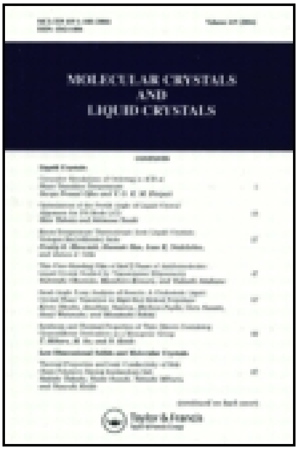


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Oxidative degradation of organic photochromes

Vincenzo Malatesta [a] , Mario Milosa [a] , Roberto Millini [b] , Luigi Lanzini [b] , Piero Bortolus [c] & Sandra Monti [c]

[a] Enichem Synthesis, via Maritano 26, San Donate Milanese (MI), 20097 (I)

[b] EniRicerche, via Maritano 26, San Donato Milanese (MI), 20097 (I)

[c] Istituto FRAE-CNR, via de' Castagnoli 1, Bologna (I)

Version of record first published: 24 Sep 2006.

To cite this article: Vincenzo Malatesta , Mario Milosa , Roberto Millini , Luigi Lanzini , Piero Bortolus & Sandra Monti (1994): Oxidative degradation of organic photochromes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 303-310

To link to this article: http://dx.doi.org/10.1080/10587259408037833

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 303–310
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

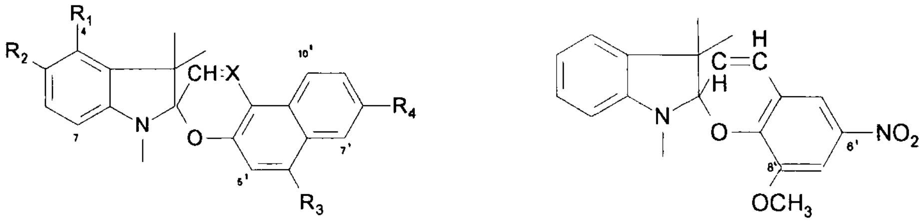
OXIDATIVE DEGRADATION OF ORGANIC PHOTOCHROMES

VINCENZO MALATESTA, MARIO MILOSA
EniChem Synthesis, via Maritano 26, San Donato Milanese (MI) 20097 (I)
ROBERTO MILLINI, LUIGI LANZINI
EniRicerche, via Maritano 26, San Donato Milanese (MI) 20097 (I)
PIERO BORTOLUS, SANDRA MONTI
Istituto FRAE-CNR, via de' Castagnoli 1, Bologna (I)

Abstract. Photo-oxidation of some representative spiropyrans and spiro-oxazines does not seem to involve singlet oxygen O_2 ($^1\Delta g$). The photochromes rather behave, in the spiro and merocyanine form, as O_2 ($^1\Delta g$) quenchers. Only a methoxy-nitro benzopyran derivative was found to promote formation of singlet oxygen. Superoxide anion $O_2^{\bar{\cdot}}$ is likely the activated oxygen species responsible for their oxidative photodegradation.

INTRODUCTION

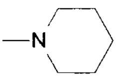
Spiropyrans, (SP), and spiro-oxazines , (SO), in solution or in polymer matrix films undergo, when exposed to UV light, a structural rearrangement from the parent colourless form to an intensely coloured merocyanine form, (MC), that in the dark thermally reverts to the starting spiro form. Repeated light-dark cycles in air result, however, in a progressive degradation of both SP and SO with a loss of photochromism. This fact severely limits their practical applications, though it has been reported that SO are endowed with a higher resistance than SP to photochemical fatigue (1). After the first study of Gautron(2) on the photodegradation of spiro[indoline-benzopyran]s in toluene solutions, Yoshida and Morinaka(3) have extended the investigation to bulk films of a spiropyran in the solid amorphous state and have shown that the decomposition was also caused by photo-oxidation. More recently Guglielmetti and coworkers(4) have compared the oxidative photodegradation of a spiro[indoline-naphthopyran], 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,2'[3H]naphth[1,2b pyran], (I), and a spiro [indoline-naphthoxazine], 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'[3H]naphth[2,1-b][1,4]oxazine], (II), SCHEME 1, in toluene solution and found that the two classes of photochromes have a somewhat different oxidative fragmentation pattern. However as no intermediate oxidation products, in which the indoline and chromene moieties were still linked together, were isolated, it was then not possible to speculate on the nature of the activated species (whether the photochrome or oxygen) that triggers the irreversible degradation. We have studied the oxidative degradation of (I), [(II)-(VI)], and (VII), 1,3-dihydro-8'-methoxy-6'-nitro-1,3,3-trimethylspiro[2H-indole-2,2'[3H]benzopyran], SCHEME 1, in different solvents and started examining also their stability towards chemical oxidation.



