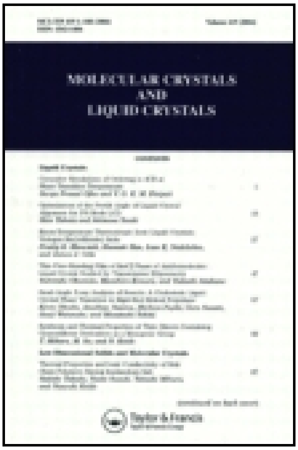

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SERS Study of 3,3-Diphenyl-naphtho[2,1-b]pyran: Another Evidence for Allenyl-Naphthol Involvement in the Photochromic Mechanism

F. Maurel [a] , S. Lau Troung [a] , J. P. Bertigny [a] , R. Dubest [a] , G. Lévi [a] , J. Aubard [a] , S. Delbaere [b] & G. Vermeersch [b]

[a] Université Denis Diderot, ITODYS, Paris, France

[b] Université de Lille 2, Laboratoire de Physique, Faculté des Sciences Pharmaceutiques et Biologiques, Lille-Cedex, France

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SERS Study of 3,3-Diphenyl-naphtho[2,1-b]pyran: Another Evidence for Allenyl-Naphthol Involvement in the Photochromic Mechanism

F. Maurel
S. Lau Troung
J. P. Bertigny
R. Dubest
G. Lévi
J. Aubard
Université Denis Diderot, ITODYS, Paris, France

S. Delbaere
G. Vermeersch
Université de Lille 2, Laboratoire de Physique,
Faculté des Sciences Pharmaceutiques et Biologiques,
Lille-Cedex, France

Surface-enhanced Raman scattering (SERS) was used to study the photochromic behaviour of 3,3-diphenyl-naphtho[2,1-b]pyran in acetonitrile solutions at room temperature. Analysis of SERS spectra of irradiated solutions (UV, UV + visible) has allowed us to separate the spectral contribution of the different photoproducts involved during the photochemical reaction and during thermal relaxation. These experiments demonstrate that, under successive UV and visible irradiation, a new species A is accumulated and then relaxes to the initial closed form (CF), via the TC photomerocyanine isomer. The SERS spectrum of A displays several analogies with the spectrum of CF and this indicates that the structure of A is near to the closed form, with no conjugation between phenyls and naphthalene moiety. On the basis of similar recent NMR experiments, it is suggested that A could be an allenyl-naphthol derivative.

Keywords: allene intermediate; 3,3-diphenyl-naphtho[2,1-b]pyran; SERS

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Address correspondence to J. Aubard, Université Denis Diderot-Paris 7, ITODYS, UMR CNRS 7086, 1 rue Guy de la Brosse 75005 Paris, France. E-mail: aubard@paris7.jussieu.fr

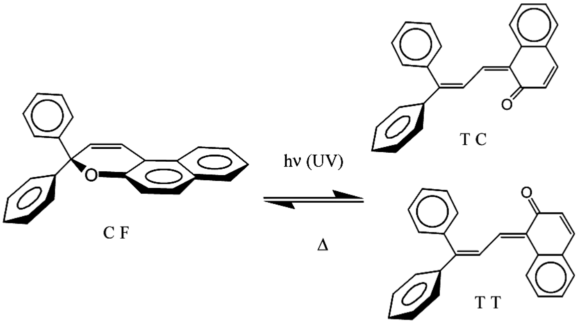
INTRODUCTION

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]. In this series, the photochromism of 3,3-diphenylnaphtho[2,1-b]pyran (Scheme 1) was the subject of a renewed interest [3–5]. Thus, very recent NMR studies, performed in polar solvents at quite high concentration and low temperature, have provided new insight on the photochromic mechanism of this compound. From these experiments, it was proved that an intermediate of allenyl-naphthol type is involved in the photochromic reaction [5]. However, in the ordinary conditions that prevail in optical spectroscopies, *i.e.* diluted solutions, room temperature, low light irradiation…, such an intermediate has never been detected probably because of the poor sensitivity of these techniques.

In previous papers, we have shown that surface-enhanced Raman scattering (SERS) could be used for the detection and characterisation of the main photoproducts in organic photochromism, even at the level of traces [6]. In this contribution, we report SERS spectra of 3,3-diphenylnaphtho[2,1-b]pyran obtained after UV and visible irradiation of acetonitrile solutions at room temperature.

EXPERIMENTAL SECTION

Synthesis and purification of 3,3-diphenylnaphtho[2,1-b]pyran (Scheme 1) was reported previously [2]. Photochrome stock solutions



SCHEME 1 Schematic representation of 3,3-diphenylnaphtho[2,1-b]pyran photochromic reaction. CF (closed form); TC and TT are the most stable trans photomerocyanine isomers.

(10^{-4} M in acetonitrile) were prepared and stored in the dark to prevent day light degradation. For the preparation of SERS samples, small aliquots of the photochrome solution were diluted in 500 µl of silver colloid, obtained from silver citrate (10^{-3} M in Ag), and 40 mM $NaNO_3$ were added just before recording spectra. SERS spectra were excited with the 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.* 60 mW or less) to avoid thermal decomposition of the samples.

