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Remarkable thermally stable open forms of photochromic new *N*-substituted benzopyranocarbazoles

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ABSTRACT

New *N*-substituted benzopyranocarbazoles were synthesized and their photochromic properties, under continuous near-UV irradiation, are described. Besides a remarkable sensitiveness to solar light, *N*-methyl and *N*-benzyl derivatives give rise to particularly stable coloured open forms. The structure of these photoisomers was characterized through NMR spectroscopy. According to our results, it was possible, after UV irradiation, to accumulate more than 90% of the long-lived TT-isomer. At ambient temperature, coloured TT state was fully photobleachable by visible light and no significant degradation was observed during cycling. This remarkable property opens a range of potential applications for these *N*-substituted benzopyranocarbazoles in photoswitchable devices.

1. Introduction

Organic photochromic compounds are capable of changing their geometrical and electronic structures under the influence of UV light and return-back to their initial state when the luminous irradiation ceases. The return to the initial state may be promoted through a thermal process (spontaneous) and/or triggered on exposure to poly- or monochromatic visible light [1,2]. As the reversible structural changes occur at a single-molecule level the phenomenon is potentially interesting to miniaturize optic components down to the molecular level [3] and for applications in molecular opto-electronics, namely for information storage (e.g. optical inscription) and photoswitch technologies offering the possibility to control, through photochromic reactions, the physico-chemical properties of materials (e.g. fluorescence, electrical conductivity, magnetism, permeability, reactivity, etc.).

The most remarkable and exploited characteristic of such systems is an observable reversible change of colour. In the last decades numerous organic photochromic compounds have been studied and they have found use in plastic materials in which a photoinduced reversible colour change is desired. These applications include lenses of variable optical density, eye-protective glasses, optical filters, diverse optical devices for use in camera systems or photographic apparatus, decorative objects, novelty items and toys, smart windows and visors, security markers, inks and cosmetic products [4,5].

The benzo and naphthopyrans constitute one of the most studied photochromic families due to their easy preparation, colour tunability and pronounced resistance to fatigue. In solutions or in polymeric matrices the photochromic behaviour is based on the reversible photochemical cleavage of the C–O bond in the pyran ring, upon UV irradiation, leading to a mixture of the closed uncoloured form (CF) and a set of isomers with quasi planar structures (the so-called "open form"—OF) where an extended π-electrons conjugation is responsible for the perceptible colour change. At room temperature the back electrocyclization reaction leading to the uncoloured state is normally a thermal process that can be significantly accelerated by irradiation with visible light (Scheme 1). The major coloured photoisomers have been assigned as the *transoid–cis* (TC), and *transoid–trans* (TT) structures. The TC-isomer is generally the predominant coloured component and exhibits a fast thermal bleaching kinetic, while the TT-isomer is the minor component thermally more stable and responsible for the residual colour that usually persists

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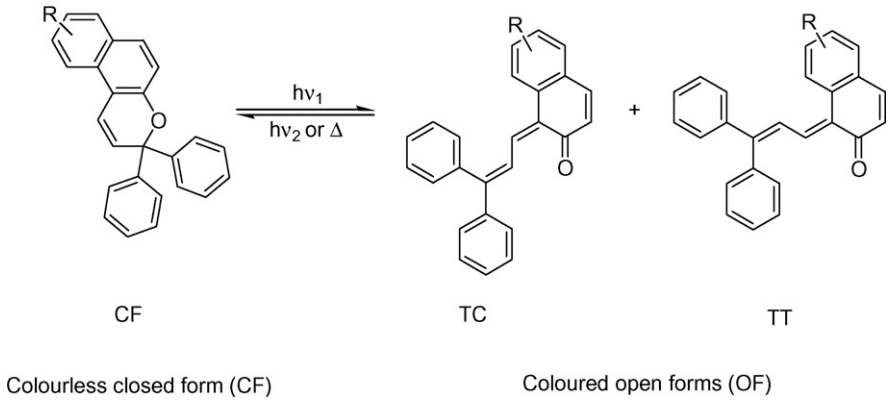
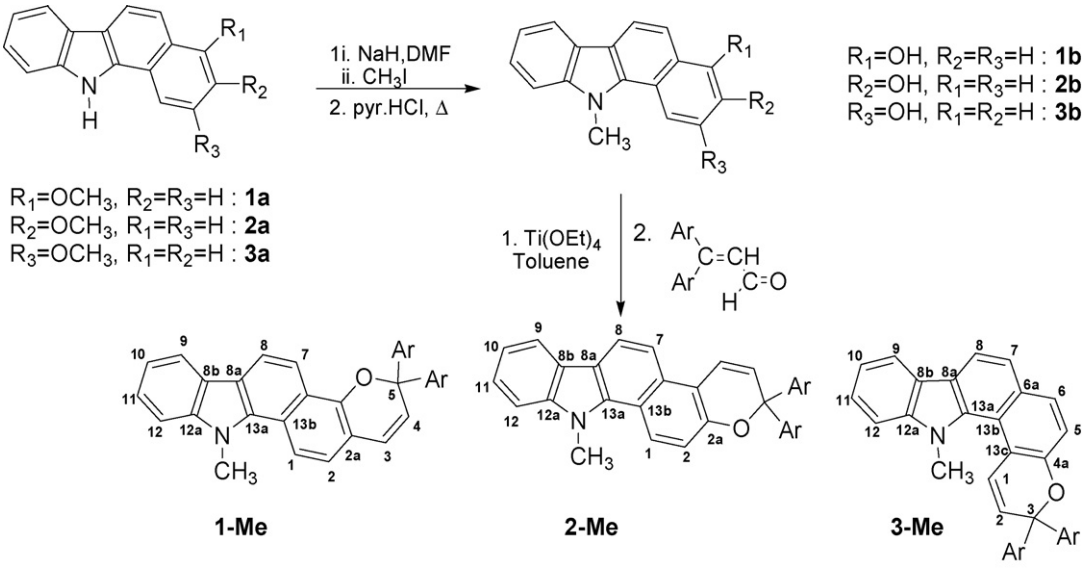
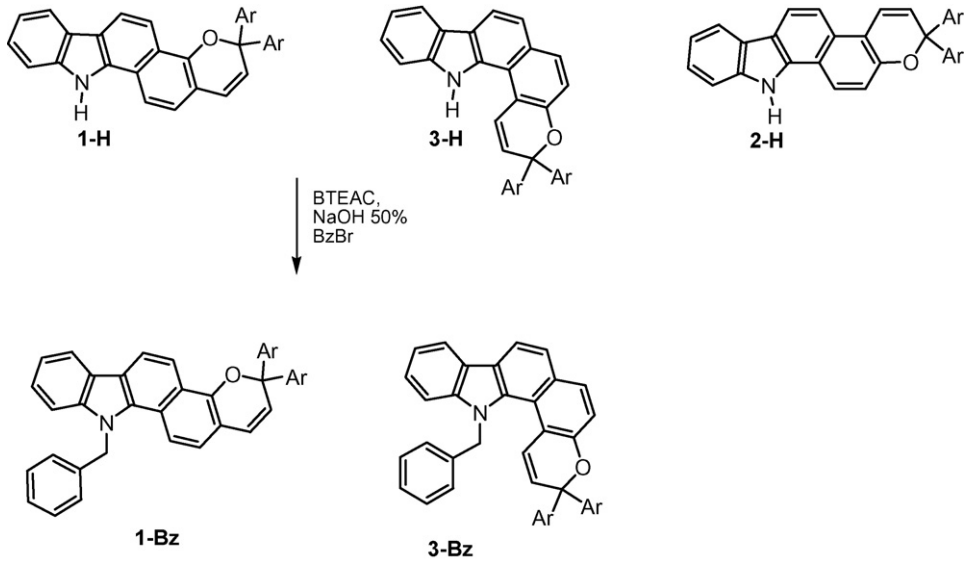


