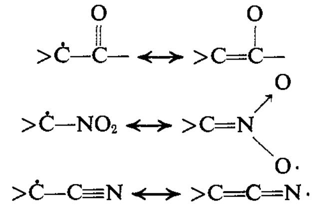
Scheme I



$$>\dot{C}-\overset{O}{\overset{\|}{C}}- \longleftrightarrow >C=\overset{O}{\overset{|}{C}}-$$

$$>\dot{C}-NO_2 \longleftrightarrow >C=N(\rightarrow O)O\cdot$$

$$>\dot{C}-C\equiv N \longleftrightarrow >C=C=N\cdot$$

Table I. Hyperfine Splitting Constants and Spin Densities for Alkyl Radicals in Water at 300°K

R	$a_{CH_3}{}^H$	$a_{CH}{}^H$	a^N	ρ^C
		A. $CH_3CO\dot{C}(CH_3)R$		
$H^{a,b}$	22.6	18.5		0.77
NO_2	22.5		4.0	0.77
$COCH_3$	22.3, 0.5			0.76
CN	21.8		3.0	0.75
OH^c	17			0.58
		B. $CH_3CO\dot{C}(H)R$		
H^a	1.2	19.3 ($a_{CH_3}{}^H$)		~0.80[d]
CN		19.1	2.8	~0.79[d]
CO_2CH_3	1.1, 0.2	19.1		~0.79[d]
$COCH_3$	0.3	18.6		~0.77[d]
$CH_3{}^{a,b}$	22.6	18.5		~0.77[d]
		C. $(CH_3)_2\dot{C}R$		
H^e	24.7	21.1		0.84
$CH_3{}^f$	22.7			0.78
$CN^{a,g}$	21.5		3.6	0.74
$CO_2H^{a,h}$	21.3			0.73
$CO_2CH_3{}^{a,h}$	21.3			0.73
$OH^{a,i}$	20.0			0.68
NO_2	19.8		3.9	0.68

[a] Prepared by the reaction of the substrate with hydrogen peroxide and titanous ion.[4] [b] For $CH_3CH_2CO\dot{C}HCH_3$.[9] The alternative structure $CH_3CH_2\dot{C}(OH)CH(OH)CH_3$ is excluded. [c] J. R. Steven and J. C. Ward, *J. Phys. Chem.*, **71**, 2367 (1967). [d] Calculated by the expression $a_{CH}{}^H = |24|\rho^C$. [e] At 188°K in liquid propane.[12] [f] At 128°K in liquid isobutane.[12] [g] Reference 7. [h] Reference 8. [i] Reference 6.

Resonance stabilization of free radicals is more important when the functional substituent is electron supplying, for example, alkoxy, thioalkyl, or amino.[6,14]

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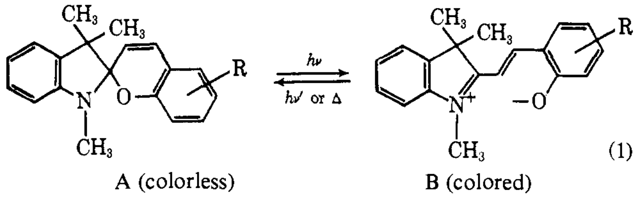
Medium Effects on Photochromism. Reversible Photobleaching of a Spiropyran on Silica Gel[1]

Sir:

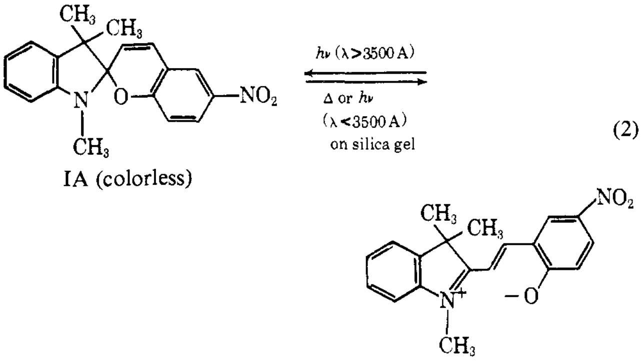
Photochromism in spiropyrans involving the reversible process A ⇄ B (eq 1) is adequately documented and has been treated in recent reviews.[2,3] The most exhaustive research in these compounds has been that of Hirshberg and Fischer[4] who have shown that the closed form A which is normally colorless undergoes photochemical ring opening to the open, colored modification B. B reverts thermally and photochemically to A, the rate of which is solvent dependent since the open, polar form B is relatively stabilized in polar solvents.[4,5]



