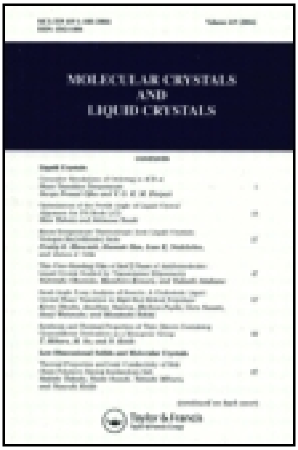

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Surface-Enhanced Raman Scattering (SERS) Studies on the Photodegradation of 3,3-diphenylnaphtho[2,1-b]pyran in Solution

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Version of record first published: 24 Sep 2006

To cite this article: F. Delepine, J. P. Bertigny, G. Levi, R. Dubest, R. Demadrille, G. Giusti, R. Guglielmetti & J. Aubard (2000): Surface-Enhanced Raman Scattering (SERS) Studies on the Photodegradation of 3,3-diphenylnaphtho[2,1-b]pyran in Solution, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 257-262

To link to this article: http://dx.doi.org/10.1080/10587250008023928

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 257-262
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Surface-Enhanced Raman Scattering (SERS) Studies on the Photodegradation of 3,3-diphenylnaphtho[2,1-b]pyran in Solution

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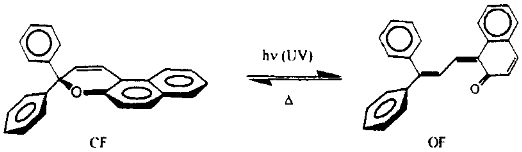
Surface-enhanced Raman scattering (SERS) was used to study the photodegradation of 3,3-diphenylnaphtho[2,1-b]pyran in acetonitrile solution. The SERS spectra obtained from long UV irradiation of photochromic solutions were compared to those of synthetic reference compounds expected in the degradation process. In order to assist the analysis of spectra, a qualitative assignment of the main SERS lines appearing during the time course of the degradation experiments was performed which allowed us to distinguish the specific spectral contributions of the different photoproducts. We were therefore able to draw hypotheses concerning the major fragments issued from the photodegradation process and to discuss the possible mechanisms for their formation.

Keywords: SERS; photodegradation; diphenylnaphthopyran

INTRODUCTION

The [2H]chromenes constitute an important class of organic photochromes which were first studied in the mid 1960's by Becker [1]. Important developments in this series were obtained by the synthesis of related derivatives, namely the diarylnaphthopyrans, which are endowed with improved photochromic properties [2]. The general photochromic equilibrium in these naphthopyrans is similar to that of spiropyrans and is shown in Scheme 1.



SCHEME 1 Photochromic equilibrium for diphenylnaphthopyran.

The increasing interest for these systems comes mainly from their new spectral features complementary to those of classical organic photochromes, spiropyrans and spirooxazines, along with high quantum efficiency of their coloration process and appropriate fading rate. Thus, coloured open forms are yellow-orange species, which have found utility in optical applications such as ophthalmic lenses, transparencies, plastic films, etc...[2]. While intense research efforts have been made in the field of applications, to our knowledge only very limited data are available concerning academic goals such as the elucidation of photochemical mechanism, the identification of short-lived species involved in the ring-opening reaction and the qualitative aspects of the photodegradation process [3].

Our recent fast absorption spectroscopic studies in solution on some of these compounds, in particular the 3,3-diphenylnaphtho[2,1-b]pyran, have allowed us to detect the short-lived species participating to the photochemical process and to propose a detailed mechanism for the ring-opening/closing reaction [4]. Moreover, in a previous paper, we have shown that surface-enhanced Raman scattering (SERS) could be used for the detection and characterisation of the main photoproducts of organic photochromes [5]. This method is used here to collect spectral data of the photofragments issued from 3,3-diphenylnaphtho[2,1-b]pyran degradation in acetonitrile solution.

