Structures of Azoic Coupling Components and Azoic Dyes

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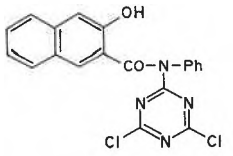
The trivial word "Naphthol" may be used for the phenol or enol (C.I. Azoic coupling component)[1] with which a diazotized primary aromatic amine (C.I. Azoic diazo component) is coupled to produce an insoluble azo dye (azoic dye) on the fibre. Colour Index lists over thirty manufacturers' names for the Naphthols, which are of two types: (a) for all shades other than yellow, derivatives of salicylanilide in which the position *para* to the hydroxyl group is blocked and coupling with the diazonium salt takes place in the second position adjacent to the hydroxyl group; and (b) for yellow shades, anilides of β-ketonic acids in which coupling takes place on the reactive methylene group. In the *Chemistry of Synthetic Dyes* (1952)[2] twenty-one Naphthols of type (a) are listed; they are all arylamides of one of the following acids: 3-hydroxy-2-naphthoic acid (I); 3-hydroxy-2-anthroic acid (II); 3-hydroxydibenzofuran-2-carboxylic acid (III); 2-hydroxycarbazole-3-carboxylic acid (IV); and 2-hydroxy-α-benzocarbazole-3-carboxylic acid (V). Colour Index mentions six additional Naphthols, redeemed from old patents, which are condensation products of (I) with *m*-chloroaniline, *p*-nitroaniline, 5-chloro-*o*-toluidine, *m*-xylidine, *o*-phenetidine, and *o*-tolidine. Naphthol AS-BI (C.I. 37566) is the *o*-anisidide of 7-bromo-3-hydroxy-2-naphthoic acid. According to a FIAT report, the IG examined "a very large number of new Naphthols with different substituents in aryl nuclei, with only one being noted of interest." This Naphthol (Naphthol AS-BI) gave brighter shades than those from standard Naphthols with improved light fastness (about 1 point on the standard 8 scale); the shades from Blue BB, Blue RR and Violet B Bases were of special interest.[3] The structures of ten Naphthols, more recently added to the commercial range, have not been disclosed in Colour Index.

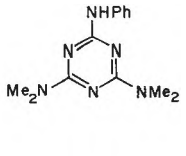
The Action of Cyanuric Chloride, 2,4-Dinitrochlorobenzene and Picryl Chloride on o-Hydroxybenzanilides

In connection with the synthesis of complex Naphthols, using the *s*-triazine ring for bridging coupling components, it was noticed that 3-hydroxy-2-naphthanilide (Naphthol AS) condensed with cyanuric chloride in presence of ethanolic sodium hydroxide. The reaction took place on the NH and not the OH group, the product being constituted as (VI).[4] Treatment of (VI) with 1% ethanolic sodium hydroxide at 50 to 55 °C for 3 hours resulted in smooth hydrolysis to 3-hydroxy-2-naphthoic acid (I) in 87% yield. Mild alkaline hydrolysis of the analogue of (VI) from Naphthol AS-GR (C.I. 37585) gives a 70% yield of (II), which is difficult to isolate under the drastic conditions of hydrolysis necessary for the Naphthol itself.

Replacement of the chlorine atoms in (VI) by dimethylamino groups and hydrolysis of the product by 1% aqueous sodium hydroxide at 85 to 90 °C yielded 3-hydroxy-2-naphthoic acid and (VII) which was easy to crystallize and identify. From Naphthol AS-LB, which can only be hydrolyzed under drastic conditions resulting in decarboxylation of the acid, the acid (IV) and the *p*-chloroaniline analogue of (VII) can be isolated in about 50% yield by mild hydrolysis.



VI



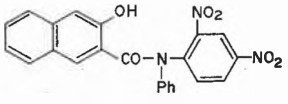
VII

The Sanger method for determining the amino acid sequence in a protein depends on the condensation of 2,4-dinitrofluorobenzene with free amino groups, leaving amide groups unaffected; but *o*-hydroxyarylamides react readily with 2,4-dinitrochlorobenzene (DNCB) in presence of a base to give the *N*-2,4-dinitrophenyl derivatives (for example VIII).[5] The reaction appears to proceed by a direct displacement of the halogen by the amide nitrogen, involving intramolecular nucleophilic catalysis by the phenoxide O: but a Smiles rearrangement is not excluded. Like the cyanuric chloride derivatives the *N*-dinitrophenyl derivatives are readily hydrolyzed by alkali, but they are very stable to acid. One advantage of the dinitrophenyl derivatives in their use for determining the constitution of Naphthols is that the aromatic amine moiety is isolated as the brightly coloured dinitrophenylamine which crystallizes readily and is also suitable for thin layer or column chromatography on alumina. The structures of three recently introduced

