PHOTOCHROMISM OF QUINOLYLHYDRAZONES

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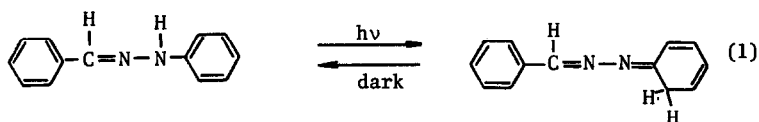
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Photochromism in hydrazones in the solid state is documented and has been recently reviewed (1). Earlier workers (2) ascribed the color change to the tautomeric shift (eq. 1),
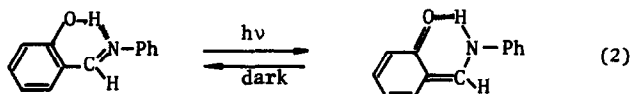

(1)

but this mechanism has not been established unequivocally (1). We wish to report the novel observation that certain quinolylhydrazones are photochromic in solutions and to propose a mechanism for the photocoloration phenomenon.

In solutions in ethyl alcohol or methylcyclohexane at room temperature, salicylaldehyde 2-quinolylhydrazone (I) is colorless but turns deep yellow on brief irradiation with the Cenco ultraviolet light (major band at 360 mμ), showing a new longest absorption maximum in the steady state at 400 mμ (Table I) and an isobestic point at 378 mμ. The color fades slowly (half life 12 hours) in the dark to regenerate the original spectrum while preserving the same isobestic point, thus indicating that a photoequilibrium between the colorless and the colored form has been attained by irradiation.

The relationship of structure to photochromism in the hydrazone I was investigated with model compounds. The first step was to vary the structure to determine what features of the molecule are essential for photocolorability. We found that the hydrazones of ortho-methoxy-(VII) and para-hydroxybenzaldehyde (VIII), and of benzaldehyde (IX) itself, are not colorable; thus the ortho-hydroxyl group is indispensable for the process. The N-methyl derivative X is not photochromic, suggesting that the N-proton of I is intimately involved in the photoequilibration. That the 2-quinolyl moiety in I is an integral part of the colored form chromophore is manifested by the lack of color change of the 2-pyridylhydrazone (XI) and the

phenylhydrazone (XII). The ultraviolet spectra of these non-photochromic hydrazones are shown in Table II. It may be concluded that the presence of the ortho-hydroxyl group, the N-proton and the quinoline ring are the essential structural features for photochromism in the hydrazone I. In accord with this hypothesis, a series of hydrazones were prepared with the same basic features and other substituents, e.g. 8'-OH; 4-OH; 3-OCH$_3$; 5-Cl; and 5-NO$_2$ (hydrazones II to VI respectively). They were photocolorable like the hydrazone I and their ultraviolet properties are compiled in Table I.

The photocoloration of the hydrazone I involves an equilibrium between the colorless and the colored forms upon irradiation. Karabatsos et al. (4) demonstrate by n.m.r. studies that phenylhydrazones exist in the imino form as in I with no detectable amounts of either azo or enamine forms. The importance of the orthohydroxyl group to photocolorability has been discussed by Cohen et al. (5) in some photochromic crystalline anils of salicylaldehyde. The color change is construed to be the result of a benzenoid-quinoid tautomerism (eq. 2).

