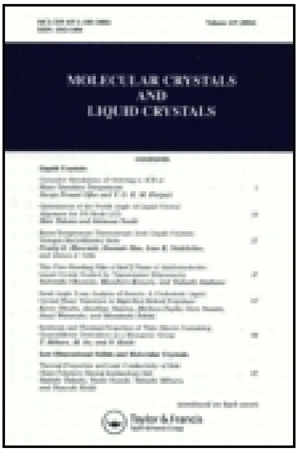


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

On the Photodegradation of 3,3-Diphenyl-[3H]-Naphtho[2,1-b]Pyrane in Solution: Mechanistic Aspect

C. Salemi-Delvaux [a], C. Aubert [b], M. Campredon [a], G. Giusti [a] & R. Guglielmetti [a]

[a] LCMOM - Université de la Méditerannée, Faculté des Sciences de Luminy, Case 901-163, avenue de Luminy, 13288, Marseille Cedex, 9, FRANCE

[b] Faculté de Pharmacie, La Timone, 27, W Jean-Moulin - 13385, Marseille Cedex, 5, FRANCE Phone: 91-26-93-42 Fax: 91-26-93-42

Version of record first published: 24 Sep 2006

To cite this article: C. Salemi-Delvaux, C. Aubert, M. Campredon, G. Giusti & R. Guglielmetti (1997): On the Photodegradation of 3,3-Diphenyl-[3H]-Naphtho[2,1-b]Pyrane in Solution: Mechanistic Aspect, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 45-51

To link to this article: http://dx.doi.org/10.1080/10587259708036141

Mol. Cryst. Liq. Cryst., 1997, Vol. 298, pp. 45–51
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in India

ON THE PHOTODEGRADATION OF 3,3-DIPHENYL-[3H]-NAPHTHO[2,1-b]PYRANE IN SOLUTION : MECHANISTIC ASPECT

C. SALEMI-DELVAUX[a)], C. AUBERT[b)], M. CAMPREDON[a)], G. GIUSTI[a)], R. GUGLIELMETTI[a)]
[a)]LCMOM - Université de la Méditerannée - Faculté des Sciences de Luminy - Case 901 -163, avenue de Luminy, 13288 Marseille Cedex 9 - FRANCE
b) *Faculté de Pharmacie - La Timone - 27, bd Jean-Moulin -*
13385 Marseille Cedex 5 - FRANCE
Telephone : 91-26-93-42 Fax : 91-26-93-04

Abstract : The present contribution is devoted to the investigation of the oxidative degradation of the 3,3-diphenyl-[3H]-naphtho[2,1-b]pyrane in toluenic solution. In order to propose some mechanisms concerning these degradation processes, we have identified the photoproducts by mean of coupled technics (GC-FID, HPLC-DAD, GC-MS). In those conditions, we have observed the production of benzophenone, β-phenylcinnamaldehyde, 2-hydroxy-1-naphthaldehyde along with an unidentified product detected by GC-MS ($m/z = 256$ g.Mol^{-1}).

1 - Introduction

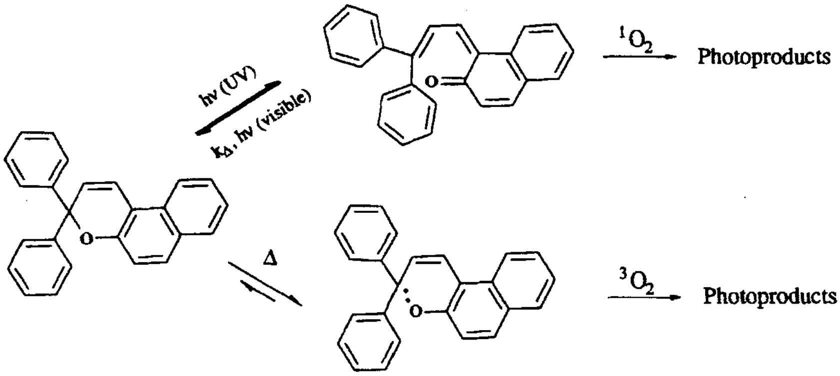
Photochromic compounds are thermally reversible dyes under UV light irradiation[1], coloured photomerocyanines being formed after the scission of the C-O bond of the closed spiranic form. However photodegradation processes represent a severe restriction for the industrial utilization of these dyes .