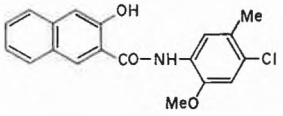
[1] *Colour Index* (Society of Dyers and Colourists, 2nd ed.), 1956; *Colour Index Supplement*, 1963.
[2] K. Venkataraman, *The Chemistry of Synthetic Dyes*, Academic Press, New York 1952.
[3] FIAT 1313, III, p. 154.
[4] B.S. Joshi, R. Srinivasan, R.V. Talavdekar and K. Venkataraman, *Tetrahedron 11* (1960) 133.
[5] P.M. Nair, R. Srinivasan and K. Venkataraman, *Tetrahedron 11* (1960) 140.

Naphthols, AS-RS (C.I. Azoic coupling component 28), AS-KN (C.I. Azoic coupling component 37), and AS-KG (C.I. Azoic coupling component 107) were thus determined.

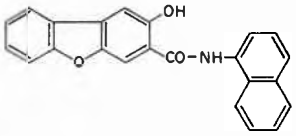
Acid and alkaline methods of hydrolysis have been used for determining the constitution of the Naphthols, but none is completely satisfactory.[6] The methods now described are of general value for determining the constitution of azoic coupling components.



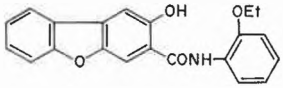
VIII



Naphthol AS-RS

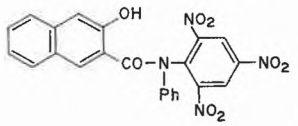


Naphthol AS-KN

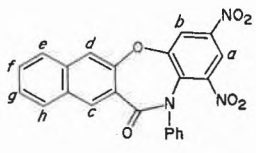


Naphthol AS-KG

Picryl chloride, as expected, reacts more readily than DNCB with Naphthol AS and with salicylanilide to give (IX) and the corresponding benzene analogue. In their behaviour towards alkali the trinitrophenyl derivatives are different from the dinitrophenyl derivatives. Instead of hydrolysis to the acid and the diphenylamine derivative, treatment of (IX) with 1% aqueous sodium hydroxide at 60 to 70 °C gave (X) and (XI) as a result of nucleophilic displacement of a nitro group and subsequent hydrolysis of (X). The NMR spectrum of (X) in dimethyl sulphoxide (DMSO) showed the following signals (chemical shifts on the τ scale): single proton doublets at 1.12 ($J = 2.5$ cps) and at 1.5 ($J = 2.5$ cps) assigned to H_a and H_b; single proton singlets at 1.3 and 1.8 (H_c and H_d); sharp singlet at 2.59 integrating for 5 protons (*N*-phenyl protons); complex pattern between 1.8 and 2.5 accounting for protons *e*, *f*, *g* and *h*.



IX



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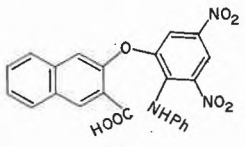


XI

[6] Ref. 2, p. 656.

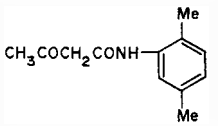
It was noticed incidentally that the picryl derivatives of arylaminesulphonic acids can be readily prepared and are useful for characterizing the reduction products of azo dyes.

Naphthol AS-SW

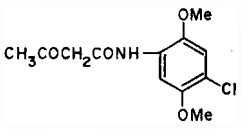
Naphthol AS-SW (C.I. 37565) is among the most important azoic coupling components, used in large quantities for dyeing cotton in scarlet, bordeaux and red shades. The usual method of making Naphthol AS-SW is the condensation of 3-hydroxy-2-naphthoic acid with β-naphthylamine in presence of phosphorus trichloride in an inert solvent. The amine is a potent carcinogen, the manufacture and handling of which have been banned in many countries. There are patent references[7] to the preparation of Naphthol AS-SW by condensing 3-hydroxy-2-naphthoyl chloride with 2-naphthylamine-1-sulphonic acid and subsequent removal of the sulphonic group; but conflicting statements have been made concerning the technical feasibility of this process. On the basis of our work on the base-catalyzed nucleophilic reactivity of *o*-hydroxybenzamides we are attempting to find conditions under which a good yield of Naphthol AS-SW can be obtained by the interaction of 3-hydroxy-2-naphthamide with 2-bromonaphthalene or naphthalene substituted in the β-position by a more suitable leaving group.