(I) X=CH; R_1=R_2=R_3=R_4=H

(II) X=N; R_1=R_2=R_3=R_4=H

(III) X=N; R_1=R_2=CH_3; R_3=R_4=H

(IV) X=N; R_1=R_2=R_4=H; R_3= 

(V) X=N; R_1=R_2=R_3=H; R_4= CO_2Me

(VI) X=N; R_1=R_3=R_4=H; R_2=Cl

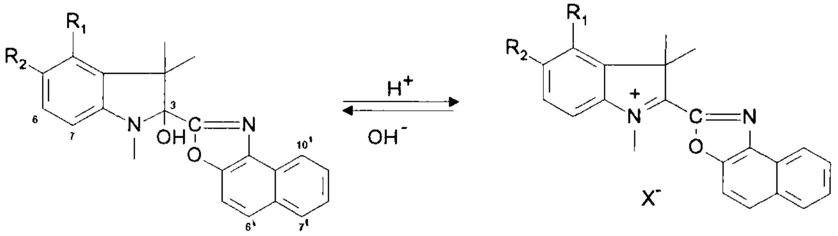
(VII)

SCHEME 1

We were able to isolate in the case of (II) and (III) a key intermediate product that allows us to suggest a preliminary likely mechanism for the interaction between photochromes and oxygen that results in their oxidative photodegradation.

RESULTS AND DISCUSSION

When aerated acetonitrile (ACN) solutions (10^{-3} M) of (II) and (III) were exposed to either sunlight or a 1 kW high pressure Xenon lamp, the formation of a compound absorbing at λ_{max} = 367 nm and having a bluish fluorescence (λ_{exc} = 350 nm; λ_{em} = 429 nm in ACN) could be monitored. If the solution, in a 1 cm path cuvette, had previously been de-aerated on a high-vacuum line (six freeze-pump-thaw cycles), sealed and then irradiated, no apparent photodecomposition of the spiro-oxazine was noticed. In irradiated air saturated toluene solutions the compound absorbing at 367 nm was not detected although the spiro-oxazines underwent extensive degradation. Similar behaviour was shown by compounds (V) and (VI). The addition of acids (HCl, H_3PO_4, etc.) to the oxidized ACN solution of (II) and (III) resulted in the development of a bright yellow colour (λ_{max} = 464 nm) with a greenish fluorescence (λ_{exc} = 430 nm; λ_{em} = 543 nm), which disappeared by neutralization of the solution while the 367 nm absorption was restored. The yellow colour formed also when aerated and acidified ACN solutions of (II) and (III) were exposed to UV light. The same behaviour was observed in ethanol. Irradiation of aerated toluene solutions of (I) or (VII) yielded extensive degradation. The intermediate formed during the photoxidation of (II) and (III) in ACN was shown, by X-Ray analysis (see experimental part), to have the following structure (VIII):



R_1=R_2=H (VIII)a R_1=R_2=H (IX)a

R_1=R_2=CH_3 (VIII)b R_1=R_2=CH_3 (IX)b

SCHEME 2

Acidification of the ACN solution of (VIII) gave the yellow compound (IX), SCHEME 2. Extensive photolysis of ACN or toluene solutions of (I)-(III) and (VII) yielded a mixture of compounds that in the case of spiro-oxazines were essentially 1,3,3-trimethyloxindole (X), 3,3-dimethyloxindole (XI), 1,2,3,4-tetrahydro-2,3-dioxo-4,4-dimethylquinoline (XII) and naphth[1,2-d]oxazole (XIII), as already reported by Guglielmetti (4). In the case of spiropyrans, besides (X)-(XII) the corresponding 2-hydroxy-1-naphthaldehyde (XIV) or 5-nitrovanillin (XV) were formed.

