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A Special Focus on the Photodegradation of 6′-Indolino-1-isobutyl-3,3-dimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine]

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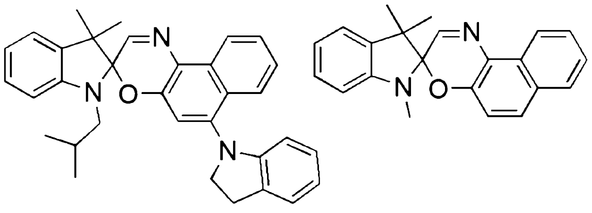
The photodegradation of 6′-indolino-1-isobutyl-3,3-dimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (**1**) following exposure to polychromatic light, was investigated in fluid solution (toluene, T) and in a solid matrix (polyurethane, PU). The photoproducts formed under irradiation were identified using HPLC and GC/MS. These included, beside the expected degradation derivatives, some new photoproducts derived from a secondary degradation pathway.

Organic photochromes are compounds that may undergo a reversible color change under the action of polychromatic light.[1,2] In early studies dating back to the late '60s, it was shown that the photodegradation of a nitrospiropyrane resulted through oxidation reactions in the formation of oxindoles and of salicylaldehyde derivatives originating from the indolinic and pyranic moieties, respectively.[3–5] Few studies followed in the '70s,[6] until in the '80s the behavior of a large number of differently condensed spiropyranes was investigated either in solution or in the solid state.[7] However, the real growth of the attention on this subject started in the '90s when the studies were extended to spiro[indoline-naphthopyranes] and spiro[indoline-naphthoxazines] both in solution[8–10] and in polymer matrices.[11]

More recently, the attention has been focused on some fluoro-2*H*-benzopyran derivatives,[12] spiro[fluorene-naphthopyrane] derivatives[13] and on degradation processes of photochromes in the presence of additives exerting an antioxidant or radical trapping activity.[14,15]

The properties of photochromic dyes are taken advantage of in a wide range of applications. While ophthalmic lenses represent by fair and large their most important end use, other major applications include children's toys, gadgets of different nature, packaging items, security markers, clothes, cosmetics as well as protective agricultural screens. 6′-Indolino-1-isobutyl-3,3-dimethylspiro[indoline-2,3′-[3*H*]-naphtho[2,1-*b*][1,4]oxazine] (**1**) (Figure 1), also known as *Palatinate Purple*, is an important member of the spiro[indoline-naphthoxazines] family due to its industrial relevance: in particular, this compound and *Berry Red* (2,2-bis(4′-methoxyphenyl)-5,6-dimethyl-2*H*-naphtho[1,2-*b*]pyran), are largely used in the production of acrylic glasses having photochromic properties. In this light and in view of the fact that after UV–vis exposure all of these materials are subject to fatigue, that is a reduction of their photochromic performance, we have endeavored in a study of the photodegradation of compound **1** in fluid solution (toluene) and in a solid matrix (polyurethane) with the aim of determining the nature of the degradation products.



1 **2**

Figure 1. Structure of the 6′-indolino-1-isobutyl-3,3-dimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]-oxazine], **1**, and of 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine], **2**.

Results and Discussion

Product Studies. A preliminary step of the degradation study consisted in determining the products derived from the photodegradation of the media where the process was taking place. Thus irradiation of pure toluene in the Atlas Suntest for 5 h, that is the time required for the complete degradation of compound **1**, resulted in the formation of several oxidation products the most abundant of which being benzylic alcohol, benzaldehyde, benzoic acid, *o*-cresol, and *p*-cresol. As for the polyurethane matrix (PU), its photostability was tested by monitoring the loss of transmission of the vibrational band at 3334 cm^{-1}, characteristic of the NH bond. After 36 h inside the Atlas Suntest, the loss of transmission only amounted to ca. 4%. No decrease of transmission at all was detected by keeping PU at 80 °C for the same time span.