The Action of DNCB, *Picryl Chloride and Cyanuric Chloride on Acylacetanilides*

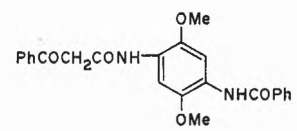
Four Naphthols for yellow shades (AS-G, AS-LG, AS-L3G and AS-L4G) were known in 1952; they are arylamides of acetoacetic or terephthaloyl-bisacetic acid. Three additions (AS-AG, AS-IRG and AS-IFG; C.I. Nos. 37611, 37613 and 37614) have the indicated structures. Naphthol AS-FGGR (C.I. Azoic coupling component 108) is of special interest; it is a nickel phthalocyanine derivative which gives green shades in combination with specified diazonium salts.[8]



Naphthol AS-AG



Naphthol AS-IRG



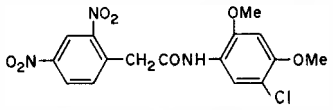
Naphthol AS-IFG

[7] CIBA, B.P. 700,024; Imperial Chemical Industries Ltd., B.P. 728,758; G.P. 1,109,288.

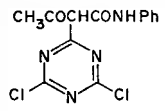
[8] Cf. Imperial Chemical Industries Ltd., French Pat. 995,964; G. RÖSCH and K.H. GEHRINGER (to Farbenfabriken Bayer) U.S.P. 2,882,267; B.P. 858,070.

The action of DNCB on β-keto-esters was studied many years ago,[9] and on β-diketones more recently.[10] From ethyl acetoacetate and from acetylacetone both the mono and di-*C*-aryl derivatives could be isolated. The reaction of DNCB with acylacetanilides has now been studied. When a solution of acetoacetanilide was refluxed with DNCB in ethanolic potassium acetate, the main product was 2,4-dinitrophenylacetanilide, accompanied by a small amount of 2,4-dinitrodiphenylamine. The interaction of DNCB with Naphthol AS-LG in presence of methanolic sodium hydroxide gave (XII) in 84% yield, together with dimethyl terephthalate in 50% yield; but no terephthalic acid was isolated.

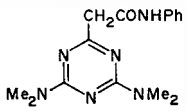
In its action on acetoacetanilide picryl chloride behaves differently from DNCB. The *O*-aryl ether, probably first formed, undergoes a nucleophilic displacement by the amide nitrogen, yielding 2,4,6-trinitrodiphenylamine as the major product, accompanied by a small amount of trinitrophenylacetanilide. Condensation of acylacetanilides with DNCB or picryl chloride provides a useful method for determining their structures. Those of Naphtol AS-AG and AS-IRG were thus determined before they were disclosed in Colour Index Supplement.



XII



XIII

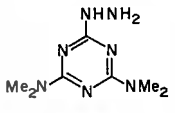


XIV

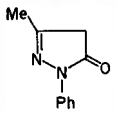
When a solution of acetoacetanilide in aqueous sodium hydroxide (molar proportion) was treated with cyanuric chloride at 0 to 5 °C, the product was (XIII); treatment of (XIII) with dimethylamine and hydrolysis of the product with hot 1% aqueous sodium hydroxide led to (XIV).

5-Pyrazolones and 4-Arylazo-5-pyrazolones

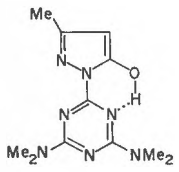
3-Methyl-1-phenyl-5-pyrazolone, a well-known dye intermediate, and its analogues have not been used so far as coupling components for yellow or orange azoic dyes, although water-soluble dyes of this type are largely used acid and acid-mordant dyes with excellent fastness properties. The reason probably is that in alkaline solution they have very poor substantivity in comparison with the technically useful azoic coupling components. By the condensation of (XV)[11,12] with ethyl acetoacetate in presence of ethanolic sodium hydroxide we have now prepared the 1-triazinyl pyrazolone (XVI). Arylhydrazines, in which the aryl group contains strong electron-withdrawing substituents, readily form hydrazones with ethyl acetoacetate, but the hydrazones resist cyclization to the pyrazolone.[13] Cyclization of (XV) to (XVI) is facilitated by the presence of the dimethylamino groups which diminish the electron-withdrawing character of the heterocyclic nitrogen atoms. The pyrazolone (XVI) in alkaline solution has high substantivity for cellulose, and on coupling with appropriate diazonium salts yields pure yellow shades, several of which have excellent fastness to chlorine.



