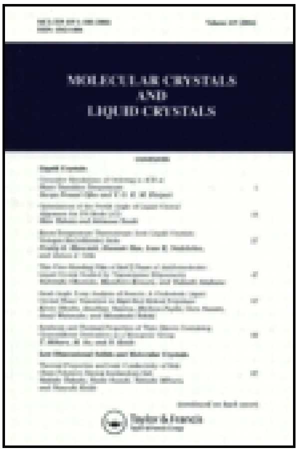

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PERFORMANCE AND MECHANISMS OF HINDERED AMINE LIGHT STABILIZER IN SPIROOXAZINE PHOTOSTABILIZATION

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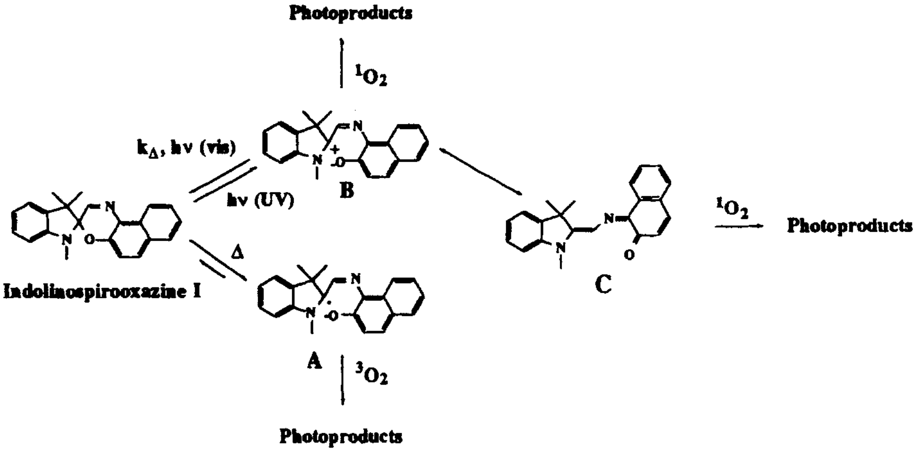
Abstract : One of the key requirements for optical switching apertures for ophtalmic, building and automobile glazing is long lived product. However, oxidation of a spirooxazine yields photoproducts such as oxindole derivatives, naphthoxazole, dihydro-2,6-quinolone and 1-N-formylimino-2-naphthoquinone devoid of photochromic activity, and limits the commercialisation of these useful systems. Achieving this long lived product can be provide by use of hindered amine light stabilizers (HALS). This paper describs the comportment of a spirooxazine irradiated in the presence of a HALS and the main stabilization mechanisms are discussed.

1 - Introduction

Photochromism of spironaphthoxazines[1] (SO) is nowadays the subject of extensive investigations owing to their higher photostability in comparison with the well-known indolinospiropyranes[2] (SP). The mechanisms of photochromism of SO is similar to SP and involves the cleavage of the C-O bond of the oxazine ring to generate highly colored isomers, photomerocyanines, which undergo ring closure to go back SO either upon heating or by irradiation with visible light (Scheme 1).

Scheme 1 : Photochromic interconversion in spiro[indoline-naphthoxazine] series



In connection with rapid development of commercial applications of these dyes, numerous studies[3-5] have been performed in order to improve photochromic properties. In this range, it has been demonstrated that photochromic parameters are strictly reliable on environment[6,7].

In a previous paper[6], we have studied the influence of acids on the fade rate. It has been shown that in toluene solutions, thermal rate constant of ring closure k_Δ increases as the concentration of acid increases. From these results, we have concluded that the colored form of unsubstituted SO has a quinonic form which can be protonated by acid and reached to a cationic charged structure more unstable in apolar solvent than the initial uncharged form.

On the other hand, data on the influence of HALS on the photochromic properties of SO are rather scarce[7] and furthermore no studies on the stabilization mechanisms of this class of antioxidant have been reported. So here, we present the results of an analytical study on the photodegradation of a spirooxazine stabilized by a HALS : decandioic acid bis-(2,2,6,6-tetramethylpiperidin-4-yl) ester (Tinuvin® 770DF).

HALS have probably been the most studied compounds in the field of polymer stabilization over the past 15 years[8]. Their excellent performance in polyolefins[9], poly(vinyl chloride)[10] and other polymers[11] has made them an attractive item for research. There have been many advances regarding the understanding of the nature of the stabilization mechanisms of these compounds, and there is still great amount of controversy particularly with regard to the relative importance of some reactive intermediates[12,13].

