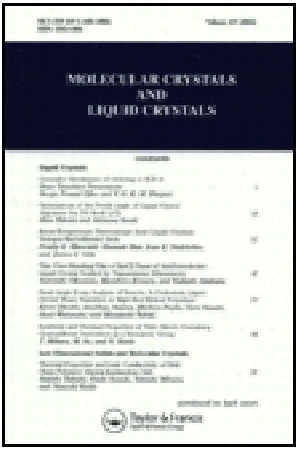


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Structural Variation and Responses in Photochromic Properties of Spirocyclic Molecular Systems Related to Spirobenzopyrans

Vladimir Minkin [a]

[a] Institute of Physical & Organic Chemistry, Rostov University, 344104, Rostov on Don, RUSSIA

Version of record first published: 24 Sep 2006.

To cite this article: Vladimir Minkin (1994): Structural Variation and Responses in Photochromic Properties of Spirocyclic Molecular Systems Related to Spirobenzopyrans, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 9-16

To link to this article: http://dx.doi.org/10.1080/10587259408037779

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 9–16
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

STRUCTURAL VARIATION AND RESPONSES IN PHOTOCHROMIC PROPERTIES OF SPIROCYCLIC MOLECULAR SYSTEMS RELATED TO SPIROBENZOPYRANS

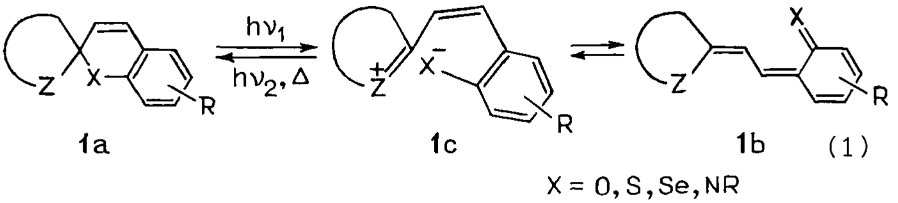
VLADIMIR MINKIN

Institute of Physical & Organic Chemistry, Rostov University
344104 Rostov on Don, RUSSIA

Abstract Synthesis, spectral properties and photochemical behavior of novel spirobenzopyrans, spiro-1,4-oxazines and 2H-chromenes with a potential of application in optical storage and erasable memory devices are overviewed. A special attention is given to elucidation of the structural modifications affording photochromic systems with near-IR absorbing photoisomers, luminescent stable forms, enhanced repetitionality of photochromic cycles and fatigue resistance as well as to spirobenzopyrans and their congeners displaying reversible photochromism in solid vacuum-deposited films. New photochromic compounds, four-coordinated main group metal chelate complexes of B(III), Be(II), Zn(II) and Cd(II), isoelectronic with 2H-chromenes and bis-spirobenzopyrans are described. Photochromism and a possibility of light to electron switching of spirocyclic cyclohexadienoneperimidines has been discovered.

INTRODUCTION

Over the past decade one focus of research of our group has been a study of novel spirobenzopyrans **1** and congeneric spirocyclic compounds exhibiting photo- and thermochromic properties,i.e. susceptible to light driven electrocyclic rearrangements of type (1), see[1-5] for reviews.



1a 1c 1b (1)

Photochromic compounds have an exciting potential of application as high density optical storage materials, in optical switching, image processing, multifrequency erasable memory and future generation optical computer devices.[6-8] A perfect photoswitching molecular system should possess a variety of specific properties, of which the following ones appear to be of primary importance.

1.Absorption spectra. Whereas the initial stable form **1a** is generally colorless, its photoisomer **1b** should absorb at visible and even better near-IR spectral region, the latter case allowing employment of diode lasers for optical recording and retrieval.

2.High quantum efficiency of the rearrangements (1) and high sensitivity. The relatively low sensitivity to light 10^{-2}- 10^{-3} J/cm^{2} is considered as the main drawback of organic photochromic materials.

3.Fatigue resistance,i.e.persistance to decomposition and back-side photoinitiated reactions providing for a possibility of multiple repetition of the photocoloration and bleaching cycles (1).

4.Variable thermodynamic and activation parameters of the equilibrium (1) By structural variation, relative stability and life times of the intercoverting isomers are to be altered in a desirable way depending upon a certain application of the photochromic system

5.Manifestation of the photochromic behavior in the solid state is of particular importance for the material to be used in erasable optical disks.

The experience accumulated in the course of very extensive study of the photochromic behavior and technical applications of spirobenzopyrans as well as other photochromic compounds [1-5,9] proved that one could hardly expect to meet all the forementioned requirements in any distinct subgroup of compounds **1**. An expedient way to the development of efficient photochromic systems (1) ought, thus, to be associated with a consistent study of responses of distinct characteristics of the photorearranging compounds to structural variation followed by unravelling of usable structure-property correlations.

