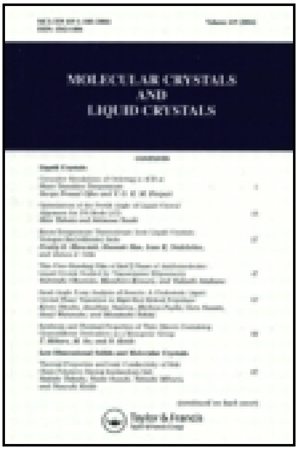


Molecular Crystals and Liquid Crystals

Revisiting Old Series and Rational Design of Novel Photochromics

A. Samat Samat [a], V. Lokshin [a], A. Heynderickx [a] & V. Khodorkovsky [a]

[a] Université de la Méditerranée, Faculté des Sciences de Luminy, Marseille, Cedex, France

Version of record first published: 31 Aug 2006

To cite this article: A. Samat Samat, V. Lokshin, A. Heynderickx & V. Khodorkovsky (2005): Revisiting Old Series and Rational Design of Novel Photochromics, Molecular Crystals and Liquid Crystals, 430:1, 23-30

To link to this article: http://dx.doi.org/10.1080/15421400590946118

Mol. Cryst. Liq. Cryst., Vol. 430, pp. 23–30, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590946118

Revisiting Old Series and Rational Design of Novel Photochromics

A. Samat
V. Lokshin
A. Heynderickx
V. Khodorkovsky
Université de la Méditerranée, Faculté des Sciences de Luminy,
Marseille, Cedex, France

The reinvestigation of photochromic systems (appeared several decades ago) involving hydrogen transfer is described. For instance sulfonyl-substituted 2-benzylpyridine (or benzothiazole) and 2-benzyl-3-benzoylchromones or quinolones undergo thermoreversible photochromic reactions at room temperature. Taking benefit of the chemical or photochemical reactivity of the enol form of the last class of compounds, novel thermoreversible or photoreversible photochromic systems have been designed (1,2-dihydrothioxanthenones and 3-(2-benzylbenzoyl)quinolones respectively), opening promising opportunities for future applications.

Keywords: 2-benzylazaheterocycles; chromone; photochromism; quinolones; thiochromone

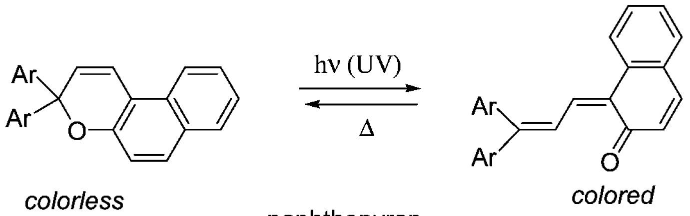
INTRODUCTION

The recent marketing of variable optical transmission glasses based on thermoreversible organic photochromes involving electrocyclisation reactions such as naphthopyrans is gaining growing success [1,2].

We are grateful to J. Aubard and R. Dubest (ITODYS, UMR 7086) for the realisation of flash photolysis experiments and to Transitions Inc. (PPG Industries/Essilor International) for their financial support at the beginning of this research program (1998–2000).

Part of this collaborative work was realised within the framework of "Groupement De recherche: Photochromes Organiques: Molécules, Mécanismes, Matériaux", GDR 2466, CNRS.

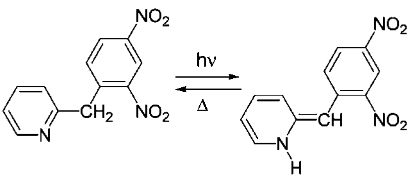
Address correspondence to A. Samat, Université de la Méditerranée, GCOM2. UMR CNRS 6114. Faculté des Sciences de Luminy. Case 901. 13288 Marseille cedex 09, France. E-mail: samat@luminy.univ-mrs.fr