This paper reviews the current understanding of the mechanism of action of HALS in the specific field of photochromic compounds and its relationship with their performance in solutions.

2 - Results and Discussion

Here, we report a comparative analytical study by chromatography (GC-FID, HPLC-DAD) after irradiation using a 500W mercury lamp (HBO Osram) of a toluenic solution containing a spirooxazine and a HALS. The analysis of the main photoproducts by gas (figures 1, 3) and high pressure liquid (figures 2, 4) chromatographies reveals the presence of oxindole derivatives (1,3,3-trimethyloxindole **1**, 3,3-dimethyloxindole **2**), dihydro-2,6-quinolone **3**, naphthoxazole **4**, 1-N-formylimino-2-naphthoquinone **5** and only both high molecular weight products (FW = 312, 342 g.Mole^{-1}). These structures were confirmed by comparing retention times with synthetized or commercial standards.

Addition of Ti®770DF in the photochromic solution is characterized by an extension of the irradiation time and leads to significant changes on the evolution of photoproducts such as an enhanced production of **2**, a quasi-disparition of **4**, a significant decrease of the quantity detected for **1**, **3**, **5** and the absence of a high molecular weight product (FW = 330 g.Mole^{-1}).

In agreement with the above mentioned results, the photooxidation of SO is partly a free radical process that involves the initial production of a macroalkyl radical[14] A and its subsequent oxidation in the presence of air. The latter leads to the formation of macrohydroperorides **B**, which are themselves photolabile and thus, a potential source of free radicals. Photolysis of hydroperoxides gives rise to amides (**1**, **2**, **3**) and naphthoxazole **4**. Secondly, the attack of singlet oxygen on the ene systems of the photomerocyanines leads, after the rearrangement of dioxetan, to a amidic structure (compounds **1**) and a 1-N-formylimino derivative (compound **5**). The photooxidation processes[15-18] are summarized in scheme 2.

Scheme 2 : Multifunctional antioxidant activities of Tinuvin® 770DF in spirooxazine stabilization