In principle the (photo) oxidation products could be formed by either the reaction of the photochrome with an activated form of molecular oxygen produced through the sensitizing action of the photochrome itself or via the interaction of an excited state of the latter with ground state molecular oxygen. We have therefore looked for the generation of excited-state singlet oxygen O_2 ($^1\Delta g$) sensitized by either the spiro or the merocyanine form of both the spiropyrans and spiro-oxazines included in this study. To this end we monitored the luminescence eimitted at 1269 nm by O_2 ($^1\Delta g$) from the forbidden transition

$$O_2\,(^1\Delta g) \xrightarrow{\qquad} O_2\,(^3\Sigma g) + h\nu\ (1269\ \text{nm}) \qquad (1)$$

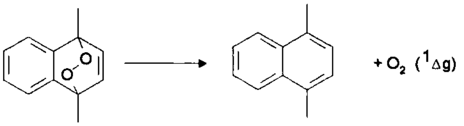
by a time resolved technique. Air-equilibrated methylene chloride solutions of the two classes of photochromes were excited with a frequency tripled Nd-YAG laser (355 nm) and the emission at 1269 nm was monitored by using a germanium photo-diode with a set-up already described (5). No singlet oxygen formation could be detected in the case of (I)-(V), ruling out a sensitizing ability of the closed forms, the only notable exception being (VII) for which a singlet oxygen quantum yield Φ_Δ = 0.19 was estimated. In two-colour experiments in which the spiro and merocyanine forms of (I)-(VII) were irradiated at 355 nm and 532 nm respectively, no O_2 ($^1\Delta g$) formed. This fact indicates that most probably the (photo)merocyanine does not participate in the sensitizing process.

Having assessed that the spiropyrans and the spiro-oxazines studied (except for (VII)) are devoid of sensitizing properties, we probed their performance as quenchers of O_2 ($^1\Delta g$) produced by irradiation, at 532 nm, of CH_2Cl_2 solutions of a known sensitizer, e.g. methylene blue (MB), for which a $\Phi_\Delta = 0.57$ has been reported $^{(6)}$. The addition of either spiropyrans or spiro-oxazines at different concentrations to the MB solutions (10^{-4} M) resulted in the shortening of the O_2 ($^1\Delta g$) luminescence lifetimes. The measured bimolecular rate constants, kq, are collected in Table 1.

Table 1 - Singlet oxygen O_2 ($^1\Delta g$) quenching rate constants in methylene chloride at 25°C

PHOTOCHROME	kq (M^{-1} s^{-1})
(I)	$(9.4 \pm 0.5) \cdot 10^6$
(II)	$(2.1 \pm 0.5) \cdot 10^6$
(III)	$(6 \pm 2) \cdot 10^7$
(IV)	$(1.9 \pm 0.5) \cdot 10^8$
(V)	$(2.1 \pm 0.2) \cdot 10^6$
(VII)	$(1.7 \pm 0.4) \cdot 10^7$

Surprisingly (VII) is not only a moderately good sensitizer but also a good quencher of singlet oxygen. The rate constants depend somewhat on the solvent polarity (e.g. for (III) kq = 7×10^7 M^{-1} s^{-1} in ACN and 1.3×10^7 M^{-1} s^{-1} in toluene). Again the two-colour experiments allowed us to find out that the quenching properties of the spiro form did not differ appreciably from those of the corresponding merocyanine(s). When O_2 ($^1\Delta g$) was generated in the dark by thermal decomposition at 50°C of 1,4-dimethylnaphthalene endoperoxide (XVI) $^{(7)}$ in either ACN or toluene,