After the 1960's initial degradation studies[2] on spiropyrans concluding that oxygen was involved in the photodegradation, few other general studies of the degradation processes have been undertaken following a qualitative approach consisting in the identification of the different photoproducts generated after the continuous irradiation of some photochromic molecules in the indolinospiropyran and indolinospirooxazine series, in toluene[3,4] solution or in the solid state[5]. We have also recently started investigation of the photodegradation of the [2H]-chromene series. Subsequently, we have carried out a qualitative study of the degradation of the photochromic compound 3,3-diphenyl-[3H]-naphth[2,1-b]pyran **I** in toluene solution (Scheme 1). This series was chosen because of its appreciable photocoloration properties in the range of the visible spectra (430 - 530 nm) giving yellow to red-purple colors[6,7].

2 - Comparative analytical qualitative study

We have developed a qualitative approach by carrying out photoproduct analysis in order to find out whether this oxidative way takes place, likewise in the indolinospiropyrans and the indolinospirooxazines,[2,4,8-11] by singlet oxygen[8-11] attack on the various diene systems[12,13] present essentially in the different open forms or by interactions between biradical species[14] and molecular oxygen.

Scheme 1 : Photochromic interconversion in [2H]-chromene series

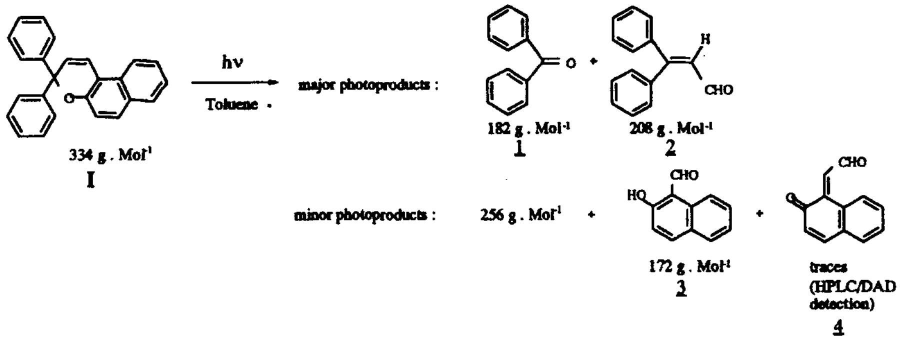


The compound **I** was degraded under UV light irradiation using a 500 W high pressure mercury lamp (HBO Osram) in toluene solution. After the analysis of the main photoproducts by gas and high pressure liquid chromatographies, their own structure was determined initially by GC-MS and confirmed by comparing the mass spectra, UV spectra and retention times with reference standards.

The chromatograms of the separated photoproducts in toluene are represented in Figures **1** and **2**. Degradation kinetics measured by regular injection into the chromatographic systems exhibit a pratically linear increase of fragment production as a function of time. The resulting structures are oxidation products identified as benzophenone **1** and β-phenylcinnemaldehyde **2** (from the left hand part of **I**) and the 2-hydroxy-1-naphthaldehyde **3** accompanied by some traces of 1-formylmethylene-2-

naphthoquinone 4 (deriving from the chromene moiety of I). Only one higher molecular weight product (FW = 256g.Mole^{-1}) is detected in toluene (Scheme 2).

Scheme 2 : Identified photoproducts by couplage (GC-MS) and by comparison with reference standards



GC-MS allowed molecular weights determination; mass spectra indicated the loss of phenyl moieties in these last systems and allows us to propose following structure corresponding to the cited mass weight (Figure 3).