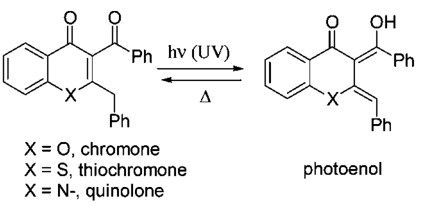


naphthopyran

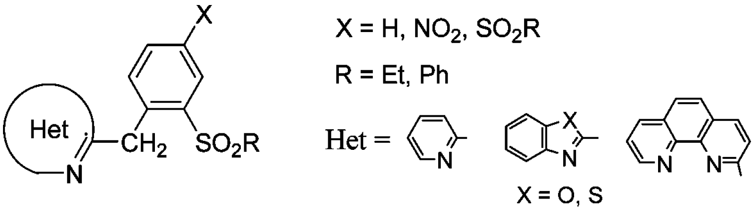
The main limitation of these compounds, regarding their applications, arise from the high dependency of the photochromic properties of these molecules on the temperature [2,3]. In order to bypass this disadvantage, the design of new systems involving hydrogen transfer has been undertaken. In such systems the reversible hydrogen shift between the two centers of the molecules induces a modification of the electronic structure and therefore a change in absorption spectra. The principal advantages of these prototropic systems are: (i) they are thermally and/or photochemicaly reversible; (ii) they do not undergo considerable structural changes: so that a lower activation energy for the thermal decoloration reaction could be expected compared to the systems involving electrocyclisation, which undergo considerable molecular reorganization. In turn, the limited molecular reorganization makes the prototropic system capable of working both in constrained (rigid polymer matrix, solid state) and not constrained media (solution, flexible polymer matrix).

Among the photochromic systems involving hydrogen (or proton) transfer, compounds such as dinitrobenzylpyridines [4], 3-benzoyl-2-benzylchromones or quinolones, described about 30 years ago [5], but not developed thereafter, seem to be promising owing to a broad range of possible structural variations and potential photochromic properties [6].





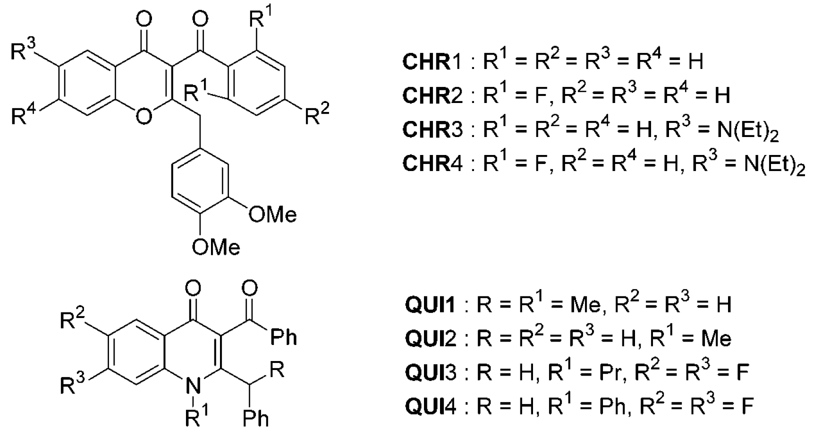
The major inconvenience of dinitrobenzylpyridines is the degradation [7] of the material after several cycles of coloration-fading. To bypass the fatigue resistance of such compounds, we decided to investigate new benzylpyridines substituted by electron withdrawing



SCHEME 1

groups other than the *o*-nitro group (which is necessary to assist the hydrogen transfer) and we selected especially sulfonyl group. Different kinds of azaheterocyclic moieties in place of pyridine were also investigated in order to better stabilize the N-H form [8] (Scheme 1).

Among the new compounds only two showed a photochromic behavior [8a,8b]. Compound **BP1** (Het = Pyridine, R = Ph, X = SO_2Ph) is photochromic both in the solid state under sunlight irradiation (purple) and in ethanolic solution under flash photolysis conditions ($\lambda_{max} = 485\,nm$, $k_\Delta = 0.27\,s^{-1}$ at 20°C). When the pyridine ring is replaced by the benzothiazole one (**BP2**: Het = benzothiazole, R = Et, X = NO_2) photochromism is observed in toluene at room temperature, giving rise to appearance of two absorption bands in the visible region with two bands: $\lambda_{max} = 445\,nm$ and $\lambda_{max} = 590\,nm$. Two rate constants for the reverse decoloration of the metastable form were observed ($15\,s^{-1}$ and $0.16\,s^{-1}$).



