

Structural Criteria for Hydrazone Photochromism in Solution

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In view of the unique photochromic property of salicylaldehyde 2-quinolyldihydrazone (1) in solution, a systematic study of the effects of hydrazone substituents on photochromism has been made. We have synthesized nine derivatives of (1) which are photochromic, eleven non-photochromic derivatives, and three non-quinolyldihydrazones for comparison. On this basis, the following structural criteria for a hydrazone $R^1R^2N=N:CR^3R^4$ to exhibit photochromism in solution are derived: R^1 and R^2 should be H and an unsaturated system containing an α -imino-group; R^3 and R^4 should be H and an α -enol, the latter being capable of internal chelation.

PHOTOCHROMISM is a reversible change of a single chemical species between two states having distinguishably different absorption spectra, such change being induced in at least one direction by the action of electromagnetic radiation; commonly, the product is more deeply coloured than the starting material.¹ Photochromic

¹ G. H. Brown in 'Photochromism, Techniques of Chemistry,' vol. III, ed. G. H. Brown, Wiley-Interscience, New York, 1971, p. 3.

behaviour of the general class of hydrazones derived from aldehydes, ketones, and α -dicarbonyl compounds has been reported hitherto only in the solid state.² Neither the structure of the coloured species nor the photochromic mechanism has been elucidated.² Salicylaldehyde 2-quinolyldihydrazone (1) is the first of its class

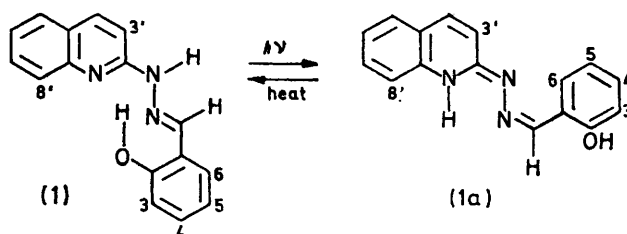
² (a) G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.*, 1961, **11**, 2; (b) R. Exelby and R. Grinter, *Chem. Rev.*, 1965, **65**, 247.

reported³ to exhibit photochromism in normal solutions, and the coloured form has been shown to possess the rare (*Z*)- α -(benzylidenehydrazono)quinoline structure (1a).⁴ We have now studied the electronic and steric factors controlling this novel solution photochromism. We have synthesized nine derivatives of (1) which are

amine \rightarrow imine and *E* \rightarrow *Z* hydrazone isomerizations, and the thermal reversion follows simple first-order kinetics. There is no apparent fatigue of the photochrome even after five cycles of changes.

Photochromic Hydrazones.—The u.v. spectra of the ten photochromic pairs are summarized in Table I.