Figure 1 : Gas chromatographic separation of photoproducts of 3,3-diphenyl-[3H]-naphtho[2,1-b]pyran I in toluene solution (Column SGE 0,32mm • 12 m capillary column (SGE Corp.) coated with BP5 (film 0,5 μm, pHe = 0,9 bar). T injector 280°C (Ross), T detector 300°C (FID), 90 to 300°C at 5°C min^{-1}).

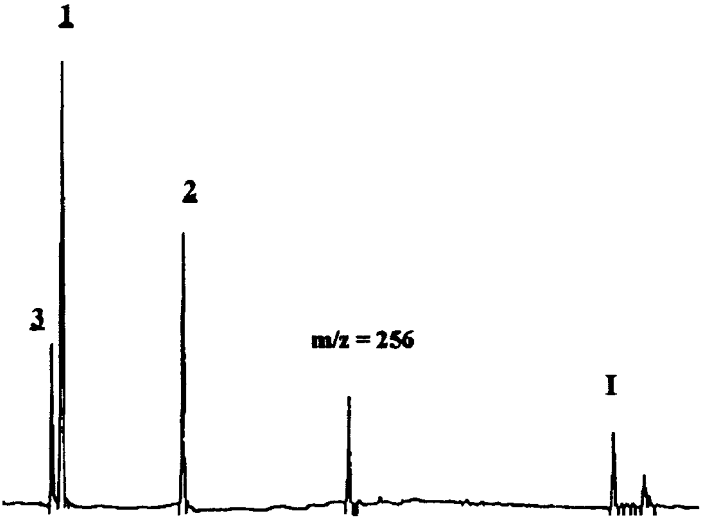


Figure 2 : Chromatographic separation (HPLC) of photoproducts issued from the degradation of 3,3-diphenyl-[3H]-naphtho[2,1-b]pyran I in toluene solution (column Zorbax Rx reversed phase, C8 4,6mm*25cm 5µm. Mobile phase : CH_3CN/H_2O 30/70 during 5 min, then 100% of CH_3CN within 40 min, flow rate $1mL.min^{-1}$. Detection 240 ± 5 nm. Room temperature).

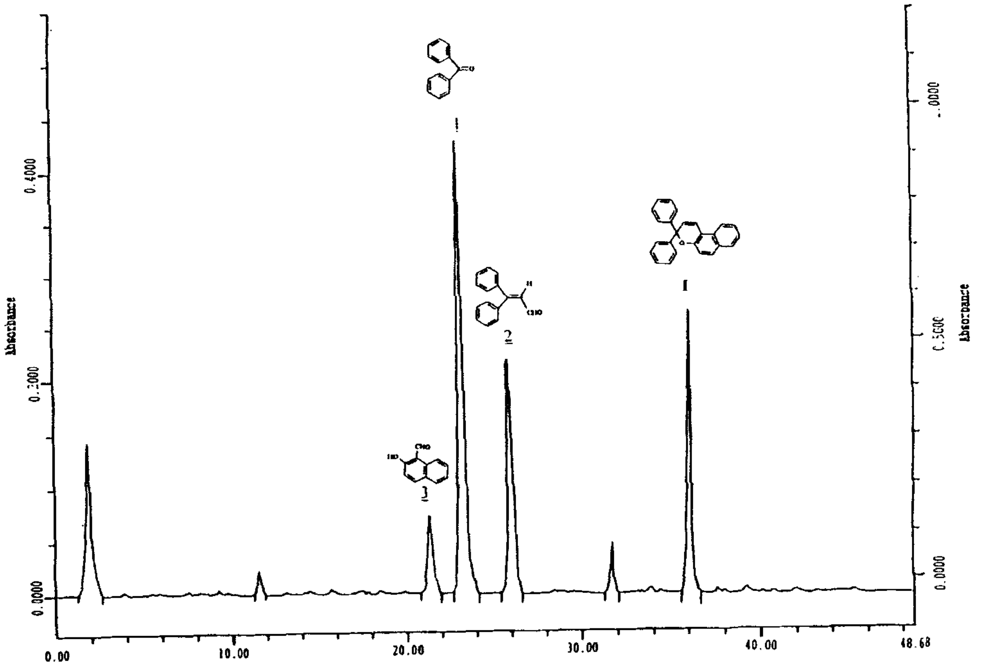
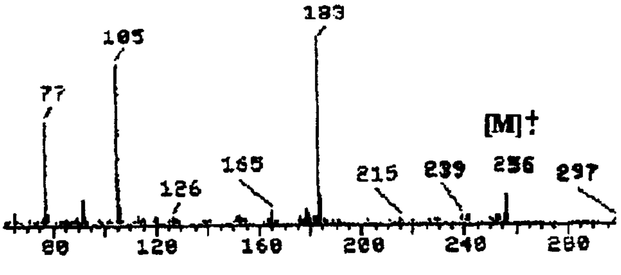