SCHEME 2 Photochromic 3-benzoyl-2-benzylchromones and -quinolones.

On the other hand, another group of compounds is presented by a large series of thiochromones, chromones and quinolones [9–11]. Among them several chromones and quinolones showed a photochromic behaviour. A selection of such compounds is presented in Scheme 2.

1. Photochromic Behavior of 3-benzoyl-2-benzyl-chromones and 3-benzoyl-2-benzyl-quinolones

Photochromic properties have been evaluated under continuous irradiation using a xenon lamp (ORIEL XBO 150 W). The light beam after crossing a water filter (absorptio1n of IR) is focalised and brought through an optical fiber to the cell put in a UV-VIS spectrometer (Varian CARY 50) allowing the monitoring of absorption spectra under irradiation or the variation of the absorption at $\lambda_{\max}$ during a coloration-thermal decolouration cycle.

The stability of the photoenol form depends markedly on the polarity of the solvent. Thus for chromones the colored forms are very unstable in acetonitrile and the photostationnary state is not observable at room temperature in this solvent. In contrast, the photoenol forms are more stable in nonpolar solvent like toluene. In the case of the colored forms of quinolones, they are stable enough in acetonitrile at 20°C to observe photocoloration cycles (colouration-decolouration) in few minutes. Depending on the nature of the heterocycle and substituents the absorption of the photoenol forms in the visible ranges from 440 nm to 513 nm. One interesting feature of these derivatives is the low values of the activation energy of the decoloration reaction. For the whole set of the studied quinolones this energy ranges from approximately $33\,\mathrm{kJ\cdot Mol^{-1}}$ to $63\,\mathrm{kJ\cdot mol^{-1}}$ showing that the fading process is less dependent on the temperature compared to the photochromic compounds involving the electrocyclization reaction, which are used for optical applications. For instance spirooxazine and naphthopyrans show activation energies for the thermal decoloration ranging from 80 to $100\,\mathrm{kJ\cdot mol^{-1}}$.

Owing to this thermodynamic characteristics associated with the acceptable fading rates, quinolones could be suitable for photochromic lenses applications. However, the narrow spectral range of the colored form, and the important fatigue phenomonon observed during long illumination times limit their applicability. Indeed, the photoenol form can undergo oxidation or photocyclization reactions making the process irreversible. Nevertheless the chemical and photochemical reactivity of this family of compounds opens new directions for the discovering of novel photochromic systems.

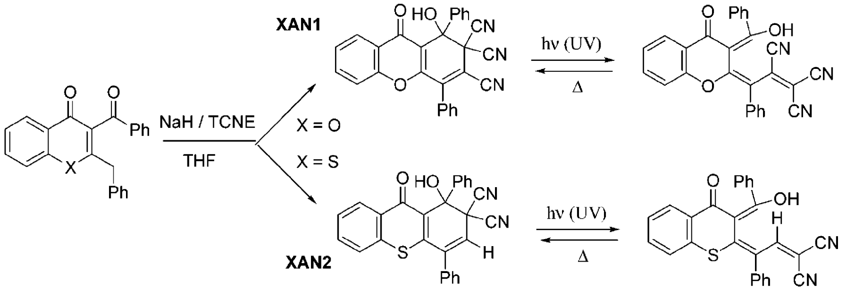
2. Photochromic 1,2-dihydro-9-xanthenone or Thioxanthenone Derivatives

When 3-benzoyl-2-benzyl chromone or thiochromone react in a basic medium with a powerful electrophilic compound like tetracyanoethylene (TCNE), an the electrocyclization reaction leading to a dihydroxanthenones [12] or a dihydrothioxanthenone occurs. These compounds undergo thermal reversible photocoloration when irradiated by UV light (Scheme 3). The photochromism is based on a electrocyclization reaction in which a C–C bond forms. The photostationary state is obtained in about 1 min in a toluene/cyclohexane (1/2) solution. The colorability and the thermal fading rates can be compared to those of the best photochromic compounds used in photochromic lenses (example with XAN2, c = 10^{-4}mol^{-1}, t = 20°C, irradiation flux 800 W·m^{-2}: λ_{max} = 520 nm, absorbance at λ_{max} at the photostationnary state = 0.46, k_{Δ} = 3.0 s^{-1}). The fatigue resistance is also comparable. In contrast to the known derivatives it seems that these systems are more sensitive to the polarity of the medium. For instance, a thermal equilibrium between the closed form and the open form is established in acetonitrile (solvatochromism).

