# Combined NMR, SERRS, and DFT study of photochemical and thermal reactions of acetylene- and thienylacetylene-substituted chromenes

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ABSTRACT: Nuclear Magnetic Resonance (NMR), Surface-Enhanced Resonance Raman Scattering (SERRS), and Density Functional Theory (DFT) were used to study 8-substituted acetylene- and thienylacetylene-diphenylnaphthopyran photochromic compounds. The purpose of this work is to determine the effect of the 8-acetylene substituent on the photochromic equilibrium. NMR spectroscopy shows that photocoloration by UV irradiation at low temperature leads to a mixture of transoid isomers (**TC** and **TT**) and a small amount of an allenyl-naphthol structure. The mixture is further enriched in this latter isomer by subsequent visible irradiation. Some photoproducts are identified by analysis of the changes in the SERRS spectra of an irradiated solution with time. To assist spectral assignment, the vibrational frequencies of compounds (**1**) and (**2**) and their photoproducts were computed at optimized geometries and compared with the observed Raman bands. Copyright © 2007 John Wiley & Sons, Ltd.

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## INTRODUCTION

Photochromic organic compounds[1] attract much attention from both fundamental and practical points of view because of their potential in various applications, optical memories, and photonic devices.[2–3] In particular, in the field of molecular electronics, the use of photochromic photon-mode switching systems is considered to be a promising approach to molecular switches. In these systems, each photo-isomer (i.e., closed or open form) could represent either a '0' or '1' information bit of a digital binary code analogous to 'on' and 'off' states. On the other hand, oligothiophenes which can be linked to a photochromic moiety[4] are interesting compounds due to their electron conducting properties when doped. Therefore, interest in the development of complex systems consisting of a photochromic unit and a conducting organic polymer has increased due to their applications in optoelectronic devices.[5] For this purpose, diphenyl-naphthopyran, 8-substituted with an oligothiophene via

an acetylenic linkage, was recently synthesized. It was shown that an acetylene or thienylacetylene substituent leads to better colorability without any further degradation. Unfortunately, the introduction of a long oligothiophene chain leads to the loss of photochromic properties; thus, compounds in this series with a terthiophene substituent are no longer photochromic under UV irradiation, since a fast radiative process from the $S_1$ singlet excited state takes place (fluorescence emission), and this prevents opening of the pyran ring.

The present work is devoted to the investigation of 3,3-diphenylnaphtho[2,1b]pyran linked to an acetylene function in the 8-position (Compound **1** in Scheme 1) and to a thienyl group via an acetylene function (Compound **2** in Scheme 1), by Nuclear Magnetic Resonance (NMR) and Surface-Enhanced Resonance Raman Scattering (SERRS). Despite their rather different sensitivities (low for NMR and high for SERRS), comparison of these two spectroscopies has recently shown that they can be complementary.[6]

It has been proved by NMR that UV irradiation of 3,3-diphenylnaphtho[2,1b]pyran leads to the formation of two colored transoid isomers, namely transoid-*cis* (**TC**) and transoid-*trans* (**TT**). Moreover, under subsequent

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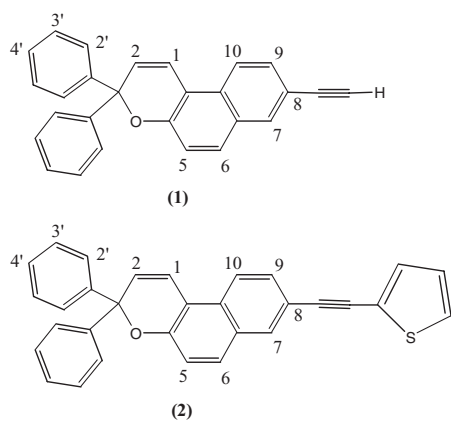
**Scheme 1.**

visible irradiation (i.e., UV + visible irradiations), it was demonstrated that an allenyl-naphthol species (**A**) accumulated during the photochromic process. This species, first identified by multinuclear NMR, relaxes to the initial closed form via the **TC** isomer.[7–8] SERRS is nowadays a powerful and well-established method for ultrasensitive chemical identification and characterization. We have shown that it is a useful approach for studying and characterizing the main transient photoproducts involved in the photochromic equilibrium.[9] In this paper, we report a spectroscopic (NMR and SERRS) and theoretical (Density Functional Theory (DFT) calculations) study of the acetylene (**1**) and thienylacetylene (**2**) 8-substituted diphenylnaphthopyran photochromic compounds. The NMR and SERRS spectral features of transient intermediates lead to useful information on the mechanism in this series.

## EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

^{1}H NMR spectra were acquired using a Bruker DPX 300 NMR spectrometer (300.09 MHz) equipped with a BBI probe-head fitted with an actively shielded z-gradient coil for delivering pulsed field gradients. UV and visible irradiation of the samples in acetonitrile-$d_3$ in the NMR tube were performed in a home-built apparatus. The emission spectrum of a 1000 W Xe–Hg high-pressure, filtered, short-arc lamp (Oriel) was focused on the end of a silica light-pipe (length 6 cm, diameter 8 mm), leading the light to the spinning sample tube, inserted in a quartz Dewar. The temperature of the sample was controlled with a variable temperature unit (B-VT1000-Bruker). The filters used are Schott 011FG09: $259 < \lambda < 388$ nm with $\lambda_{max} = 330$ nm and $T = 79\%$, and Oriel 3-74: $\lambda > 400$ nm for UV and visible irradiation, respectively.