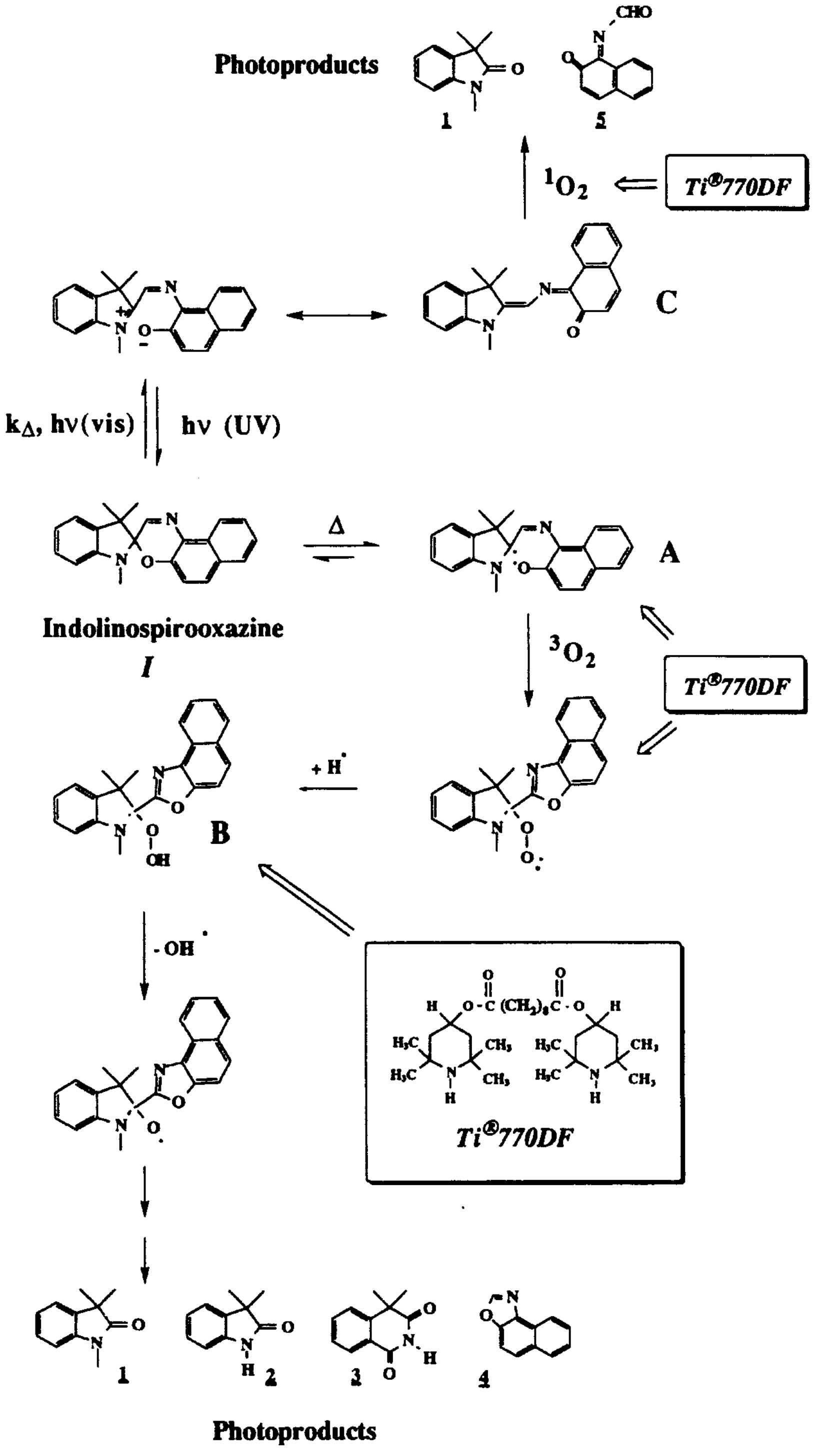


Figure 1 : Gas chromatographic separation of photoproducts of spiro[indoline-naphthoxazine] I in toluene solution (a) without or (b) with Ti®770DF. (Column SGE 0,32mm * 12 m capillary column (SGE Corp.) coated with BP5 (film 0,5 µm, pHe = 0,9 bar). T injector 280°C (Ross), T detector 300°C (FID), 90 to 300°C at 5°C min^{-1}).

