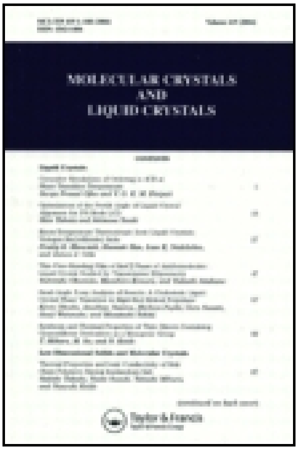

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Picosecond Time-Resolved Resonance Raman Spectroscopy and Vibrational Analysis in Spirooxazine Photochromism

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Picosecond Time-Resolved Resonance Raman Spectroscopy and Vibrational Analysis in Spirooxazine Photochromism

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Picosecond time-resolved resonance Raman (TR^3) spectroscopy was used to study the dynamics and structure of transient species involved in the photochromic process in solution of 1,3,3-trimethylspiro[indoline-naphthoxazine]. TR^3 spectra recorded in n-hexane, at 10 ps and 50 ps time-delays were compared with those obtained on the ns-ms timescale and to the resonance Raman spectrum of a permanent opened form. These data and the results of a detailed *ab initio* vibrational analysis, have allowed us to determine the structure of the transoid isomer already present at 10 ps and to precise the photochromic mechanism.

Keywords: ps TR^3 spectroscopy; indolinospironaphthoxazine; isomer structure

INTRODUCTION

Spiropyran and spirooxazine photochromism has been widely studied by means of transient spectoscopy during the last 20 years. In this context, time-resolved resonance Raman (TR^3) has proved to be a useful technique for investigating the molecular structure of transient species involved in the photochromic process over ms to ns [1] and recently in the ps time range [2,3]. These works were developed aiming to precise the number and the structure of photomerocyanine isomers and which electronic configuration they adopt (quinoidic or zwitterionic). Thus, our recent TR^3 experiments have suggested that in indolinospironaphthoxazine photochromism the colored open forms present a quinoidic electronic distribution and a dominant TTC isomeric structure [1]. However in this work, TR^3 spectra were recorded in ms-ns time range, which is not sufficient to probe primary photochemical events. These studies were now completed by recording picosecond TR^3 spectra of 1,3,3-trimethylspiro[indoline-naphthoxazine] in solution. In this paper, we report the TR^3 study of this photochrome in n-hexane solutions. Particular attention in the spectra recorded was given to very short time (10 - 50 ps), since it was recently suggested that the ring-opening in spirooxazine series involved the formation of a cisoid intermediate within 6 - 30 ps [3]. A detailed analysis of these spectra was achieved, from the comparison with the resonance Raman spectra of a permanent opened form and the results of *ab initio* vibrational calculations on the TTC and CTC most stable trans photomerocyanine isomers.

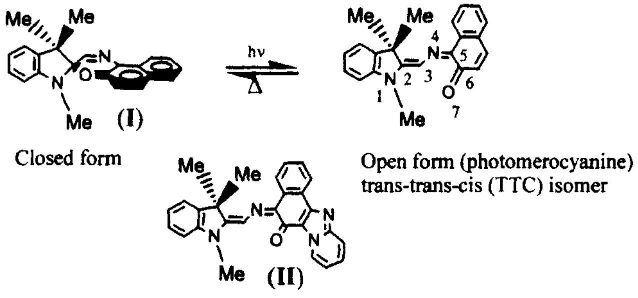

FIGURE 1 Photochromic equilibrium for compound I and structure of the permanent opened form II.