To prepare SERRS samples, small aliquots of the stock solution of the photochrome (*ca.* $10^{-4}$ M in acetonitrile) were diluted in 500 μL of silver colloid, obtained from silver citrate (Ag, $10^{-3}$ M), and 40 mM NaNO$_3$ were

added just before recording the spectrum. SERRS spectra were excited with the 514.5 nm line of a 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 a 1 cm quartz cell, filled with 3 mL of 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 regular time intervals after irradiation, were poured into 500 μL of Ag colloid and their SERRS spectra recorded. All the Raman and SERRS spectra were normalized with respect to the solvent (acetonitrile) band at 921 cm$^{-1}$.

DFT calculations were performed using Gaussian 98.[10] All calculations of wavenumbers in the harmonic approximation were performed on fully optimized geometries. DFT geometry optimization was carried out with a combination of Becke's 1988 exchange functional[11] and the Perdew 86 gradient-corrected correlation functional (BP86).[12] The 6-31G(d) basis set was used for all atoms in the geometry optimization and the vibrational calculations. No scaling factor was applied to improve the fitting of the experimental and theoretical Raman spectra, since it has been shown that the DFT force field using BP86 functional yields vibrational wavenumbers in very good agreement with experiment.[6] It should be noted that in the present calculations, there is no possibility of taking into account the SERRS selection rules (arising from SERRS mechanisms, i.e., electromagnetic and chemical enhancement contributions), so the calculated line intensities can hardly be compared with those observed. To investigate the ring-opening mechanism in the ground, first singlet and triplet states we used a coupled semiempirical AM1/configuration interaction (AM1-CI) method[13] available in the AMPAC program package.[14] The ring-opening profile was determined by elongating the C—O bond step-by-step while the other geometric parameters were fully optimized.

## RESULTS AND DISCUSSION

### NMR studies

A solution of (**1**) in acetonitrile-$d_3$ ($10^{-2}$ M) was irradiated at 228 K with UV light for 20 min then with visible light for 12 min. ^{1}H NMR spectra (Fig. 1) were recorded before and after UV irradiation and then after subsequent visible irradiation (UV + visible irradiations). After UV irradiation (Fig. 1b), the initial form (**1**) is largely converted into a structure characterized by a doublet ($^3J = 11.9$ Hz) at 8.5 ppm. Such a high chemical shift is assigned to the H-2 proton in the **TC** isomer of the
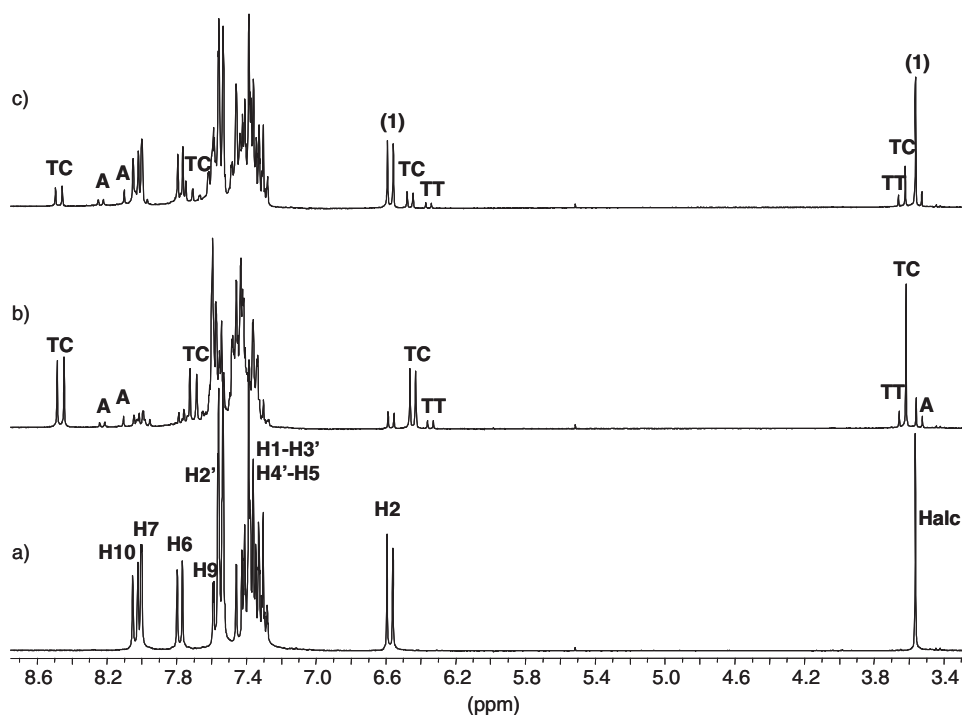
**Figure 1.** $^{1}$H NMR spectra at 228 K of (**1**). (a) before, (b) after 20 min of UV irradiation, (c) after 12 min of visible irradiation

photomerocyanine, which is deshielded by the C=O group.[15] Other signals are also detected, in particular in the region of acetylene protons. Two weak signals at 3.52 and 3.65 ppm indicate the presence of two supplementary photoproducts, assigned to the allenyl-naphthol (**A**) and the other isomer of photomerocyanine (**TT**).[7] Figure 1c displays the results of visible light irradiation. The initial closed form is mainly recovered in spite of a small increase in the concentration of **A**. We recently reported that visible light does not bleach photomerocyanines directly to the closed form but to the allenyl-naphthol.[8]