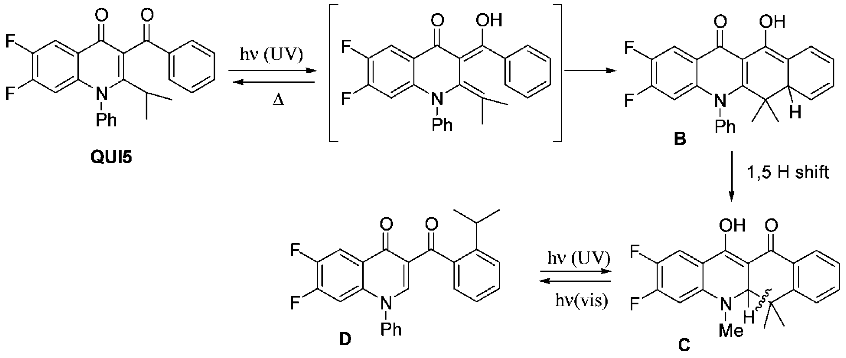
3. Photochromic 3-(2-alkyl(benzyl)benzoyl)quinolones.

During our investigations aiming at the development of the series of photochromic quinolones involving hydrogen transfer, we discovered an unusual behavior of the compound **QUI5** under irradiation. Beside the formation of the expected photoenol **A** responsible for the thermoreversible coloration, a by-product **C** (Scheme 4) showing a photoreversible photochromism was also isolated.

This by-product, coming from a photocyclisation reaction followed by hydrogen shift, undergoes a C–C bond break when irradiated by



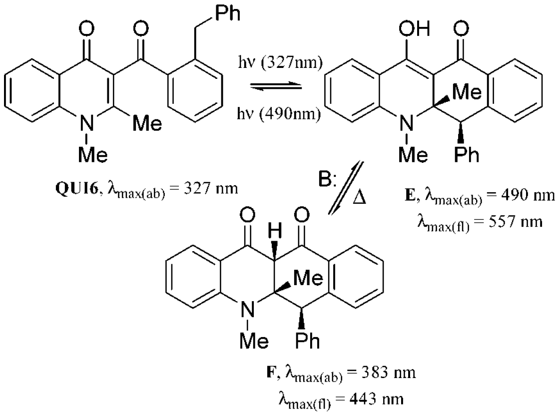
SCHEME 3



SCHEME 4

UV light. This phenomenon prompted us to investigate compounds analogous to **D** in which the substituent bearing the transferable hydrogen atom is localized on the benzoyl moiety. An example is given by compound **QUI6**, which represents a novel photoreversible photochromic system involving a hydrogen transfer/cyclization sequence [13] (Scheme 5).

Irradiation of degassed solutions of **QUI6** at 327 nm in toluene led to the formation of the dihydrobenzo-acridione **E**. Upon irradiation at 490 nm, **E** can be converted back to **QUI6**. In the dark, derivative **E** is slowly converted into the dihydrobenzoacridine-dione **F** ($\lambda_{max} = 386$ nm). In the presence of catalytic amount of a base, the equilibrium $\mathbf{E} \rightleftharpoons \mathbf{F}$ is established rapidly and irradiation of such



SCHEME 5

solutions at 490 nm led to the recovery of **QUI6**. Both **E** and **F** are fluorescent. No transients were detected and two isosbestic points were observed before the photostationary state was reached [13].