Scheme 1. Photochromic equilibrium of a substituted diphenylnaphthopyran.



Scheme 2. General synthesis for compounds **1-Me**, **2-Me** and **3-Me**.



Scheme 3. General synthesis for compounds **1-Bz**, **2-Bz** and **3-Bz**.

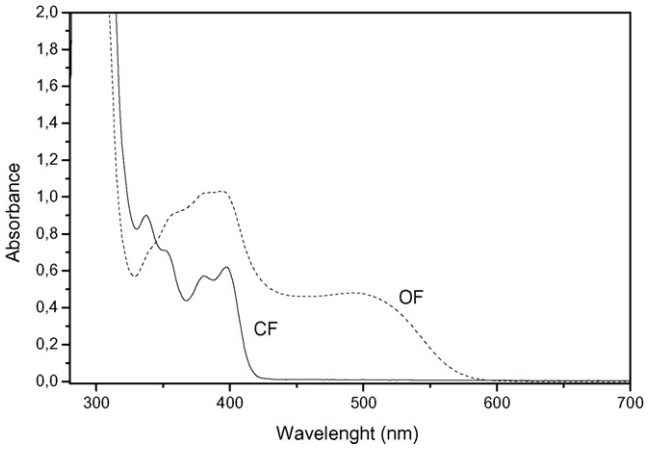


Fig. 1. Absorption spectra before (CF) and after (OF) UV irradiation of **3-Me** (toluene solution: irradiation at 330 nm until the photo steady state).

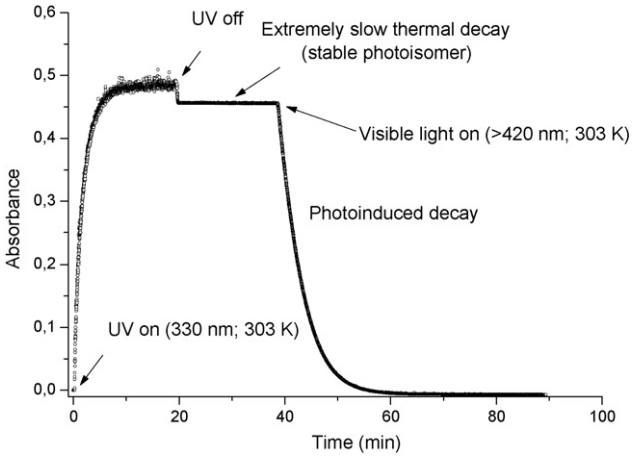


Fig. 2. Temporal evolution of the absorbance at 494 nm of compound **3-Me** (toluene solution: irradiation at 330 nm until the photo steady state and visible irradiation with $\lambda > 420$ nm).

for variable length of time after the UV irradiation has ceased [6].

The use of this family of compounds in fully photon-controlled applications such as recording media (optical memories) and photoswitches is not usually considered due to the thermal reversibility, a prohibitory property for those applications. References to benzo and naphthopyrans for such applications are scarce in the literature certainly because few of them possess two thermally stable states [4,7]. Moreover, they are not attractive due to the low concentration of the thermally more stable TT-isomer (0–15% [6]) that can be reached under conventional irradiation. Indeed diarylethenes and fulgides constitute by far the most promising and extensively studied families of bistable organic photochromes that are suitable for such applications [8,9].

Here, we report the synthesis and the photochromic properties of new *N*-substituted benzopyranocarbazoles (**1-Me**–**3-Me** and **1-Bz**–**3-Bz**). Studies were performed under continuous UV irradiation, in order to accumulate the long-lived photoisomers [10], and it was observed that **3-Me** and **3-Bz** give rise to more than 90% of unusual long thermal stable isomers. The efficient use of steric effects to enhance the thermal stability of open forms without the loss of other photochromic properties pave the way to the possibility to apply photochromic naphthopyrans as photoswitching units and to transform a known T-photochrom into a possible P-photochrom.

Table 1
Maximal wavelengths of the coloured forms (λ_{max}, nm), colourability (A_{PSS} = maximum absorbance at λ_{max} attained at the photostationary state), rapid (k_1) and slow (k_2) fading rate constants (s^{-1}) and their respective amplitude for compounds **1-Me**, **1-Bz**, **2-Me**, **3-Me** and **3-Bz**, and the three reference compounds **1-H**, **2-H** and **3-H** in toluene solutions (1.0×10^{-4} M at 30 °C) under continuous irradiation

Compound	λ_{max}	A_{PSS}	k_1	k_2
1-H	414, 517	1.34, 1.38	1.0×10^{-3} (75)	1.6×10^{-6} (25)
1-Me	420, 542	1.45, 1.36	1.1×10^{-3} (85)	9.5×10^{-6} (15)
1-Bz	417, 532	0.24, 0.11	1.0×10^{-3} (75)	4.0×10^{-6} (25)
2-H	485	0.37	0.13 (76)	2.0×10^{-5} (24)
2-Me	485	0.30	0.25 (75)	6.0×10^{-5} (25)
3-H	467	0.61	3.0×10^{-2} (70)	2.0×10^{-5} (30)
3-Me	494[a]	0.48	0.32 (4)	$<10^{-6}$ (96)
3-Bz	477[a]	0.37	0.26 (8)	$<10^{-6}$ (92)

[a] Absorption of the broad band exhibits almost the same absorbance between 436 nm and 504 nm (see Fig. 1).