In the present case, this phenomenon is not obvious. To understand it better, a fresh solution was irradiated with UV light only and thermal bleaching at 228 K was followed by recording the NMR spectrum at regular time intervals. Measurement of peak intensities at 3.52, 3.55, 3.61, and 3.65 ppm makes it possible to plot the curve of concentration *versus* time for the four species (**A**, **1**, **TC**, and **TT**) in solution (Fig. 2). The **A** curve follows a mono-exponential decay (**A** → **TC**, $k_1 = 5.1 \times 10^{-4}\,\mathrm{s}^{-1}$) while the bleaching of the **TC** isomer (**TC** → (**1**), $k_2 = 1.4 \times 10^{-4}\,\mathrm{s}^{-1}$) is bi-exponential (Eqns 1 and 2).

$$[\mathbf{A}]_t = [\mathbf{A}]_0 \cdot \exp(-k_1 \cdot t) \qquad (1)$$

$$[\mathbf{TC}]_t = (k_1/(k_2 - k_1)) \cdot [\mathbf{A}]_0 \exp(-k_1 \cdot t)$$
$$+ ([\mathbf{TC}]_0 - (k_1/(k_2 - k_1))\,[\mathbf{A}]_0)$$
$$\cdot \exp(-k_2 \cdot t) \qquad (2)$$

A solution of (**2**) in acetonitrile was prepared at $9 \times 10^{-5}$ M due to its low solubility. Such a concentration,

which is low for NMR measurements, is in almost the same concentration range, however, as solutions studied in SERRS (*vide supra*). The $^{1}$H NMR spectrum recorded after 5 min of UV irradiation (Fig. 3, spectrum b) indicates the formation of **TC** photomerocyanine, which has doublets at 6.47 and 8.45 ppm for the H-5 and H-2 protons, respectively. A brief visible irradiation (2 min) converts it to a new photoproduct, identified as the allenyl-naphthol. This is fully confirmed by observing the NMR spectra recorded during the thermal evolution of the sample at 228 K. Indeed, it is clear that the signals of **A** decrease while those of **TC** increase. After the total disappearance of **A**, bleaching of **TC** to the initial closed
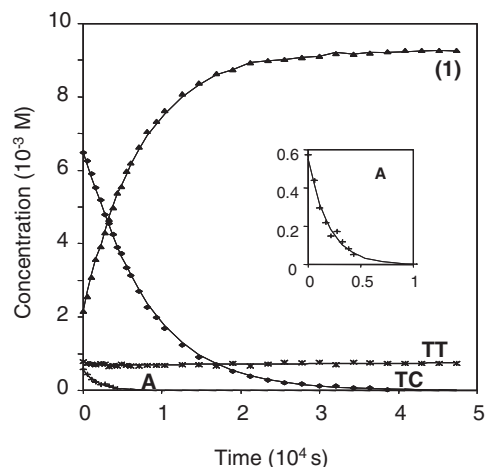


**Figure 2.** Time dependence of concentrations of (**1**), **TC**, **TT**, and **A** in the dark at 228 K after UV irradiation
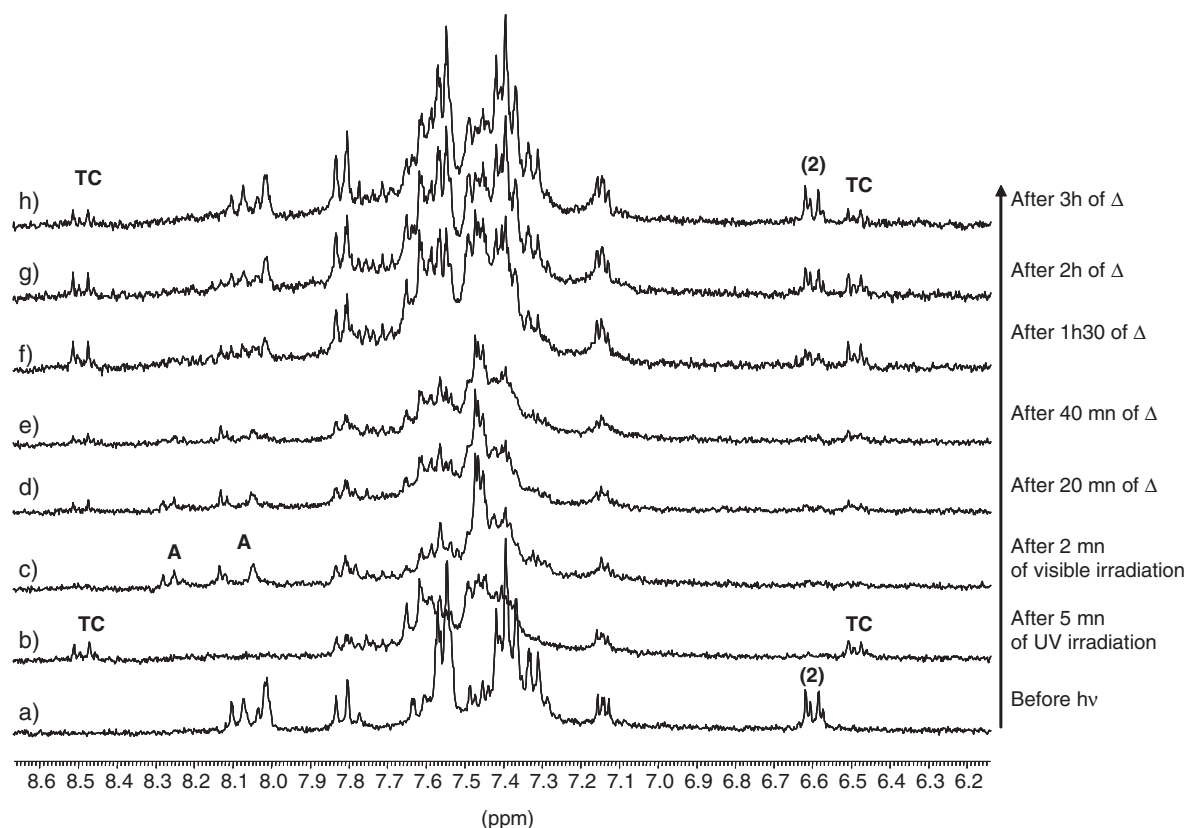
**Figure 3.** $^1$H NMR spectra at 228 K of (**2**) during photochromic reaction

