



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photogeneration of an ADADA H-bonding cleft based on a naphthopyran-decorated triazine

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ARTICLE INFO

Article history:

Available online 23 April 2008

Keywords:

NMR spectroscopy
Photochromism
Triazine
Naphthopyran
Rotamers

ABSTRACT

Bis-capped DAD H-bonding triazine units have been designed and synthesized, the two masking building blocks being 3,3-diphenyl-3H-naphtho[2,1-b]pyrans. Upon photoirradiation, the ring opening of both photochromic units leads to the formation of a five ADADA H-bonding site molecule. The conversion between the closed, mono-open and bi-open forms has been elucidated using NMR technique which has allowed to assign the corresponding rotamers and isomers, and their relative abundance. No self-aggregation has been observed for the closed form but more importantly also for the photogenerated structures.

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1. Introduction

The development of molecular systems that respond to light by undergoing reversible changes in their structures and physico-chemical behaviours is of paramount importance as it can deeply impact nanotechnologies related to functional and bio-inspired materials [1]. Transcribing such molecular variation to the supramolecular level and the desire to control self-assembly processes by means of light have promoted the design of numerous photochromic supramolecular systems [2]. These nanosized architectures are usually obtained by specific molecular recognition between complementary components (function, size, geometry), *i.e.* recognition between a guest and a host. The intrinsically molecular trend to self-assemble relies on non-covalent interactions such as hydrogen bonding, metal coordination, donor-acceptor or π -stacking. Based on the unique property offered by organic photochromes to modify the self-assembling process, various systems possessing recognition modules have been synthesized in fulgide [3], diarylethene [4], azobenzene [5], benzopyran [6] and spirooxazine families [7]. Up to now, the 2H-chromenes and more precisely the 3,3-diphenyl-3H-naphtho[2,1-b]pyrans have been mainly used in ophthalmic applications due to their easy access and pronounced resistance to fatigue [8]. Besides their colour changes, their unprecedented use as photoswitchable aggregative units could be

envisaged. Indeed, one can hypothesize that the electrocyclization process will serve as a double-lock towards the accessibility to a recognition unit and therefore to the formation of supramolecular arrays. However, before developing new insights, the photochromic response of the system has to be investigated. The present paper details the synthesis and the NMR structural elucidation of the biphotocromic system C–C, consisting of two naphthopyrans joined through a diaminotriazine central unit (Scheme 1).

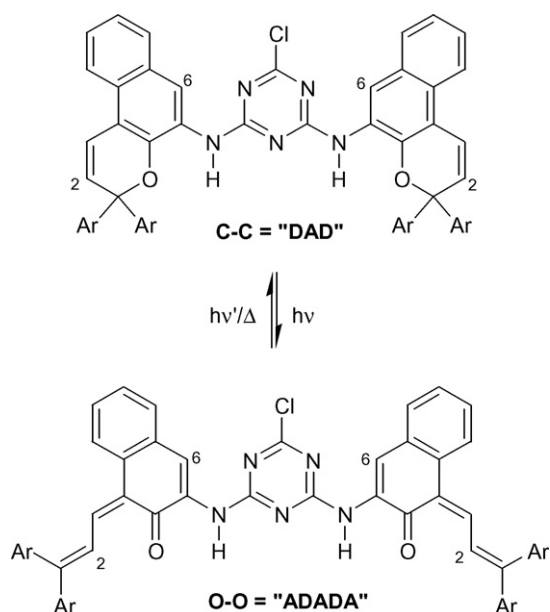
In the naphthopyran closed form, the phenyl units linked to the Csp³ of the pyran ring surround the aggregative core. The photoinduced ring-opening leads to the formation of open forms which are less sterically crowded and possess a carbonyl group that could also participate to a H-bond network. The ability of 1,3,5-triazine derivatives to generate non-covalent aggregates has been thoroughly exploited, as an example, the interaction between melamine and cyanuric acid has been fully documented [9]. The present system C–C has been chosen as it allows to generate from irradiation of a DAD network, the formation of a five ADADA H-bonding site molecule.