2. Results and discussion

2.1. Synthesis

Naphthopyrans are usually prepared through the reaction of naphthols with 1,1-diarylprop-2-yn-1-ol under acid catalysis. For basic naphthols, such as *N*-substituted hydroxybenzo[*a*]carbazoles, an alternative method involving the organotitanium mediated condensation with an α,β-unsaturated aldehyde is more adequate. The methylation of methoxybenzo[*a*]carbazoles (**1a**, **2a** and **3a**) and the subsequent reaction with pyridinium hydrochloride afforded *N*-methyl-hydroxybenzo[*a*]carbazoles (**1b**, **2b** and **3b**) with appropriate yields (Scheme 2).

Naphthopyrans **1-Me**, **2-Me** and **3-Me** were obtained in low yields (10–30%) [11] through the reaction of β-phenylcinnamaldehyde with a Ti^{IV} "phenolate", obtained by adding $Ti(OEt)_4$ to the corresponding *N*-methylhydroxybenzo[*a*]carbazoles and separating the ethanol formed by azeotropic distillation.

Under the same conditions, the chromenization reaction of the corresponding *N*-benzylhydroxybenzo[*a*]carbazoles failed. *N*-Benzylated benzopyranocarbazoles **1-Bz** and **3-Bz** were then prepared in good yield (>95%) (Scheme 3) by phase transfer catalysis [12] benzylation (benzyl triethyl ammonium chloride (BTEAC), NaOH 50%, BzBr) of the unsubstituted benzopyranocarbazoles (**1-**

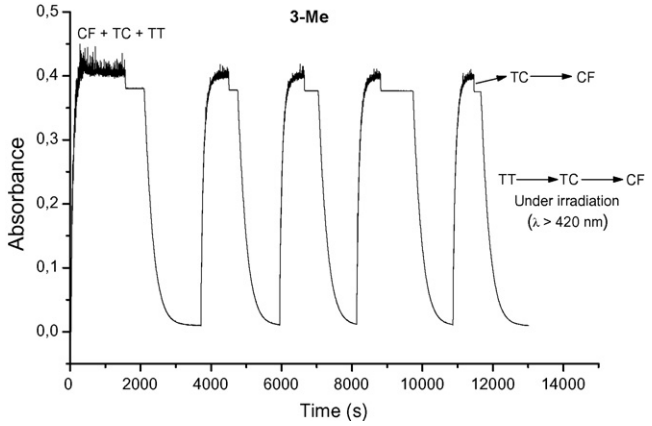


Fig. 3. Cycles of colouration–decolouration for **3-Me** compound at 30 °C (toluene solution, colouration: irradiation at 330 nm until the photo steady state and decolouration: visible irradiation with $\lambda > 420$ nm; absorbance at 494 nm).

H and **3-H**) [12]. The very low yield observed in the synthesis of compound **2-H** [13] discouraged us to perform the *N*-benzylation of this compound.

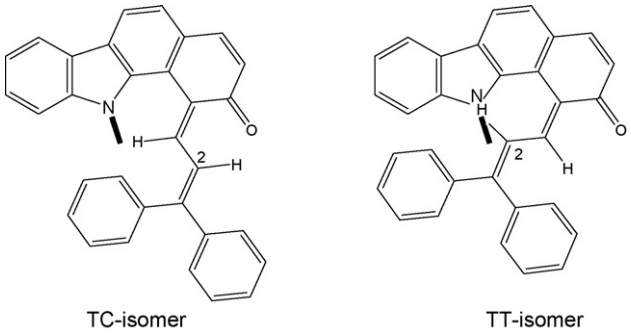
2.2. Photochromic properties

The new naphthopyran derivatives described herein exhibit photochromic behaviour at room temperature in toluene solutions. The relevant spectrokinetic parameters (activation wavelengths of closed forms, maximal wavelengths of the coloured forms, relative steady-state colourability and thermal fading rates) were evaluated under continuous UV irradiation. The UV spectra of the closed forms are described in the experimental part; for the open forms, data are summarized in Table 1 together with data obtained with the corresponding benzopyranocarbazoles without *N*-substituents (**1-H**, **2-H** and **3-H**) [13] for comparative purposes.

From a general point of view, the fusion of an *N*-substituted indole ring to the naphthopyran core led to the presence of strong activation bands in the near-UV and consequently improvement of the sensitivity to solar light (Fig. 1). Fatigue resistance is also expected because these compounds can be isomerised without the use of the more photodegradative short UV wavelengths. These effects originate from the presence of the fused carbazole ring [13].

Compared to reference benzopyranocarbazoles (**1-H**, **2-H** and **3-H**) the open forms of the new compounds exhibit the same band profile in the visible absorption spectra. Minor shifts in the localization of these bands point to the absence of relevant electronic effects due to the presence of the *N*-alkyl substituent at the carbazole moiety.

In toluene solutions, under UV irradiation, the colouration curves for all the described compounds show the usual pattern with the absorbance of the solution increasing until photo steady state was reached. When the irradiation light was turned off, all the described compounds exhibited a biexponential bleaching kinetics that is the usual behaviour of the naphthopyran family at room temperature. The photolytic cleavage of the C–O bond usually leads to the generation of two coloured ring-opened structures (TC and TT) with similar absorption spectra but different thermal stabilities. The slowest thermal decay is normally assigned to the TT-type isomers [6]. This apparent thermal stability is justified by the need of a double-bond rotation for the direct reversion to the closed form while the TC-type molecules are able to do it with a single-bond rotation [14].



Scheme 4. Structure of the **3-Me** photoisomers showing the strong steric effect between H-2 and the *N*-substituent for the TT-isomer.

Table 1 shows the absorbances reached at the photo steady state (A_{PSS}) and rate constants of the thermal back return. Compounds **1-H**, **1-Me** and **1-Bz** exhibit a large amplitude slow decay, while for compounds **2-H** and **2-Me** the decay is faster. The former compounds (**1-Me** and **1-Bz**) can be considered 2*H*-naphtho[1,2-*b*]pyran derivatives while compound **2-Me** a 3*H*-naphtho[2,1-*b*]pyran derivative. For the latter, the rapid fade and low steady-state optical density at room temperature is assigned, at least in part, to the steric destabilization of the *trans* quinoidal open form [4]. As expected, in part due to the absence of important nonbonding interactions in the open forms, compounds **1-Me** and **1-Bz** give rise to longer-live open forms than **2-Me**.

