


FIG 1.



I

representing the azophenol and quinone hydrazone forms respectively. The corresponding mobile proton signals are seen at 4.6 and -2.7; the low field signal indicates the bonding of the NH and COOMe groups. In dimethylacetamide the dye exists solely in the azophenol form.

Both 2-phenylazo-1-naphthol and the 1,2-isomer exist as hydrazones. The two well-resolved groups of signals below 2.5 centered at 1.85 and 2.25 in the spectrum of 1-naphthol (Fig. 2A) may be assigned to the protons in the 8 and 5 positions respectively. A complex multiplet between 2.48 and 2.75 represents the protons in the 4, 6 and 7 positions and the quartet at 3.34 the C_2 proton. Fig. 2B shows the spectrum of 2-phenylazo-1-naphthol. If the compound exists in the azophenol form, we may expect to find at least four protons, excluding that of the OH group, in the region below 2.4 in the spectrum. The fact that only one is seen indicates the

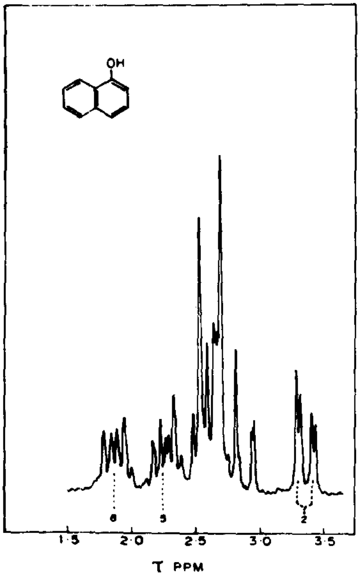


Fig 2(A)

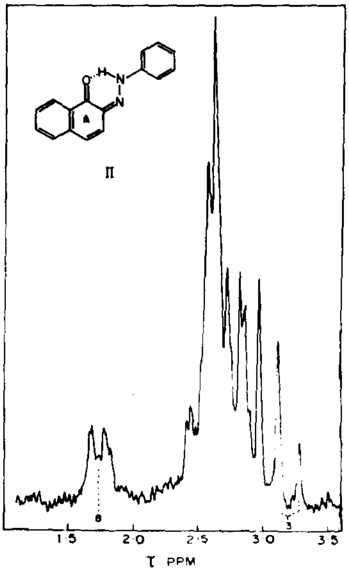


Fig 2(B)

hydrazone structure (II) for the compound. Since ring A of (II) is not aromatic, the proton at C_5 may be expected to absorb at higher field than the corresponding one of 1-naphthol. The C_8 proton remains at low field in the hydrazone because of the neighbouring C=O group. The doublets at 3.2 and 2.88 may be assigned to the C_3 and C_4 protons and they confirm structure (II). The methyl ether, which has to be in the azophenol form, shows absorptions for four protons in the region 1.7 to 2.4, and no aromatic proton signal is seen above 2.75. 1-Phenylazo-2-naphthol and 1-phenylazo-2-anthrol also exist as quinone hydrazones. In the light of our experience with 1-hydroxy-4-azo systems, it may be expected that the azophenol forms would be present at least as minor components in these solutions. We have examined their spectra for the possible presence of small amounts of the azophenol forms in both CCl_4 and $CDCl_3$ solutions, but could not detect any. Rapid exchange between the two forms is apparently making it impossible to observe the minor component.

Unlike 1-phenylazo-2-naphthol, its 4'-methoxy derivative seems to exist entirely in the azophenol form. The protons of the p-methoxyphenyl group in this compound and in 2-hydroxy-5-methyl-4'-methoxyazobenzene show nearly identical chemical shifts. This is in agreement with the observation that electron donor groups tend to stabilize the azophenol form. However, 1-p-methoxyphenylazo-2-anthrol retains the hydrazone structure, one methoxyl group being inadequate to effect even a partial conversion to the azophenol form.

The tautomerism of 4-arylazo-5-pyrazolones and three possible structures have been discussed recently by Jones *et al*.[8]

The NMR spectrum of 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone showed a highly deshielded proton (-3.8 to -4.2) which was readily exchangeable with D_2O. The hydrazone structure (III) was preferred on the doubtful ground that the low-field resonance was very broad. More convincing evidence for (III) becomes available when the NMR data on pyrazolones are examined using the criterion now employed. The spectrum of 3-methyl-1-phenyl-5-pyrazolone shows a two-proton multiplet centered at 2.15, representing the *ortho*-protons of the benzene ring on which the adjacent C=O group has a deshielding effect. The spectrum (in $CDCl_3$; Fig. 3A) of the 4-phenylazo derivative has a two-proton multiplet centered at 2.03, corresponding to the *ortho*-protons of ring A; but the *O*-methyl derivative (IV) has four protons which give a complex multiplet centered at 2.3 (Fig. 3B), and the two additional low-field protons of

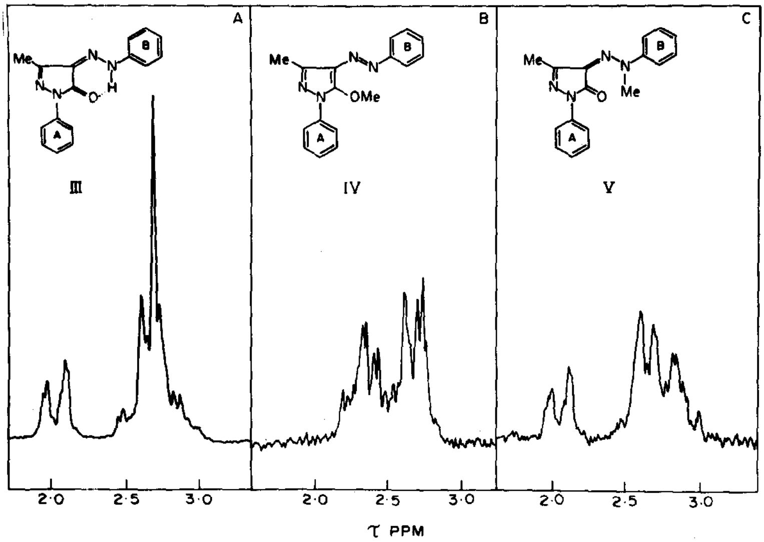
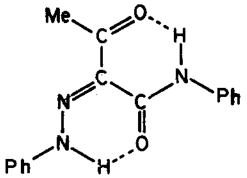


FIG 3

the *O*-methyl derivative are clearly the *ortho*-protons of ring B. The parent pigment must therefore exist in the hydrazone form (III). The spectrum of the *N*-methyl derivative (V) (Fig. 3C) confirms this conclusion, since it resembles Fig. 3A. The *p*-methoxyphenylazo analogue of (III) is found to retain the hydrazone structure like 1-*p*-methoxyphenylazo-2-anthrol and unlike the corresponding α- and β-naphthol derivatives.

The spectrum of the phenylazo derivative of acetoacetanilide shows that it exists as the hydrazone of structure (VI). The hydrazone and amide NH groups occur at -4.63 and -1.47 respectively. A hydrazone form is also indicated for the *p*-methoxyphenylazo derivative.



(VI)

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