2. Results and discussion

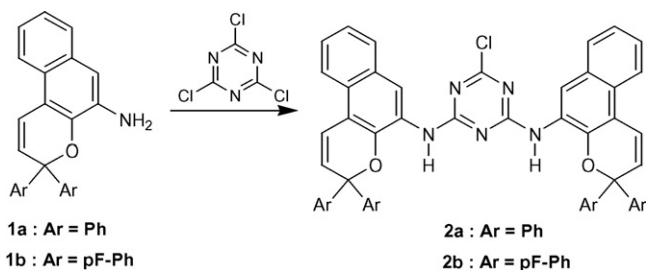
2.1. Synthesis and UV–vis measurements

The synthesis of target molecules with hydrogen bond sites requires first the 5-amino-3,3-diphenyl-[3H]naphtho[2,1-b]pyran **1a** which was obtained in three steps from the 3-amino-2-naphthol as previously described [10]. The dinaphthopyrans **2a** and **2b** were

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Scheme 1. Photochromic equilibrium of targeted dinaphthopyrans linked to diaminotriazine. (C and O denote closed and open forms, respectively, A and D, acceptor and donor).



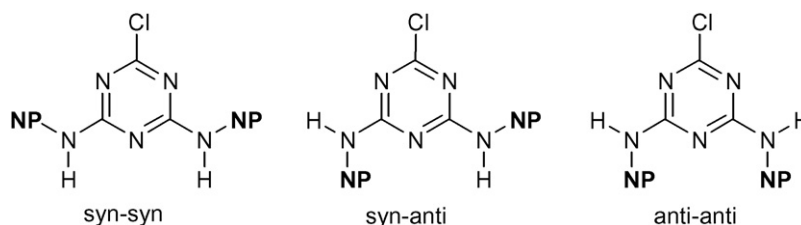
Scheme 2. Synthetic pathway to **2a** and **2b**.

Table 1
Spectrokinetic data for compounds **2a** and **2b** in toluene at 20 °C

Compound	λ_{\max} (nm)	A_{eq}	k_{Δ} (s ⁻¹)
2a	449	0.81	0.023
2b	452	0.84	0.019
3,3-Diphenyl-3H-naphtho[2,1-b]pyran	425	1.12	0.112

prepared by the reaction of cyanuric chloride with the amino derivatives in THF using diisopropylethylamine (Scheme 2). The two derivatives were selectively obtained by a sequential procedure and by controlling the temperature [11].

UV irradiation of the two toluene solutions of **2a** and **2b** was carried out at 20 °C. As reported in Table 1, there is no significant difference between the spectrokinetic parameters measured. The



Scheme 3. Possible conformations of the closed forms (NP: naphthopyran).

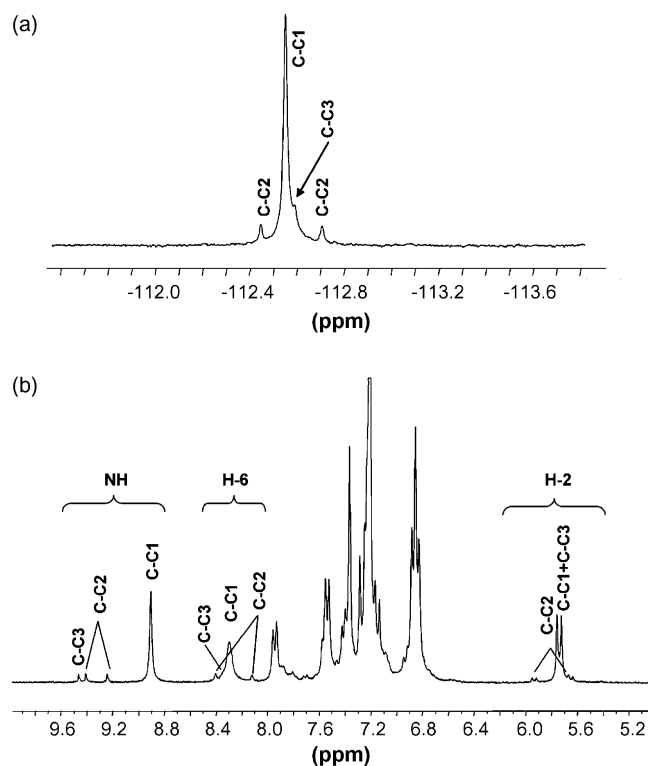


Fig. 1. ¹⁹F (a) and ¹H (b) aromatic spectra of C–C at 213 K.

maximal absorption wavelength, the relative steady-state colourability and the thermal fading rate are very similar, thus indicating that the fluorine atoms do not modify the photochromic process. However, the substitution pattern on the 5-position induces bathochromic shifts of λ_{\max} and more interestingly decreases the thermal fading rate constants (k_{Δ}) for both compounds in comparison with the unsubstituted parent naphthopyran.