LONG WAVE ABSORBED PHOTOISOMERS OF SPIROBENZOPYRANS AND THIAPYRANS

In photochromic dyes applied to the erasable disks for the diode lasers, such as GaAlAs and InP, the photocolored form **1b** must absorb in near- IR spectral region, i.e.beyond about 700 nm to which are extended the tails of long wave-bands of only a few of merocyanines **1b** (X=O). Becker and Kolc[10] were the first to demonstrate that by substitution of oxygen atom by sulfur in 1',3',3'-trimethylspiro/2H-1-benzopyran-2,2'-indoline/ (BIPS), long-wave absorption of **1b** (X=S) could be shifted about 100 nm deeper. Even longer-wavelength shift had been achieved in 2H-selenachromenes **1** (X=Se,Z=H, Ph), which photoisomers absorbed beyond 900 nm in isopentane isopropanol at 77K.[11] In both cases, however, the merocyanine isomers were found to be unstable at room temperature in solution and in a polymer film.

To stabilize the colored forms **1b** (X=S), introducing a nitro group to the position 6 in the benzothiopyran moiety has been suggested by analogy with the effect known for spirobenzopyrans **1** (X=O).[1,5] A good number of derivatives of spiro-6-nitroindolinobenzothiopyrans has been recently prepared,[12-14] some of these showing up to 30 repetitive cycles (1) at room temperature before fading. A further step towards diode-laser susceptible spiro-indolinobenzothiopyrans was the synthesis and successive polymerization of their 8-methacryloxymethyl derivatives.[14,15] The colored cast films of these induced by UV irradiation have been reported to retain the initial color for 200 days.Whereas the way to solving the problem of thermal stability of spirobenzothiopyrans thus seems to be unraveled, their main drawbacks remain to be insufficient cyclicity and low quantum yields of the photocoloration, the latter being estimated an order of magnitude smaller than those of congeneric spirobenzopyrans.[5,13]

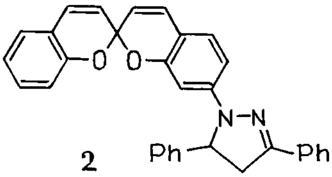
In view of this observation attempts have been undertaken to identify and then realize those structural modifications of spirobenzopyrans **1** (X=O) that would lead to the long-wavelength absorbed photoisomers **1b** (X=O) without loss of high efficiency of the photocoloration inherent in this class of photochromic compounds.[1,2,5] Semiempirical quantum mechanical calculations of excited state properties by use of SCF PPP, CNDO/S, MNDO and INDO/1 methods have been carried out in systematic series of the type **1** compounds[16-18] and their sufficient predictive accuracy proved by comparison of computational and available experimental data. The principal conclusions may be summarized as follows.

a) Variation of the spiro-heterocyclic moiety Z in **1** does not markedly affect absorption of **1b**, which origin is due to electron transitions located within the quinoneallyde fragment.

b) No batochromic shifts are brought about by an extension of the π-system in **1b** through benzo- or naphtoannelation of the 2H-chromene ring unless the annelation is linear (at positions 6,7).

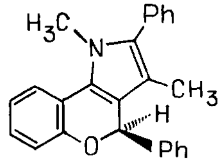
c) Significant batochromic shifts of the long-wave absorption bands in **1b** may be achieved by either introducing of strong electron releasing (i.e.amino) groups at position 7 of 2H-chromene moiety or by attachment of such groups to position 4.It is precisely the type of substitution that warrants the greatest extension of the conjgate system of **1b.**

The validity of the latter prediction has been recently proved by observation of the long wave absorption of the photomerocyanines of compounds **2-4.**

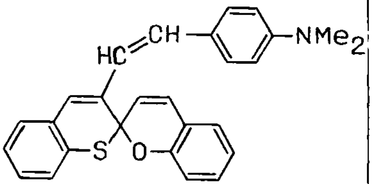


2

$\lambda_{max}(1b) = 770 nm$[19]



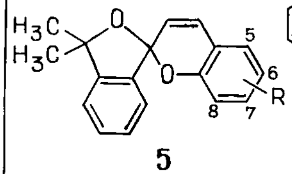
3 $\lambda_{max}(1b) = 678 nm$[20]



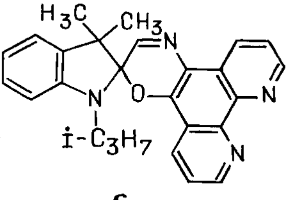
4 $\lambda_{max}(1b) = 786 nm$[21]

