Mechanistic understanding of the photochromism of a hybrid dithienylethene–naphthopyran system by NMR spectroscopy

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ABSTRACT: Detailed ^{1}H NMR kinetic investigations of the photochemical and thermal behaviour of a recently described poly-photochromic molecule including both dithienylethene and naphthopyran groups are reported. The combination of two photochromic moieties allows the selective controlled extension of the conjugated pi-electron system and the modulation of the absorption behaviour between $\sim$380 to $\sim$750 nm. It is shown that the two photochromic entities are coupled and do not behave independently. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: naphthopyran; dithienylethene; photochromism; kinetics

INTRODUCTION

Photochromism is defined as a reversible change of a single species between two states having distinguishably different absorption spectra.[1–3] Among the large family of photochromic compounds, naphthopyrans[4] have been the subject of intense investigations due to their high colourability, fast bleaching and good resistance to degradation. More recently, owing to their suitable photochromic properties (high thermal stability and high resistance to degradation), dithienylethene and related compounds have emerged as promising candidates for various applications in optoelectronic devices.[5–13]

Combination of these two entities in a unique molecular system allows the controlled selective extension of the conjugated pi-electron system. We have recently reported the synthesis and photochromic properties of a hybrid system, Open Dithienylethene–Closed Naphthopyran (OD-CN): namely, the 3-(1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene), 3-phenyl-naphthopyran.[14] Four different steady states were detected by UV–visible spectroscopy. The system was then investigated by ^{1}H NMR spectroscopy and the coexistence of eight different isomers was underlined.[15]

A general mechanism has been proposed: while 365 nm irradiation of OD-CN gives rise to the thermally reversible opening of naphthopyran ring, irradiation at 313 nm leads both to the closure of the dithienylethene moiety and the thermally reversible opening of the naphthopyran group, thus generating seven photoisomers of OD-CN in different concentrations: OD-TTC, OD-CTC, OD-TTT, (CD-CN1 + CD-CN2), CD-TTC and CD-CTC (Scheme 1).

However, the different pathways along which the various photo-generated species are interconverting still remain to be examined in more detail. In particular the investigation of the competing photoreactions, mainly the photo-opening of naphthopyrans and the photo-cyclisation of dithienylethene require more investigation to reach a full understanding of the photochromic properties of such a hybrid system.

In previous papers,[16] some of us have reported the kinetic investigations of poly-photochromic systems including naphthopyrans units. They have shown that unambiguous information about the location and the relative strengths of the various photochemical and thermal isomerisation pathways connecting the photo-isomers manifold can be provided by the simultaneous nonlinear least-square fitting of the concentration *versus* time profiles recorded under continuous irradiation or during the thermal relaxation in the dark.

In this paper, we report the results of our quantitative analysis of the photochemical and thermal isomerisation processes among the seven coexisting species: OD-CN,