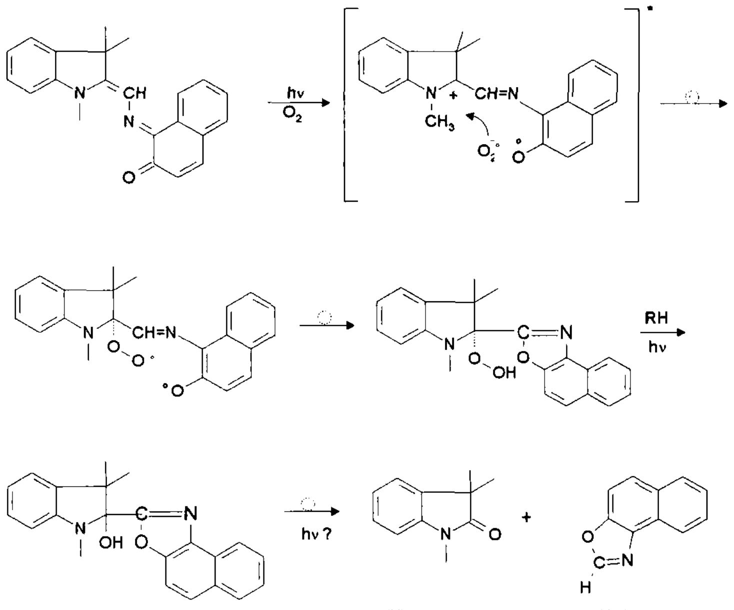
(XVI)

(2)

no apparent chemical degradation of the photochromes (photochrome/endoperoxide: 1/150) was noticed. This indicates once more that the spiro forms do not react with O_2 ($^1\Delta g$). It can be concluded that in ACN or toluene the singlet oxygen quenching by the photochromes is to a largest extent physical in nature. On the other hand the photodegradation of aerated ACN solutions of (I)-(VII) strongly indicates the involvement of an activated oxygen species, other than O_2 ($^1\Delta g$), formed following the interaction of the excited photochrome with ground state oxygen O_2 ($^3\Sigma g$). The superoxide anion $O_2^{\bullet-}$ is proposed to be the reactive species. Its formation could occur via an electron-transfer process from the excited merocyanine form to O_2 ($^3\Sigma g$). The oxidation products observed should then derive from the nucleophilic attack of $O_2^{\bullet-}$ (8) on the merocyanine radical cation. The photoassisted charge-transfer (C.T.) complex formation and reaction may be formulated as follows:

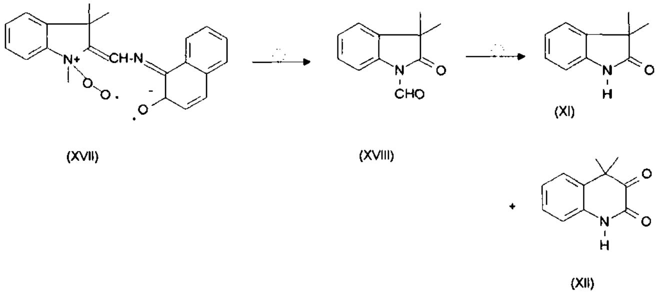
$$\text{SP (or SO)} \xrightarrow{h\nu} \text{MC} \xrightarrow{h\nu'} {}^1\text{MC} \xrightarrow{\text{ISC}} {}^3\text{MC} \xrightarrow{O_2} [\text{MC}^{\bullet+}\ O_2^{\bullet-}] \longrightarrow \text{MCO}_2$$

More specifically in the case of spiro-oxazine we may write (SCHEME 3):



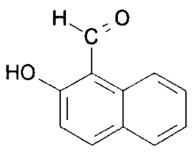
SCHEME 3

(XI) and (XII) could on the other hand form from the intermediate (XVII) that yields the observed

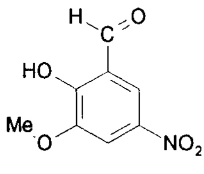


SCHEME 4

N-formyl oxindole (XVIII) that may be the precursor of (XI) and (XII), SCHEME 4. Indeed as already reported by Guglielmetti et al. (4), in control experiments the trimethyloxindole (X) does not undergo oxidative demethylation to (XI) that should be formed then from an intermediate having still the photochrome skeleton. In the case of spiropyrans we were not able to detect the formation of the naphthofuran, the analogous of (XIII) where CH has replaced N, but only the corresponding hydroxyaldehydes (XIV) and (XV).