UV and visible irradiation experiments were carried out in 1 cm quartz cuvette, filled with 3 ml stock solution, using a collimated beam from a 250 W xenon lamp (XBO Osram) equipped with appropriate filters (Schott WG 295 for UV irradiation and Schott GG 400 for visible irradiation). Under these conditions, a short UV exposure (max. 20 s) ensured that degradation was negligible. Small aliquots (50 µl), taken at the end of the irradiation and at regular time intervals, were poured into 500 µl Ag colloid and their SERS spectra recorded.

RESULTS AND DISCUSSION

Two different experiments were undertaken. In the first one, photochromic solution was UV irradiated ($\lambda > 300$ nm) and SERS spectra were recorded as a function of time. In the second experiment, the solution was irradiated successively with UV and visible irradiation ($\lambda > 400$ nm) and SERS spectra were recorded at the end of the visible irradiation.

SERS Analysis of UV Irradiated Solutions

SERS spectra of a UV irradiated photochrome solution (10^{-4} M in acetonitrile), recorded at the end of the irradiation (20 s duration) and then at regular intervals up to 30 s, are shown in Figure 1 (spectra b, c and d) and compared with the SERS spectrum of the non-irradiated solution (spectrum a), prepared and stored in the dark. It should be noted that UV irradiation leads to important spectral changes (line intensities and positions).

Thus, one can notice, in spectra b, c and d, the absence of the main SERS lines typical of the closed form (CF); these lines are observed in spectrum a, at *ca.* 1360, 1380, 1500, 1570, 1600 and 1640 cm^{-1} and assigned to "in plane" ring vibrations (ν and δ) of the naphthopyran moiety in the closed form [6]. The very intense Raman lines observed in the spectra of irradiated solution can thus be attributed to open

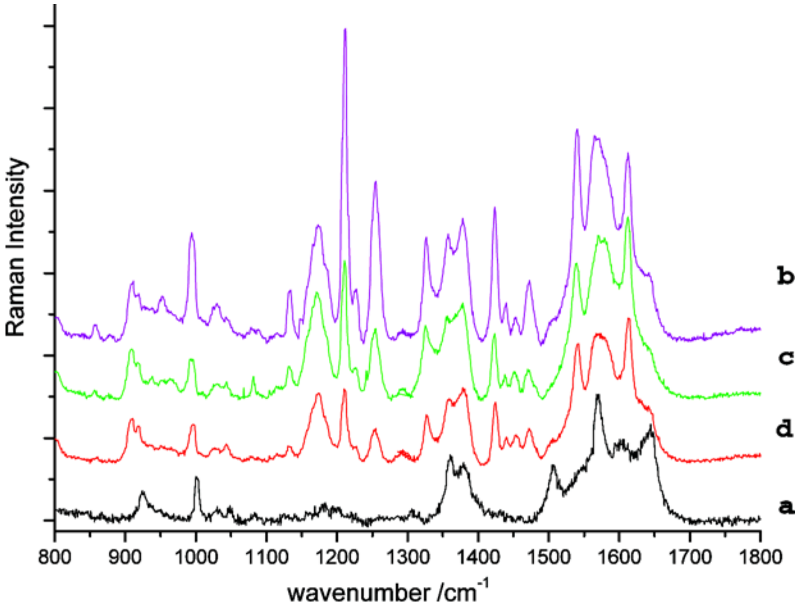


FIGURE 1 SERS spectra in silver colloids of 3,3-diphenyl-naphtho[2,1-b]-pyran (10^{-5} M); (a) spectrum of non-irradiated solution; (b, c and d) spectra taken at 0 s, 15 s and 30 s respectively, after the end of 20 s UV irradiation.

forms (OF). Indeed, in our experimental conditions, there is no noticeable photodegradation (*vide supra*) and the evolution of SERS spectra can only be attributed to UV induced photoisomerisation process, leading to photomerocyanines isomers (Scheme 1). Since photomerocyanines are blue-purple absorbing species, they display resonance SERS (SERRS) under laser excitation at 514.5 nm; their detection in silver colloidal solutions is thus favoured with respect to the non resonant closed form [6]. After the end of the UV irradiation, the decrease in Raman intensities observed on spectra recorded at 0, 15 and 30 s (Fig. 1, spectra b, c and d) points out that back thermal relaxation takes place. Finally, when kept in the dark for more than 30 min, the UV irradiated solution displayed a SERS spectrum identical to the spectrum of CF. Assignment of the Raman lines was performed by Density Functional Theory (DFT) calculations (BP86/6-31G(d)); details of this vibrational analysis will be given elsewhere. Briefly, concerning SERS spectra of UV irradiated solution, this analysis indicates that all the main Raman lines observed in the spectral range 800–1800 cm^{-1} can be assigned to a mixture of TC and TT trans photomerocyanine isomers with a large excess in TC.