MATERIALS AND METHODS

Experimental 1,3,3-trimethylspiro[indoline-naphthoxazine] photochrome, I, (Fig. 1), is commercially available (Aldrich) and was used as received. Synthesis and purification of the opened form model, II (Fig.1), were reported previously [4]. Recording of nanosecond TR^3 spectra of I and resonance Raman spectra of II have been described in details elsewhere [1]. Picosecond TR^3 spectra were obtained using a pump/probe spectrometer based on a Ti-sapphire laser system working in the picosecond regime [5]. This system provides at 800 nm, 0.8 mJ, 2.5 ps pulses at 1 kHz repetition rate. Pump pulses (266 nm, 20 μJ) were obtained by frequency tripling the Ti-sapphire fundamental. Probe pulses (600 nm, 15 μJ) were generated by using a narrow band optical parametric generator and amplifier system, pumped by the second harmonic of the Ti-sapphire laser (400 nm). In our experiments the probe pulse has a duration of 1.4 ps and a spectral bandwidth of *ca.* 10 cm^{-1}. The probe pulses were time-delayed with respect to the 266 nm pump pulses using a computerized optical delay line. Pump and probe beams are focused on a cylindrical jet of solution (*ca.* 10^{-3}M) using the same lens. Raman light is collected at 90° and focused onto the entrance slit of the spectrometer. It consists of a highly rejective Notch filter followed by a single stage monochromator equipped with a CCD multichannel detector. In our experiments the analyzed spectral field is *ca.* 1000 cm^{-1}.

Theoretical methods Ground state geometries of the trans photomerocyanine isomers were fully optimized with the Hartree Fock and DFT approximations using the 3-21G basis set. The frequencies, obtained by diagonalization of the force constants (calculated at the DFT level using the BP86 functional), were unscaled. The spontaneous Raman intensities were obtained at the Hartree Fock level.

RESULTS AND DISCUSSION

Picosecond TR^3 spectra of photochrome I, excited at 600 nm, were recorded in various solvents (n-hexane, ethanol and acetonitrile) and at different time-delays. We focused the present analysis on the results obtained in n-hexane, of which a typical example is shown in Fig. 2, for 10 ps and 50 ps time-delays (spectra a and b). The TR^3 spectrum of I, obtained in the same solvent but at 10 ns time-delay is also depicted in Fig. 2 (spectrum c). It should be noted that, except an increase in the signal–to-noise ratio on going from ps to ns, the spectra are very similar (intensities and positions). This demonstrates that the TR^3 spectrum of I at 10 ps time-delay arises from open photomerocyanine species. Moreover, since it was previously established that TR^3 spectra in apolar solvents recorded at 10 ns time-delay, were identical to those obtained at longer time-delays respectively, 10 μs and 1ms, this indicates that the species detected at 10 ps is typical of trans isomers and remains unchanged up to ms timescale [1]. In these conditions there is no evidence, at the shortest time measured here (10 ps), for the formation of another transient species, namely a cisoid photomerocyanine isomer. This conclusion is in agreement with the results of transient absorption measurements in spirooxazine and naphthopyran series, which suggest that the formation of a cisoid intermediate occur on the sub-ps timescale [2]. All these results evidence that in the photochromism of I; i) the opening process is complete at 10 ps, the shortest time available with the Raman equipment, ii) the observed 10 ps TR^3

spectrum is typical of trans open forms in apolar solvents, iii) these species do not (or slightly) change over a wide time scale.

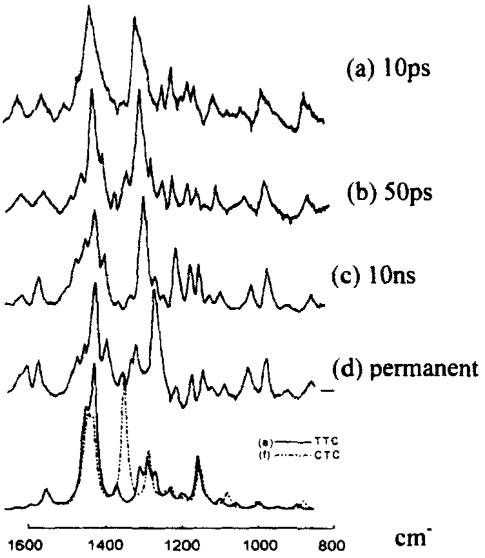

FIGURE 2 TR^3 spectra of I in n-hexane, recorded at different time-delays (a, b and c); RR spectrum of II (d) and calculated Raman spectra of TTC and CTC trans isomers of I (e and f).