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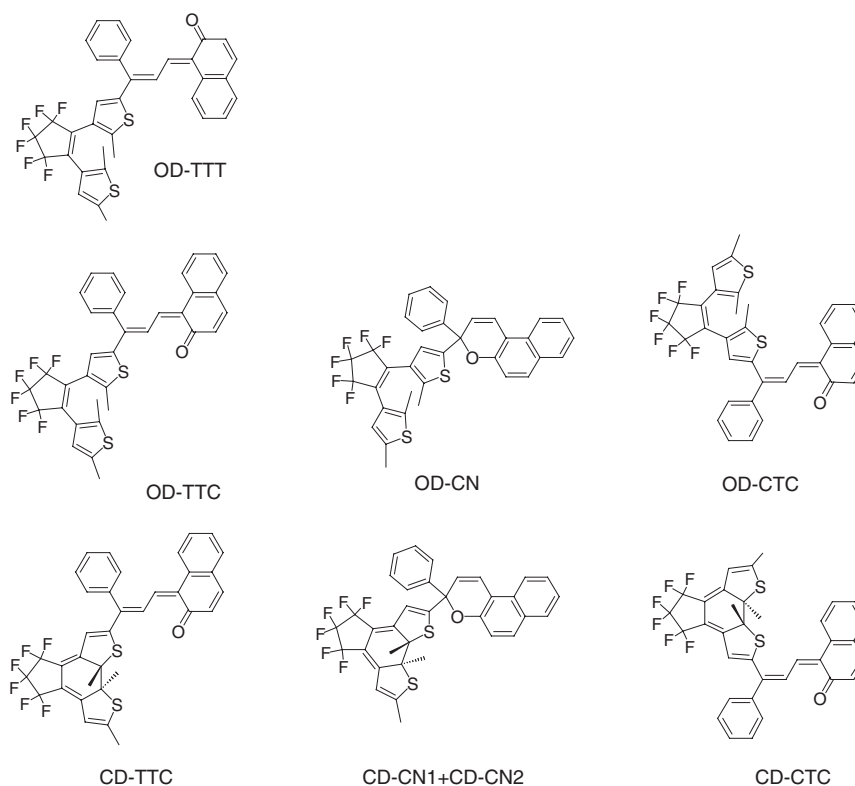
Scheme 1. Structures of photoproducts. The two molecules identified as CD-CN1 and CD-CN2 were attributed to diaster-eomers (*R,R-l* = *S,S-d*) and (*R,R-d* = *S,S-l*), due to the presence of asymmetric carbons in the dithienylethene cycle (*R,R*) or (*S,S*) and in the closed naphthopyran (*l* or *d*). In the present work, they have been merged as CD-CN = (CD-CN1 + CD-CN2)

OD-TTC, OD-CTC, OD-TTT, CD-TTC, CD-CTC and CD-CN (= CD-CN1 + CD-CN2).

RESULTS AND DISCUSSION

Thermal bleaching analysis

The bleaching behaviour of the biphotochromic molecule was analysed prior to any investigation of the photo-reaction kinetics. The evolution of the thermal relaxation at 227 K after UV irradiation with 313 nm, was monitored by recording ^{1}H NMR spectra at regular time intervals. By measuring several specific NMR signals, the peak-intensities of the seven photoproducts were integrated and the time-evolution of their respective concentrations was plotted (Fig. 1). The data sets were analysed on the basis of the general reaction pathway scheme shown in Scheme 5. The structures having the open naphthopyran in the CTC configuration (OD-CTC and CD-CTC) decreased along a mono-exponential curve, towards OD-CN and CD-CN, respectively. The rate constant for the bleaching at 227 K is $^{227}k = 1.6 \times 10^{-4}\,\mathrm{s}^{-1}$ for OD-CTC → OD-CN and this is about six times higher than the rate $^{227}k = 2.5 \times 10^{-5}\,\mathrm{s}^{-1}$ for CD-CTC → CD-CN. The photoproduct OD-TTT decayed very slowly

with a mono-exponential evolution towards OD-TTC ($^{227}k = 5.8 \times 10^{-6}\,\mathrm{s}^{-1}$) which in turn is converted thermally to OD-CN ($^{227}k = 1.0 \times 10^{-5}\,\mathrm{s}^{-1}$) (Scheme 2). These results help to better understand the thermal stability of the photoproducts and their isomerisation pathways at low temperature. They confirm the earlier observations for other naphthopyran compounds, namely that the XTC (CTC or TTC) configuration is directly connected to the closed form.[16] The results also confirm that the state of the dithienylethene ring, either closed or open, affects the stability of the naphthopyran open forms. Finally, it is noted that the attachment of a naphthopyran to a dithienylethene group does not affect the thermal stability of the closed form CD-CN.