A (colorless) B (colored) (1)

In general, most photochromic materials of various types behave in the above manner; *i.e.*, the colorless form is converted by ultraviolet irradiation to a metastable colored form. A well-known exception to this general behavior has been the system 15,16-dimethyldihydropyrene (colored) which may be transformed to the isomeric colorless metacyclophane by visible radiation, the latter isomer reverting in the dark to the more stable dihydropyrene.[6]

We should now like to report that this same "inverse photochromism" is observed in the spiropyran series when the medium is a cyclohexane–silica gel matrix; that is, in this matrix the open or colored tautomer of 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran (IB) is the stable form which, upon irradiating with wavelengths greater than 3500 A, is rapidly photobleached to the colorless tautomer IA (eq 2). The latter reverts in the dark to the intensely colored IB ($t_{1/2}$ = 41 min measured at either 373 or 525 mμ) and partially reverts to IB in a few seconds with 2537-A light (all irradiations with ultraviolet light lead to wavelength-dependent photostationary mixtures of IA and IB).



IA (colorless) (2)

IB (colored)

Solutions 5 × 10^{-4} *M* in I in cyclohexane or methanol solvent are colorless in the dark but become intensely blue upon irradiation for 10 sec with light from an unfiltered 500-w PEK high-pressure mercury arc lamp. Upon standing in the dark the cyclohexane solution bleaches rapidly while the methanol solution bleaches much more slowly, as expected. The unimolecular rate constant for bleaching in ethanol[5] has been determined as 4.3 × 10^{-5} sec^{-1} at 6°, and our qualitative observations indicate that bleaching in nonpolar solvents is about 100 times faster.

Addition of silica gel[7] to a colorless 5 × 10^{-4} *M* solution of I in cyclohexane produces a bright red matrix

(1) Electronic Spectra and Photochemistry of Adsorbed Organic Molecules. V. Part IV: P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *J. Am. Chem. Soc.*, **88**, 5075 (1966).

(2) R. Dessauer and J. P. Paris, *Advan. Photochem.*, **1**, 288 (1963).

(3) R. Exelby and R. Grinter, *Chem. Rev.*, **65**, 254 (1965).

(4) R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *J. Phys. Chem.*, **66**, 2465, 2470 (1962), and preceding papers in this series.

(5) E. Berman, R. E. Fox, and F. D. Thomson, *J. Am. Chem. Soc.*, **81**, 5605 (1959).

(6) V. Boekelheide *et al.*, *ibid.*, **89**, 1695, 1704, 1709 (1967), and references therein.

(7) The silica gel was Fisher 60–200 mesh, heated to 200° then partially hydrated by contact with the atmosphere for several hours. Rigorously dried silica gel was less effective in promoting IA → IB thermal conversion.

which develops to *full* color intensity in a few hours, the half-life being 43 ± 5 min. Exposure to the PEK lamp with a 3500-A cut-off filter for a period of 10 sec results in complete bleaching, the original color being restored in the dark with a half-life of 41 ± 5 min (with apparent color re-formation beginning almost immediately).[8]

It is necessary to demonstrate that the red, stable form on silica gel was indeed the same species as the open, unstable, blue photochromic species in solution. It is known that adsorption produces electronic spectral shifts, so the fact that one colored form is red to the eye while the other is blue is not surprising (in fact, the recorded visible spectra are quite similar as indicated in Figure 1; *vide infra*). Two experiments have demonstrated that these are the same species.[9] (1) Elution of bright red IB from a silica gel chromatography column with methanol yielded a deep blue solution with a visible spectrum identical with that of IB produced photochemically in methanol. The blue eluent bleached in the dark after 1 hr. (2) Addition of silica gel to blue IB produced photochemically in cyclohexane yielded immediately the red IB with substantial color development; *i.e.*, the visible optical density was equivalent to that attained after 20 min from the time of adding silica gel to an initially colorless solution of IA in cyclohexane in the dark.