form (**2**) is observed. Due to the low concentration, the spectral resolution was too poor for it to be possible to get accurate values of the peak intensities, and no bleaching rate constants were calculated. However, in less than 40 min **A** disappeared completely, and comparison of spectra f and h in Fig. 3 shows that the concentration of **TC** is about two times smaller, whence a half-life of 90 min can be estimated. These two observations are in complete agreement with values deduced from investigations on (**1**) and are summarized in Scheme 2.

## SERRS studies

**Experimental SERRS and theoretical Raman spectra of (1) and (2).** SERRS spectra of compounds (**1**) and (**2**) excited at 514.5 nm, and recorded at 900–1700 cm$^{-1}$, are shown in Figs 4b and 5b. The DFT//BP86/6-31G(d) Raman spectra are also depicted for comparison in the same figure (Figs 4a and 5a). It should be emphasized that the calculated Raman spectrum represents the vibrational signatures of molecules in their gas phase. Hence, the experimentally observed SERRS spectrum may differ significantly from the calculated spectrum. However, as shown in Figs 4 and 5, the calculated Raman spectra compare quite well with the experimental ones, particularly in the case of (**1**); since for (**2**) there are dis-

crepancies regarding the intensities of several Raman lines.

The SERRS spectrum of (**1**) is dominated by six bands at *ca.* 1608, 1461, 1422, 1379, 1159, and 1004 cm$^{-1}$. These bands were assigned on the basis of the vibrational eigenvectors (Supplementary Material Figure S1) derived from the DFT calculations. These indicate that these SERRS lines arise mainly from in-plane vibrations of the naphthopyran moiety and phenyl rings.

The SERRS spectrum of (**2**) is very similar to that of (**1**) and shows six bands at *ca.* 1606, 1461, 1421, 1378, 1158, and 1004 cm$^{-1}$. These bands are assigned to the calculated frequencies at 1613, 1443, 1428, 1385, 1158, and 980 cm$^{-1}$. As for compound (**1**), the vibrational eigenvectors corresponding to these frequencies (Supplementary Material Figure S2) indicate that the modes of vibration contributing to the SERRS spectrum arise mainly from the naphthalene and phenyl rings. However, it should be noted that the 1443 cm$^{-1}$ mode is strong in the calculated spectrum but appears as a medium band. Inspection of this normal mode indicates that it corresponds to stretching vibrations spreading over the whole $\pi$-conjugated system from the naphthalene to the thiophene substituent with a significant contribution on this latter ring. It is clear that the involvement of the thiophene ring in the $\pi$-conjugated system is at the origin of extra lines observed in the SERRS spectrum of (**2**). The huge enhancement of the Raman signal can generally be
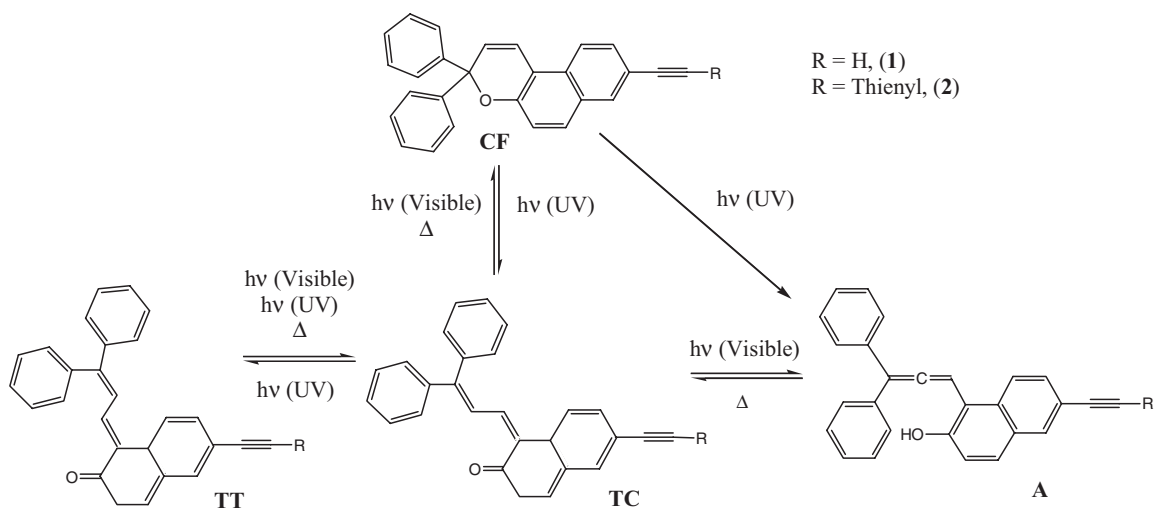
**Scheme 2.**