Figure 3 : Mass spectra of the unidentified photoproduct (m/z = 256) under electronic impact (70 eV)

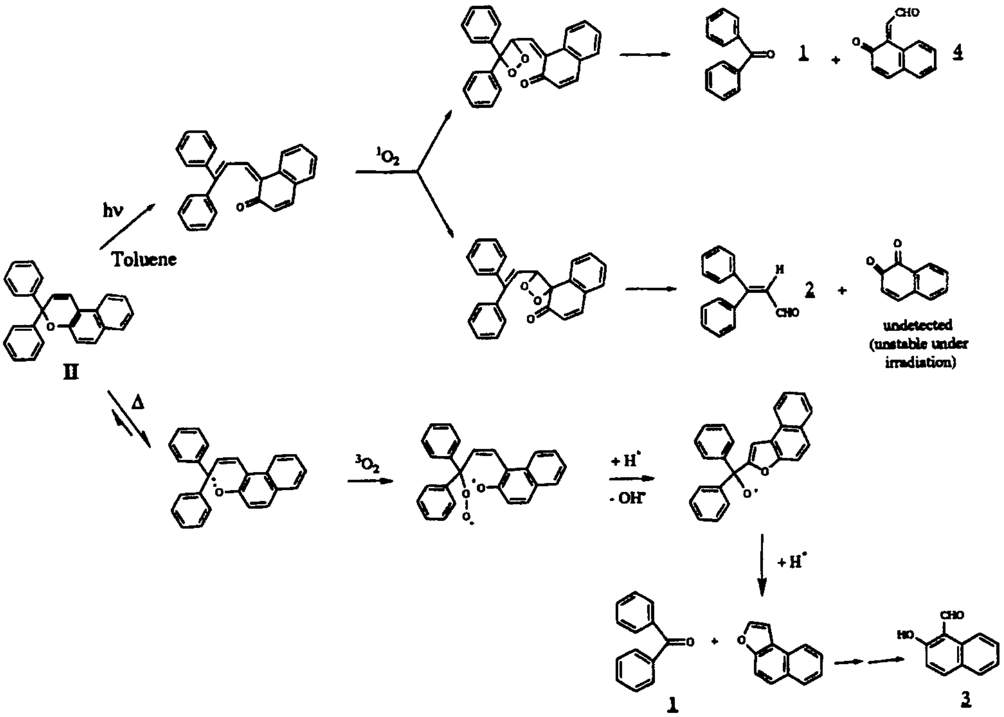


3 - Conclusion

The most striking feature emerging from the strictly examination of the photodegradation of I in toluene, is the abundance of **1** against the other photoproducts.

Thus, similarly to indolinospiropyrans, very few high molecular weight products were found and fragments (**1** and **2**) issued from the left diarylic part of the molecule are the most abundant. These results confirmed that similar oxidation processes take place for the two series. These mechanisms (Scheme 3) of photodegradation involve[9] singlet oxygen attack on the double bonds of the open forms giving dioxetan as intermediates or take place via the reaction of molecular oxygen with radical species. As found for indolinospirooxazines, different protective agents as the hindered amine light stabilizers and singlet oxygen quenchers should be able to improve the fatigue resistance of [2H]-chromenes.