In order to further analyze TR^3 spectra obtained at very short time, the resonance Raman spectrum of the permanent opened form, II, was recorded (Fig. 2d). This compound was chosen on purpose since it presents a TTC isomeric structure and a quinoidic electronic distribution very close to that expected for the trans open forms of I. Comparison of TR^3 spectra (Fig. 2, respectively, a, b and c) with the RR spectrum of II (Fig. 2d) reveals similarities in line positions but more interestingly analogies in the relative intensity distribution. This suggests that TR^3 spectra of I arises mainly from a species of which the structural features and the electronic distribution are very close to those of the permanent opened form II. All these observations provide strong arguments indicating that in n-hexane, the open form of 1,3,3-trimethylspiro[indoline-naphthoxazine], which already exists at 10 ps after

266 nm UV pulse, presents a quinoidic electronic distribution and a dominant TTC isomeric structure (Fig. 1).

To complete the interpretation of TR^3 spectra, a vibrational analysis based on DFT and *ab initio* calculations was performed for the two most stable trans photomerocyanines isomers of I namely, TTC and CTC. The calculated Raman spectra are shown in Fig. 2 (spectra e and f); the experimental and calculated frequencies and their assignment are summarized in table 1. It should be noted that the experimental frequencies are correctly reproduced by the calculation for TTC isomer (Fig. 2e) while in the case of CTC (Fig. 2f) the agreement is poor. On the other hand, important differences are observed between the calculated and experimental Raman intensities. This discrepancy arises from the classical approach for the calculation of Raman intensities which does not take into account the contribution of the resonance Raman effect. In the present case, this effect leads to selective enhancement for in-plane vibrations originating from the azomethinic bridge and the naphthalenic moiety (Fig. 1 and Table 1).

TR^3 (10 ns) (n-hexane)	TTC (BP86/3-21G)	Assignment*
867	865	δ naphthalene ring
932	928	δ benzene indoline ring
977	974	δ C_3-N_4-C_5 + $\nu_{C=C}$ naphthalene
1027	1045	δ indoline ring
1095	1081	δ C-H naphthalene ring
1132	1133	δ naphthalene ring + δ C-H benzene indoline
1151	1165	ν C_3-N_4 + ν C_5-C_6 naphthalene
1173		
1202		
1230	1237	δ naphthalene ring + ν C-C naphthalene
1259	1246	ν naphthalene ring + ν indoline ring
1294	1291	ν naphthalene ring (ν C=C) + δ C-H naphthalene
1321	1313	ν indoline ring
1354	1343	ν indoline ring + δ C-H benzene indoline
1402		
1424	1402	ν C_5=N_4 + ν C_2=C_3
1447	1446	δ CH_3 (umbrella) + δ C-H naphthalene
1470	1461	δ CH_3 (umbrella) + δ C_3-H
1555	1579	ν ring (ν C=C) naphthalene
1603	1601	ν C=O + ν C=C naphthalene

ν and δ : in plane stretching and bending.

TABLE 1 Experimental and calculated (TTC) Raman frequencies (cm^{-1}) of I.

CONCLUSION

TR^3 spectra of 1,3,3-trimethylspiro[indoline-naphthoxazine] in n-hexane, recorded on the picosecond timescale, were very similar to those obtained in apolar solvents at ns, μs and ms time-delays. Comparison with the resonance Raman spectrum of a permanent opened form and the results of a detailed *ab initio* vibrational analysis, have proved us that these TR^3 spectra originated mainly from a TTC photomerocyanine isomer which is already present at 10 ps. On the other hand, TR^3 spectra of I, in polar solvents (*e.g.* acetonitrile), showed quite different spectral features with respect to those in polar solvents [1]. These spectra slightly changed over the whole time range investigated (10 ps - 1 ms) but were substantially different to the resonance Raman spectrum of the permanent opened form (spectra not shown). Moreover, TR^3 spectra in polar solvents could not be correctly simulated from TTC or CTC calculated Raman spectra (Fig. 2, spectra e and f). Therefore, in polar solvents it is likely that an equilibrium between the most stable trans photomerocyanine isomers, TTC and CTC, takes place and is already established within 10 ps. Further calculations, in particular resonance Raman intensities, could permit in a near future to estimate the abundance of each isomeric species.

Acknowledgments

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