$$(2)$$

However, the quinoid tautomer of I cannot contribute significantly to the coloration process since the N-methyl hydrazone X is not photochromic. The O-methyl derivative VII and the para-hydroxybenzaldehyde hydrazone VIII are not photocolorable, hence the ortho-hydroxyl group of I must be actively participating in hydrogen bonding with the imino nitrogen. Such intra-molecular hydrogen bonding would stabilize both the electronic excited and the ground states of I thereby facilitating the photochromic change (6). The hydrogen bonding is not possible in the syn form of I because of steric hindrance and the resulting lack of planarity. Thus the anti-imino form as shown in I should be the colorless form responsible for the absorption maximum at 358 mμ. Irradiation of I generates a new colored form with longer conjugated chromophore which absorbs at 400 mμ. This may be accounted for by a proton transfer from the exocyclic nitrogen to the ring nitrogen as in Ia. The amine-imine tautomerism leads to an expanded chromophore with concomitant deepening of color.
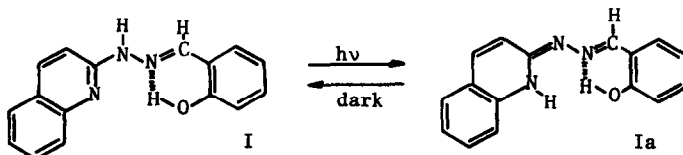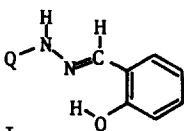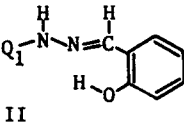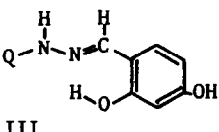

I   Ia
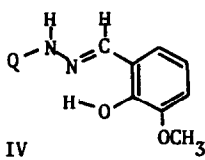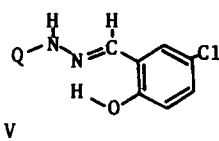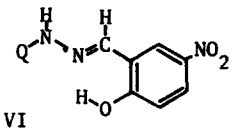
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Table I

Ultraviolet Spectra of Photochromic Hydrazones (3)

λmax (ε) in 95% Ethanol

I

a 358 (38500) 310s (27250) 237 (40050)

b 400 (25000) 298 (26500) 289 (27400) 247 (37900)

II

a 415 (3000) 345 (23380) 310 (20730) 300 (21380)

278 (14030) 255 (19500) 245 (21000)

b 405 (15130) 303 (22280) 254 (18200)

III

a 360 (33000) 340 (34250) 325 (33500)

310s (25500) 251 (42300)

b 408 (25750) 295 (26950) 255 (43600)

IV

a 360 (48100) 320 (47900) 293s (29000) 238 (55000)

b 400 (25500) 364 (31000) 303 (36900)

295s (34000) 244 (47550)

V

a 365 (28800) 290s (12600) 317s (15700) 237 (27600)

b 403 (18750) 298 (15000) 290 (15000) 253 (27860)

VI

a 363 (20360) 310 (13400) 230 (17140)

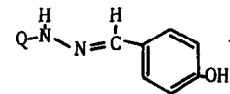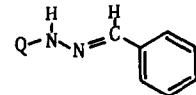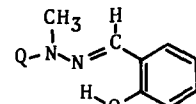b 435 (7490) 403 (14020) 380 (16180)

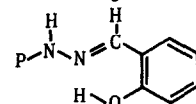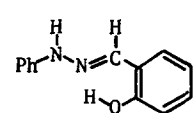302 (11850) 235 (13100)

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a before irradiation

b after irradiation to reach a photo-steady state

Q = 2-Quinolyl Q_1 = 8-Hydroxy-2-quinolyl

Table II

Ultraviolet Spectra of Non-Photochromic Hydrazones (3)

λmax (ε) in 95% Ethanol

Compound				
VII	318s (8130)	284 (1550)	250s (19250)	
VIII	355s (22450)	326 (28050)	240s (21500)	
IX	350s (28500)	323 (33500)	290s (15050)	231 (42900)
X	355 (34750)	340s(32000)	309 (20500)	236 (30550)
XI	336 (17030)	275 (30000)	270 (32000)	
XII	348 (23500)	303s(9700)	243s (13630)	235s (13780)

Q = 2-Quinolyl   P = 2-Pyridyl   Ph = Phenyl

References

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(3) The hydrazones are prepared by established procedure: T. Rudolph, F. Przystal, and
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(4) G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. Hsi, J. Am. Chem. Soc., 86, 3351 (1964).

(5) M. D. Cohen and G. M. J. Schmidt, J. Phys. Chem., 66, 2442 (1962).

(6) G. Gabor and E. Fischer, ibid., 66, 2478 (1962).