### Photocolouration analysis

For a more detailed investigation of the photocolouration process, a sample of OD-CN was irradiated with 313 nm light at 227 K and NMR spectra were recorded periodically. By measuring the peak-intensities of each photoproduct, time-evolution of concentrations of individual isomers can be plotted (Fig. 2). As some photoproducts are not completely thermally stable even
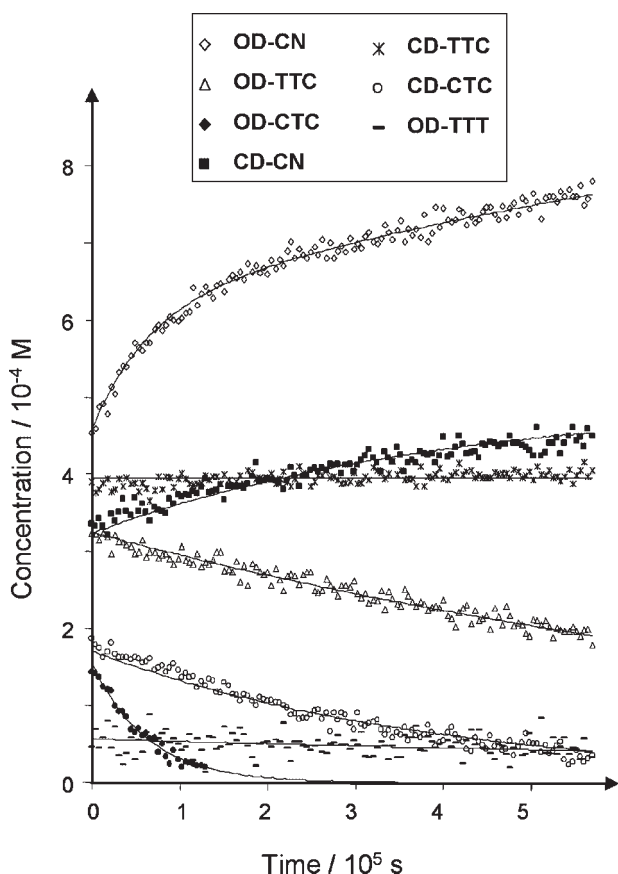
Figure 1. Thermal relaxation of OD-CN and its isomers at 227 K (starting time $t = 0$ corresponds to the end of UV irradiation of the thermostated sample). Experimental data points and all the simultaneous fitted continuous curves ($\chi^2 = 8.76 \times 10^{-11}$)

at 227 K, thermal bleaching has been taken into account, an approach in line with earlier experiments.

The results confirm the previously suggested processes[15] (Scheme 3). Irradiation of OD-CN generates the opening of naphthopyran moiety into the TTC and CTC configurations and the cyclisation of dithienylethene towards CD-CN. Additionally, the species CD-CN reacts
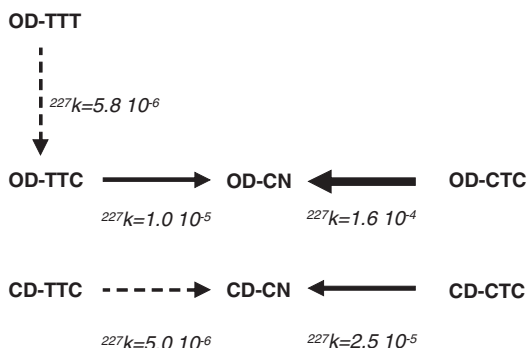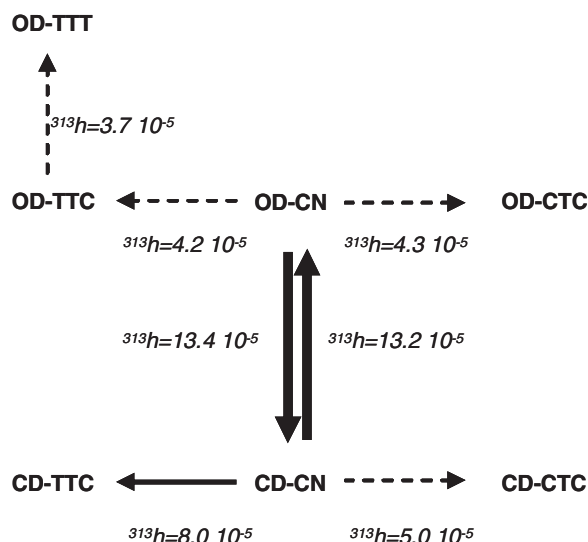