XV



XVII



XVI

The 5-pyrazolones have been regarded as equilibrium mixtures of keto-enol tautomers. From IR and NMR data it has been proved unequivocally that 3-methyl-1-phenyl-5-pyrazolone has the structure (XVII).[14] In the IR spectrum there is a strong CO band at 1710 cm^{-1}; in the NMR spectrum a two-proton singlet at 6.63 corresponds to the methylene group, the reactivity of which is shown by the rapid exchange of the two protons with D_2O.[14] The IR spectrum of (XVI) in chloroform shows no absorption in the neighbourhood of 1710 cm^{-1}; an absorption band at 1615 cm^{-1} is assignable to the C=N group, which appears at 1610 cm^{-1} in (XVII). The NMR spectrum in $CDCl_3$ supports the hydrogen-bonded structure (XVI). In addition to the *C*-methyl group at 7.74 and the two dimethylamino groups at 6.88, there is a one-proton singlet at 4.6 (proton in the 4-position) and the hydroxyl appears at −3.43 (rapidly exchanging with D_2O), being therefore assignable to a chelated hydroxyl.

[9] A. REISSERT and H. HELLER, *Ber. dtsch. chem. Ges. 37* (1904) 4364 and later papers.

[10] S. S. JOSHI and I. R. GAMBHIR, *J. Amer. Chem. Soc. 78* (1956) 2222; *J. Org. Chem. 27* (1962) 1899.

[11] D. S. BAPAT, Ph. D. Thesis, University of Bombay, 1960.

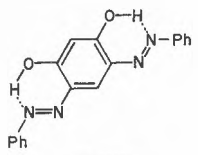
[12] For the preparation of the diethylamino homologue, described as a substance possessing valuable pharmacological properties, see CIBA, B. P. 825,072.

[13] S. V. KHROMOV-BORISOV, *J. Gen. Chem.* USSR (English Trans.) *25* (1955) 123.

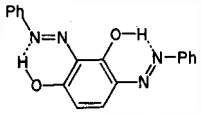
[14] R. JONES, A. J. RYAN, S. STERNHELL and S. E. WRIGHT, *Tetrahedron 19* (1963) 1497. See also P. E. GAGNON, J. L. BOIVIN and R. J. PAQUIN, *Can. J. Chem. 31* (1953) 1025.

Chelation in Azophenols and Chromatographic Adsorbability on Alumina

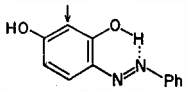
Chelation plays an important part in the chromatographic adsorption of hydroxyazobenzenes on alumina.[15,16] Using thin layer technique, R_f values can be determined rapidly and provide useful data on the number and position of hydroxyl and azo groups. In chromatography water-insoluble azophenols behave differently from the water-soluble azo dyes examined by RUGGLI and JENSEN.[17] In the water-soluble dyes containing sodium suphonate groups the azo groups are the determining factor. However, *p*-hydroxyazobenzene is more strongly adsorbed than 2,4-bisphenylazophenol. 4-Phenylazoresorcinol,4,6-bisphenylazoresorcinol(XVIII), 2-phenylazoresorcinol and 2,6-bisphenylazoresorcinol (XIX) are adsorbed in the given order of decreasing strength of adsorption. The weaker adsorption of (XIX) is related to its stronger chelation in comparison with (XVIII). In the canonical structure (XIX) each of the chelate rings contains one C=C bond; but in (XVIII) one chelate ring cannot implicate a double bond of the benzene ring in either of the two Kekulé structures. The resonance stabilization of the chelate rings in (XIX) is therefore greater; and in (XVIII) the hydroxyl groups are partially free for hydrogen bonding with alumina, (XVIII) consequently being more strongly adsorbed than (XIX).