SERS Analysis of Solutions Under Successive UV and Visible Irradiation

A fresh solution of 3,3-diphenyl-naphtho[2,1-b]pyran was UV irradiated for 20 s then to visible light ($\lambda > 400\,\mathrm{nm}$) for also 20 s. SERS spectra were recorded at the end of the visible irradiation and at regular intervals. Evolution of SERS spectra is depicted in Figure 2. Important differences are observed between the spectra. Thus, the spectrum 2b, recorded at the end of visible irradiation, displays several analogies with the spectrum of the closed form (spectrum 2a); indeed, the lines at 1360/1380 cm^{-1} and 1500/1570/1640 cm^{-1}, typical of the SERS spectrum of CF, are clearly evident in spectrum 2b. Moreover, in this spectrum, most of the lines typical of open forms are either absent or weak (compared with spectrum 2e) and some

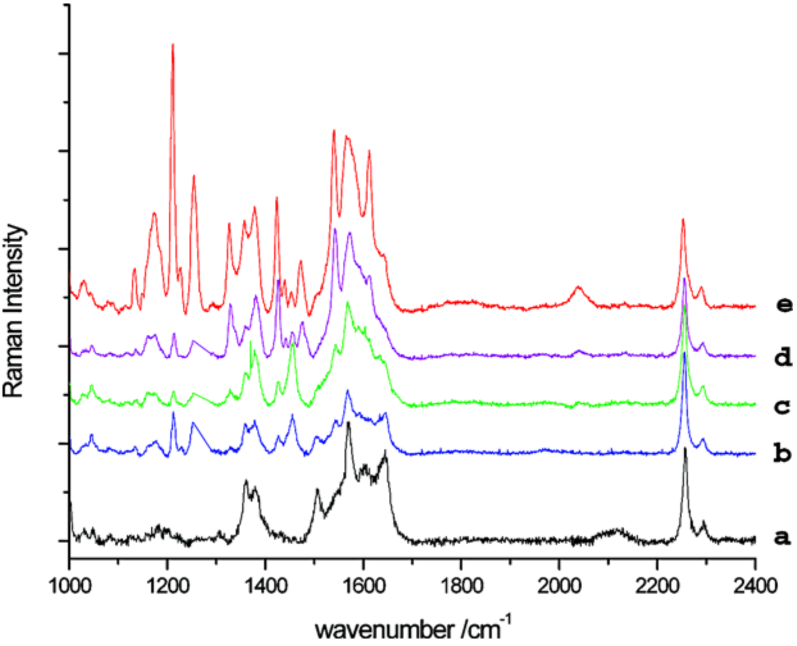


FIGURE 2 Evolution of SERS spectra of 3,3-diphenyl-naphtho[2,1-b]pyran acetonitrile solution, under successive UV (20 s) and visible (20 s) irradiation (all spectra were normalised with respect to 2255 cm^{-1} solvent line); spectra b, c and d were taken 0 s, 15 s and 30 s from the end of visible irradiation. Spectra a and e are those of closed and open forms, respectively, and shown for comparison.

new lines observed at *ca.* 1045, 1160, 1365 and 1455 cm^{-1} appear with medium or weak intensities.

Spectra recorded 15 s and 30 s after the end of irradiation (2c and 2d) show that, during the thermal relaxation, SERS spectra change again and resemble more and more to the spectrum of open forms. Final evolution of the solution (after storing in the dark) lead to a SERS spectrum similar to the spectrum of the initial closed form (Fig. 2a).

Discussion

On the basis of the present set of SERS experiments some conclusions can be drawn:

1) Under stationary UV irradiation the main photochemical process is the CF → OF photoisomerisation, in which OF represents a mixture of TC and TT isomers with a large excess in TC.
2) Thermal relaxation after UV irradiation corresponds to the expected thermal ring closure process with the recovery of initial closed form.
3) After successive UV and visible irradiation, SERS spectra recorded at the end of visible irradiation display spectral features with evident similarities to those of CF.
4) During the thermal relaxation following visible irradiation, SERS spectra change and resemble open forms; final evolution leads to the initial closed form.

To take into account the two latter conclusions, one can consider that a new species A is involved in the photochromism mechanism. Under successive UV and visible irradiation, this species is accumulated, leading to the SERS spectrum of Figure 2b. This spectrum displays several analogies with the SERS spectrum of CF and this suggests that the structure of A is near to the closed form. During thermal relaxation, A reconverts to open forms (OF) and finally to CF. Since the predominant open form is the TC isomer, it is likely that A isomerizes to CF via TC.

Recently, in similar NMR experiments [5], an allenyl-naphthol intermediate was produced after consecutive UV and visible irradiation of 3,3-diphenyl-naphtho[2,1-b]pyran in acetonitrile/acetone solutions (10^{-2} M) at low temperature (213 K). The complete structure elucidation of this intermediate was obtained and a detailed mechanism was proposed [5]. The present SERS experiments suggest that A could be the allenyl-naphthol species identified in NMR. In favor of this hypothesis, one could invoke i) that the structure of A is near to the closed form with probably no conjugation between phenyls and naphthalene moiety, ii) the presence in the SERS spectrum of A (spectrum 2b) of new lines, some of which being typical of allenic linkage.

Experiments are currently underway attempting to provide more details on the vibrational characteristics of A.

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