Scheme 2. Thermal processes occurring during relaxation at 227 K. The sizes of the arrows are a visual indication of the relative values of the corresponding rate constants, ^{227}k in s^{-1} (Residual error RE $= 8.76 \times 10^{-11}$)
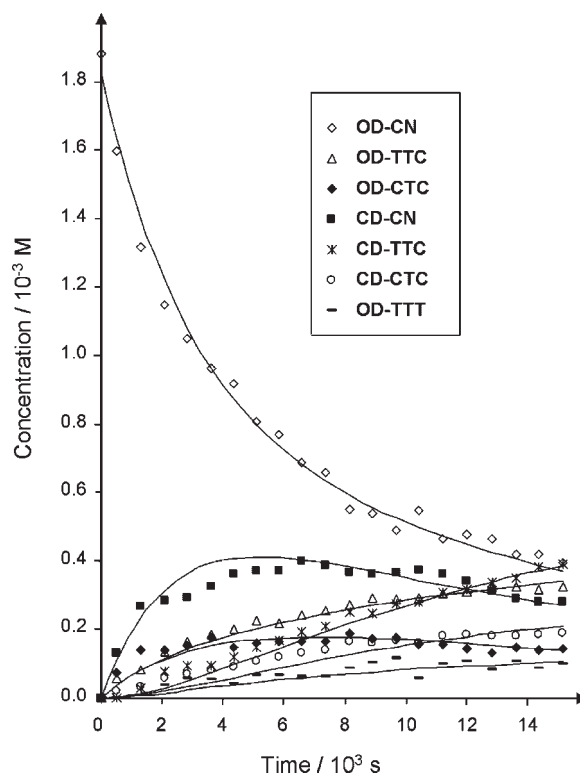
Figure 2. Time-evolution of concentrations at 227 K during irradiation with 313 nm. Experimental data points and all the simultaneous fitted continuous curves ($\chi^2 = 8.09 \times 10^{-10}$)

further on irradiation involving a ring-opening of the naphthopyran moiety. The only photoisomerisation process between open naphthopyrans concerns the path from OD-TTC towards OD-TTT. No evidence for a photoreaction between TTC and CTC could be detected.
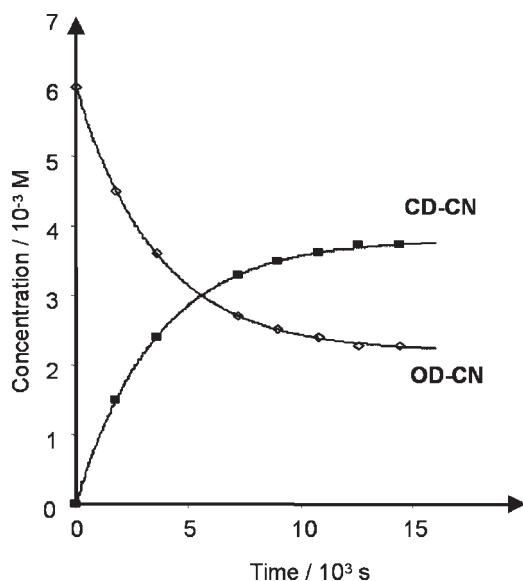

Scheme 3. Photoisomerisation processes occurring under irradiation with 313 nm at 227 K. The sizes of the arrows give a visual indication of the relative values of the corresponding rate parameters, ^{313}h in s^{-1} (Residual error RE $= 8.09$ 10^{-10}).

The configuration of the adjacent dithienylethene group, whether open or closed, has no influence on this reaction pathway. Moreover, no cyclisation of dithienylethene was found when the naphthopyran is in an open configuration.