TABLE I
U.v. spectra of photochromic quinolyhydrazones

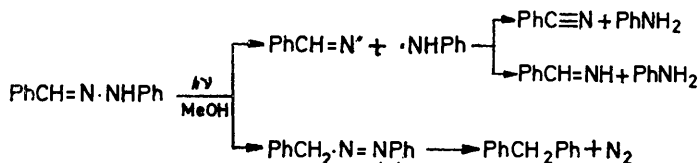


Substituents	Uncoloured			Coloured		
	Compd.	M.p. (°C)	$\lambda_{\max.}$ (EtOH)/nm (log ϵ)	Compd.	$\lambda_{\max.}$ (EtOH)/nm (log ϵ)	
None	(1)	203	358 (4.387), 310 (4.230), 237 (4.406)	(1a)	400 (4.220), 298 (4.176), 289 (4.204), 247 (4.196)	
3-NO ₂	(2)	201—203	350 (4.352), 315 (4.385), 231 (4.422)	(2a)	400 (4.217)	
3-OMe	(3)	195—196	360 (4.682), 320 (4.680), 238 (4.740)	(3a)	400 (4.406), 364 (4.491), 303 (4.567), 244 (4.677)	
4-OH	(4)	252	360 (4.518), 340 (4.535), 325 (4.250), 251 (4.626)	(4a)	408 (4.411), 295 (4.430), 255 (4.639)	
3,6-Me ₂	(5)	171—172	367 (4.354), 326 (4.283), 240 (4.350)	(5a)	390 (4.021), 300 (4.134), 292 (4.134), 247 (4.196)	
4,6-(OMe) ₂	(6)	179—180	363 (4.542), 343 (4.536), 326 (4.256), 248 (4.558)	(6a)	398 (4.342), 310 (4.346), 249 (4.474)	
3,5-Cl ₂	(7)	215—216	366 (4.447), 238 (4.439)	(7a)	405 (4.270), 300 (4.097), 254 (4.417)	
3'-Me	(8)	145—146	378 (4.307), 320 (4.127), 288 (4.134), 242 (4.418), 236 (4.428)	(8a)	392 (4.386), 296 (4.155), 289 (4.158), 248 (4.418)	
8'-NO ₂	(9)	204—206	370 (4.182), 335 (4.279), 302 (4.369), 240 (4.450)	(9a)	442 (4.164), 295 (4.415), 238 (4.433)	
8'-OH	(10)	206	345 (4.369), 310 (4.316), 300 (4.330), 278 (4.147), 255 (4.290), 245 (4.322)	(10a)	405 (4.180), 303 (4.348), 254 (4.260)	

photochromic, eleven non-photochromic derivatives, and three non-quinolyhydrazones for comparison. We present here structural criteria for a hydrazone to exhibit photochromism in solution.

Photochemistry of Hydrazones.—A non-destructive photochemical reaction of a hydrazone is typified by the isomerization of (*E*)-salicylaldehyde phenylhydrazone [$\lambda_{\max.}$ (benzene) 345 nm] to the *Z*-form [$\lambda_{\max.}$ (benzene) 308 nm] upon irradiation of a solution in benzene at 365 or 313 nm.⁵ When a shorter wavelength is applied, a hydrazone may undergo cleavage and reduction as

The hydrazones (2)—(10) are condensation products of known α -quinolyhydrazines and salicylaldehydes bearing ring substituents. In terms of the electron delocalization induced by these substituents, the 3-nitro-group in (2) and the 3-methoxy group in (3), *ortho* to the enol function, confer respectively positive and negative character to the enol carbon atom. The 4-hydroxy-group in (4), *para* to the imine, enhances the six-membered ring chelation, as do the 4- and 6-methoxy-groups in (6). The benzene ring in (7) experiences a mild electron deficiency due to inductive withdrawal by the chloro-substituents. An 8'-substituent on the quinoline ring [NO₂ in (9) and OH in (10)] withdraws or donates electrons respectively to the α -carbon atom to which the hydrazine group is attached. The remaining two hydrazones possess bulky substituents. Thus, the 3- and 6-methyl groups of (5) flanking the chelate ring should twist the chelate out of coplanarity. The 3'-methyl group in (8) limits the likely conformations of the α -amino-group to that shown in (1). If the alternative conformation with the aldimine nitrogen close to the quinoline 3'-position is required for photocoloration, this



SCHEME 1

illustrated in Scheme 1 for benzaldehyde phenylhydrazone.⁶ Unlike these hydrazones, the quinolyhydrazone (1) is readily convertible into the coloured form (1a) on irradiation 250—400 nm in normal solutions by

³ J. L. Wong and F. N. Bruscatto, *Tetrahedron Letters*, 1968, 4593.