2.2. NMR investigations

The targeted compounds may exist in various forms as restricted rotations about the Nsp³–Csp² bonds have to be considered. The exclusion of isomers arising from the restricted rotation about the amino–naphthopyran bond is not obvious but considering the sterical hindrance between the two phenyl groups in both photochromic units and the triazine entity, the closed forms may adopt predominantly three different conformations (*syn-syn*, *syn-anti* and *anti-anti*) as depicted in Scheme 3.

At 293 K, the ¹H and ¹⁹F NMR spectra of the fluorinated dinaphthopyran **2b** show the presence of a unique form as proved by the unique chemical shift value observed for the four fluorine atoms, although broadened ¹H aromatic resonances are observed, in particular for the characteristic and well distinguishable NH, H-

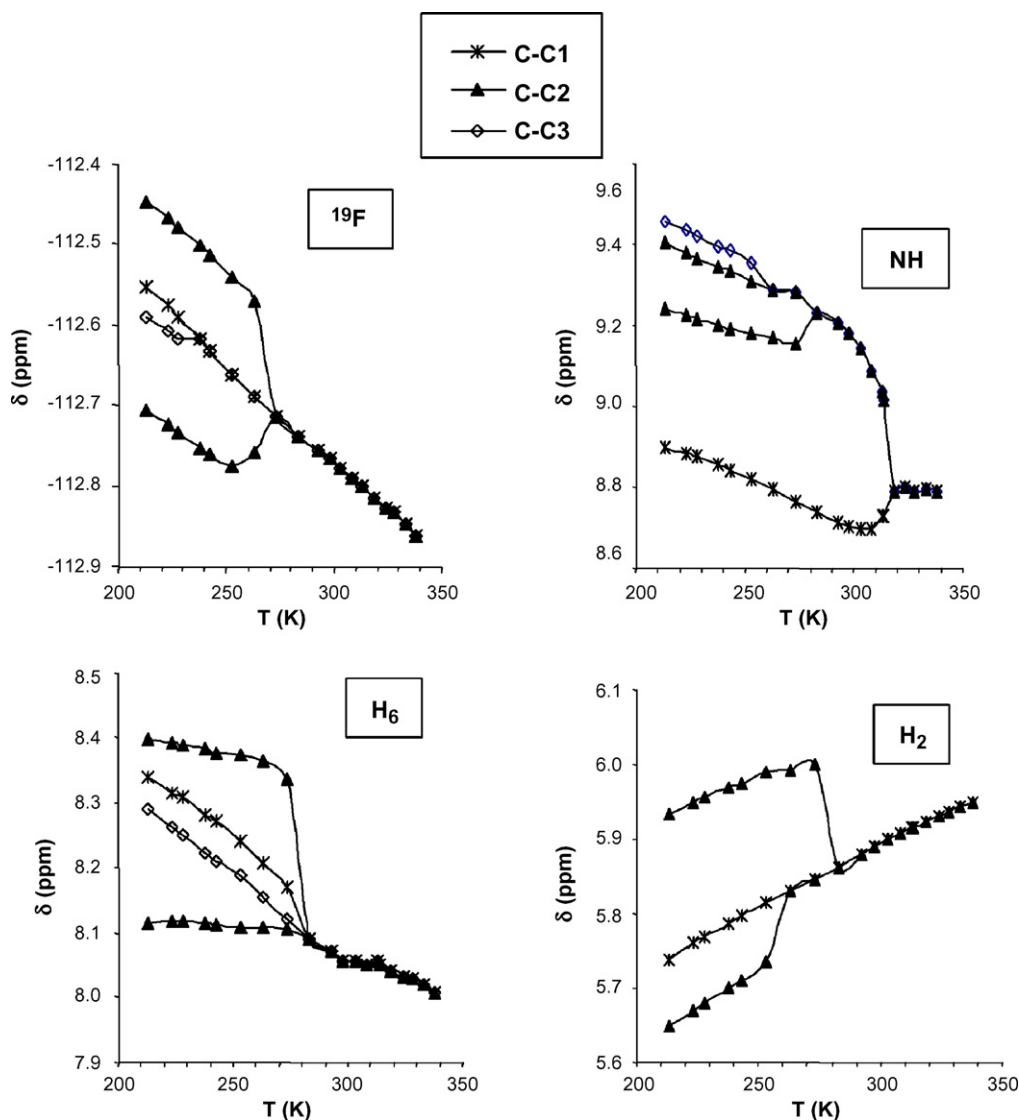


Fig. 2. Temperature dependence of the ^{19}F , NH, H₆, and H₂ chemical shifts in the C–C rotamers.