explained by an increase in the local electromagnetic field near the silver particle surface when localized surface plasmons are excited. Since the calculated Raman spectrum corresponds to the normal (spontaneous) Raman spectrum, the marked decrease in the SERRS intensity of the 1443 cm$^{-1}$ mode suggests that the thiophene ring is not in direct interaction with the silver surface.

**SERRS spectra of UV-irradiated solutions of (1) and (2).** Photochromic solutions were UV irradiated ($\lambda > 300$ nm) for 20 s and the SERRS spectrum was recorded at regular intervals up to 300 s (Fig. 6). In order to establish the appearance of a new photoproduct these spectra were compared with that of a non-irradiated solution prepared in the dark. Surprisingly, UV irradiation does not lead to marked changes, and the SERRS spectra are quite similar to that of the non-irradiated solution (Fig. 6a). However, careful examination of the spectra

reveals some minor changes. Immediately after UV excitation (Fig. 6b), the spectrum of the irradiated solution closely resembles that of the non-irradiated solution but with a poorer signal-to-noise ratio than that of the closed form (Fig. 6a). This could indicate the presence of metastable allenyl-naphthol species **A**, the SERRS spectrum of which is very similar to that of the initial closed form, **CF** (Scheme 2).[6] This observation is in agreement with the above NMR data for compound (**1**). On the contrary, in spectrum c, recorded after 15 s, appear new weak lines at *ca.* 1570, 1540, 1490, 1400, and 1360 cm$^{-1}$. All these lines progressively disappear in the following spectra (from 30 to 300 s) indicating thermal relaxation toward the closed form. In order to characterize the photoproducts appearing at 15 s (Fig. 6c) we calculated the Raman spectra of **TC** and **TT**, the open isomers of (**1**). As it appears in Fig. 7, the Raman spectra of **TC** and **TT** are found much more intense than the closed form spectrum. It could be noted that Raman
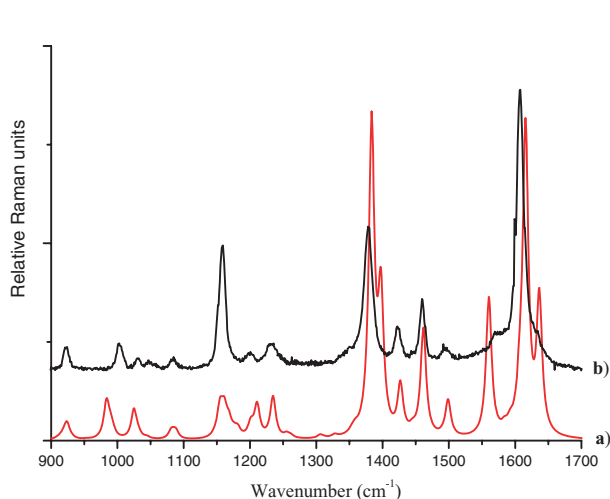


**Figure 4.** (a) BP86/6-31G(d) and (b) SERRS spectra for (**1**). This figure is available in colour online at www.interscience. wiley.com/journal/poc
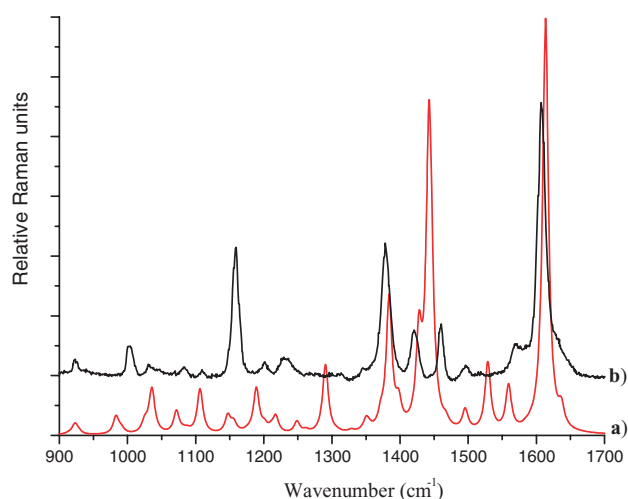