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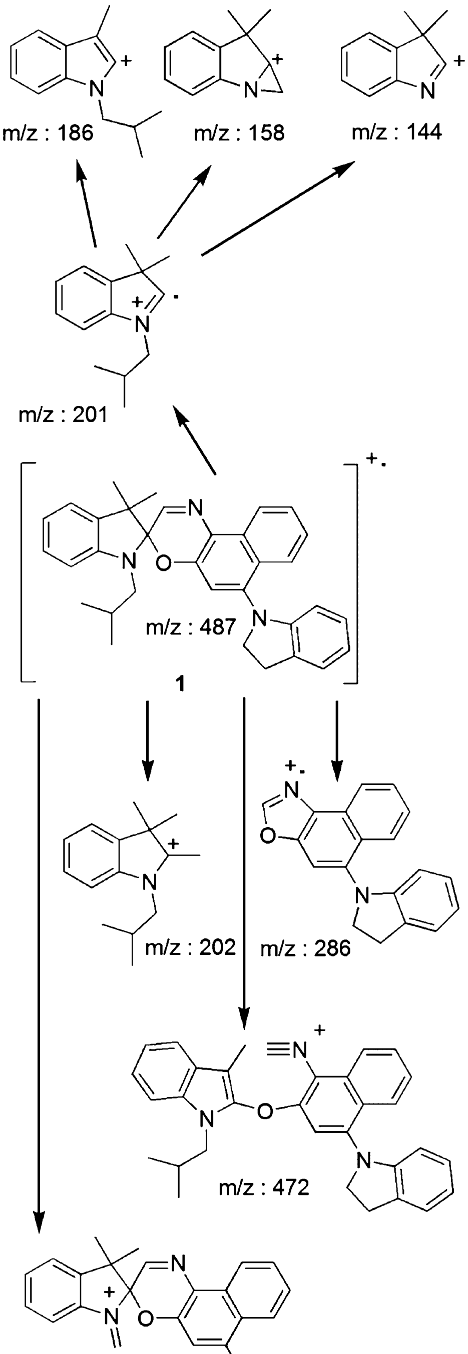


Scheme 1. Proposed fragmentation of **1** following electron impact.

The main peaks in the MS spectrum of **1** are m/z 487 ($M^{\bullet+}$, 45), 472 (26), 444 (33), 286 (71), 230 (28), 202 (43), 201 (30), 186 (15), 158 (100), and 144 (41). A fragmentation pattern accounting for these peaks is outlined in Scheme 1. Cleavage of the initially formed radical cation ($m/z = 487$) leads to fragment $m/z = 201$ which, by further loss of a methyl, propyl, or butyl residue leads to fragments $m/z = 186$, $m/z = 158$, and $m/z = 144$, respectively. Conversely, cleavage of the oxazinic ring in the initial radical cation followed by fragmentation leads to either $m/z = 202$ or $m/z = 286$.

The photodegradation of **1** resulted in a fairly large number of different products. The twelve most abundant species **P1**–**P12** were identified on the basis of their HPLC retention time and their GC retention time in addition to their mass spectra (Table 1).

With a few exceptions all the products had markedly shorter HPLC elution times with respect to **1** due to their smaller mass and/or to a greater polarity. Actually, products **P8** and **P9** have longer elution times than **1** (23.97 and 24.94 min, respectively), their main structural difference with the starting compound being the lack of the alkyl group bound to the nitrogen atom of the indolinic moiety. Two other products, **P10** and **P11**, that mainly differ from **1** due the expansion of the spiro-indolic ring, have an elution time only slightly shorter or fairly similar (22.34 and 23.16 min, respectively) than that of **1**. Finally, **P12**, a photoproduct differing from **1** only for the presence of an "external" indolic rather than indolinic moiety, had a retention time only slightly shorter than that of **1**.