2 and H-6 protons. To assess the involved conformations of the closed form **2b**, hereafter C–C for convenience, NMR temperature-dependent experiments were monitored. At 213 K, the signals were split, the ^{19}F NMR spectrum consisting of three sets (C–C1, C–C2 and C–C3) of fluorine resonances with unequal peak-intensities (Fig. 1a).

The rotation about the C_{triazine}–NH bond is typically rapid at room temperature and a single, time-averaged signal is observed. As the temperature is decreased, the rotation becomes slower and four separate resonances appear, one signal of high intensity (70%), two similar signals of medium intensity (20%) and one signal of minor intensity (10%). Even if a more complicated spectrum is obtained in ^1H NMR spectroscopy (Fig. 1b), similar results are obtained for NH and H-6 protons, for H-2 proton only three doublet signals have been clearly detected. From the spectra recorded at different temperatures from 213 until 338 K, the chemical shift variations of each ^{19}F , NH, H-6 and H-2 signals have been extracted as displayed in Fig. 2. The chemical shifts of ^{19}F , H-6 and H-2 for C–C1 and C–C3 are close together while signals for unsymmetrical molecule (C–C2) which follow the same slope are rather different.

In contrast, the NH signal of C–C3 is shifted greatly upfield compared to NH for C–C1. This result is not surprising as the three

rotamers arise from the rotation around the C_{triazine}–NH bond that exhibits the most affected chemical environment. Consequently, the three isomeric compounds are assigned to two symmetrical rotamers, C–C1, adopting folded *anti-anti* conformation in preference to C–C3, having extended *syn-syn* conformation, and one asymmetrical rotamer C–C2 in *syn-anti* conformation. The major conformation is assumed to be the *anti-anti*, as the steric hindrance caused by the naphthopyran moiety is supposed to be less prevalent than the stabilization through π – π interactions, due to the face-to-face naphthyl rings. No signals corresponding to self-aggregation of one of those rotamers have been detected. Upon UV irradiation, 2H-chromenes undergo a bond breaking, leading to the formation of open coloured isomers being assigned as the Transoid-Cis (TC) and the Transoid-Trans (TT) reversible by an electrocyclization process [12]. TC isomers have been found to be the predominant structure exhibiting a faster thermal decay, TT open forms representing usually 0–15%. The lifetime of these photomerocyanines at room temperature is short, then justifying that the NMR investigations were performed at lower temperatures [13]. In these conditions ($T < 253$ K), as three conformations of C–C exist in solution before irradiation, taking into account that two isomers can be produced (TC and TT) and that the two naphthopyran entities do not open

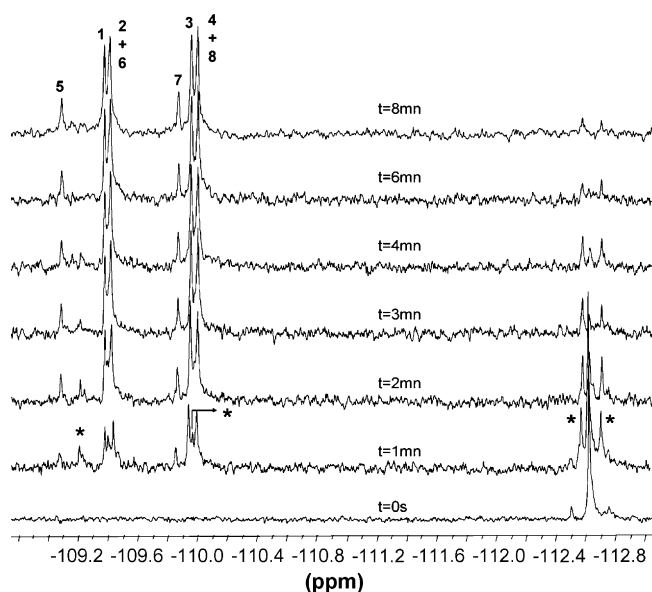


Fig. 3. ^{19}F NMR spectra of CC at 238 K. The times indicated are the cumulated UV irradiation periods (*: signals of C–O1 and C–O2, 1–4: signals of O–O1, and 5–8: signals of O–O2).

simultaneously, up to fifteen additional photoinduced structures could be produced. Due to this high number of expected structures, ^{19}F NMR spectroscopy has been chosen as it greatly simplifies the assignment of the NMR signals to the open and closed structures. Indeed, the chemical shift of a fluorine atom in a closed naphthopyran is situated at around -112.6 ppm, while the range of ^{19}F in open entities is shifted at around -110 ppm.