For compounds **3-Me** and **3-Bz** the bleaching curves at room temperature in the dark exhibit a very distinct pattern with thermal decay of small amplitude (<10%), followed by an unexpectedly large amplitude (>90%) slow decay ($k_{\Delta} < 10^{-6}\ s^{-1}$ in the temperature range 298–353 K). As a consequence, at room temperature and under the irradiation conditions used, a significant residual colour could remain almost unchanged for more than 10 days. The residual colour can only be completely bleached upon visible irradiation (>420 nm) (Fig. 2).

These observations point to the formation, under continuous UV irradiation, of an unusually long-lived open form, at least in the temperature range examined, that is probably locked due to the strong steric effect of the *N*-substituent. The relative position of pyran ring seems to be very relevant for this behaviour as in these compounds the *N*-substituent can directly affect the open/close photochromic mechanism (Scheme 4).

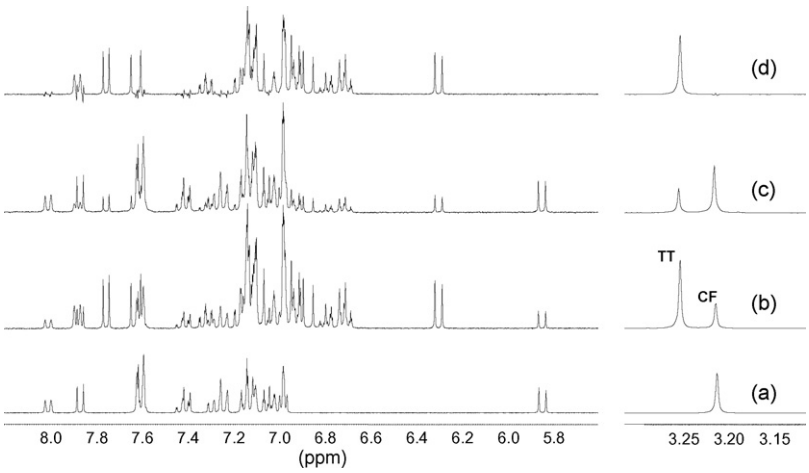


Fig. 4. ^{1}H NMR spectra of compound **3-Me** in toluene at 295 K. (a) Before irradiation, (b) after 25 min of UV irradiation, (c) 2 months after UV irradiation and (d) ^{1}H NMR spectrum obtained by (b) – (a) difference spectra.

The remarkable thermal stability of the major component, not common to naphthopyrans, and the possibility to repeat the cycles colouration–decolouration without a noticeable photodegradation (Fig. 3) persuaded us to accomplish a closer study of these systems.

2.3. Spectral characterization of the thermally stable photoinduced species

The ^{1}H NMR spectrum of a toluene solution of compound **3-Me** at 295 K was recorded in the dark (Fig. 4a), 25 min after irradiation with UV light (Fig. 4b) and 2 months after irradiation (Fig. 4c). Besides the original diminished signals, the raise of one singlet (δ_H 3.24 ppm, *N*–C*H*$_3$) indicates that only one additional species is present. Difference between spectra 4a and 4b makes it possible to obtain the ^{1}H NMR spectrum, displayed in Fig. 4d, of only the stable coloured form. Two new doublets (δ_H 6.87 ppm and 7.62 ppm, J = 12.7 Hz) confirm that the photoproduct is an open form, as such a coupling constant is typical of *transoid* open isomers [15]. The integration of the *N*–C*H*$_3$ signals (δ_H 3.24 ppm for the open form and δ_H 3.20 ppm for the closed form) allowed to establish the composition

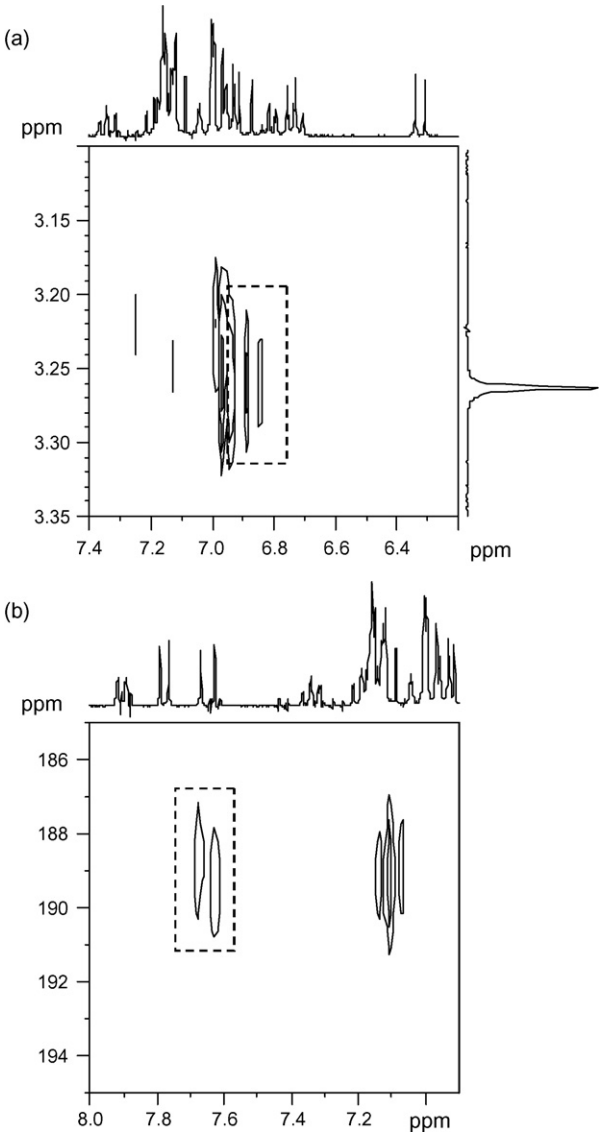
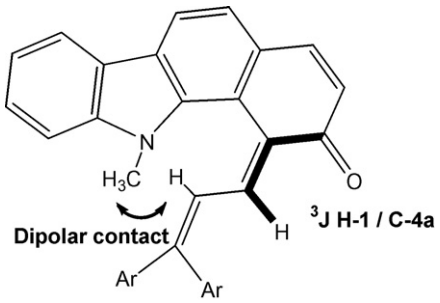


Fig. 5. Part of 2D: (a) ^{1}H–^{1}H Roesy and (b) ^{1}H–^{13}C HMBC for the open form (TT-isomer) of **3-Me**.