That the photobleached material is the spiropyran is indicated by the identity of the half-lives for color formation in a cyclohexane solution of the spiropyran upon adsorbing it onto silica gel and by color re-formation in a photobleached sample on silica gel.

Ultraviolet and visible spectra of IA in cyclohexane and IB in cyclohexane–silica gel and in methanol are given in Figure 1. The blue shift in the S_1 transition and red shift in the S_2 transition in IB in going from methanol to the silica matrix are not unreasonable with respect to magnitude,[1] but we make no attempt to rationalize them with respect to direction since the respective transitions have not been assigned.

The observations reported in this communication are in accord with the following simple mechanistic view. In solution, even in polar solvents, the most stable tautomer of I is IA which may, however, be photochemically converted to relatively unstable IB with quantum yield on the order of 0.1–0.01.[4] On highly polar, partially hydrated silica gel, the open, polar IB is stable relative to IA, to which it may be photoconverted with quantum efficiency qualitatively of similar magnitude. The "driving force" of either photoconversion is maintained simply by the relative extinctions of the two tautomers at the exciting wavelengths.[10]

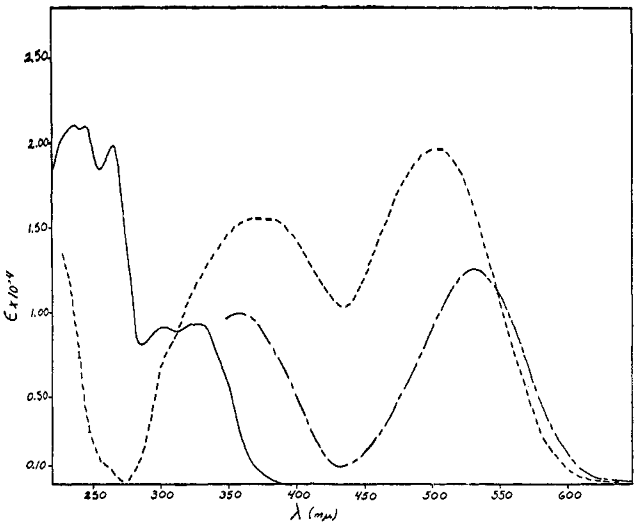


Figure 1. Ultraviolet and visible spectra of IA and IB: ——, IA in silica gel–cyclohexane; - - - - -, IB in cyclohexane; — - — -, IB in methanol.

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[8] All irradiations were carried out in 0.1-cm path-length quartz cells, which were also used directly for visible and ultraviolet spectral analyses.

[9] We do not mean to imply that the red species on silica gel and the blue species in solution are necessarily the same mixture of geometrical isomers of IB (see ref 4).

[10] This discussion is essentially in agreement with that pertaining to a related system, 1,3,3-trimethylindolino-6′-nitro-8′-methoxybenzopyrylospiran adsorbed on silicic acid, which has been the subject of a very recent preliminary report by C. Balny and P. Douzou, *Compt. Rend.*, C264, 477 (1967). We thank a referee for bringing this to our attention.

Spectroscopy and Photochemistry of *all-trans*-Retinal and 11-*cis*-Retinal

Sir:

Because of the important role of 11-*cis*- and *all-trans*-retinals in the visual process,[1–3] we wish to report several new results relative to their spectral and photochemical behavior.

While the absorption spectra[4,5] at different temperatures and nmr spectra[6,7] of these isomers have been reported, the low-temperature emission spectra and excitation spectra have not appeared.

Irradiation of any of the isomers in alcohol solution at room temperature is said to produce a photostationary equilibrium with the *all-trans* isomer as the predominant isomer.[8] *all-trans*-Retinal at 77°K showed some unknown reversible photochemical behavior as determined by monitoring intensity changes of the long-wavelength absorption band.

all-trans-Retinal was obtained from Sigma Biochemicals and recrystallized twice from 95% ethanol. The 11-*cis*-retinal was a gift from Hofmann-La Roche Co. and had been purified by them. In addition, nmr spec-

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