The photodegradation of **1** may be envisaged to proceed through several different mechanistic pathways. A homolytic opening of the oxazinic ring with formation of a biradical has long since been proposed,[16] and indeed the formation of such biradical has been proven in a double-trapping ESR experiment in the presence of nitric oxide, whereby a 7-membered cyclic oxynitroxide was identified.[17] **P1**–**P12** are new photoproducts detected in the photodegradation of **1** in solution and polymer matrix. Scheme 2 shows a possible route to products **P1**–**P4**, based on a reaction between the biradical and triplet oxygen. The formation of **P4** analogue has been previously observed under various experimental conditions during the photodegradation of **2**.[18]

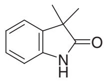
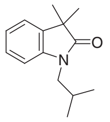
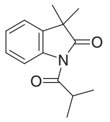
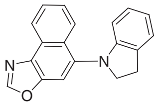
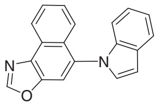
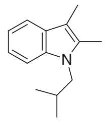
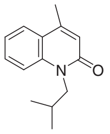
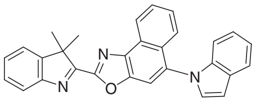
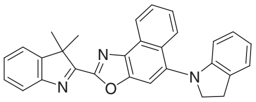
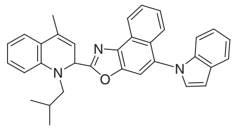
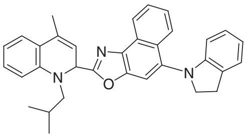
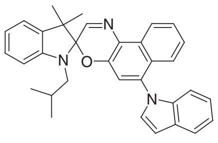
P1 has been detected in the degradation of previously investigated spiro[indoline-naphthoxazine] derivatives,[9] however, it is interesting to note its presence in the mixture of the photodegradation products of **1**. The formation of **P5** is expected to result from a secondary degradation pathway involving a photochemical aromatization of the indoline substituent of **P4** as it is presented in Scheme 3. Such reaction has already been evidenced to take place on nitroindoline derivatives by Papageorgiou and co-workers.[19]

The same type of reaction could explain the formation of **P12** starting from **1**. Photoproducts **P1**–**P7** have been identified on the basis of their HPLC retention times that were found identical to those of authentic samples previously synthesized in our laboratory or provided by our industrial partner.

A photodegradation mechanism involving a radical intermediate can also be invoked to account for the initial stage of the processes leading to higher molecular weight photoproducts.[20]

The identification of the heavier **P8**–**P12** is based on the rationalization of their MS fragmentation pattern. In this respect, we wish to point out that the pair of products **P8** and **P9**, **P10** and **P11**, **P12** and **1** exhibit the same fragmentation pattern with a two mass units difference, consistently with their proposed structures.

Table 1. Photoproducts Detected in the Photodegradation of Compound **1** after Two Hours of Irradiation in Toluene (T) and Polyurethane (PU)

Structure	Mass /g mol^{-1}	Retention time /min	T[a]	PU[a]	Code	MS most important fragments
	161	6.16	+	+	**P1**	M$^+$ = 161 (3), 117 (100), 104 (19), 90 (40), 76 (15)
	217	9.00	++++	+++	**P2**	M$^+$ = 217 (29), 174 (57), 146 (100), 130 (33)
	231	10.18	+++	+++	**P3**	M$^+$ = 231 (14), 188 (100), 160 (29), 144 (19), 130 (23)
	286	15.90	++	++++	**P4**	M$^+$ = 286 (100), 230 (15), 115 (13)
	284	15.30	++++	++	**P5**	M$^+$ = 284 (100), 228 (37), 114 (51)
	201	9.84	++	++	**P6**	M$^+$ = 201 (31), 158 (100), 143 (16), 135 (12), 115 (10)
	215	8.61	+	+	**P7**	M$^+$ = 215 (48), 200 (27), 172 (51), 159 (100), 144 (76), 115 (13)
	427	23.97	+	+	**P8**	M$^+$ = 427 (100), 412 (16), 282 (21), 228 (18), 205 (21), 144 (14)
	429	24.94	++	+	**P9**	M$^+$ = 429 (100), 414 (11), 230 (15), 207 (17), 144 (10), 91 (14)
	483	22.34	+	+	**P10**	M$^+$ = 483 (97), 468 (73), 442 (27), 338 (100), 228 (41), 200 (58), 184 (62), 144 (60)
	485	23.16	+	+	**P11**	M$^+$ = 485 (89), 470 (67), 444 (21), 340 (85), 230 (30), 200 (100), 184 (48), 144 (54)
	485	22.73	+++	+++	**P12**	M$^+$ = 485 (34), 470 (27), 442 (22), 284 (17), 228 (24), 202 (23), 201 (30), 186 (12), 158 (100), 144 (42)