Scheme 5. Structure of TT-isomer showing dipolar contact between N–CH$_3$ and H-2.

of the mixture after UV irradiation and rapid thermal decay to be at: 72% of the open form (OF) and 28% of the original one (CF). After 60 days in the dark, at room temperature, the new resonances have diminished to 33% with the complementary increase of the closed form to 67% confirming an extremely slow thermal decay. From these results k_2 is estimated around 1.5×10^{-7} s^{-1}.

Structural assignments of new signals were made through 2D NMR experiments. More particularly, the ^{1}H–^{1}H Roesy experiment makes it possible to observe a dipolar interaction between the *N*–C*H*$_3$ and signal at 6.87 ppm (Fig. 5a). In the HMBC spectrum (Fig. 5b), long-range ($^3J_{1H-13C}$) cross peak between the signal at 7.62 ppm and the carbonyl signal at 189.1 ppm (C=O) is observed. These key features allowed to identify the thermally stable isomer as the TT-isomer (Scheme 5).

The set of extracted ^{1}H and ^{13}C NMR data for isomers TT from **3-Me** and **3-Bz** are reported in experimental data part.

2.4. Bleaching processes

As illustrated in Fig. 2, when the irradiation (λ = 330 nm) is stopped at the photo steady state, absorbance diminished characterizing a relatively rapid low amplitude thermal decay of one open form, deduced to be the TC-isomer. This isomer could not be observed in the NMR studies because it is formed in low quantities and completely reverts thermally to the closed form before the beginning of the NMR recordings. Temperatures below 298 K could not be used due to precipitation. Experiments have been repeated from 298 K to 343 K. The thermal decay follows a monoexponential curve, from which the rate constant of bleaching of TC → CF for **3-Me** and **3-Bz** can be determined. Using Arrhenius plots (Fig. 6), the activation energies for the thermal TC → CF processes have been determined at 66 ± 2 kJ mol^{-1} for **3-Me** and 60 ± 2 kJ mol^{-1} for **3-**

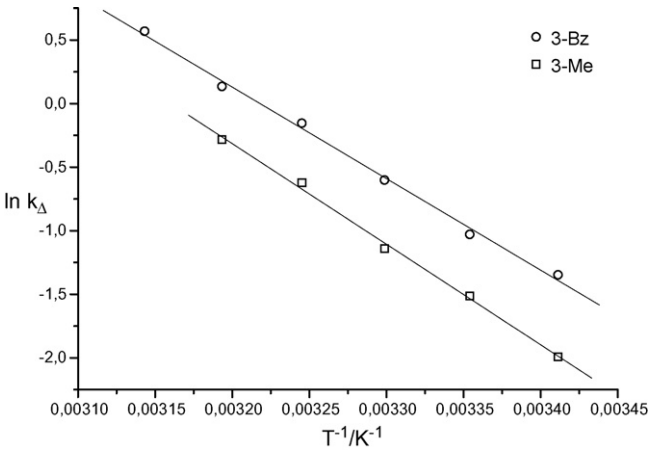
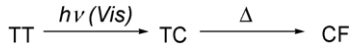


Fig. 6. Arrhenius plots for the fast thermal bleaching of **3-Me** and **3-Bz**.



Scheme 6. Kinetic scheme of the visible light photobleaching of the long-lived isomer TT of the **3-Me** and **3-Bz** benzopyranocarbazoles.

Bz. These values are in accordance with those already observed for typical of chromenes [15,16].

The complete bleaching was only achieved under longer wavelength irradiation (>420 nm). This bleaching follows a monoexponential behaviour with an apparent rate constant (k_{obs} = 0.010 s^{-1} at 303 K) more than one order of magnitude slower that the TC → CF fast thermal step. All these considerations are in agreement with the mechanistic assumption given in Scheme 6 [6,13,17].

The photochemical step is rate determining in our experimental conditions.

3. Conclusions

Several new *N*-alkylated benzopyranocarbazoles have been synthesized using known synthetic methods. Under continuous near-UV irradiation, they give rise to coloured solutions. In the dark, at room temperature, these solutions exhibit a thermal bleaching and reach a second thermally *quasi* stable state. This residual colour remains almost unchanged for a long time and could be readily and efficiently removed upon irradiation with visible light (>420 nm). This photo reversible behaviour could be repeated several times without any loss of its characteristics. The NMR spectral characterization, including 2D experiments, of the long-lived state revealed a two component mixture containing only the closed form CF and the open TT-isomer. For **3-Me** and **3-Bz** compounds, there is a remarkable formation of a large proportion of the very long-lived TT-isomer. This unusual behaviour is a result of a steric effect of the *N*-substituent and opens the use of *N*-alkylated benzopyranocarbazoles as possible future alternatives to the diarylethenes and fulgides for some applications as photoswitches.

4. Materials and methods

4.1. Materials

All the chemicals were obtained from commercial suppliers as reagent grade materials and were used as received. Column chromatography (CC) was performed on silica gel 60 (70–230 mesh).

4.2. Methods

UV–vis spectra were recorded on a Cary 50 Varian spectrophotometer using 1×10^{-5} M toluene solutions. Maximal wavelengths (λ_{max}) are given in nm and molar absorption coefficients of closed forms (ε) in L mol^{-1} cm^{-1}. Mass spectra were obtained under electronic impact (EI = 70 eV) on an AutoSpecE spectrometer. Melting points (°C) were measured in capillary tubes on a Büchi 535 apparatus and are uncorrected. All new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy.

NMR spectra of compounds **3-Me** and **3-Bz** (5×10^{-3} M in toluene-d_8) were acquired using Bruker DPX300 NMR spectrometer operating at 300 MHz (^{1}H) or 75 MHz (^{13}C). Chemical shifts are given in ppm.

UV irradiation of the samples in the NMR tube was performed in a home-built apparatus with a 1000-W Xe–Hg lamp, equipped with filter Schott 011FG09 (259 nm < λ < 388 nm with λ_{max} = 330 nm and *T* = 79%). During irradiation, the sample was kept spinning for homogenization and the temperature was controlled with a variable temperature unit. After irradiation had been stopped, the tube was transferred into the thermoregulated NMR probe.