FATIGUE RESISTANT SPIROPYRANS OF 2-OXAINDAN SERIES AND SPIROOXAZINES

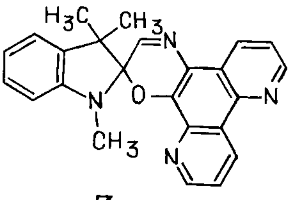
Although 6-NO_2 group in the 2H-chromene moiety enhances thermal stability of **1b**, it also tends to fast irreversible photodegradation due to population upon photoexcitation of the reactive triplet state. The photodegradation may be retarded on retention of sufficiently long life-times of the colored forms **1b** (at ambient temperature in solution) in the case of spiro-naphto-(antraceno-,phenantreno-)pyrans of 2-oxaindan series **5.**[22-24]



5



6



7

TABLE 1. Quantum and Coloration (A_0) Efficiency, Cyclicity and Kinetical Parameters of Thermal Coloration and Bleaching Reactions of Spiropyrans **5** (in toluene solution at 20°C)

R	Φ	A_0*	Z_{exp}**	k_{b-a}, s^{-1}	$\Delta G^{\ddagger}_{a-b}$, kcal/mol***
H				30	19.7
7,8 Benzo-	1.0	0.2	530	0.4	20.2
7,8 Naphto (b)-	0.3	0.7	900	0.025	20.5
7,8-Benzo-6-NO_2-	0.2	0.5	925	0.009	21.3
7,8 Benzo-6-Br-	0.9	0.4	280	0.2	22.5
5,6-Benzo,7,8 Benzo-	-	-	215	-	-
5,6-Benzo-8-OH-	-	-	2500	8.7	20.1
6-NO_2-BIPS	0.6	1.0	25	0.03	21.9****

* Relative to 6-NO_2-BIPS, defined from the slope of a photocoloration curve according to[25] (photolysis energy 800J).

** The number of flashes (Xe lamp,800 J) after which a decrease at e times of the initial optical density occurs ($C=5\cdot10^{-4}M$)

*** The energy barrier to the thermal **1a**→**1b** coloration reaction as defined by proton dynamic NMR technique.

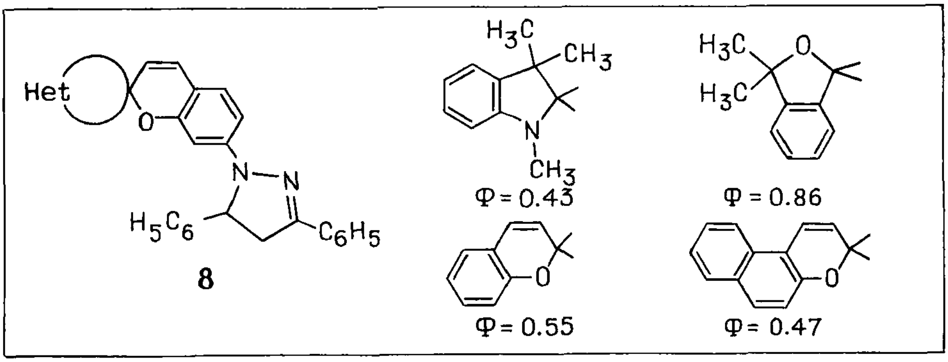
**** In DMSO.

We also studied properties of a series of novel spirooxazines which class is noteworthy for the distinguished fatigue resistance.[26] New method employing hydroxyamino aromatics, instead of hydroxynitroso derivatives, in coupling with methylene bases has been developed[27] and proved to be most expedient route to spiroindolinobenzoxazines with fused pyridine rings **6**, **7**. These compounds showed high coloration efficiency (A_0 = 0.4-1.0 relative to 6-NO_2 BIPS) and cyclicity at room temperature both in solution and polymeric films. The number of coloration - bleaching cycles after which initial absorption of the type **1b** photoisomers of spirooxazines is half-decreased is in the range of 210-1320 in PMMA films (11 for 6-NO_2 BIPS). By complexation of **6** with metal ions further enhancement in fatigue resistance may be achieved.

FLUORESCENT SPIROPYRANS

An efficient way to substantial increasing of the photosensitivity of photochromic materials lies in the development of systems (1) with luminescent image reading. Some of spiroindolinobenzopyrans are known to luminescence in both ring-closed **1a** (in rigid glasses, 77K) and ring-opened **1b** forms.[5,6,29] Quantum yields of photoluminescence were found, however, to be of very low value 0.001-0.02.