**Figure 5.** (a) BP86/6-31G(d) and (b) SERRS spectra for (**2**). This figure is available in colour online at www.interscience. wiley.com/journal/poc
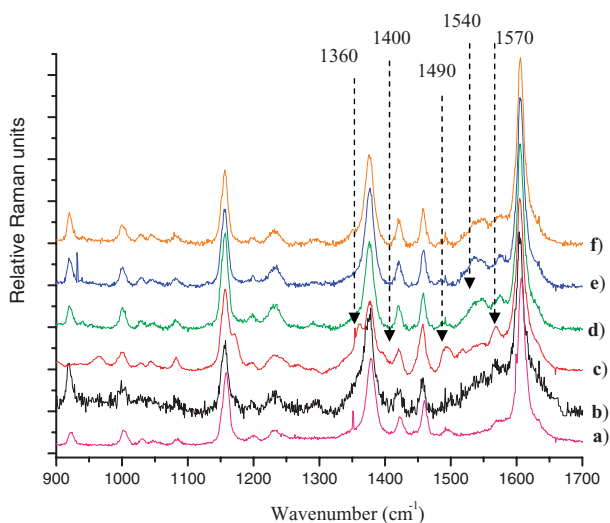
**Figure 6.** SERRS spectra of compound (**1**) ($10^{-5}$ M) in acetonitrile after UV (20 s) irradiation. Spectra b, c, d, e, and f were recorded at 0, 15, 30, 60, and 300 s after irradiation. That of a non-irradiated solution (**CF**, spectrum a) is presented for comparison. This figure is available in colour online at www.interscience.wiley.com/journal/poc

intensity depends on the change of the molecular polarizability along the normal mode. Vibrational analysis shows that the strongest calculated Raman bands in the opened spectra arise mainly from in plane vibration involving the extended conjugated system (from the C-3 atom to thienyl substituent) and thus, the strong enhancement of the polarizability when going from closed to opened form is the result of better electronic delocalization in the $\pi$ conjugated system. The calculated Raman normal modes of **TC** and **TT** at 1590, 1543, and 1485 cm$^{-1}$, probably correspond to the SERRS lines observed at 1570, 1540, and 1490 cm$^{-1}$. The doublet calculated at 1365 and 1385 cm$^{-1}$ in the **TT** isomer could

correspond to the lines at 1360 and 1400 cm$^{-1}$. Therefore, the changes in the SERRS spectra with time combined with vibrational analysis indicate that in the course of the photochromic relaxation process, a very small amount of the allenyl-naphthol (**A**) species is involved, along with the expected colored isomers, **TC** and **TT**. These species then relax to the closed form, as depicted in Scheme 2.

The time dependence of a 20 s UV-irradiated solution of (**2**) was followed at room temperature in the same way (Fig. 8). The SERRS spectrum of the non-irradiated solution of this compound is also displayed for comparison and to highlight the main lines which appear after UV irradiation (Fig. 8a). In contrast with compound (**1**), significant spectral changes are observed. Several strong new Raman lines are observed at 1552, 1483, 1310, 1270, 1110, and 1025 cm$^{-1}$ immediately after irradiation (0 s, Fig. 8b) the intensities of which decrease rapidly in the subsequent spectra. Finally, from 60 to 300 s (Fig. 8d–f) the spectra resemble that of the non-irradiated solution (**CF**, spectrum a). A straightforward explanation for the appearance of the new lines can be based on the large amount of colored open forms. Quantum chemical calculations were carried out on the **TC** and **TT** isomers of (**2**), and their Raman spectra are depicted in Fig. 9.

It can be seen that the spectra of **TC** and **TT** are very similar and show several strong bands at *ca.* 1544, 1520, and 1448 cm$^{-1}$ and medium bands at *ca.* 1485, 1111, and 1038 cm$^{-1}$. However, the calculated Raman bands at 1363 and 1383 cm$^{-1}$ are specific to the **TT** isomer while the strong one at 1270 cm$^{-1}$ with a shoulder at 1300 cm$^{-1}$ fingerprints the **TC** isomer. Comparison of the SERRS and calculated Raman spectra makes it possible to assign the SERRS lines at 1552, 1483, 1110, and 1025 cm$^{-1}$ to the Raman bands of **TC** or **TT** calculated at 1544, 1520, 1485, 1111, and 1038 cm$^{-1}$. The two SERRS lines at
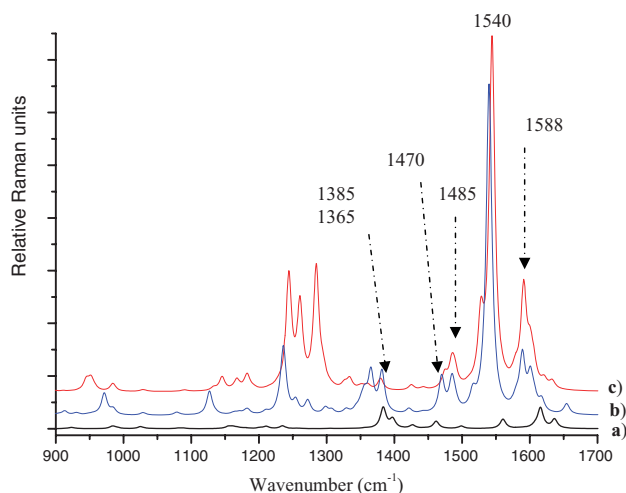