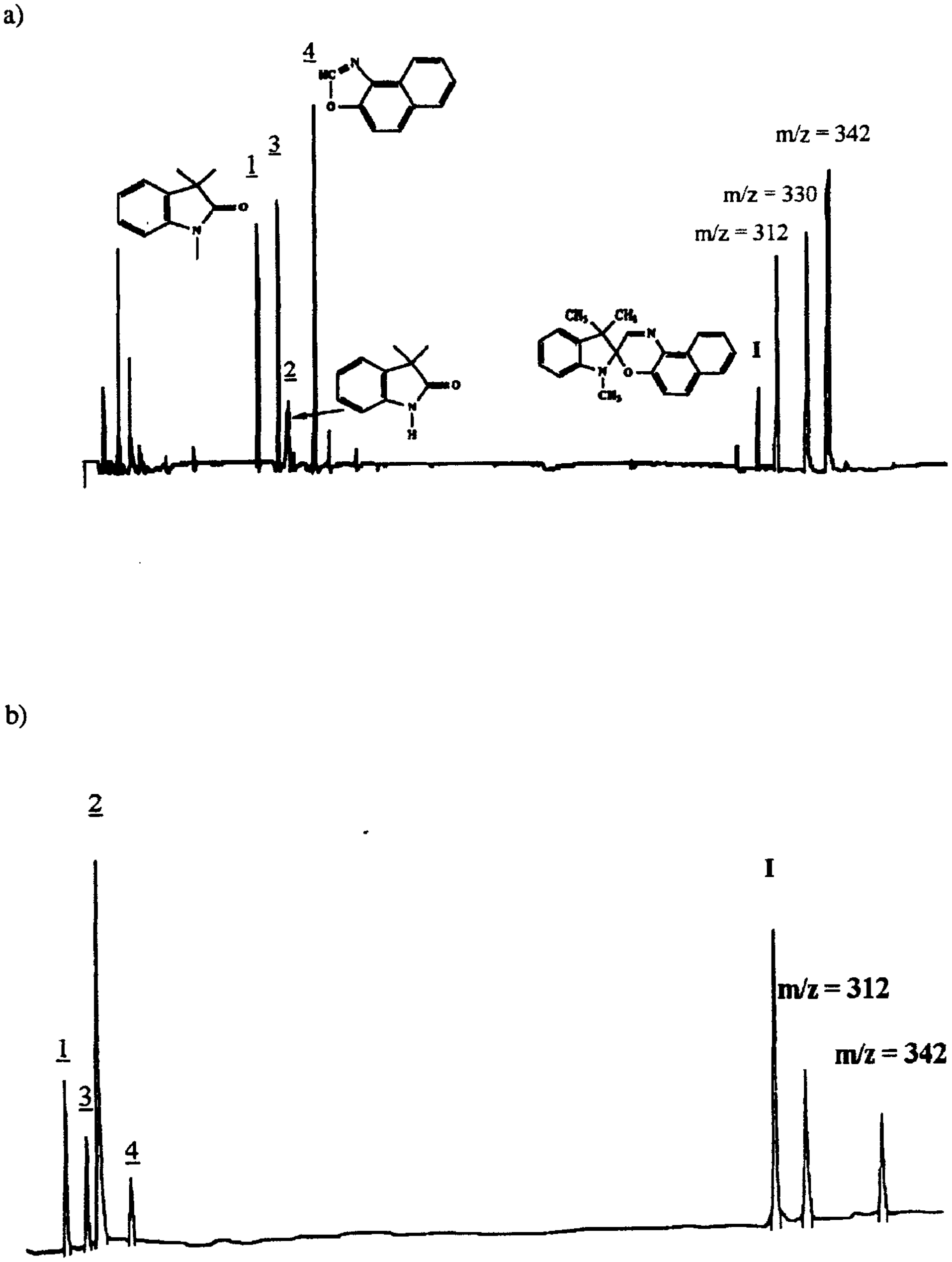


Figure 2 : Chromatographic separation (HPLC) of photoproducts issued from the degradation of spiro[indoline-naphthoxazine] I in toluene solution (a) without or (b) with Ti®770DF.

(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 $1 mL.min^{-1}$. Detection 240 ± 5 nm. Room temperature).