Our approach implies an attachment of a fluorescent label to the benzopyran ring of **1a** which should emit under excitation at wave length longer than that (313-365 nm) causing photorearrangement (1). As the appropriate fluorescent label, 3,5-diphenylpyrazoline unit has been chosen which shows intense green fluorescence under excitation at 420-430 nm. The merocyanines **1b** formed upon exposition to UV light absorb at 560-770 nm and possess no fluorescence. Sufficiently high quantum yields of the fluorescence (in PMMA films at room temperature) have been achieved for the spiropyrans **8**. The back reaction restoring the fluorescent type **1a** form is initiated by either irradiation of polymeric films by visible light or by heating them at 70-80°C.



8

PHOTOCHROMISM OF VACUUM-DEPOSITED SOLID FILMS OF SPIROPYRANS

Vacuum evaporation has recently been recognized as the most advantageous dry process for preparing thin solid films of photochromic compounds. The known examples of spiropyrans displaying reversible photochromism in microcrystalline or amorphous state are, however, rare.[30] Our study disclosed an important structural factor favoring to manifestation of the reversible photochromism of spirobenzopyrans in solid which is the presence in 2H-chromene moiety of formyl or/and methoxycarbonyl groups in positions 6,8 By evaporation under a pressure of 10^{-5}- 10^{-6} Torr at 250°-450°C with the rate of 3-30 Å /s, stable amorphous films of a number of spirobenzopyrans were deposited on fused quartz and KBr plates. When being subjected to the UV irradiation (365 nm), the spiropyran films underwent photocoloration due to **1a**⟶**1b** transformation. The merocyanine forms **1b** possess in solid sufficiently long half-times at ambient temperature (from several minutes to about 10 hours) and in some cases can be irreversibly fixed in the colored form by heating at 80-90°C.[31] The following are the spectral-kinetical characteristics of a number of spirobenzopyrans prone to reversible photochromism in thin solid films given in the order: type of a compound and substituents in the 2H-chromene moiety;λ_{max} (**1a**); λ_{max} (**1b**) in nm; half-life time in hs at room temperature; relative (to 6-NO_2 BIPS) rate of photocoloration under irradiation (365 nm) by high pressure Hg lamp.

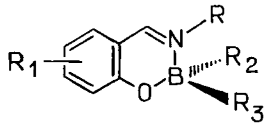
1',3',3'-Trimethylspiro-(2H-1-benzopyran-2,2'-indolines):6-CH_3,8-CHO, 365, 625, 0.7, 23; 6-CHO, 8-CH_3, 335, 590, 2.7, 29; 6-$COOCH_3$, 8-CHO, 360, 588, 9.6, 19; 6-$COOC_2H_5$,8-CHO, 365, 595, 16.1, 15.

3-Methylspiro-(2H-1-benzopyran-2,2'-benzo-1,3-oxazol-4-one): 6-CH_3, 8-CHO, 345, 590, 0.3, 3.

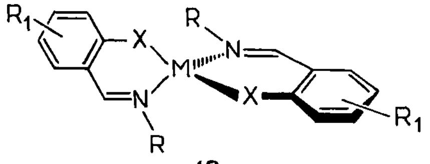
3,3'-Dimethylspiro-(2H-1-benzopyran-2,1'-2-oxaindan): 6-OCH_3,8-CHO, 350, 580, 0.2, 2.

PHOTOCHROMIC BEHAVIOR OF METAL CHELATE COMPLEXES OF o-HYDROXYARALDIMINES

The type **9** and **10** metal chelate complexes are isoelectronic to respectively 2H-chromenes and bis-spirochromenes which makes probable manifestation of photochromic behavior.



9



10

M= Be,Zn,Cd,Hg; X=O,S; R=Alk , R_1,R_2,R_3 =Alk,Ar

It was found indeed that irradiation of toluene or methanol solutions of **9** and **10** by light of the xenon photolytic lamp (500 J,2·10^{-4} s) results in immediate coloration of the solutions due to appearance of the long wave absorption at 440-660 nm. It totally disappears within 80 ms after switching off pulse of the photolytic lamp. By use of laser nanosecond flash photolysis, the life-times of the colored forms were found to fall into the range of 60-100 ns. Compounds **9** and **10** display very high cycle-repeating durability, i.e.stability against photodecomposition.[32] No measurable loss in intensity of the long-wave absorption of the colored species was observed in toluene solution after 100 pulses of the xenon lamp taken with 1-3 min intervals. Although no definite conclusion as to the nature of the photoisomers of **9,10** can be drawn on the ground of the data currently available, photocleavage of the Met-O bonds seems to be the most probable primary reaction occurring in the first singlet excited state.