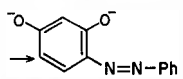
XVIII



XIX



XX A

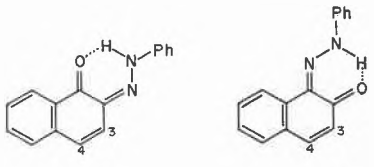


XX B

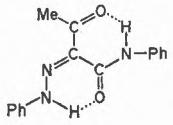
Coupling Behaviour of Resorcinol

When resorcinol is coupled with two molecules of diazotized aniline at *p*H 5 to 8, the main product is (XIX). It was suggested by us[16] that the entry of the second azo group in the 2-position of 4-phenylazoresorcinol was the result of the chelation indicated in (XX A), "in which one of the Kekulé structures makes a larger contribution to the resonance of the benzene ring; coupling then takes place at the end of the double bond attached to the hydroxylated carbon atom. Under strongly alkaline conditions the hydrogen bond is broken (XX B), and coupling takes place in the positions *ortho* and *para* to the two hydroxyl groups" with formation of (XVIII). We added that "bond fixation in ring structures has not found adequate support in experimental evidence or theoretical considerations and attempts are being made to explain such facts as the diazonium coupling of β-naphthol solely in the 1-position and 5-hydroxyindane mainly in the 6-position on other grounds, which do not postulate a static system involving the fixation of bonds and which take into account the relative stability of the activated complexes, the number of resonance structures in which the favoured position is activated, and the electron densities at the sites available for attack by a given reagent."

This problem has been re-examined by ZOLLINGER[18] in the background of his important work on the kinetics of diazonium coupling. He has shown that the formation of (XVIII) is subject to general base catalysis and that at constant *p*H the ratio between (XVIII) and (XIX) can be varied by altering the basic components of the buffer solutions in which coupling is carried out. It has been claimed that these results make the explanation suggested by us quite untenable. We feel that this is an overstatement of the implications of the newer results. There was no suggestion in our paper that the formation of (XVIII) or (XIX) was solely *p*H-dependent. In acid solutions ZOLLINGER was able to obtain only a 11.7% yield of (XVIII), and only 25.4% of (XVIII) under the best of conditions employed by him below *p*H 8.18. The possibility of the predominant formation of (XVIII) in acidic or nearly neutral solutions has not so far been realized, and until this is done, it is difficult to see why one has to accept general base catalysis as the sole factor determining the orientation of the second diazo substituent and how rationalizations of the type suggested by us earlier can be ruled out completely.



XXI XXII



XXIII

[15] T.S. GORE, T.B. PANSE and K. VENKATARAMAN, *Proc. Indian Acad. Sci. 29 A* (1949) 289.

[16] T.S. GORE and K. VENKATARAMAN, *Proc. Indian Acad. Sci. 34 A* (1951) 368.

[17] P. RUGGLI and P. JENSEN, *Helv. Chim. Acta 18* (1935) 624, *19* (1936) 64.

[18] H.F. HODSON, O.A. STAMM and H. ZOLLINGER, *Helv. Chim. Acta 41* (1958) 1816.

ZOLLINGER's results are summarized in two tables. According to Table 1 (composition of reaction products of resorcinol coupling) 83.6 to 88.3% of (XIX) was obtained when the *p*H was varied between 5.49 and 7.01; when the *p*H was increased to 9.72, 11.66 and 12.46, the 4,6-isomer (XVIII) was obtained in yields of 85, 90 and about 100% respectively; at a *p*H of 8.10 (XVIII) and (XIX) were obtained in yields of 24.9 and 70.5%. According to Table 2 (influence of buffer composition on the proportion of disazo isomers in resorcinol coupling) the *p*H was varied from 6.97 to 8.18 and the yields of (XIX) varied from 67.5 to 93.5%; however in the two experiments in which substantial amounts (21.0 and 25.4%) of the 4,6-isomer (XVIII) were obtained, triethanolamine and pyridine were used in the buffer mixtures. There is no evidence to show that these two bases have no effect on the intramolecular hydrogen bond in 4-phenylazoresorcinol (XX A). It also seems to us that the behaviour of *m*-phenylenediamine, demonstrated only by paper chromatography,[19] is not relevant to the discussion concerning resorcinol, because of the differences in the conditions of coupling of amines and phenols with diazonium salts and in the strengths of the hydrogen bonds of azo groups with amino and hydroxyl groups.