A supplementary process had to be taken into account to obtain a good fit between experimental data and calculated curves. It concerns the decyclisation of CD-CN towards OD-CN. The apparent rate parameters are quasi equal at 227 K, $^{313}h_{\text{OD-CN}\to\text{CD-CN}} = 13.4 \times 10^{-5}\,\text{s}^{-1}$ and $^{313}h_{\text{CD-CN}\to\text{OD-CN}} = 13.2 \times 10^{-5}\,\text{s}^{-1}$.

Examination of the data reported in Scheme 3 indicates that the photoconversion of OD-CN to CD-CN is playing a major role (60% of the whole photoreactivity) whilst the photoconversion of OD-CN into OD-TTC and OD-CTC make up the reminder with a contribution of approximately 20% each of these processes. Viewed in a similar manner, the data indicates that 50% of the CD-CN photoreactivity is associated with the dithienylethene ring opening, whilst 31% and 19% of the photoreactivity are directed towards the formation of CD-TTC and CD-CTC.

The photocolouration was investigated also at ambient temperature by NMR spectroscopy. In these conditions, only cyclisation of the dithienylethene group can be monitored, because the lifetime of photomerocyanines is very short at ambient temperature. These photomerocyanine species are not accumulated sufficiently to be detected by NMR spectroscopy. Only signals of structures with closed naphthopyran and cyclised dithienylethene are produced at the timescales of the experiment and the course of reaction was followed by measuring peak-intensities of OD-CN and CD-CN (Fig. 3). A conversion maximum of 64% for the formation of CD-CN was detected. Analysis of this data allowed to identify a photoreversible mechanism between the two species with $^{313}h_{\text{OD-CN}\to\text{CD-CN}} = 17.6 \times 10^{-5}\,\text{s}^{-1}$ and

$^{313}h_{\text{CD-CN}\to\text{OD-CN}} = 10.2 \times 10^{-5}\,\text{s}^{-1}$. In this two-species system, the kinetic equation includes thus only a single variable, for example OD-CN, giving:

$$\frac{d[\text{OD-CN}]}{dt} = -^{313}h_{\text{OD-CN}\to\text{CD-CN}}[\text{OD-CN}] + ^{313}h_{\text{CD-CN}\to\text{OD-CN}}[\text{CD-CN}] \tag{1}$$

which, when combined with the law of conservation of matter and the expression of $h_{i\to j} = \Phi_{ij}\,\varepsilon_i\,l\,I_0\,F$ leads to:
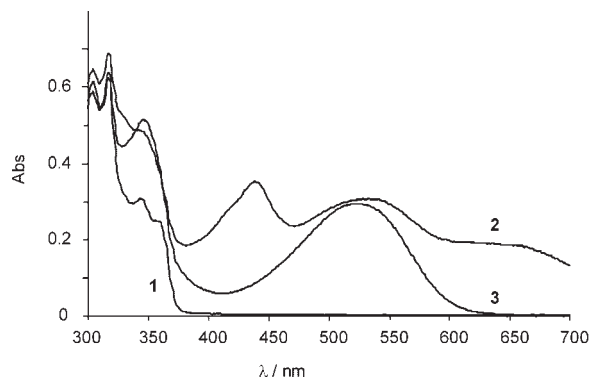
$$\frac{d[\text{OD-CN}]}{dt} = -^{313}\Phi_{\text{OD-CN}\to\text{CD-CN}}\varepsilon_{\text{OD-CN}}lI_0F[\text{OD-CN}] + ^{313}\Phi_{\text{CD-CN}\to\text{OD-CN}}\varepsilon_{\text{CD-CN}}lI_0F[\text{OD-CN}]_0 - ^{313}\Phi_{\text{CD-CN}\to\text{OD-CN}}\varepsilon_{\text{CD-CN}}lI_0F[\text{OD-CN}] \tag{2}$$