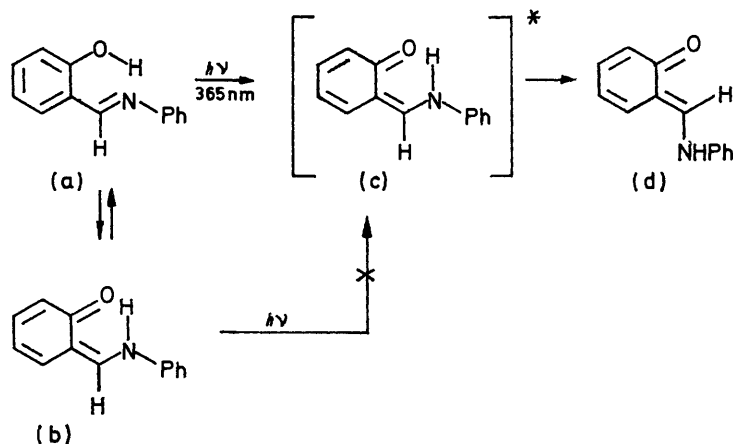
⁴ J. L. Wong and M. F. Zady, *J.C.S. Chem. Comm.*, 1973, 684.

⁵ G. Condorelli and L. L. Costanza, *Boll. Accad. Gioenia Sci. nat.*, 1966, **8**, 753, 775.

⁶ R. W. Binkley, (a) *Tetrahedron Letters*, 1969, 1893; (b) *J. Org. Chem.*, 1970, **35**, 2796.

TABLE 2

U.v. spectra of nonphotochromic quinolyhydrazones $R^1R^2N:N^3R^4$							
Compd.	R^1	R^2	R^3	R^4	M.p. ($^{\circ}\text{C}$)	λ_{max} . (EtOH)/nm (log ϵ)	
(11)	2-Quinoly	H	H	2-Methoxyphenyl	168—170	351 (4.441), 344 (4.438), 232 (4.431)	
(12)		H	H	3-Hydroxyphenyl	195—196	345 (4.352), 325 (4.398), 228 (4.371)	
(13)		H	H	4-Hydroxyphenyl	252	326 (4.448)	
(14)		H	H	2-Hydroxynaphthyl	216—218	391 (4.474), 333 (4.243), 321 (4.204), 260 (4.534), 247 (4.619)	
(15)		H	Ph	2-Hydroxyphenyl	212—214	358 (4.549), 311 (4.438), 239 (4.617)	
(16)		H	Me		151	358 (4.326), 321 (4.238), 304 (4.260), 289 (4.286), 240 (4.486)	
(17)		Me	H		147—148	355 (4.541), 390 (4.312), 236 (4.485)	
(18)		2-Quinoly hydrochloride	H		H	286—288	383 (4.480), 286 (4.450)
(19)		1-Methyl-2-quinolyldene	H		H	144	398 (4.371), 355 (4.330), 340 (4.297), 300 (4.093), 248 (4.362), 236 (4.236)
(20)		3-Quinoly	H	H	249—251	372 (4.072), 336 (4.176), 244 (4.170)	
(21)		8-Hydroxy-2-quinoly	H	H	Phenyl	204—205	330 (4.132), 315 (4.142), 260 (4.034), 240 (4.046)



property of the hydrazone (8) should be less apparent. However, the wide range of electronic and steric effects brought about by the various substituents is not manifested in the photochromic behaviour of these hydrazones. Thus, $4 \times 10^{-5}\text{M}$ -solutions of the hydrazones (1)—(10) in 95% ethanol developed a deep colour immediately after irradiation at room temperature at 365 nm. The coloured forms (1a)—(10a) are isolable by preparative t.l.c. Their u.v. spectra (Table 1) reveal a bathochromic shift of the longest wavelength absorption of the uncoloured forms at *ca.* 360 nm to the 400 nm region. Apparently, the variations of the electronic and steric environment neither prevent the basic chromophore from participating in the photocolouration step nor destabilize the coloured structures so as to preclude their isolation. Those structural modifications which disallow photochromism are represented by the hydrazones listed in Table 2.