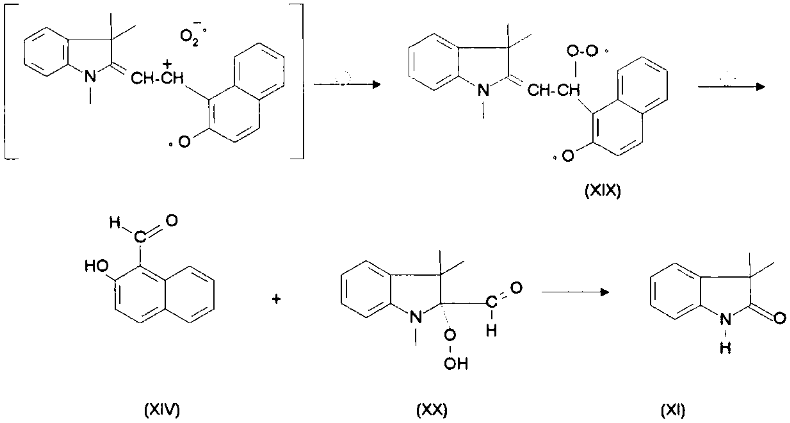


(XIV)



(XV)

Furthermore we have no evidence that the analogous of (VIII) is formed. If we suppose that the oxidizing species is still $\overline{O_2}$ then the different fragmentation pattern through which (XIV) and (XV) are formed in the spiropyrans requires that $\overline{O_2}$ attacks, within the C.T. complex, at a different position which is more electrophilic than the former spiro carbon atom. A likely candidate is the benzylic carbon atom for which the corresponding (pseudo)carbocation is stabilized by the naphthyl or phenyl groups, SCHEME 5.



SCHEME 5

According to SCHEME 3 and 4 in the case of spiro-oxazines the major products should be (as found experimentally) (XIII) and (X), but the consistent presence of (XII) and (XI) suggests that the attack on the indoline N is equally probable. For spiropyrans the products distribution ((XI) and (XIV) major products, (X) and (XII) in very low concentration) seems to support the attack of $O_2^{\bar{\cdot}}$ at a position remote from the indoline N atom, SCHEME 5.

It is not immediately clear the reason why the merocyanines behave as quenchers rather than sensitizers of singlet oxygen formation. It has been reported that azomethine dyes (9) are very poor sensitizers of O_2 ($^1\Delta g$) because their excitation energy is most likely dissipated by rotation about the $>C = N-$ double bond. Their efficiency in quenching singlet oxygen may stem from the large amount of charge-transfer in the dye/ O_2 ($^1\Delta g$) complex and /or be due to their low lying triplet states. We have calculated triplet energy values of ca. 20-24 Kcal/mol for the merocyanine forms of spiro-oxazines and spiropyrans respectively (10)

Finally we have found that (IX) is formed by treatment of ACN solutions of (II) and (III) with either $CuCl_2$ or $FeCl_3$ in the presence or absence of oxygen thus giving more support to the suggested electron-transfer process responsible for the formation of oxidized and rearranged products. The rearrangement (cyclization to oxazole) of the oxidized intermediate must be very fast as we have found from preliminary electrochemical experiments (11), carried out on the merocyanines of (II) and (III) in ACN. An oxidation wave is observed at 790 mV (vs SCE). Further studies are in progress on (IV) and other derivatives of photochromes and the results will be reported elsewhere.

EXPERIMENTAL PART

UV-VIS spectra were recorded on a HP-3520A diode array spectrophotometer, the fluorescence spectra on an Aminco Bowman S2 luminescence spectrometer. The gas chromatographic analysis was carried out on a HP-5890II cromatograph (injector at 180°C; FID at 280°C; 5m crosslinked silicon gum capillary column; temperature kept at 70°C for 3 min and then ramped at 10°C/min up to 280°C). Toluene and acetonitrile, Rudi-Pont HPLC grade, were used as received. The photochromes were synthetised in the EniChem Synthesis laboratories according to reported literature methods (1). The 10^{-3} M solutions of the photochromes in either solvents were photolysed with a 1 kW HP-Xenon lamp in a quartz reactor in which oxygen was slowly bubbled during the photolysis. The light was focussed. Alternatively air equilibrated solutions were exposed to sunlight on the roof top. The reaction progress was monitored by GC and GC/MS and the products identification was carried out on a FINNIGAN INCOS 50 mass spectrometer. When available authentic samples of the photolysis products synthesized as reported in ref. (4) were used.