When the system reaches a photostationary state (PSS), $d[\text{OD-CN}]/dt = 0$, giving:

$$\frac{[\text{OD-CN}]_0}{[\text{OD-CN}]_{\text{PSS}}}$$
$$= ^{313}\Phi_{\text{OD-CN}\to\text{CD-CN}}\varepsilon_{\text{OD-CN}}\big/^{313}\Phi_{\text{CD-CN}\to\text{OD-CN}}\varepsilon_{\text{CD-CN}}$$
$$+ 1$$
$$= ^{313}h_{\text{OD-CN}\to\text{CD-CN}}\varepsilon_{\text{OD-CN}}\big/^{313}h_{\text{CD-CN}\to\text{OD-CN}}\varepsilon_{\text{CD-CN}}$$
$$+ 1 \tag{3}$$

Equation 3 was fully checked with data extracted from Fig. 3 ($[\text{OD-CN}]_0 = 6 \times 10^{-3}\,\text{M}$ and $[\text{OD-CN}]_{\text{PSS}} = 2.2 \times 10^{-3}\,\text{M}$).

Finally, the molar absorption coefficients of OD-CN and CD-CN were determined at 313 nm by UV–Visible spectroscopy. From the absorbance values measured at 313 nm (Fig. 4) and knowing that the concentrations at PSS are 36/64 % (established with the NMR experiment),

Figure 3. Time-evolution of concentrations at 293 K during irradiation with 313 nm. Experimental data points and all the simultaneous fitted continuous curves ($\chi^2 = 2.07 \times 10^{-10}$)

Figure 4. UV–Visible spectra of OD-CN before irradiation (1), after 40 min of irradiation (2) and after thermal evolution in the dark (3)
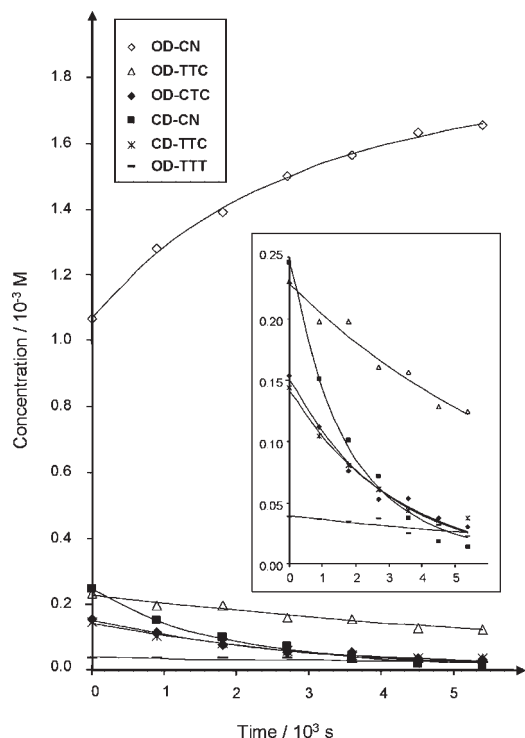
Figure 5. Time-evolution of concentrations at 227 K during visible light irradiation at 434 nm. Experimental data points and all the simultaneous fitted continuous curves ($C^2 = 3.71 \times 10^{-11}$). Insert: Evolution of the low-concentration photoproducts