UV–vis irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150-W ozone free xenon lamp (6255 Oriel Instruments), equipped with filter Schott 011FG09 (259 nm < λ < 388 nm with λ_{max} = 330 nm and *T* = 79%). The light from the UV lamp was filtered using a water filter (61945 Oriel Instruments) and then carried to the spectrophotometer holder at the right angle to the monitoring beam using an optical fiber system (77654 Oriel Instruments). 40 W/m^2 light flux was used (Goldilux Photometer with UV-A probe). Visible irradiation experiments were performed using a long-pass filter, Schott GG 420 (Oriel 59480). A thermostated (20 °C) 10-mm quartz cell, containing the sample solution (3.5 mL, 1.0×10^{-4} M) at specified temperatures, equipped with magnetic stirring was used. In a preliminary experiment, the UV–vis absorption spectra of the closed and open forms and the λ_{max} of the open form were determined. In a second experiment the absorbance at photostationary equilibrium, A_{PSS}, was measured at λ_{max} and then the decrease in the absorbance *versus* time was monitored. The rate constants were calculated using mono- and multiexponential models.

4.3. Synthetic procedures

4.3.1. General method for the synthesis of compounds *1b–3b*

A suspension of NaH (0.19 g, 7.92 mmol) in dry DMF (20 mL), under Ar, was stirred in an ice bath. The methoxy-1,2-benzocarbazoles **1a–3a** [18–20] (1.2 g, 4.86 mmol) were added to the suspension and the temperature was raised to 50 °C. Five equivalents of CH_3I (3.5 mL, 56.2 mmol) was added and the mixture was kept at 50 °C for 3 h and overnight at room temperature (r.t.). The reaction mixture was poured into ice water (100 mL) and the solid formed was filtered, washed with water and dissolved in Et_2O. The organic solution was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was purified by CC (silica gel; AcOEt/pentane 1:4) to afford the *N*-methylmethoxybenzo[*a*]carbazoles [21]. A mixture of *N*-methylmethoxybenzo[*a*]carbazole (1.24 g, 5 mmol) and pyridine hydrochloride (3.47 g, 30 mmol) was gently boiled for 30–40 min. After cooling, water (120 mL) was added, and the precipitate thus obtained was filtered off. The solid was redissolved in acetone and evaporated to dryness affording the *N*-methylhydroxybenzo[*a*]carbazoles **1b–3b** [22].

4.3.2. General method for the synthesis of compounds *1-Me*, *2-Me* and *3-Me*

A suspension of *N*-methylhydroxybenzo[*a*]carbazole **1b–3b** (1.5 g, 6 mmol) in dry toluene (30 mL), under Ar, was stirred until all the *N*-methylhydroxybenzo[*a*]carbazole was dissolved. A solution of titanium (IV) ethoxide (1.37 g, 6 mmol) in dry toluene (25 mL) was added over a period of 10 min. The mixture was refluxed for 30 min, and the ethanol formed was slowly distilled (up to 1/3 of the initial volume). The mixture was cooled to r.t. and a solution of β-phenylcinnamaldehyde (1.25 g, 6 mmol) in dry toluene (20 mL) was added dropwise. The mixture was refluxed for a period of 2–6 h, cooled to r.t., quenched with NaOH (2 M aq., 40 mL), and extracted with CH_2Cl_2 (3× 40 mL). The combined organic extracts were dried (Na_2SO_4), evaporated to dryness and the residue was purified by CC (CH_2Cl_2/pentane 1:1).

*4.3.2.1. 5,13-Dihydro-13-methyl-5,5-diphenyl-1-benzopyran[7,8-a]carbazole (**1-Me**).* Off-white solid. Yield 24%. mp 239–240. UV–vis (closed form): 374 (92,700), 394 (121,700). ^{1}H NMR (DMSO, 300 MHz): 4.35 (3H, s, N–CH_3), 6.62 (1H, d *J* = 9.7 Hz, H-4), 6.95 (1H, d *J* = 9.7 Hz, H-3), 7.22–7.29 (3H, m), 7.34 (4H, t *J* = 7.6 Hz,

H-3′, 5′, 3″ and 5″), 7.40 (1H, d J = 8.8 Hz), 7.48 (1H, t J = 7.7 Hz) 7.56–7.58 (4H, m, H-2′, 6′, 2″ and 6″), 7.76 (1H, d J = 8.4 Hz), 8.19 (1H, d J = 8.8 Hz), 8.22 (1H, d J = 8.1 Hz), 8.32 (1H, d J = 8.9 Hz), 8.34 (1H, d J = 8.9 Hz). ^{13}C NMR (DMSO, 75 MHz): 35.0 (*N*–*C*H$_3$), 83.2 (C-5), 110.2 (d), 113.6 (d), 115.8 (s), 115.82 (d), 119.4 (s), 119.6 (d), 120.0 (d), 122.7 (s), 123.6 (s), 123.9 (s), 124.0 (d), 124.2 (d), 125.5 (d), 126.6 (4C, d), 127.9 (2C, d), 128.5 (d), 128.7 (4C, d), 135.6 (s), 141.2 (s), 145.5 (2C, s), 148.3 (s). MS: *m*/*z* (%): 437 (100), 360 (29), 345 (7), 219 (5), 180 (6), 165 (8). Exact mass for $C_{32}H_{23}NO$: 437.1773. Found: 437.1780.

*4.3.2.2. 4,13-Dihydro-13-methyl-4,4-diphenyl-1-benzopyran[6,5-a]carbazole (**2-Me**).* Off-white solid. Yield 10%. mp >250. UV–vis (closed form): 369 (78,000), 388 (88,600). ^{1}H NMR (DMSO, 300 MHz): 4.22 (3H, s, *N*–C*H*$_3$), 6.49 (1H, d J = 10.0 Hz, H-5), 7.11–7.15 (3H, m), 7.21–7.28 (5H, m), 7.33 (1H, dt J = 7.7 Hz and 1.2 Hz, H-11 or H-10), 7.39–7.42 (4H, m, H-2′, 6′, 2″ and 6″), 7.46 (1H, d J = 10.0 Hz, H-6), 7.58 (1H, d J = 8.5 Hz, H-2), 7.77 (1H, d J = 8.5 Hz, H-1), 8.04 (1H, d J = 7.7 Hz, H-9), 8.12 (1H, d J = 8.8 Hz, H-7), 8.58 (1H, d J = 8.8 Hz, H-8). ^{13}C NMR (DMSO, 75 MHz): 34.4 (*N*–*C*H$_3$), 83.2 (C-4), 110.1 (d), 114.0 (d), 115.8 (s), 117.0 (s), 118.3 (d), 119.7 (d), 119.9 (s), 120.6 (d), 120.7 (d), 122.8 (s), 124.9 (d), 125.0 (d), 126.8 (4C, d), 127.9 (2C, d), 128.6 (4C, d), 129.2 (d), 130.0 (d), 136.3 (s), 141.0 (s), 145.3 (2C, s), 149.8 (s). MS: *m*/*z* (%): 437 (100), 360 (80), 271 (5), 247 (20), 180 (17), 165 (8), 149 (15), 83 (18), 69 (21). Exact mass for $C_{32}H_{23}NO$: 437.1785. Found: 437.1780.

