An α-Quinolylimine as the Long-lived Photocoloured Form

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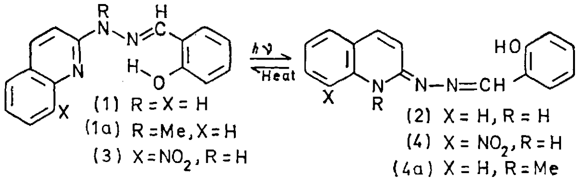
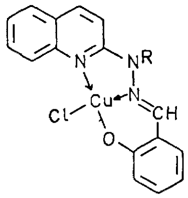
Summary The structure of the coloured species of the photochromic quinolylhydrazone (**1**) is postulated to be *Z,Z*-(**2**).

SALICYLALDEHYDE 2-quinolylhydrazone (**1**) containing a *N*-salicylidene group is the only example in the general classes of hydrazones[1] and anils[2] which is photochromic in normal solutions. Previously,[3] we have determined the structural criteria in (**1**) for photocolourability, and suggested prototropic tautomerism for an extended chromophore as shown in (**2**). We now report† the structural study of the coloured species (**2**).

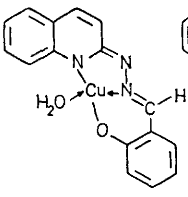
An ethanol solution of the photochrome (**1**), m.p. 204°; λ_{max} 358 nm (ϵ 23,800), was brought to the photostationary state [9·7% (**1**) and 90·3% (**2**)] by irradiation at 365 nm at room temperature. Preparative t.l.c. allowed the isolation of the coloured species (**2**), m.p. 151°; λ_{max} 395 (16,600), which is stable indefinitely in the solid form and has a half-life of 91 h at 24° in ethanol. The 8-nitro-substituted photochromic pair (**3**) and (**4**), also obtained, provide evidence for the tautomeric process. The i.r. absorptions, *viz.* $\nu_{asym,sym}$ of 8-nitroquinoline at 1530 and 1352 cm^{-1},[4] of (**3**) are reduced to a weak band at 1530 cm^{-1} in the i.r. spectrum of (**4**), denoting a strongly hydrogen-bonded nitro-function in the latter coloured species. This would require the presence of the quinoline *N*-hydrogen thus lending credence to the postulated α-iminoquinoline structure of (**2**) and (**4**). A corollary of this hydrogen-bonding scheme is the retarded rate of thermal decay of the nitro-coloured form (**4**) [$t_{1/2}$ 78° 27·5 h *vs.* 5·6 h for (**2**) in ethanol]. Compounds (**2**) and (**4**) decayed quantitatively to the uncoloured forms



(1) R = X = H
(1a) R = Me, X = H
(3) X = NO_2, R = H
(2) X = H, R = H
(4) X = NO_2, R = H
(4a) X = H, R = Me



(5) R = H
(5a) R = Me



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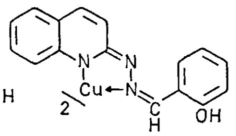

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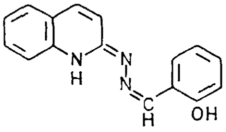
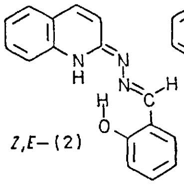
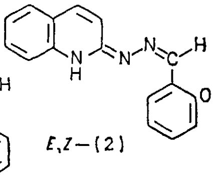


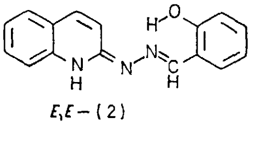
Z,Z-(2)



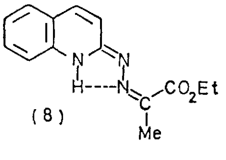
Z,E-(2)



E,Z-(2)



E,E-(2)



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† Satisfactory elemental analyses were obtained for all new compounds, and were characterized as to purity by t.l.c. and spectral data (u.v. in 95% ethanol and i.r. in KBr). The longest λ_{max} (in nm) and its extinction coefficient are reported here.

(**1**) and (**3**), respectively. As a u.v. model, we have synthesized (**4a**), the *N*-methyl analogue of (**2**) starting from the known 2-hydrazino-1-methylquinolinium chloride[5] according to the reported procedure,[3] m.p. 144—145°; λ_{max} 398 (23,500) which resembles that of (**2**).

The metal complex formations of these polyfunctional quinolylhydrazones provide evidence of the geometry of the two imino-groups in (**2**). Thus, in an aqueous ethanolic copper(II) chloride solution, both (**1**) and the exocyclic *N*-methyl derivative (**1a**) yielded an immediate precipitate, the elemental analyses of which allow the monochelate formulation (**5**), λ_{max} 422 (14,200), and (**5a**), λ_{max} 424 (16,100), which resemble each other. The latter chelate did not show a base shift in the u.v. spectrum, indicating that the ligand acts as a tridentate similar to that in the copper-salicylaldehyde α-pyridylhydrazone complexes reported earlier.[6] The copper chelate (**5**), however, readily deprotonated in aqueous base to form (**6**), λ_{max} 470 (15,500), which is also obtainable directly by shaking a chloroform solution of (**1**) with an aqueous copper(II) chloride solution saturated with bicarbonate. Similar treatment of the coloured form (**2**) produced the copper chelate (**7**), analysing for 2 moles of ligand per mole of copper, λ_{max} 420 (15,000). Upon heating in an aqueous solution, this bischelate underwent disproportionation to yield one mole each of the monochelate (**6**) and the uncoloured ligand (**1**). While the phenolic C–O stretching mode is shifted from 1282 cm^{-1} in (**1**) to 1310 in (**5**) and (**6**), as in the formation of copper–salicylidene anil complexes;[7] this band in the spectrum of (**2**) remains unchanged after chelation. The coloured species (**2**) must have therefore acted as a bidentate ligand in forming the bischelate (**7**). Under the same conditions, the *N*-methyl model (**4a**) did not yield a copper complex. Thus, of the four diastereoisomeric structures: *Z,Z*, *Z,E*, *E,Z*, and *E,E* that are possible for the two conjugated imino-bonds, the *Z,Z*-form is the most likely one to behave as a bidentate ligand in bischelation. Stabilization of the unusual α-quinolylimine fraction in *Z,Z*-(**2**) may be derived from the extensive conjugation in the molecule as well as from the internal 5-membered hydrogen bond that is possible. This is analogous to the structure suggested by Reimlinger *et al.*[8] for an isomer of ethyl pyruvate 2-quinolylhydrazone (**8**).

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