it was found that the values for the respective absorption coefficients are very similar, with values of: $\varepsilon_{OD\text{-}CN} = 11085 \pm 463$ and $\varepsilon_{CD\text{-}CN} = 11194 \pm 468\ L\,mol^{-1}\,cm^{-1}$. This data allows to conclude that at 293 K, using light at 313 nm the following ratio $^{313}\Phi_{OD\text{-}CN\rightarrow CD\text{-}CN} = 1.74 \times {}^{313}\Phi_{CD\text{-}CN\rightarrow OD\text{-}CN}$ at 293 K, describes the system.
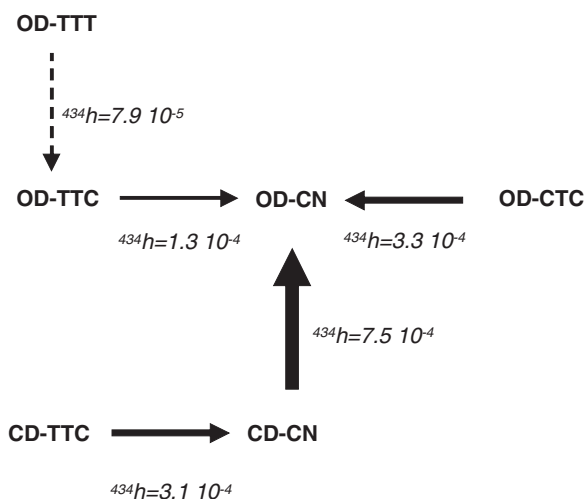
Scheme 4. Photoisomerisation processes occurring under irradiation with 434 nm at 227 K. The sizes of the arrows give a visual indication of the relative values of the corresponding rate parameters, ^{434}h in s^{-1}. (Product CD-CTC was not accumulated sufficiently to be detected.) (Residual error RE $= 3.71 \times 10^{-11}$)
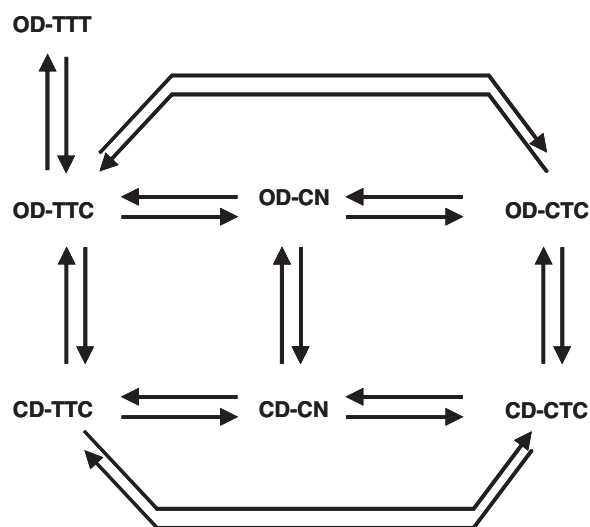
Scheme 5. General scheme used for the fitting procedure. In principle forty-two processes could be formulated, however taking into account that some processes are impossible. For example, no reaction is expected between OD-CTC and CD-TTC, as it would require at less two elementary pathways to perform the two isomerisations

Photobleaching analysis

The photobleaching was investigated at 227 K by irradiating with a 434 nm visible light a sample which had been firstly irradiated with UV light (Fig. 5). The analysis of the data was relatively simple as all decay kinetics follow mono-exponential curves, with the exception of OD-TTC and CD-CN which displays a biexponential one, due to the path OD-TTT $\rightarrow$ OD-TTC and CD-TTC $\rightarrow$ CD-CN, respectively (Scheme 4). This result clearly confirms our observations under UV irradiation. All the photochemical paths are reverted. When the naphthopyran is in an open configuration, no decyclisation of the dithienylethene moiety occurs.

CONCLUSION

The photochromism of a biphotochromic molecule involving both a naphthopyran and a dithienylethene moiety has been investigated by kinetic analysis of the concentration *versus* time profiles recorded by ^{1}H NMR spectroscopy. Up to seven photoisomers have been monitored. It has been shown that the two photochromic entities do not behave independently. The cyclisation of dithienylethene at 313 nm and the reverse process at 434 nm can only occur if naphthopyran is in closed configuration. On the contrary, naphthopyran can produce photomerocyanines in different isomeric states whatever the nature of dithienylethene (open or closed).

