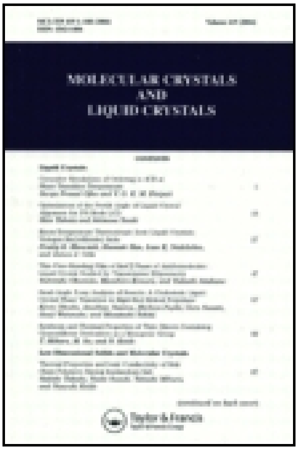

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Stanislav Neŝpûrek , Stanislav Böhm & Josef Kuthan (1994): Photochromism of 4H-Thiopyrans and 1,4-Dihydropyridines, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 139-142

To link to this article: http://dx.doi.org/10.1080/10587259408037801

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 139–142
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Printed in the United States of America

PHOTOCHROMISM OF 4*H*-THIOPYRANS AND 1,4-DIHYDROPYRIDINES

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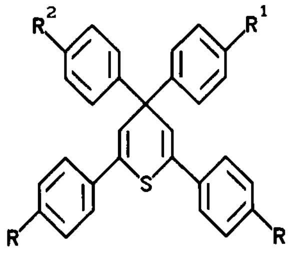
Abstract New type of photochromic reactions of 3,5-bridged isomers of thiopyrans and phenyl migration from position 4 to 3 of dihydropyridine ring are presented.

INTRODUCTION

There is current interest in reversible photochemical recording systems. In addition to known photochromic reactions [1,2]., such as cis-trans isomerism, homolytic or heterolytic bond cleavage and tautomeric shift of hydrogen, new types of photoreactions are generally possible.

RESULTS AND DISCUSSION

Synthesis and preparation of samples for optical measurements were described elsewhere [3-5]. After the illumination of samples with UV light new absorption bands appear (see Fig. 1 for 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine, IIb). Spectral characteristics are given in Table I.



I

II

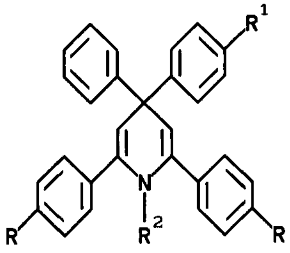
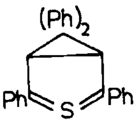


TABLE I Solution ground state λ^1 and solid state photochromic λ^2 absorption maxima (in nm).

Comp.	R	R^1	R^2	λ^1		log ε		λ^2 I	λ^2 II	Rel. int.
Ia	H	H	H	250		4.47		381	564	0.60
Ib	OMe	H	H	260		4.62		394	600	0.30
Ic	Bu	H	H	242		4.57		382	545	0.40
Id	Me	H	H	242		4.57		399	572	0.30
Ie	F	H	H	250		4.34		393	602	0.40
If	Br	H	H	255		4.62		398	594	0.30
Ig	H	Me	H	255		4.62		380	547	0.30
Ih	H	Cl	H	250		4.46		388	567	0.30
Ii	H	Br	H	238		4.53		387	564	0.30
Ij	H	Bu	Bu	250		4.00		378	552	0.10
Ik	H	Me	Me	238		4.57		404	598	0.20
Il	H	F	F	238		4.51		384	559	0.20
Im	H	Br	Br	250		4.57		362	554	0.20
IIa	H	H	H	239	290	4.42	3.83	405	568	0.39
IIb	H	Me	H	249	310	4.46	3.88	420	580	0.35
IIc	H	Cl	H	234	297	4.48	3.82	408	572	0.36
IId	H	Br	H	236	303	4.52	3.68	410	588	0.10
IIe	Me	H	H	242	302	4.48	3.73	432	627	0.10
IIf	F	H	H	233	294	4.34	3.68	418	600	0.27
IIg	Br	H	H	249	305	4.57	3.81	440	632	0.14
IIh	H	H	Me	235	288	4.45	3.83	405	550	0.32
IIi	H	Me	Me	234	295	4.50	3.91	408	545	0.25
IIj	H	Cl	Me	232	290	4.52	3.81	420	560	0.11
IIk	H	Br	Me	233	290	4.57	3.86	408	555	0.20
IIl	Me	H	Me	240	288	4.52	3.90	405	580	0.13
IIm	F	H	Me	235	286	4.42	3.78	410	575	0.07
IIn	Br	H	Me	246	293	4.56	3.88	410	560	0.26
IIo	H	H	Bz	235	290	4.44	3.78	396	560	0.32
IIp	H	H	Ph	228		4.46		400	560	0.34
IIq	H	H	PhMe	227		4.52		380	580	0.24
IIr	H	H	PhOMe	231		4.52		410	560	0.21
IIs	H	H	PhBr	229		4.51		389	585	0.21
IIt	H	H	PhCl	227		4.55		380	584	0.25

Me - methyl, Bu - butyl, Bz - benzyl, Ph - phenyl



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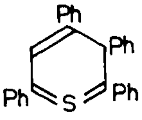