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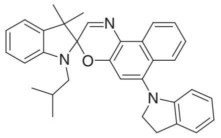
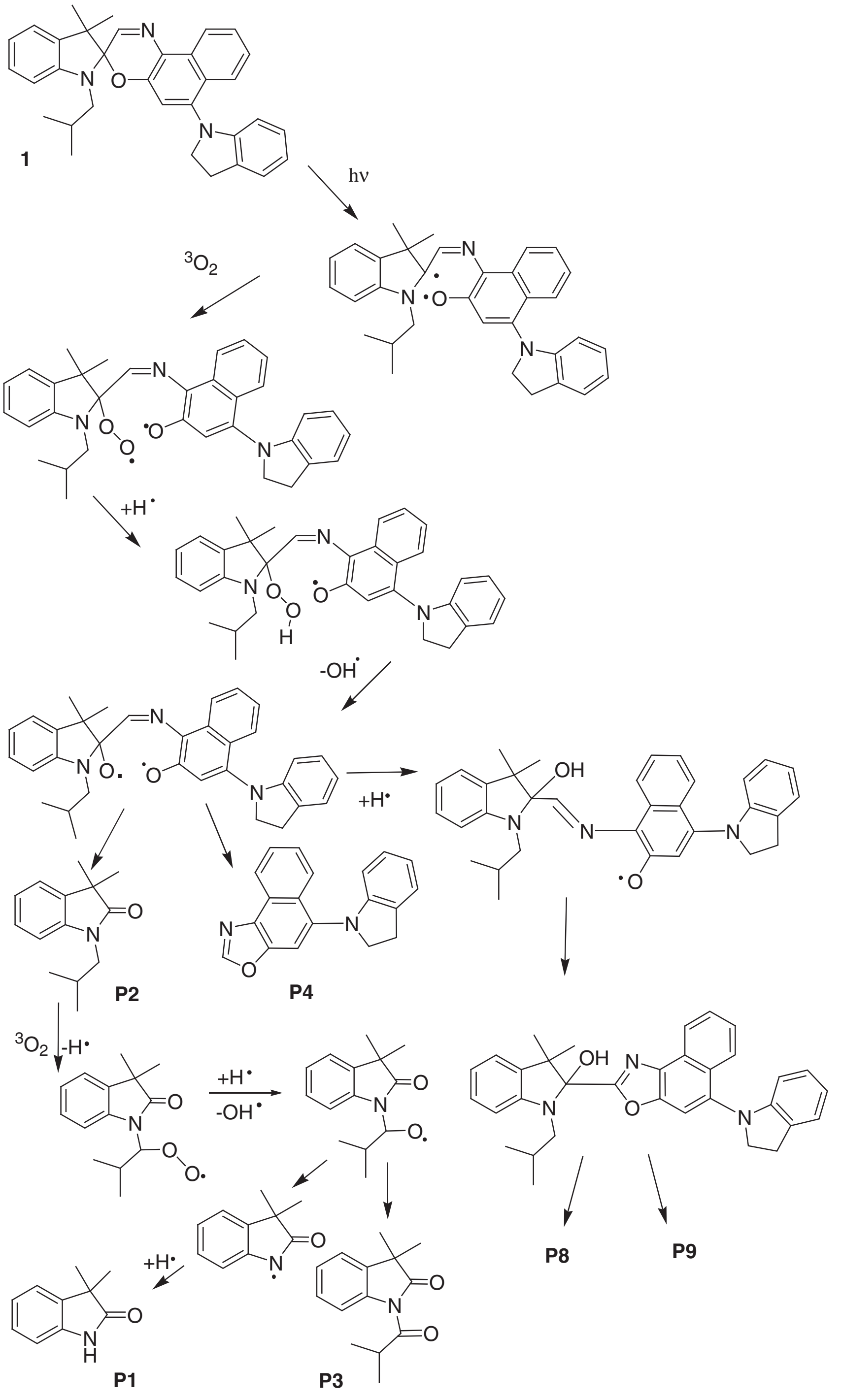
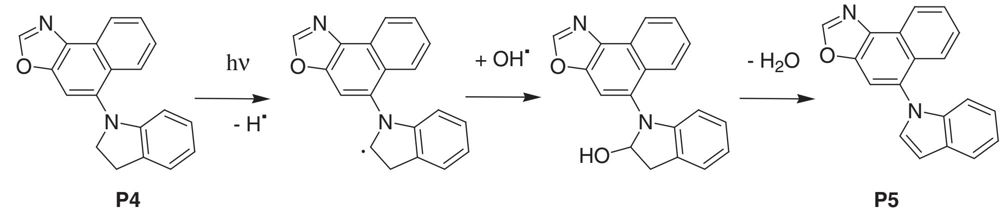
Structure	Mass /g mol^{-1}	Retention time /min	T$^{a)}$	PU$^{a)}$	Code	MS most important fragments
	487	23.47			**1**	M$^+$ = 487 (45), 472 (26), 444 (33), 286 (71), 230 (28), 202 (43), 201 (30), 186 (15), 158 (100), 144 (41)