EXPERIMENTAL

Degassing and irradiation

Experiments were carried out in degassed toluene-d_8 at 2–3 mmol dm^{-3} concentration. The degassing of solution to remove oxygen was made by the technique of freeze-pump-thaw cycles (five cycles: 2.25×10^{-6} Torr) directly in the J. Young valve NMR sample tubes (Wilmad 507-JY-7). Photoirradiation was carried out directly into the NMR tube in a home-built apparatus with a 1000 W high-pressure Hg–Xe lamp equipped with filters. Monochromatic UV light was obtained by passing the light through a first filter (Schott 11FG09: $259 < \lambda < 388$ nm with $\lambda_{max} = 330$ nm, $T = 79\%$), then through an interferential one ($\lambda = 313$ nm and $T = 7\%$). Monochromatic visible light was obtained by passing the light through a first filter (Schott SCFIKG1503: $295 < \lambda < 800$ nm with $T = 50\%$ at $\lambda = 330$ and 700 nm), then through an interferential one ($\lambda = 434$ nm and $T = 16\%$). NMR spectra were recorded on a Bruker 500 spectrometer (^{1}H, 500 MHz) equipped with TXI probe, using standard sequences. Data sets were processed using Bruker Topspin 1.3 software.

UV–Visible spectroscopy

UV–Visible spectra were performed in toluene solution ($5.02 \pm 0.21 \times 10^{-5}$ M) of spectrometric grade (Aldrich) at 20°C. The analysis cell (optical path length 1 cm) was placed in a thermostated copper block with magnetic stirring inside the sample chamber of a Varian Cary 50 spectrometer. An Oriel 200 W high-pressure Xe–Hg lamp was used for irradiation equipped with interferential filter ($\lambda = 313$ nm and $T = 17\%$). The photostationary state was attained after 40 min of irradiation, then the sample was kept in the dark for thermal evolution (Fig. 4).

Kinetic data analysis

A general scheme involving the seven species (OD-CN, OD-TTC, OD-CTC, OD-TTT, CD-CN, CD-TTC and CD-CTC) has been reduced to 20 processes. Each process transforming the species i into the species j is characterised by a rate v_{ij}. (Scheme 5).

These rate can be expressed either thermally ($v_{ij} = {}^{227}k_{ij} [X_i]$) or photochemically ($v_{ij} = {}^{\lambda}h_{ij} [X_i] = \Phi_{ij} \varepsilon_i l I_0 F [X_i]$) or both ($v_{ij} = ({}^{227}k_{ij} + {}^{\lambda}h_{ij}) [X_i]$). ${}^{227}k_{ij}$ is the thermal rate constant of bleaching at 227 K of compound 'X_i' into compound 'X_j'. ${}^{\lambda}h_{ij}$ corresponds to an apparent first order rate parameter at $\lambda = 313$ nm or 434 nm, Φ_{ij} is the quantum yield of the photochemical transformation, ε_i is the molar absorption coefficient of compound X_i at the irradiation wavelength, l is the optical path, I_0 is the incident monochromatic photon flux and F the photokinetic factor. Its variations during the UV irradiation period have been neglected. This assumption is fully justified if F is strictly constant when the irradiation wavelength is close to an isobestic point or if the absorbance of the photochemical reacting solution is sufficiently low. As the irradiation light was not strictly monochromatic, Φ_{ij} and ε_i values must be considered as wavelength-averaged.

The calculated evolution in concentrations of different species was obtained by numerical integration of the set of differential equations written from the Scheme 5, using homemade curve fitting software.[17]

From the general Scheme 5, all the values are taken into account to start a fitting procedure. Starting values for the k_{ij} or the h_{ij} were chosen around 10^{-3}, and were then refined by trial and error until a good fit was obtained. Finally, the parameters were fitted automatically using an iterative algorithm of the Powell type, designed to minimize the residual error (RE = $\Sigma_n \Sigma_m [Y_{cal} - Y_{obs}]^2$/nm), between the experimental and the calculated curves (n is the number of experimental data points and m the number of kinetic curves). Parameters which were estimated either too small or not significant were removed one by one until a systematic increase of the residual error was observed.

We found that the fitting procedure was very selective among the various possible processes taken under consideration. For instance, the simulated kinetic curves were significantly distant from their corresponding experimental data if some important pathway was omitted or if the presence of a forbidden process was artificially imposed.

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