Moreover, the ring-opening leads to spiro carbon hybridization change, from sp^3 to sp^2 . The two phenyl groups and consequently the two fluorine atoms therefore are no longer equivalent in each photomerocyanine, resulting in two distinguishable resonances [14].

UV irradiation of C–C was monitored at 238 K by recording ^{19}F NMR spectra as displayed in Fig. 3. After 1 min of UV irradiation, two new resonances are detected in the part characteristic of ^{19}F in closed entity. Their intensities increase, and then decrease while the sample is irradiated longer. In the part of spectrum characterising open entities, signals at -109.2 , -109.3 and at about -110 ppm follow the same evolution. As their peak-intensities are twice lower than the intensity of the first cited, these signals can be associated to two open–closed structures (C–O1 and C–O2) with two different resonances for the open side ($I = 1 \cdot ^{19}\text{F}$), and only one for the closed side ($I = 2 \cdot ^{19}\text{F}$). All these signals totally disappear when the time of irradiation is increased. As they result from mono-opening reaction, irradiation converts them to open–open structures. Indeed, only signals in part characterising photomerocyanines are detected after several minutes of irradiation. Four intense signals (1, 2, 3, and 4, see Fig. 3) are observed, as well as four other ones (noted 5, 6, 7, and 8), but less intense.

In spite of the signals proximity impeding accurate peak-intensity measurements, it is possible to monitor the time-evolution of concentrations. The thermal evolution of fresh solutions of C–C after 5 min of UV irradiation at four low temperatures (228, 238, 243 and 253 K) has been monitored by recording NMR spectra at regular time intervals and by measuring the peak-intensities (Fig. 4). This enables not only to gather the different signals, but also to assign all of photomerocyanine entities to Transoid-Cis isomers, due to the kinetic rate of relaxation, which is in agreement with values reported for naphthopyran family [15].

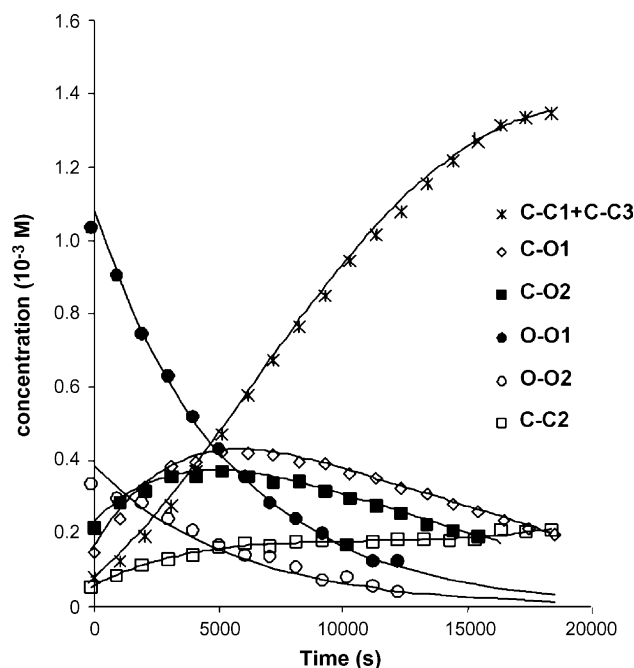


Fig. 4. Time-evolution concentrations of C–C after UV irradiation at 243 K.

Table 2
Thermal rate constants of bleaching (k_{Δ} in s^{-1})

T (K)	$k_{1(\text{O}-\text{O} \rightarrow \text{C}-\text{O})}$	$k_{2(\text{C}-\text{O} \rightarrow \text{C}-\text{C})}$
228	1.6×10^{-5}	NS
238	7.6×10^{-5}	3.0×10^{-5}
243	18.8×10^{-5}	9.0×10^{-5}
253	79.0×10^{-5}	56.2×10^{-5}

Consequently, the four intense signals (previously named 1, 2, 3 and 4 = O–O1) follow the same monoexponential decay, as well as the four less intense (5, 6, 7 and 8 = O–O2). As for the two open–closed structures (C–O1 and C–O2), as expected their time-dependences are bi-exponential curves. Nevertheless, it is not possible to correlate an open–open structure to a particular open–closed one, for example, $\text{O}-\text{O}1 \rightarrow \text{C}-\text{O}1$ and $\text{O}-\text{O}2 \rightarrow \text{C}-\text{O}2$ or $\text{O}-\text{O}1 \rightarrow \text{C}-\text{O}2$ and $\text{O}-\text{O}2 \rightarrow \text{C}-\text{O}1$. But, one can get a good fit by considering the reaction: $\text{O}-\text{O}1 + \text{O}-\text{O}2 \rightarrow \text{C}-\text{O}1 + \text{C}-\text{O}2 \rightarrow \text{C}-\text{C}$, with parameters k_1 and k_2 respectively. The kinetic equations are deduced from this consecutive mechanism:

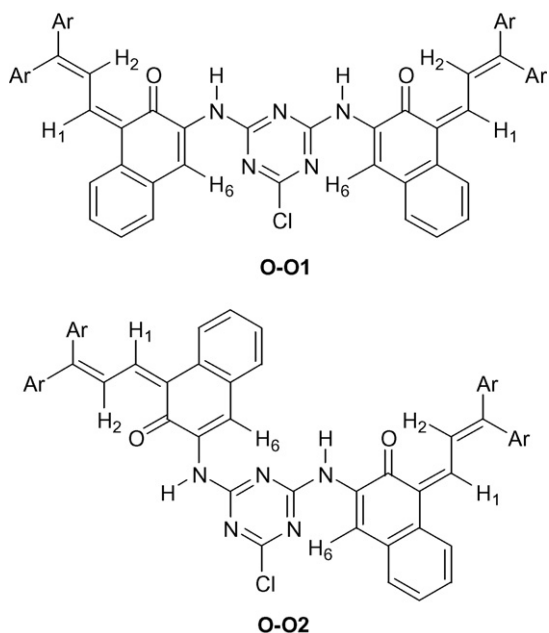
$$[\text{O}-\text{O}]_t = [\text{O}-\text{O}]_0 \exp(-k_1 t)$$

$$[\text{C}-\text{O}]_t = [k_1 / (k_2 - k_1)] [\text{O}-\text{O}]_0 (\exp(-k_1 t) - \exp(-k_2 t)) + [\text{C}-\text{O}]_0 \exp(-k_2 t)$$

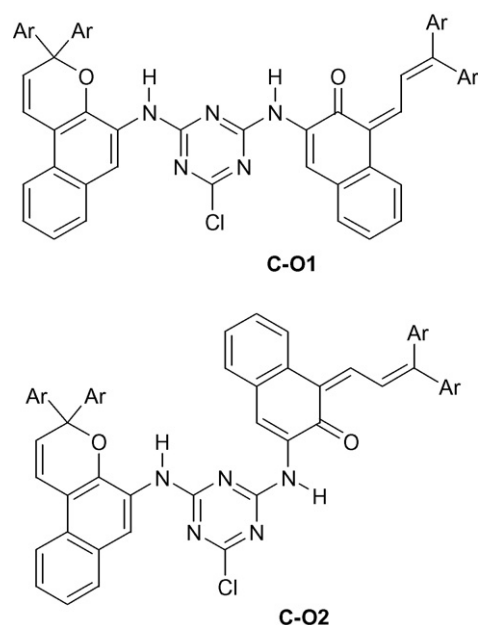
$$[\text{C}-\text{C}]_t = [\text{C}-\text{C}]_{\infty} - [\text{O}-\text{O}]_t - [\text{C}-\text{O}]_t$$

where $[\text{O}-\text{O}]_0$, $[\text{O}-\text{O}]_t$ are the sum of concentrations of O–O1 and O–O2 at $t=0$ and at the instant t , $[\text{C}-\text{O}]_0$ and $[\text{C}-\text{O}]_t$, the sum of concentrations of C–O1 and C–O2 at $t=0$ and at the instant t , $[\text{C}-\text{C}]_t$, the initial concentration of solution, and k_1 and k_2 , the rate parameters for the bleaching (Table 2).

The set of above-mentioned results has been obtained from ^{19}F NMR spectroscopy. Nevertheless, ^1H NMR spectra have also been recorded as they can bring more accurate structural information. Indeed, in spite of the overlapping aromatic signal complexity, close examination enables to distinguish some characteristic resonances.



Scheme 4. Structures for bi-open forms O-01 and O-02.



Scheme 5. Structures for mono-open forms C-01 and C-02.

In the first ^1H spectrum recorded at 238 K after irradiation (Fig. 5), the signals belonging to open–open structures (identified in ^{19}F spectroscopy) can be detected.