^{1}H-NMR (200 MHz) ($CDCl_3$/TMS) of (VIII)b: $\delta = 7.00$ (C6-H); 6.42 (C7-H); 7.73 (C5'-H); 7.34 (C6'-H); 7.98 (C7'-H); 7.58 (C8'-H); 7.71 (C9'-H); 8.58 (C10'-H); 1.13, 1.59 (2-CH_3 at C3); 2.24 (C4-CH_3); 2.28 (C5-CH_3); 2.80 (N-CH_3); 3.88 (OH) ppm. For (IX)b (DMSO-d_6/TMS) : $\delta = 8.00$ (C6-H); 7.61 (C7-H); 8.24 (C5'-H); 8.41 (C6'-H); 8.29 (C7'-H); 7.82 (C8'-H); 7.94 (C9'-H); 8.67 (C10'-H); 2.06 (2-CH_3 at C3); 2.43 (C4-CH_3); 2.54 (C5-CH_3); 4.66 (N-CH_3) ppm.

Crystal data of (VIII)b (Figure 1) : $C_{24}H_{24}N_2O_2$,M = 372.466; monoclinic, space group C2/c; a = 11.990(2) Å, b = 31.492(8) Å, c = 12.174(2) Å; β = 112.65(2)°; V = 4242.2(16)$Å^3$; z = 8; D_{calc} = 1.1663 Mg m^{-3}; F(000) = 1584; λ = 1.54178 Å (Cu Kα); μ = 5.569 cm^{-1} (CuKα). The data were collected on a Siemens AED diffractometer at 298 K in v/2v scan and corrected for Lorentz and polarization effects. The structure was solved by direct methods. All non-H atoms were refined anisotropically, while H atom positions were calculated on geometrical ground. Refinement convergence R = 0.0635 (R_w = 0.0712); 2569 reflections observed out of 4054 unique reflections measured (I>2α(I)).

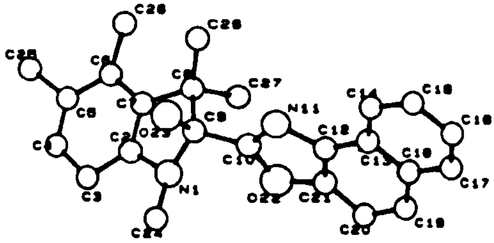


FIGURE 1 - PLUTO drawing of (VIII)b

ACKNOWLEDGEMENTS

We thank dr. W.Giroldini and dr. P.Allegrini for providing us with samples of the photochromes, Mr. E. Palmieri for the GC/MS analyses and M.U.R.S.T. for financial support.

REFERENCES

1. H.Durr and Bovas-Laurent, Eds, Photochromism: molecules and systems (Elsevier, Amsterdam, 1990).
2. R.Gautron, Bull.Soc.Chim.Fr., 8, 3190 and 3200 (1968).
3. T.Yoshida and A. Morinaka, J.Photochem.Photobiol. A, 49, 75 (1992).
4. G. Baillet, G.Giusti and R.Guglielmetti, J.Photochem.Photobiol., 70, 157 (1993).
5. P. Bortolus, S. Monti, A. Albini, E.Fasani and S. Pietra, J. Org. Chem., 54, 534 (1989).
6. F. Wilkinson, W.P. Helman and A.B. Ross, J.Phys. Chem.Ref. Data, 22(1), 113 (1993).
7. N.J. Turro, M.F.Chow and J. Rigandy, J.Am.Chem.Soc., 103, 7218 (1981).
8. D.T. Sawyer and J.S. Valentine, Acc.Chem. Res., 14, 393 (1981).
9. W.F.Smith, Jr. W.G. Herkstroeter and K.L.Eddy, J.Am. Chem.Soc., 97, 2764 (1975).
10. V. Malatesta, L.Longo, R.Fusco and G. Marconi, ISOP93, Iles des Embiez (F), 12-16 Sept., (1993).
11. V. Malatesta, to be published.