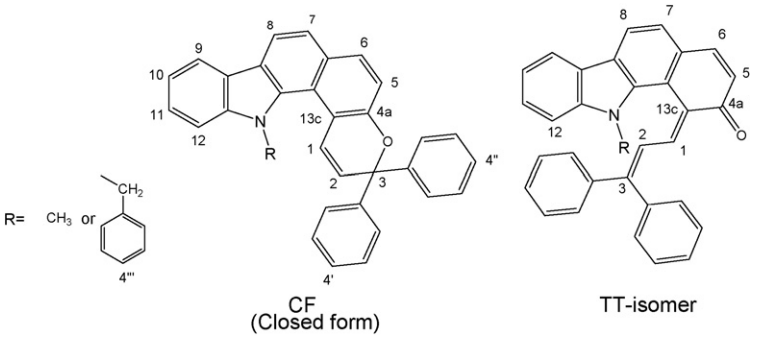
*4.3.2.3. 3,13-Dihydro-13-methyl-3,3-diphenyl-1-benzopyran[5,6-a]carbazole (**3-Me**).* Off-white solid. Yield 30%. mp 228–229. UV–vis (closed form): 338 (16,813), 339 (18,279), 352 (15,129), 378 (11,554), 393 (12,803), 395 (12,892). ^{1}H NMR (toluene-d_8, 300 MHz): 3.20 (3H, s, *N*–C*H*$_3$), 5.84 (1H, d J = 9.5 Hz, H-2), 6.98 (1H, d J = 9.5 Hz, H-1), 7.04 (2H, dd J = 8.3 Hz and 2.0 Hz, H-4′ and 4″), 7.14 (4H, m, H-3′, 5′, 3″ and 5″), 7.24 (1H, d J = 8.4 Hz, H-5); 7.24 (1H, dd J = 7.3 Hz and 1.0 Hz, H-12), 7.28 (1H, dt J = 8.5 Hz and 1.0 Hz, H-10), 7.39 (1H, d J = 8.10 Hz, H-7), 7.42 (1H, dt J = 7.3 Hz, H-11), 7.60 (1H, d J = 8.4 Hz, H-6), 7.61 (4H, dd J = 8.8 Hz and 2.0 Hz, H-2′, 6′, 2″ and 6″), 7.87 (1H, d J = 8.4 Hz, H-8), 8.01 (1H, dd J = 8.0 Hz and 1.2 Hz, H-9). ^{13}C NMR (toluene-d_8, 75 MHz): 36.5 (*N*–*C*H$_3$), 81.8 (C-3), 110.8 (C-12), 114.5 (C-13c), 116.4 (C-5), 117.2 (C-8), 120.0 (C-9), 120.5 (C-10), 121.5 (C-7), 122.4 (C-8a), 123.2 (C-2), 125.0 (C-8b), 125.3 (C-11), 126.7 (C-1), 127.2 (C-13b), 127.2 (C-2′, 2″, 6′ and 6″), 127.6 (C-4′ and 4″), 128.0 (C-3′, 3″, 5′ and 5″), 130.0 (C-6a), 131.7 (C-6), 138.1 (C-13a), 145.1 (C-12a), 145.4 (C-1′ and 1″), 151.6 (C-4a). MS: *m*/*z* (%): 437 (100), 422 (14), 360 (38), 345 (11), 257 (12). Exact mass for $C_{32}H_{23}NO$: 437.1785. Found: 437.1770.

*4.3.3. General method for the synthesis of compounds **1-Bz** and **3-Bz***

To a mixture of **1-H** or **3-H** (0.500 g, 1.18 mmol), a 50% NaOH solution (1 mL), benzene (5 mL), BTEAC (0.092 g, 0.4 mmol) and benzyl bromide (0.344 g, 2.01 mmol) was added dropwise, under stirring and Ar. The mixture was left for 2 h at r.t., poured into hot water (10–20 mL) and stirred again for 4 h. The solids formed were filtered, washed with water and dissolved in CH_2Cl_2. The organic solution was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was purified by CC (CH_2Cl_2/pentane 1:1).

*4.3.3.1. 5,13-Dihydro-13-benzyl-5,5-diphenyl-1-benzopyran[7,8-a]carbazole (**1-Bz**).* Brown solid. Yield 95%. mp 219–220. UV–vis (closed form): 392 (18,800), 372 (17,700), 317 (43,600), 333 sh (26,400). ^{1}H NMR (toluene-d_8, 300 MHz): 5.41 (2H, s, C*H*$_2$–Ph), 5.99 (1H, d J = 9.7 Hz, H-4), 6.43 (1H, d J = 9.7 Hz, H-3), 6.76 (1H, d J = 8.5 Hz, H-2), 6.95 (2H, m, H-2‴ and 6‴), 7.00 (2H, m, H-4′ and 4″), 7.02 (1H, m, H-4‴), 7.10 (1H, m, H-12), 7.11 (4H, m, H-3′, 5′, 3″ and 5″), 7.12 (2H, m, H-3″ and 5″), 7.29 (1H, m, H-10), 7.31 (1H, m, H-11), 7.61 (4H, dd J = 7.2 Hz and 1.3 Hz, H-2′, 6′, 2″ and 6″), 7.68 (1H, d J = 8.5 Hz, H-2), 8.10 (1H, dd J = 7.0 Hz and 1.6 Hz, H-9), 8.18 (1H, d J = 8.5 Hz, H-8), 8.54 (1H, d J = 8.5 Hz, H-7). ^{13}C NMR (toluene-d_8, 75 MHz): 49.6 (*C*H$_2$–Ph), 83.6 (C-5), 109.8 (C-12), 115.1 (C-7), 115.5 (C-1), 115.5 (C-2a), 119.6 (C-8), 120.2 (C-9), 120.6 (C-10), 123.6 (C-13b), 124.3 (C-2), 124.4 (C-3), 124.9 (C-6b), 125.3 (C-8a), 125.6 (C-11), 125.9 (C-8b), 126.4 (C-2‴ and 6‴), 127.5 (C-2′, 2″, 6′ and 6″), 128.2 (C-4‴), 128.3 (C-4), 128.3 (C-4′ and 4″), 128.4 (C-3′, 3″, 5′ and 5″), 128.5 (C-3‴ and 5‴), 135.8 (C-13a), 137.3 (C-1‴), 141.7 (C-12a), 145.5 (C-1′ and C-1″), 149.2 (C-6a). MS: *m*/*z* (%): 513 (100), 436 (15), 422 (25), 345 (19), 315 (6), 191 (6), 149 (6), 91 (28). Exact mass for $C_{38}H_{27}NO$: 513.2093. Found: 513.2092.