**Figure 7.** BP86/6-31G(d) Raman spectra of **CF** (a), **TT** (b), and **TC** (c) isomers of (**1**). This figure is available in colour online at www.interscience.wiley.com/journal/poc
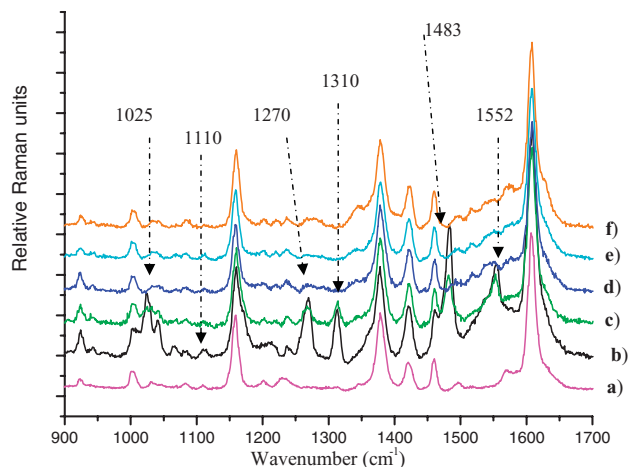


**Figure 8.** SERRS spectra of compound (**2**) ($10^{-5}$ M) in acetonitrile after UV (20 s) irradiation. Spectra b, c, d, e, and f were taken 0, 30, 60, 120, and 300 s after irradiation. That of a non-irradiated solution (**CF**, spectrum a) is presented for comparison. This figure is available in colour online at www.interscience.wiley.com/journal/poc
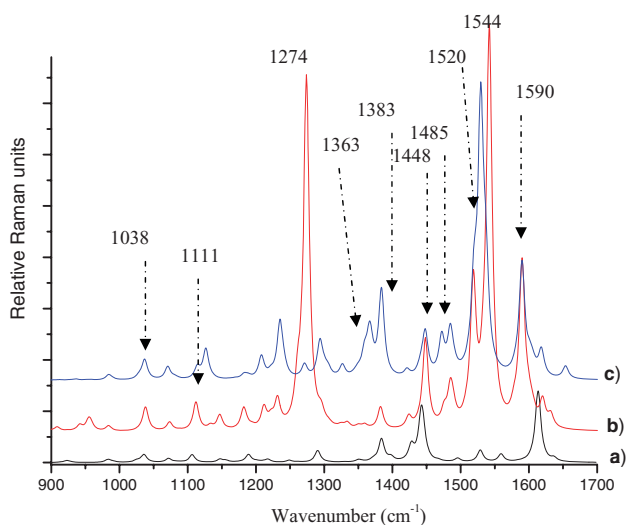
**Figure 9.** BP86/6-31G(d) Raman spectra of **CF** (a), **TC** (b), and **TT** (c) isomers of (**2**). This figure is available in colour online at www.interscience.wiley.com/journal/poc



**Figure 10.** SERRS spectra of compound (**1**) ($10^{-5}$ M) in acetonitrile after successive UV (20 s) and visible irradiations (20 s). Spectra b, c, d, e, f, and g were taken 0, 15, 30, 60, 120, and 300 s after irradiation. That of a non-irradiated solution (**CF**, spectrum a) is presented for comparison. This figure is available in colour online at www.interscience. wiley.com/journal/poc

1270 and 1310 cm$^{-1}$ could probably be assigned to the 1270 and 1300 cm$^{-1}$ bands calculated for the **TC** isomer. It can been seen from Fig. 8 that after UV irradiation there are no lines in the SERRS spectrum at 1363 and 1383 cm$^{-1}$, which suggests that the mixture of open colored forms is strongly enriched in the **TC** isomer. The calculated Raman medium band at 1448 cm$^{-1}$ corresponds to a stretching vibration of the thiophene ring. As for the **CF** form, the thiophene ring is probably remote from the metallic surface and, therefore, this vibration does not contribute to the SERRS spectrum.

**SERRS spectra of UV + Visible irradiated solutions of (1) and (2).** Fresh solutions of compounds (**1**) and (**2**) were UV irradiated for 20 s then with visible light ($\lambda > 400$ nm) also for 20 s. SERRS spectra were recorded at the end of the visible irradiation and at regular intervals thereafter. The spectra of (**1**) are depicted in Fig. 10. They show no change from 0 to 300 s and all are similar to that of the non-irradiated solution spectrum (**CF**, spectrum a). Even a close analysis of the whole set fails to reveal any intermediate in the relaxation process. This is distinctly different from what was obtained in the NMR experiments. In the present case, this result suggests that under the conditions of SERRS experiments (ambient temperature and $10^{-5}$ M concentration), consecutive UV + visible irradiation does not lead to any transient species, such as colored isomers or allenyl-naphthol photoproducts. This can probably be explained by a fast ring closure induced by the visible irradiation.