a) +: small amount, +++: high amount.



Scheme 2. Possible degradation pathway from **1** to **P1**–**P4** and **P8**, **P9**.



Scheme 3. Possible secondary degradation pathway from **P4** to **P5**.

Experimental

Chemicals. Compound **1** was purchased from James Robinson Ltd. and recrystallized from ethanol before use. The polyester–polyurethane copolymer (poly[4,4′-methylenebis(phenyl isocyanate)-*alt*-1,4-butanediol/poly(butylene adipate)]) (Aldrich) was used to prepare polymer films. The thermal stability of the polymer matrix was checked using a Perkin-Elmer1605 FT-IR spectrophotometer. The T_g value measured using differential scanning calorimetry was −18 °C.

Photochromic polymer films were prepared mixing the dye and PU in THF that had been previously distilled in order to eliminate the BHT stabilizer. The mixture was deposited on glass plates (ORMA CR39 support) after soaking. The polymer samples were 14 µm thick and contained $2 \times 10^{-5}\,\mathrm{mol\,g^{-1}}$ (dye/polymer). Polymer films formulated without dye afforded blank samples.

Degradation Experiments. All the degradation experiments were performed in a Sun Test apparatus (Atlas) equipped with a 1500 W Xenon lamp and a 290 nm filter at 25 °C. Light intensity, as measured between 300 and 400 nm, was $80\,\mathrm{W\,m^{-2}}$. Mass spectra were obtained under electronic impact (EI 70 eV). The GC/MS (6890 HP GC system and 5973 MS detector) apparatus was equipped with a short column (0.2 µm, 12 m × 0.2 mm). The injector was heated at 255 °C. The best separation was obtained using the following temperature sequence: 5 min at 70 °C (solvent delay), increment to 310 °C ($5\,^\circ\mathrm{C\,min^{-1}}$) and then isotherm at 310 °C for 25 min.

HPLC analyses were run on a Beckman Gold system coupled with a UV–vis diode array detector. Separations were carried out using a 4.6 mm × 25 cm, C18 (5 µm) reversed-phase column with a linear gradient of ACN (acetonitrile) in deionized water from 30% to 100% during a 45 min set at the flow rate of $1\,\mathrm{mL\,min^{-1}}$.

Conclusion

We have investigated the photodegradation mechanism of 6′-indolino-1-isobutyl-3,3-dimethylspiro[indoline-2,3′-[3*H*]-naphtho[2,1-*b*][1,4]oxazine] (compound **1**) in toluene solution (T) and in a polyurethane matrix (PU).

Most of the photoproducts formed in the degradation of **1** following its prolonged irradiation indicate separation of the indolic and naphthopyranic moieties due to cleavage of both the tertiary carbon–oxygen and the tertiary-carbon–carbon bonds of the oxazinic ring, while photoproducts retaining both the indolic and naphthoxazinic reflected the cleavage of only the tertiary carbon–oxygen bond.

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