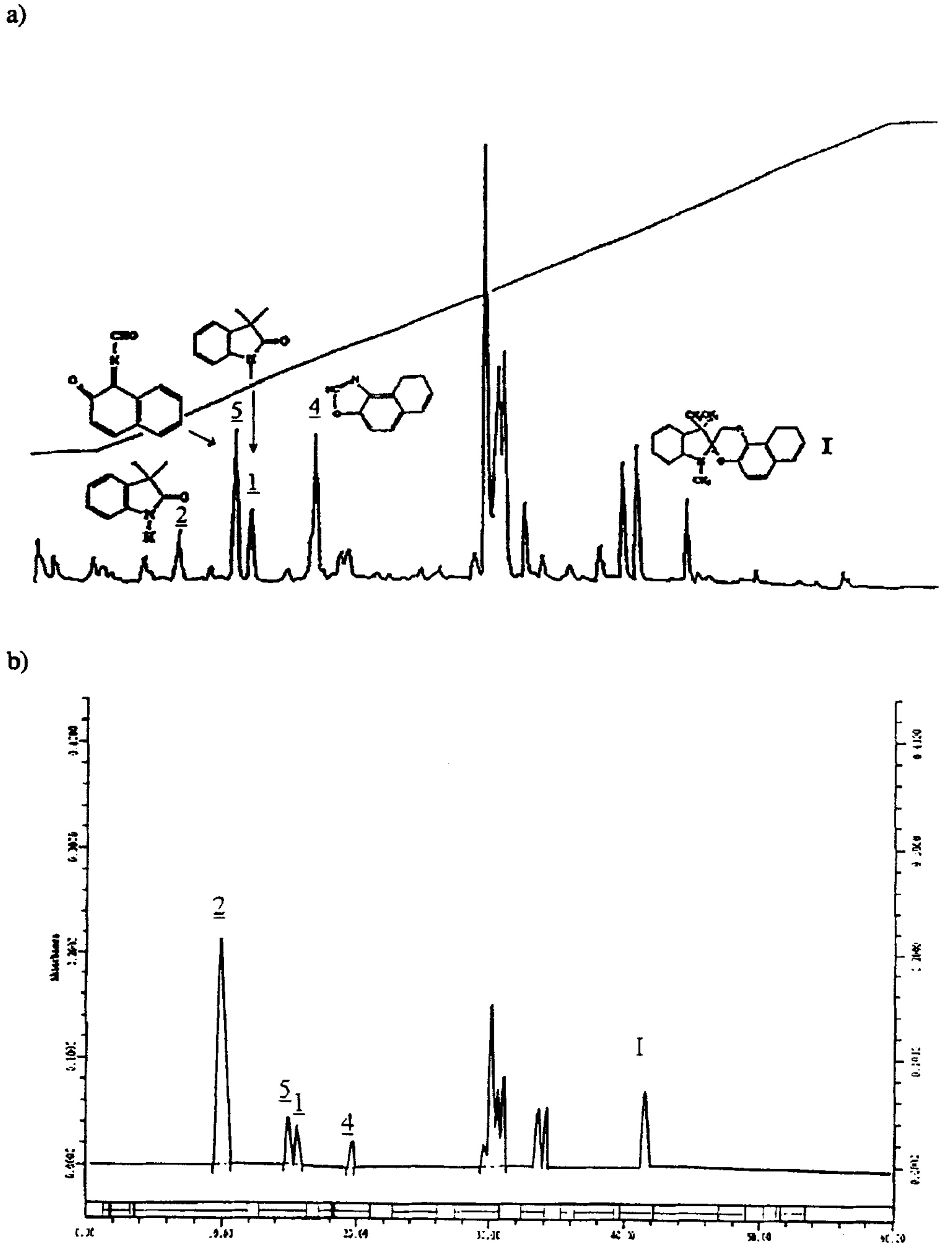
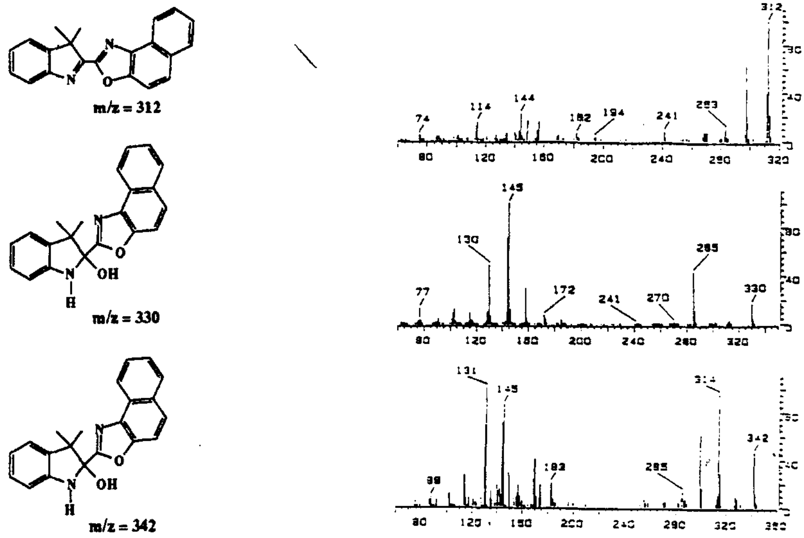


Figure 3 : Mass spectra of high molecular weight photoproducts under electronic impact (70 eV)



3 - Conclusion

By mean of fragment identification (GC/MS-LC/MS), we have shown the ability of Tinuvin® 770DF[19] to react with singlet oxygen and to act as a spin trap, an hydroperoxide decomposer towards the oxygen-centred radicals and the hydroperoxides derived from the initially formed biradical A.

These results demonstrate the multifonctional antioxidant performance of HALS in photochromic system stabilization.

4 - Experimental details

4. 1 - Materials

Compound I used in this work was prepared as described in the literature[20,21] and purity was controlled by HPLC-DAD chromatography. Toluene (SDS France, anhydrous for analysis) was used as solvent. Tinuvin® 770DF was commercially available (Ciba-Geigy). Oxindole derivatives and naphthoxazole were synthetized according to the literature[15].

4. 2 - Analytical study

All degradations were carried out using a 500 W high pressure mercury arc lamp (HBO Osram) in a quartz flask with magnetic stirring and temperature ambient conditions. The concentration of the compounds were fixed to 5×10^{-4} M for **I** and $3,3 \times 10^{-4}$M for Ti$^{\circledR}$770DF.

Separation profiles were performed with a gas chromatography system 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. This system was equipped with a reversed phase column (Zorbax Rx C8 25 cm * 4,6 mm 5 µm).

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).

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