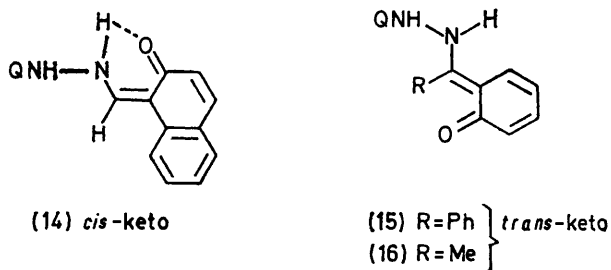
Nonphotochromic Hydrazones.—None of the hydrazones (11)—(21) (Table 2) developed a more coloured solution after irradiation in the u.v. region. By com-

parison with the photochromic hydrazone (1) the following structural requirements for photochromism in solution were inferred: (i) the *ortho*-hydroxy-group of (1) is needed since (11)—(13) and (21) are not photochromic; (ii) the phenol ring of (1) is vital for it cannot be replaced by 2-naphthol (14); (iii) the ketone hydrazones (15) and (16) are not photochromic, hence R^3 must be H; (iv) R^2 must also be H as indicated by (17) which is *N*-methylated; and (v) the hydrazine group should be adjacent to the quinoline nitrogen atom, which must not be quaternized as deduced from (20) and (18).

The requirements of features (i)—(iii) can be adequately accounted for by analogy with the mechanism of photochromism in the salicylidene anils⁷ (Scheme 2). Thus, the salicylaldimine (a) undergoes a π - π^* transition to yield eventually the excited *cis*-keto-structure (c) followed by isomerization to the *trans*-keto-form (d). The *cis*-keto-form (b), when frozen in this form and

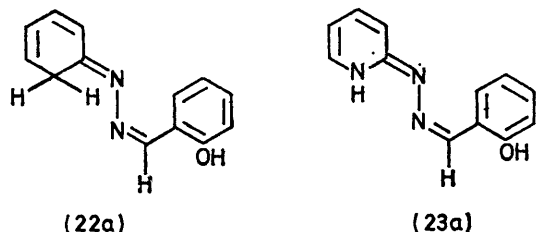
⁷ (a) R. S. Becker and W. F. Richey, *J. Amer. Chem. Soc.*, 1967, **89**, 1298; (b) M. Ottolenghi and D. S. McClure, *J. Chem. Phys.*, 1967, **46**, 4620.

irradiated,^{7a} does not isomerize to the *trans*-structure (d), suggesting that the phenol form (a) is necessary for photoexcitation. Hence, the integrity of the salicylaldimine unit of the hydrazone (1) cannot be compromised. The 2-hydroxy-1-naphthylhydrazone (14) may owe its loss of photochromic property to its existence in the *cis*-keto-form,* and the *trans*-keto-structure of either (15) or (16) is rendered unlikely by the bulky R group. The necessity of the structural features (iv) and (v) is rooted in the presence of an α -iminoquinoline in all



the coloured forms which extends the π -chromophore to provide for a more highly coloured isomer. However, the pre-existence of a conjugated chromophore as in 1-methyl-2-quinolyldenehydrazone (19) probably pre-empt the photoexcitation from being localized on the salicylaldimine unit, leading to no reaction.

Structural Criteria for Photochromism.—The following criteria must be met in order for a hydrazone $R^1R^2N=N:CR^3R^4$ to exhibit normal photochromism in solution: R^1 and R^2 must be H and an unsaturated system containing an α -imino-group; R^3 and R^4 must be H and an α -enol, the latter being capable of internal chelation. An aryl system containing an imino-group adjacent to the hydrazone satisfies the R^1 or R^2 requirement, and the enol feature is usually accommodated in an α -phenol. On this basis, salicylaldehyde phenylhydrazone (22) is predictably nonphotochromic in solution since its hypothetical coloured form (22a) would command an unstable extended π -system. By the same token, the salicylaldehyde α -pyridylhydrazone (23) should be more susceptible to photochromic behaviour even though its



coloured form (23a) is still not as stable as (1a). Indeed, when an ethanolic solution of (23) [λ_{\max} (EtOH) 335 (log ϵ 4.456), 309 (4.309), and 237 nm (4.267)] was

* 2-Hydroxy-1-naphthylmethyleneamine is virtually all present in alcoholic solution as the keto-isomer.⁸