REFERENCES

1. R.C.Bertelson, in "Photochromism" (Ed.G.H.Brown),Ch.3, J.Wiley Inc., New York.1971. **2.** V.Barachevskii, G.Lashkov, V.Czekhomskii "Photochromism and Its Application" Khimiya,Moscow. 1977. **3.** F.Dietz, A.V.Eltsov, in "Organic Photochromes" (Ed.A.Eltsov), Ch.1, Consultants Bureau,New York.1990. **4.** H.Dürr, Angew Chem ,101,427 (1989).**5.**R.Guglielmetti, in "Photochromism Molecules and Systems" (Ed.H.Dürr and H.Bouas-Laurent), Ch.8, Elsevier, Amsterdam. 1990. **6.** D.A.Parthenopoulos, P.M.Rentzepis, Science, 245, 845 (1989). **7.** G.A.Ashwell, Nature, 347,617 (1990).**8.**U.P. Wild, S.Bernet, B.Kohler, A.Renn, Pure Appl.Chem., 64, 1335 (1992).
9 .J.Fabian, H.Nakazumi, M.Matsuoka, Chem.Rev., 92, 1197 (1992).**10.** R.S. Becker, J.Kolc, J.Phys.Chem., 72, 997 (1968). **11.** B.S.Lukyanov, M.I. Knyazhanskii, Yu.V.Revinskii, L.E.Nivorozhkin, V.I.Minkin, Tetr Lett., 2007 (1973). **12.** S.Arakawa, H.Kondo, J.Seto, Chem.Lett., 1805 (1985).
13. S.Tamura, N.Asai, J.Seto, Bull.Chem.Soc.Japan, 62, 358 (1989).
14. M.Hirano, A.Miyashita, H.Nohira, Chem.Lett., 209 (1991).
15.A.Miyashita, M.Hirano, S.Nakano, H.Nohira, J.Mater.Chem., 3,221(1993)
16. V.A.Pichko, B.Ya.Simkin, V.I.Minkin, J.Mol.Struct.(THEOCHEM), 188, 129 (1989) .**17.** B.Ya.Simkin, S.N.Makarov, V.I.Minkin, V.A.Pichko, Khim.Het.Soed., 310 (1991). **18.** V.A.Pichko, B.Ya.Simkin, V.I.Minkin, J.Org.Chem., 57, 7087 (1992). **19.** N.V.Voloshin, N.E.Shelepin, N.V.Volbushko, V.I.Minkin, unpublished. **20.** A.V.Metelitsa, A.V.Koblik, V.I. Minkin, unpublished. **21.** S.Watanabe, H.Nakazumi, K.Maed, T.Kitao, Chem. Commun., 420 (1990). **22.** S.M.Aldoshin, V.A.Lokshin, A.I.Rezonov, N.V. Volbushko, N.E.Shelepin, M.I.Knyazhanskii, L.O.Atovmyan, V.I.Minkin, Khim.Het.Soed.,744 (1987). **23.** S.P.Makarov, B.Ya.Simkin, V.I.Minkin, Khim .Het.Soed., 172 (1988). **24.** Ya.N.Malkin, T.B.Krasieva, V.A.Kuzmin, J.Photochem.Photobiol.Chem., 49, 75 (1989). **25.** P.Appriou, R.Guglielmetti, F.Garnier, J.Photochem., 8, 145 (1978). **26.** N.Y.C.Chu, in "Photochromism Molecules and Systems" (Ed. H.Dürr and H.Bouas-Laurent), Ch.10, Elsevier, Amsterdam. 1990. **27.** O.A.Zubkov, V.A.Palchkov, V.I. Minkin, N.E.Shelepin, Russ.Pat. 1744952 (1992). **28.** A.V.Metelitsa,M.I. Knyazhanskii, O.A.Zubkov, V.A.Palchkov, N.E.Shelepin, V.I.Minkin,Mol. Crystals and Liquid Crystals, this issue. **29.** M.G.Kuz'min, M.V.Koz'menko, in "Organic Photochromes" (Ed.A.Eltsov), Ch.6, Consultants Bureau,New York .1990. **30.** T.Yoshida, A.Morinaka, N.Funakoshi, Chem.Commun., 437 (1986); Thin Solid Films, 162, 343 (1988). **31.** N.V.Volbushko, N.A.Voloshin, A.V.Metelitsa, V.I.Minkin, Russian Pat.1610834 (1988).
32 .V.I.Minkin, N.V.Volbushko, M.S.Korobov, L.E.Nivorozhkin, Mendeleev Commun.,No 3, 102 (1993).