Two doublet signals at 9.2 and 9.3 ppm present scalar coupling constant equal to 11.8 Hz in correlation with two doublet signals at 7.95 ppm. The same coupling system is observed for the signals of small intensities around 9.25 and 8.0 ppm. They characterise the two protons of transoid bond, H-2 and H-1, in each photomero-cyanine entities, inside two open–open structures, named O-01, major in concentration and O-02, less intense in concentration. Four intense and four small singlet resonances are assigned to NH and H-6, in each bi-open system. Consequently, in the same way as the four fluorine atoms are non-equivalent in the open–open structure, the protons are also differentiated. The chemical shifts in both structures are quite similar excepted for the H-6 protons, and more particularly in O-02. For this latter form, chemical shifts for H-6 were found at 8.5 and 8.95 ppm (Scheme 4).

This can be explained by a different electronic environment and therefore, O-02 is attributed the *syn-anti* structure, whereas O-01 is identified to the *syn-syn* one, both having TC conformations for

the open forms. By varying the temperature, the concentration and/or the time of irradiation, no chemical shifts or broadening were detected for the bi-open structures. This clearly indicates that no self-aggregation takes place in our conditions. Similar treatment of the NMR data corresponding to the two mono-open forms C-01 and C-02 affords one major *syn-syn* and one minor *syn-anti* having a TC conformation for the open-ring part (Scheme 5).

3. Conclusion

Triazine possessing two photoswitchable side-arms based on diphenylnaphthopyran acts as a simple and efficient biphotochromic compounds, upon photoirradiation both pyran rings give rise to open forms which exist as TC-forms. More interestingly the two photogenerated carbonyl groups may be considered as two additional H-bond sites. The predominant bi-open structure is found to be a *syn-syn* rotamer with regard to the diamino-triazine core, and it corresponds to the most appropriate geometrical isomers to be involved in an ADADA H-bond sequence. Specific recognition experiments are under current investigation. This sys-

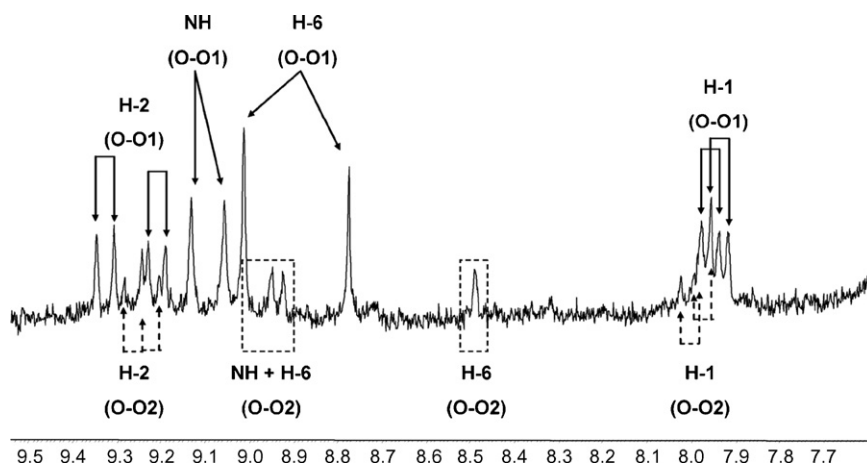


Fig. 5. Aromatic part with characteristic signals in O-01 and O-02.

tem can be remotely photoswitched from an hindered DAD to a potentially highly efficient aggregative unit which may open new prospects for the use of well-known 2H-chromene derivatives in the field of addressable self-assembled structures.

4. Experimental

4.1. Methods

Photochromic measurements (UV–vis) were performed in toluene solution (5×10^{-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 Beckman-DU-7500-diode-array spectrometer. An Oriel 150 W high pressure Xe lamp was used for irradiation.

For NMR investigations in the photochromic process, samples ($1-3 \times 10^{-3}$ M in toluene- d_8) were irradiated directly in the NMR tube (5 mm), thermo-regulated, using a 1000 W Xe-Hg HP filtered short-arc lamp (Oriel) equipped with filter for UV irradiation (Schott 011FG09, $259 < \lambda < 388$ nm). After irradiation, the sample was transferred into the thermoregulated probe of a Bruker Avance-DPX or AC-300P NMR spectrometer (^1H , 300 MHz, ^{19}F , 282 MHz).

Flash column chromatography was performed on silica gel (Merck 40–63 μm). Melting point was determined on an Electrothermal Eng. Ltd melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were determined on a Bruker AC 250 NMR spectrometer with CDCl_3 or $\text{DMSO}-d_6$ as solvent and TMS as internal standard ($\delta = 0$ ppm). Mass spectra were recorded on a VG AutoSpec apparatus using electronic impact at 70 eV. Microanalyses were determined in the microanalytical laboratory at the CNRS, Vernaison.