Reversible regio and stereoselective photocyclisation of **QUI6** affords not only colored but also, unlike furylfulgides and dithienylethemes [14], fluorescent products which is important for the non-destructive readout and makes them suitable for potential applications as components of optoelectronic devices [15].

In summary, the future of the photochromic applications of derivatives compounds of the 2-benzylazoheterocycles, 2-benzoyl-2-benzyl-chromone and quinolone families seems limited due to low photosensitivity and/or low fatigue resistance. In contrast, derivatives of such compounds like dihydroxanthenone or thioxanthenones and 3-(2-alkyl(benzyl)benzoyl) quinolones constitute novel photochromic systems having potential applications in the field of materials with variable optical transmission for the first and in the field of optoelectronics or optical memories for the second.

REFERENCES

[1] Durr, H. & Bouas-Laurent, H. (1990). *Photochromism: Molecules and Systems*, (Elsevier): Amsterdam, NL.

[2] Crano, J. C. & Guglielmetti, R. J. (1999). *Organic Photochromic and Thermochromic Compounds*, Kluwer Academic: Plenum Publishers, New York.

[3] Crano, J. C., Kwak, W. S., & Welch, C. N. (1992). In: *Applied Photochromic Polymer System*, Mc Ardle, C. B. (Ed.), chapter 2, Blackie: New York.

[4] (a) Eichen, Y., Lehn, J. M., Scherl, M., Haarer, D., Caselegno, R., Corval, A., Kuldova, K., & Trommsdorff, H. P. (1995). *J. Chem. Soc., Chem. Commun.*, 713.
   (b) Frank, I., Grimme, S., & Peyerimhoff, S. D. (1996). *J. Phys. Chem.*, *100*, 16187.
   (c) Corval, A., Kuldova, K., Eichen, Y., Pikramenou, Z., Lehn, J. M., & Trommsdorff, H. P. (1996). *J. Phys. Chem.*, *100*, 119315.
   (d) Scherl, M., Haarer, D., Fischer, J., Decian, A., Lehn, J. M., & Eichen, Y. (1996). *J. Phys. Chem.*, *100*, 16175.
   (e) Shinohara, S., Takeda, J., Ooike, T., & Kurita, S. (1999). *J. Phys. Soc. Jpn.*, *68*, 1725.

[5] Huffman, K. R., Loy, M., & Ullman, E. F. (1965). *J. Am. Chem. Soc.*, *87*, 5417.

[6] Patent, J. P. (1973). (Sumitomo Chemicals), No. 49-110583.

[7] (a) Hardwick, R., Mosher, H., & Passailaigue, S. P.(1960). *J. Chem. Soc., Faraday Trans.*, 44.
   (b) Klemm, D. & Klemm, E. (1978). *J. Prakt. Chem.*, 551.

[8] (a) Heynderickx, A., Samat, A., & Guglielmetti, R. (2001). *J. Heterocyc. Chem.*, *38*, 737.
   (b) Heynderickx, A., Samat, A., & Guglielmetti, R. (2002). *Synthesis*, 1747.
   (c) Heynderickx, A., Guglielmetti, R., Dubest, R., Aubard, J., & Samat, A. (2003). 1112.

[9] Rossollin, V., Lokshin, V., Samat, A., & Guglielmetti, R. (2003). *Tetrahedron*, *59*, 7725.

[10] Rossollin, V., PhD. (2001). Dissertation, Marseille France.

[11] Valès, M., PhD. (2002). Dissertation, Marseille France.

[12] Fijiwara, Y., Ishikawa, R., Akiyama, F., & Taranishi, S. (1978). J. Org. Chem., *43*, 2477.

[13] Lokshin, V., Valès, M., Samat, A., Pèpe, G., Metelitsa, A., & Khodorkovsky, V. (2003). *Chem. Commun.*, 2080.

[14] Whittal, J. (1990). In: *Photochromism: Molecules and Systems*, Dürr, H. & Bouas-Laurent H. (Eds.), Elsevier: Amsterdam, NL, Chapter 9, p. 467.

[15] Irie, M. (1994). *Photoreactive Materials for Ultrahigh Density Optical Memory*, Elsevier: Amsterdam, NL.