Scheme 3 Possible mechanisms for the formation of the main photoproducts



4 - Experimental part

4.1 - Photodegradation experiments

The photochromic compound I[15] (C = 5 x 10^{-4} M.l^{-1}) was dissolved in anhydrous toluene (SDS France). The aerated solutions were irradiated in a quartz flask with magnetic stirring with a 500 W high pressure mercury lamp HBO Osram housed in a light box (Arquantiel, Ile St Denis, France). The solution irradiated was regularly analyzed by gas chromatography till the complete bleaching of the solutions (2 days).

4.2 - Photoproducts analyses

The gas chromatography system (GC) consisted of a Girdel equipped with a Ross injector, a FID detector and a column SGE 0,32mm * 12 m capillary column (SGE Corp.) coated with BP5 (film 0,5 µm, pHe = 0,9 bar). The high performance liquid separations were carried out with a Beckman HPLC Gold system coupled with a 168 UV-visible diode array detector to allow screening for peak purity and peak comparison. The column consisted of a reversed phase Zorbax Rx C8 25 cm * 4,6 mm 5 µm. The separations were performed with a mobile phase : CH_3CN/H_2O 30/70 for 5 min, then 100 % of CH_3CN with 40 min. The flow rate was fixed at 1 mL.min^{-1} system.

Mass spectra were obtained with an HP 5985 spectrometer under electronic impact mode (EI) (70 eV) and positive chemical ionisation mode (CI+) with methane (150 eV). Benzophenone **1**, β-phenylcinnemaldehyde **2** and 2-hydroxy-1-naphthaldehyde **3** were commercially available (Aldrich).

Acknowledgements :
The authors thank the French "Ministère de l'Enseignement Supérieur et de la Recherche" and Transitions Optical Inc. for financial support of this work.

References

1 H. Dürr and H. Bouas-Laurent (Eds.), *"Photochromism Molecules and Systems"*, Elsevier, Amsterdam, (1990).
2 R. Gautron, *Bull. Soc. Chim. Fr.*, 8, 3200-3204(1968).
3 R. Gautron, Thèse en Sciences, Strasbourg, (1967).
4. G. Baillet, G. Giusti, R. Guglielmetti, *J. Photochem. Photobiol. A : Chem.*, 70, 157-161(1993); G. Baillet, M. Campredon, R. Guglielmetti, G. Giusti, C. Aubert,*J. Photochem. Photobiol. A : Chem.*, 83, 147-151(1994).

5 T. Yoshida and A. Morinaka, *J. Photochem. Photobiol. A: Chem.*, 63, 227-234(1992).
6. R. Becker, J. Michl, *J. Am. Chem. Soc.*, 88, 5931(1966); R. Becker, *USP 3, 567, 605*, (1971).
7. B. V. Gemert, M. P. Bergomi, *US 5, 066, 818* (1991); B. V. Gemert, M. P. Bergomi, *Mol. Cryst. Liq. Cryst.*, 246, 67-73(1994).
8.C. Salemi, G. Giusti, R. Guglielmetti, *J. Photochem. Photobiol. A : Chem.*, 86, 247-252(1995).
9.C. Salemi-Delvaux, B. Luccioni-Houzé, G. Baillet, G. Giusti, R. Guglielmetti, *Tet. Lett.*, 37(29), 5127-5130(199).
10 D. Eloy, P. Escaffre, R. Gautron and P. Jardon, *Bull. Soc. Chim. Belg.*, 101(9), 779-790(1992).
11 A.A. Firth, D. J. McGarvey and T. G. Truscott, *Mol. Cryst. Liq. Cryst.*, 246, 295-298(1994).
12 A. A. Frimer, *Chem. Rev.*, 79, 359-387(1979).
13 A. M. Braun, M. T. Maurette and E. Oliveros (Eds.), Technologie photochimique, chap.11, (1986).
14. M. Campredon, A. Samat, R. Guglielmetti, A. Alberti, *Gazz. Chim. Ital.*, 123, 261-264(1993).
15. H. G. Heller, S. N. Olivier, J. Whittall, I. Tomlisen, *USP 4,826, 977*, (1989).