The time dependence of the SERRS spectra of (**2**) is depicted in Fig. 11. The lines observed at 15 and 30 s appear in the same positions as those observed after UV irradiation alone and can, therefore, be attributed to the colored isomers, **TC** and **TT**. The changes in the spectra
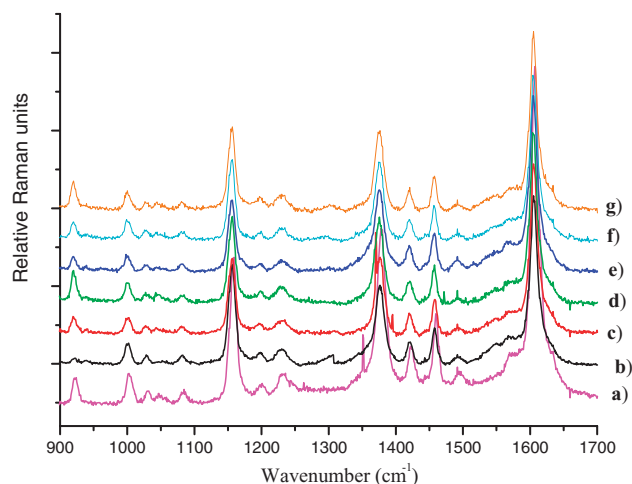
from 60 to 300 s are also similar to those observed after UV irradiation alone. Therefore, analysis of all the spectra suggests that only the metastable photomerocyanines occur, and that they rapidly revert thermally to the initial closed form, as shown by the large decrease in the intensities of the lines at 1552, 1483, 1310, 1270, and 1025 cm$^{-1}$.

Surprisingly, these experiments did not reveal the involvement of any photoproducts such as **TT** and **TC**. Therefore, the question is open, in the case of compound (**2**), as to why the allenyl-naphthol species does not
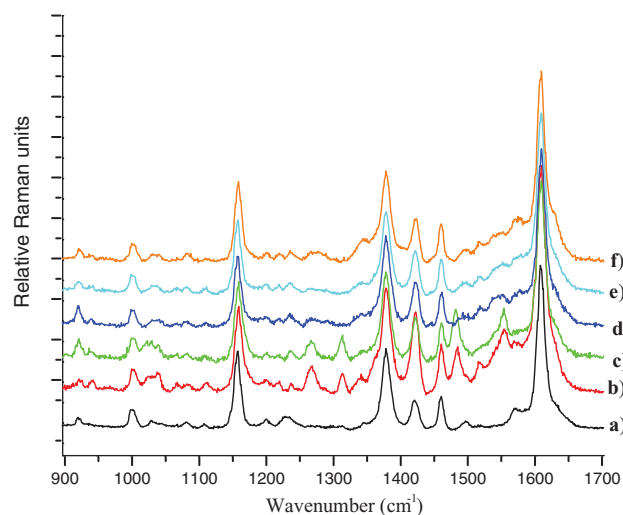


**Figure 11.** SERRS spectra of compound **2** ($10^{-5}$ M) in acetonitrile after successive UV (20 s) and visible irradiations (20 s). Spectra b, c, d, e, and f were taken 15, 30, 60, 120, and 300 s after irradiation. That of a non-irradiated solution (**CF**, spectrum a) is presented for comparison. This figure is available in colour online at www.interscience.wiley.com/journal/poc

**Table 1.** Calculated activation barrier (in kcal mol$^{-1}$) of (**1**) and (**2**) for ring opening in ground, first singlet, and triplet excited states

| Compound | $E_a$ (S$_0$) | $E_a$ (S$_1$) | $E_a$ (T$_1$) |
|---|---|---|---|
| (**1**) | 28.9 | 0.6 | 17.09 |
| (**2**) | 29.0 | 0.1 | 28.7 |

accumulate. It was shown very recently that fast relaxation of the closed form of an 8-substituted diphenylchromene in the triplet state could be a deactivation pathway competing with the singlet excited state ring-opening reaction. To check this hypothesis, we carried out the calculation for ring opening of both compounds (**1**) and (**2**) in the excited singlet and triplet states at the semi-empirical level using CI (see computational method). The calculated activation barriers are presented in Table 1. As previously observed for other photochromes, it is found that the singlet electronic excited state ring opening is an almost barrierless process for both compounds, leading to merocyanine through conical intersection.[16] In contrast, the triplet ring-opening activation barrier is very sensitive to the substituent effect and is found to be 17 and 28.7 kcal mol$^{-1}$ for (**1**) and (**2**), respectively. Therefore, if we assume that the triplet state of the closed form is also populated; theoretical calculations clearly suggest that the ring opening of (**1**) could lead to open merocyanine forms, while this process is inhibited for (**2**). As a consequence, triplet state of **CF** of (**2**) should rapidly deactivate towards the closed form in the singlet ground state (S$_0$) through an intersystem crossing (ISC) mechanism. The triplet state of the initial form of compound (**1**) could lead to the colored isomers (**TC** or **TT**) through a ring-opening reaction. Unfortunately, this hypothesis cannot be verified in the present photostationary experiments in spite of very high sensitivity of SERRS spectroscopy and complementary experiment are needed to validate it.

## SUMMARY AND CONCLUSIONS

In this paper, NMR and SERRS spectroscopic studies were compared and quantum chemical DFT calculations were run on two closely photochromic compounds (**1**) and (**2**) namely, acetylene- and thienylacetylene-8-substituted diphenylnaphthopyrans. In spite of very different experimental conditions, a detailed mechanism of the relaxation process after UV and subsequent visible irradiation was deduced from the NMR and SERRS data for compound (**1**). However, the picture is not so clear for compound (**2**). Thus, while NMR suggests that relaxation proceeds by a similar mechanism, SERRS experiments clearly demonstrate that no photoproducts other than **TC** and **TT** are involved. Semi-empirical calculations show that efficient ISC to a stable and resonant triplet state in

the closed form takes place which could inhibit the formation of **A** species.

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