Azophenol-quinonehydrazone Tautomerism

The existence of tautomerism in azophenols has been recognized since 1884 when ZINCKE showed that the product of the action of phenylhydrazine on 1,4-naphthoquinone is identical with 4-phenylazo-1-naphthol obtained by coupling α-naphthol with diazotized aniline. There is now an extensive literature on azophenol-quinonehydrazone tautomerism, which has so far been followed mainly by studying UV and IR spectra in addition to chemical properties.[20–22] UV and IR data broadly led to the conclusions that *o*- and *p*-hydroxyazobenzene are essentially azophenols, 2- and 4-phenylazo-1-naphthol and 1-phenylazo-2-naphthol are equilibrium mixtures of the tautomers in which the hydrazone form is more favoured, and 1-phenylazo-2-anthrol and 4-phenylazo-1-anthrol are almost entirely in the hydrazone form. The equilibrium depends on substituents in the diazonium component, electron-withdrawing groups favouring the hydrazone form, and on the solvent. 1-Phenylazo-2-naphthol and 2-phenylazo-1-naphthol can possess chelate structures in both the azophenol and quinonehydrazone forms. A further complication arises in 1-phenylazo-2-hydroxy-3-naphthanilide because of the presence of the amide group. The IR spectra of Naphthol AS and its analogues were determined by HOYER[23] in the 5000 to 2500 cm^{-1} region using molten hexachlorobenzene (230°) as solvent; the presence of a strong intramolecular hydrogen bond was shown by broad absorption between 3370 cm^{-1} and 3000 cm^{-1}. We have examined the IR spectrum of Naphthol AS in *s*-tetrachloroethane, which shows a bonded carbonyl at 1655 cm^{-1} and NH at 3440 cm^{-1}. Benzanilide in the same solvent shows CO absorption at 1670 cm^{-1} (broad because of intermolecular bonding) and NH at 3435 cm^{-1}.

We are examining the NMR spectra of a series of azophenols, including derivatives of Naphthol AS, and of azoic dyes derived from acylacetanilides, which will be reported in detail in the *Indian Journal of Chemistry;* but some of the results may be briefly mentioned here. The NMR spectrum of 2-phenylazo-*p*-cresol (in CCl_4) shows the hydroxyl group at −2.25 and the aromatic protons in the 5- and 6-positions at 2.98 (quartet) and 3.22 (doublet, $J = 9$ cps), supporting the hydrogen-bonded azophenol structure. 4-Phenylazoresorcinol (in DMSO) also has the hydrogen-bonded azophenol structure (XX A), the chelated hydroxyl appearing at −2.77 and the unchelated hydroxyl at −0.68. 2,4-Bisphenylazoresorcinol (XIX) (in $CDCl_3$) shows strongly chelated protons at −6.62 and −5.68. The large paramagnetic shifts of the chelated protons in (XIX) indicate much stronger chelation in comparison with (XX A) and (XVIII), as well as the possibility of the existence of (XIX) in the quinonehydrazone form. In the 4,6-isomer (XVIII) (in $CDCl_3$) the two hydroxyls appear as a sharp signal at −4.03. Attention should also be drawn to the observation of GORE *et al.*[15] that in the ultraviolet-visible region (XIX) has a high-intensity band at about 415 mμ, and (XVIII) has a high-intensity band at about 340 mμ, together with a relatively low-intensity band at about 415 mμ (solvent cellosolve). The spectra of 2-phenylazo-1-naphthol and 1-phenylazo-2-naphthol (both in CCl_4) show a strongly chelated proton at −5.85 and −5.90 respectively, supporting the hydrazone structures (XXI) and (XXII); these are further confirmed by doublets at 3.2 and 1.75 in (XXI) and at 3.2 and 1.47 in (XXII), corresponding to the protons in positions 3 and 4. 1-Phenylazo-2-hydroxy-3-naphthanilide (in *s*-tetrachloroethane) shows a strongly chelated proton at −6.8 and the amide proton at −1.6, indicating a quinonehydrazone structure in which the sandwiched carbonyl is bonded with both the NH protons.

Acetoacetanilide Derivatives

The IR spectrum of acetoacetanilide now examined in chloroform shows that it exists almost entirely in the keto-anilide form (bands at 1710 and 1675 cm^{-1} in the 1600 to 1750 cm^{-1} region); a sharp band at 3435 cm^{-1} and a broad band at 3320 cm^{-1} correspond to NH in the free and bonded forms. The IR spectra of Naphthol

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