4.2. Synthetic procedures

The synthetic method of biphotochromic triazines was shown in Scheme 2 and experimental details were carried out as following.

4.2.1. Synthesis of 2-chloro-4,6-di- $\{[3,3\text{-diphenyl-}[3\text{H}]\text{-naphtho}[2,1\text{-}b]\text{pyran}]$ -5-amino}-1,3,5-triazine (**2a**)

A solution of cyanuric chloride (84 mg, 0.455 mmol) in THF (5 mL) under nitrogen was stirred at 0 °C. A solution of **1a** (150 mg, 0.43 mmol) and *N,N*-diisopropylethylamine (56 mg, 0.434 mmol) in THF (5 mL) was added and then the mixture was stirred for 1 h at ambient temperature. A second solution of **1a** (150 mg, 0.43 mmol) and *N,N*-diisopropylethylamine (56 mg, 0.434 mmol) in THF (10 mL) was added and the reaction mixture was stirred for 40 h at 55 °C. The solution was filtered and the solvent was evaporated. The crude product was purified by column chromatography using dichloromethane/petroleum ether (2:3) as eluent. Yield 172 mg (49%); mp 164–165 °C; δ_{H} (250 MHz, CDCl_3): 6.31 (1H, d, J 10.1 Hz, H-2), 6.92 (1H, s, H-8), 7.04–7.30 (7H, m, H-9,4',3'), 7.34–7.60 (6H, m, H-1,7,2'), 7.87 (1H, s, H-6), 8.18 (1H, d, J 8.5 Hz, H-10), 9.58 (1H, s, NH); δ_{C} (62.5 MHz, CDCl_3): 144.2, 129.4, 129.3, 128.7, 128.5, 127.6, 126.2, 124.7, 121.3, 119.7, 85.6; MS (LSIMS) m/z 811.3 (MH^+ , 100). Calcd. for $\text{C}_{53}\text{H}_{19}\text{ClN}_5\text{O}_2$, C, 78.56, H, 4.48, N, 8.64, O, 3.95, Cl, 4.38; Found C, 78.71, H, 4.52.

4.2.2. Synthesis of 2-chloro-4,6-di- $\{[3,3\text{-}(\text{di-4-fluorophenyl})\text{-}[3\text{H}]\text{-naphtho}[2,1\text{-}b]\text{pyran}]$ -5-amino}-1,3,5-triazine (**2b**)

A solution of cyanuric chloride (81 mg, 0.439 mmol) in THF (5 mL) under nitrogen was stirred at 0 °C. A solution of **1b** (150 mg, 0.39 mmol) and *N,N*-diisopropylethylamine (55 mg, 0.426 mmol) in THF (5 mL) was added and then the mixture was stirred for 1 h at ambient temperature. A second solution of **1b** (150 mg, 0.39 mmol) and *N,N*-diisopropylethylamine (55 mg, 0.426 mmol) in THF (10 mL) was added and the reaction mixture was stirred for 40 h at 50 °C. The solution was filtered and the solvent was evaporated. The crude product was purified by column chromatography using dichloromethane/petroleum ether (2:3) as eluent. Yield 112 mg (29%); mp 300–301 °C; δ_{H} (250 MHz, CDCl_3): 6.31 (1H, d, J 10.1 Hz, H-2), 6.92 (1H, s, H-8), 7.04–7.18 (5H, m, H-9,2'), 7.32–7.60 (6H, m, H-1,7,3'), 7.87 (1H, s, H-6), 8.07 (1H, d, J 8.5 Hz, H-10), 9.69 (1H, s, NH); δ_{C} (62.5 MHz, CDCl_3): 164.8, 160.8, 139.8, 139.7, 129.5, 129.4, 128.1, 126.4, 126.3, 124.9, 124.8, 121.3, 120.1, 115.9, 115.5, 114.6, 83.7; δ_{F} (toluene- d_8): –112.4; MS (LSIMS) m/z 883.3 (MH^+ , 100). Calcd. for $\text{C}_{53}\text{H}_{15}\text{F}_4\text{ClN}_5\text{O}_2$, C, 72.15, H, 3.66, N, 7.94, O, 3.63, Cl, 4.02, F, 8.61; Found C, 72.01, H, 3.71.

Acknowledgements

The 300 MHz NMR facilities were funded by the Region Nord-Pas-de-Calais and MENRT. This collaborative study was realized within the framework GDRI CNRS no. 93.

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