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

⁸ G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, 1966, **88**, 2407.

irradiated at 365 nm, a new longest wavelength absorption band emerged at 395 nm. This reaction mixture, containing both (23) and (23a), decayed rapidly to an uncoloured solution of (23) only, and attempts to isolate the coloured species (23a) by preparative t.l.c. were of no avail. In the same α -pyridyl series, we would expect that 2-hydroxy-1-naphthaldehyde α -pyridylhydrazone (24) [λ_{\max} (EtOH) 368 (log ϵ 4.348), 332 (4.246), and 247 nm (4.534)] should give no sign of reaction upon u.v. irradiation, because the enol requirement of photochromism is violated just as in the quinolyldenehydrazone (14).

EXPERIMENTAL

U.v. spectra were obtained with a Cary 14 recording spectrophotometer. Microanalysis on all new compounds, performed by M-H-W Laboratories, Garden City, Michigan 48135, were satisfactory and are available as Supplementary Publication No. SUP 21461 (2 pp.).[†]

Hydrazone Preparation.—Equimolar amounts of the hydrazine and aldehyde or ketone were heated at reflux in 95% ethanol for 5 h. The solution was concentrated, and the crystalline precipitate recrystallized from ethanol; yield 40–80%. Hydrazones (10),⁹ (20),¹⁰ and (22)⁵ have been reported previously.

All the carbonyl reagents used are known, and, with the exception of 3,6-dimethylsalicylaldehyde, are available from Aldrich Chemical Co., Eastman, or K and K Laboratories. 3,6-Dimethylsalicylaldehyde was prepared by the procedure developed by Duff,¹¹ and was obtained as fine needles (from ethanol), m.p. 62–63° (lit.,¹² 58–59°). 2-Hydrazinoquinoline was purchased from Eastman. The 8-hydroxy- and 8-nitro-derivatives were prepared by reported methods.⁹ 2-Hydrazino-1-methylquinolinium chloride was prepared according to the procedure described by Huenig and Herrmann.¹³

2-Hydrazino-3-methylquinoline.—A mixture of 2-chloro-3-methylquinoline¹⁴ (0.15 g, 0.85 mmol) and 85% hydrazine hydrate (1.0 ml) in propan-1-ol (10 ml) was refluxed for 40 h. The solution was evaporated, the residue was distributed between ether and water, the ether layer was dried and evaporated, and the residue was recrystallized from hexane to yield the *quinolyldenehydrazone* (0.084 g, 59%), m.p. 128–130°; λ_{\max} (EtOH) 330 (log ϵ 3.812) and 240 nm (4.384). (Found: C, 69.15; H, 6.45; N, 24.35. $C_{10}H_{11}N$ requires C, 69.4; H, 6.35; N, 24.25%).

Photocolouration Studies.—A 3×10^{-2} M-solution of the hydrazone (1)—(10) in ethanol was irradiated at room temperature with a Sylvania Black Lamp Blue (365 nm) to the photostationary state. The solution was evaporated to dryness and the residue was dissolved in ether (25 ml) and chromatographed on silica gel G plates (1 mm thick) with chloroform as eluant. The u.v.-fluorescent band nearest to the solvent front was eluted with ether and a 50–90% yield of the corresponding coloured form was isolated (Table 1).

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⁹ T. Rudolph, F. Przystal, and J. P. Phillips, *J. Medicin. Chem.*, 1967, **10**, 981.

¹⁰ R. G. Anderson and G. Nickless, *Talanta*, 1967, **14**, 1221.

¹¹ J. C. Duff, *J. Chem. Soc.*, 1941, 547.

¹² O. Anselmino, *Ber.*, 1902, **35**, 4108.

¹³ S. Huenig and H. Herrmann, *Annalen*, 1960, **636**, 21.

¹⁴ R. E. Lyle, D. E. Portlock, M. J. Kane, and J. A. Bristol, *J. Org. Chem.*, 1972, **37**, 3967.