EXPERIMENTAL

Synthesis and purification of compounds I to V (Figure 1) were reported previously [3,6]. For the preparation of SERS samples, a few microliters of stock solutions (*ca.* 10^{-2} to 10^{-3} M) were diluted in 500 µl of silver colloid, obtained from silver citrate (10^{-3} M in Ag), and 20 mM $NaNO_3$ were added just before recording spectra. In our experiments, the final concentrations were in the range 10^{-4}-10^{-5} M. SERS spectra of Ag sols were excited with 514.5 nm line of Ar^+ laser and recorded on a Dilor XY multichannel Raman spectrometer. In all experiments the laser power was kept low enough (*ca.* 100 mW or less) to avoid thermal decomposition of the samples. Degradation experiments were performed by UV irradiating 10^{-3} M solutions of I in acetonitrile using a focused 250 W xenon lamp (XBO Osram). Under these conditions, it was observed that the degradation process was almost complete (more than 90%) for approximately three hours exposure time. Small aliquots (a few μl), taken from the irradiated solutions at regular time intervals, were poured into 500 μl Ag colloid and their SERS spectra recorded.

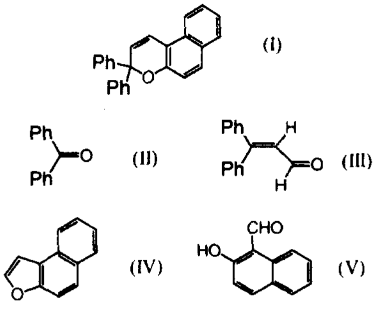


FIGURE 1 Chemical formula of 3,3-diphenylnaphtho[2,1-b]pyran photochrome (I) and the reference compounds, benzophenone (II), β-phenylcinnamaldehyde (III), naphtho[1,2]furan (IV) and 2-hydroxy-1-naphthaldehyde (V).

RESULTS AND DISCUSSION

SERS spectra of UV irradiated photochrome solutions (10^{-3} M in acetonitrile) for long exposure (from 45 min to 3 h) are shown in Figure 2 (spectra b, c and d) and compared with the spectrum of non-irradiated photochrome (spectrum a). It should be noted that UV irradiation leads to important spectral changes (intensities and positions). Thus, one can observe, in the whole spectral range investigated (800-1700 cm^{-1}), the decrease of the SERS lines typical of the closed form (CF) with the concomitant appearance of new lines. In order to assign these lines to the various species involved in the photochromic process, one must take into account that two competitive mechanisms take place, respectively photoisomerisation (leading to open forms: OF) and photodegradation. Therefore, the following experiment was undertaken.

Two different SERS samples were prepared from the same UV irradiated solution (*ca.* 2 h of extensive UV irradiation; see experimental section). The first sample was obtained by depositing immediately a few μl aliquot of the irradiated solution in the silver colloid, while the second sample was prepared from the irradiated solution after it was stored in the dark for more than half an hour. As a result of this experiment it was observed that a certain number of lines present in the SERS spectrum of the first sample at *ca.* (cm^{-1}) 910, 940, 975, 1175, 1250, 1270, 1490 and 1550 (spectrum c; Figure 2) were absent in the spectrum of the second one (not shown). This suggests that these lines originate from open forms. Moreover, in the SERS spectrum obtained from the solution where more than 90% of the starting compound was photodegradated (spectrum d; Figure 2), most of the OF lines were either absent or display very small intensities. This observation confirms that open forms are present in partially degradated solutions under our UV irradiation conditions. Although open merocyanine isomers (OF) are transient species, which revert back thermally to the closed form, it seems that once absorbed onto Ag colloid, the ring closure reaction did not further develop and the SERS spectrum was stable. Moreover, since coloured photomerocyanines are blue-purple absorbing species, they present a strong resonance Raman effect. Therefore, their detection in silver colloidal solutions with 514.5 nm laser excitation is favoured by resonant SERS (SERRS) [5], leading to the observed OF lines.

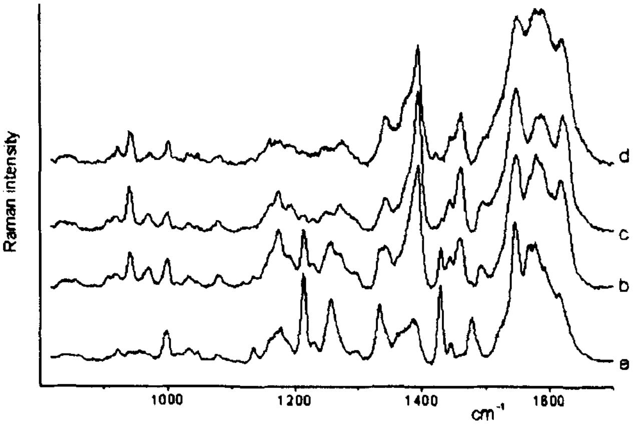


FIGURE 2 SER spectra in silver colloids of I ($3x10^{-5}M$); non-irradiated (a), after 45 min UV irradiation (b), 2h (c) and 3h (d).