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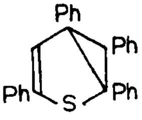

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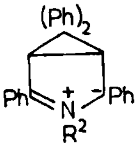

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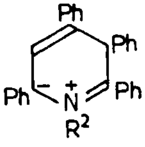

VII

The illuminated samples showed changes in two absorption regions. The longer wavelength band seems to be the pure photochromic one. The short wavelength bands (shoulders) are connected with both the photochromism and the formation of photodegradation products. From the inset of Fig. 1a it is evident that the time dependence of the normalized concentration of the photochromic species $[M]_t/[M]_0$ obeys the equation $[M]_t /[M]_0 = \exp [- \beta t]$, where t is the time and β is the decay rate constant. The life time τ ($= 1/\beta$) of coloured species of IIb in acetonitrile solution was determined as $\tau = 22$ μs, the rise time could be estimated from flash photolysis measurements as 20 to 50 ns. The coloured species arose quickly and directly from the parent material. An addition of poly(methyl methacrylate) (IIb/PMMA/chloroform - 0.008 g/7.2 g/200 ml) changed the monomolecular reaction to that with a non-exponential time dependence that could be analyzed in terms of a dispersive first-order reaction, i.e. $[M]_t/[M]_0 = \exp [-(\beta_1 t)^{\alpha}]$. The best fit yielded the parameters $\alpha = 0.8$ and $\beta_1 = 4.8 \times 10^3$ s^{-1}. A similar behaviour was found for crystalline samples (see Fig. 1b). Here, $\alpha = 0.8$, $\beta_1 = 1.8 \times 10^{-4}$ s^{-1} at room temperature. This non-exponential dependence can be accounted for by a Gaussian distribution of activation energies whose width decreases with increasing temperature. The mechanism of the photochromism was studied by quantum chemical calculations. The molecular geometries of possible photoisomers (see below) were optimized by the AM 1 procedure, the CNDO/S-CI method was used for the calculations of electronic absorption spectra. An example of the calculated spectrum of IIb is given in Fig. 1b (lines).

CONCLUSION

The photochromic reactions can be schematically written as:

$$\text{III [568 nm]} \underset{kT}{\overset{h\nu}{\leftrightarrows}} \text{I} \underset{kT}{\overset{h\nu}{\rightleftarrows}} \text{IV [618 nm]} \longrightarrow \text{V [275 nm]}$$

The major coloured species is the 3,5-bridged isomer III. Di-π-methane rearrangements I ⟶ IV is apparently followed by bleaching process involving V-like intermediates. The transformation I ⟶ III is photochemically allowed according to the Woodward-Hoffmann rules provided one of the sulfur free pairs participates in the formation of an additional C=C double bond (theoretical absorption wavelengths are given for Ia).

$$\mathrm{VI}\ [473\ \mathrm{nm}]\ \underset{kT}{\overset{h\nu}{\leftrightarrows}}\ \mathrm{II}\ \underset{kT}{\overset{h\nu}{\rightleftarrows}}\ \mathrm{VII}\ [559\ \mathrm{nm}]$$

The major coloured species is the isomer VII formed by the phenyl migration from position 4 to 3 of the dihydropyridine ring (theoretical absorption wavelengths are given for IIb).

REFERENCES

1. G. H. Dorion and A. F. Wiebe, Photochromism (The Focal Press, London, New York, 1970).
2. G. H. Brown, Photochromism (Wiley-Interscience, New York, London, Sydney, Toronto, 1971).
3. S. Nešpůrek, M. Schwartz, S. Böhm and J. Kuthan, J. Photochem. Photobiol. A: Chem., 60, 345 (1991).
4. S. Nešpůrek and W. Schnabel, J. Photochem. Photobiol. A: Chem., 62, 151 (1991).
5. P. Šebek, S. Nešpůrek, R. Hrabal, M. Adamec and J. Kuthan, J. Chem. Soc. Perkin Trans. 2, 1301 (1992).

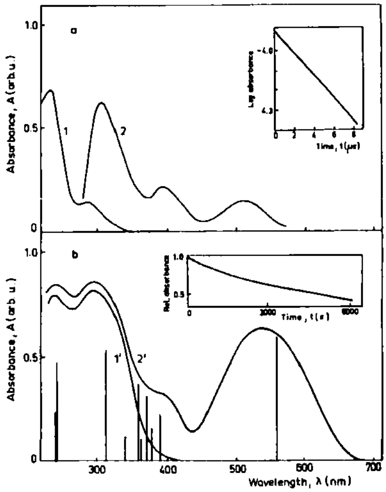

FIGURE 1 The photochromic spectra of IIb in acetonitrile solution (a) and in the solid state (b). Curves 1 and 1′ represent the ground state spectra, 2 and 2′ - spectra of the photochromic species, lines - calculated spectrum. The insets show the time decays of the absorbance of the coloured species at room temperature.