Identification and assignments of the main Raman lines are summarised in Table 1. Vibrational analysis was performed using *ab initio* calculation with Gaussian 94 (HF 6-31G*).

CF	OF	II - III	IV	V	Assignment
	940				
	975				
1000		1000			v phenyl rings
1140					δ C-H naphthalene ring
				1160	v naphthalene ring + δ C-H + δ O-H
	1175				
				1190	
1214					v naphthalene ring
	1250				
1258					v naphthalene ring
	1270				
1335					v naphthalene ring
			1345	1345	v naphthalene ring
				1395	δ O=C-H + δ C-O-H
1430					v naphthalene ring
				1440	v naphthalene ring + v C-O
			1460		v naphthalene ring + v C-O
1478					v naphthalene ring
	1490				
1545					δ C-H phenyl rings
	1550				
			1580		v naphthalene ring + δ C-H furan
				1590	v naphthalene ring
				1620	v naphthalene ring

TABLE 1 SERS wavenumbers (cm^{-1}) of I and main photoproducts. CF (closed form); OF (open forms); II to V (reference compounds; Figure 1). v and δ: in plane stretching and bending.

The SERS spectrum of the almost totally degradated solution (spectrum d; Figure 2) is then expected to give structural information on the main final products resulting from the photodegradation process. Since a direct vibrational analysis of this complex SERS spectrum is difficult, only comparison with spectra of reference compounds (II to V; Figure 1) was proposed. Thus, the presence of broad lines at *ca.* (cm^{-1}) 1345, 1395, 1440, 1460, 1580, 1590 and 1620 is typical of compounds IV and V [5], while the observation of a remaining line at *ca.* 1000 cm^{-1}, arising from phenyl ring vibrations, indicates the presence of either compound II or III, or a mixture of both.

Although very rough, this analysis establishes that photodegradated solutions of diphenylnaphthopyran contain a mixture of products originating from diphenyl and naphthopyran moieties. However, quantitative analysis is difficult since SERS effect is more efficient for largely delocalised π-electron systems than for less conjugated molecules. Thus, although SERS spectra of the reference compounds were recorded under the same experimental conditions and line intensities measured with respect to acetonitrile line at *ca.* 920 cm^{-1}, used as an internal standard, it appeared that the SERS spectrum of compound V is five times more intense than that of compound IV and ten times than spectra of II and III (spectra not shown).

CONCLUSION

Ag colloidal SERS experiments on the photodegradation of the 3,3-diphenylnaphtho[2,1-b]pyran seems to indicate that this process leads to photoproducts II to V (Figure 1). Since SERS is a highly sensitive method with molecular specificity, we were able in the present study to detect traces of these species but we failed to estimate their proportion in the mixture. Moreover, the detection of naphtho[1,2]furan, which had not been found in previous analytical degradation studies of diarylnaphthopyrans [3] and indolinospironaphthopyrans [7] reveals that the degradation mechanism is different between acetonitrile and toluene solvents.

Since the detected products are clearly oxidised species, different hypotheses for the oxidation mechanisms must be considered. One possible mechanism involves singlet oxygen attack on the double bonds of the open form (see Scheme 1). Although it was postulated that neither closed nor open forms are in general able to sensitise formation of singlet oxygen, this oxidative pathway has to be taken into account since it leads to the formation of the main observed photoproducts. Another proposed mechanism involves the reaction of molecular oxygen with biradical species induced during the C-O bond cleavage. This is the sole possible oxidation process which could explain the formation of the naphthofuran (product IV) and it was suggested that this derivative could be an intermediate for the formation of the photoproduct V.

Finally, this work complements previous studies and indicates that the photodegradation of the 3,3-diphenylnaphtho[2,1-b]pyran in acetonitrile is governed by competitive oxidation reactions.

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