*4.3.3.2. 3,13-Dihydro-13-benzyl-3,3-diphenyl-1-benzopyran[5,6-a]carbazole (**3-Bz**).* Off-white solid. Yield 96%. mp 179–180. UV–vis (closed form): 336 (76,300), 352 (63,200), 378 (48,600), 395 (54,500). ^{1}H NMR (toluene-d_8, 400 MHz): 4.86 (2H, s, C*H*$_2$–Ph), 5.57 (1H, d J = 9.6 Hz, H-2), 6.92 (2H, m, H-2‴ and 6‴), 6.97 (3H, m, H-3‴, H-4‴ and H-5‴), 7.00 (2H, dd J = 8.2 Hz and 1.2 Hz, H-4′ and 4″), 7.08 (4H, m, 4H, H-3′, 5′, 3″ and 5″), 7.14 (1H, d J = 9.6 Hz, H-1), 7.16 (1H, dd J = 7.0 Hz and 1.3 Hz, H-12), 7.18 (1H, m, H-11), 7.20 (1H, m, H-10), 7.23 (1H, d J = 8.8 Hz, H-5), 7.44 (1H, d J = 8.6 Hz, H-7), 7.50 (4H, dd J = 7.0 Hz and 1.2 Hz, H-2′, 6′, 2″ and 6″), 7.62 (1H, d J = 8.8 Hz, H-6), 7.89 (1H, d J = 8.6 Hz, H-8), 7.99 (1H, dd J = 8.0 Hz and 1.6 Hz, H-9). ^{13}C NMR (toluene-d_8, 75 MHz): 52.7 (*C*H$_2$–Ph), 81.8 (C-3), 112.8 (C-12), 114.5 (C-13c), 116.4 (C-5), 117.0 (C-8), 119.9 (C-9), 120.6 (C-13b), 120.9 (C-10), 122.4 (C-7), 123.1 (C-2), 123.7 (C-8a), 125.2 (C-11), 125.9 (C-8b), 126.3 (C-2‴ and C-6‴), 126.7 (C-1), 127.1 (C-4‴), 127.2 (C-2′, 6′, 2″ and 6″), 127.9 (C-3′, 5′, 3″ and 5″), 128.0 (C-4′ and 4″), 128.6 (C-3‴ and 5‴), 129.9 (C-6a), 131.9 (C-6), 138.0 (C-1‴), 138.1 (C-13a), 144.9 (C-1′ and 1″), 145.0 (C-12a), 151.1 (C-4a). MS: *m*/*z* (%): 513 (63), 422 (100), 345 (19), 328 (11), 256 (10), 91 (21). Exact mass for $C_{38}H_{27}NO$: 513.2093. Found: 513.2081.



Scheme 7. Skeleton correspondence of closed (CF) and open (TT) isomer.

4.3.4. NMR data of the TT-isomer

For better spectral comparison, the numbering of the closed forms (CF) and the open forms (TT) was the same (Scheme 7).

4.3.4.1. ***3-Me*** *open form (TT).* ^{1}H NMR (toluene-d_8, 300 MHz): 3.24 (*N*–C*H*$_3$), 6.30 (1H, d *J* = 9.5 Hz, H-5), 6.71 (2H, m, H-2′ and 6′), 6.79 (2H, m, H-3′ and 5″), 6.87 (1H, d *J* = 12.7 Hz, H-2), 6.95 (1H, dd *J* = 7.2 Hz and 1.1 Hz, H-12), 6.96 (1H, d *J* = 7.8 Hz, H-7), 7.01 (2H, m, H-2″ and 6″), 7.08 (1H, d *J* = 9.5 Hz, H-6), 7.11 (2H, m, H-3″ and 5″), 7.16 (1H, dt $^3J_{10-9}$ = 7.5 Hz, $^3J_{10-11}$ = 8.3 Hz and $^4J_{10-12}$ = 1.1 Hz, H-10), 7.31 (1H, dt $^3J_{11-10}$ = 8.3 Hz, $^3J_{11-12}$ = 7.5 Hz and $^4J_{11-9}$ = 1.3 Hz, H-11), 7.62 (1H, d *J* = 12.7 Hz, H-1), 7.76 (1H, d *J* = 7.8 Hz, H-8), 7.88 (1H, dd *J* = 7.5 Hz and 1.3 Hz, H-9). ^{13}C NMR (toluene-d_8, 75 MHz): 32.7 (*N*–C*H*$_3$), 120.1 (C-8), 120.8 (C-10), 121.2 (C-9), 122.6 (C-7), 124.4 (C-2), 126.6 (C-5), 127.5 (C-11), 129.2 (C-12), 130.0 (C-6a), 139.8 (C-1), 141.1 (C-13a), 144.3 (C-6), 144.8 (C-12a), 152.0 (C-13c), 189.1 (C=O).

4.3.4.2. ***3-Bz*** *open form (TT).* ^{1}H NMR (toluene-d_8, 300 MHz): 5.34 (2H, s, C*H*$_2$–Ph), 6.14 (1H, d *J* = 9.6 Hz, H-5), 6.63 (5H, m, H-2‴, 3‴, 4‴, 5‴ and 6‴), 6.78 (2H, m, H-3″ and 5″), 6.87 (1H, m, H-4″), 6.88 (1H, d *J* = 7.8 Hz, H-7), 6.92 (1H, d *J* = 9.6 Hz, H-6), 6.98 (1H, d *J* = 12.6 Hz, H-2), 7.04 (2H, m, H-2″ and 6″), 7.14 (1H, d *J* = 12.6 Hz, H-1), 7.21 (3H, m, H-12, H-2′ and 6′), 7.30 (1H, m, H-11), 7.71 (1H, d *J* = 12.6 Hz, H-1), 7.72 (1H, d *J* = 7.8 Hz, H-8), 7.87 (1H, m, H-9). ^{13}C NMR (toluene-d_8, 75 MHz): 47.9 (*C*H$_2$–Ph), 110.8 (C-12), 119.5 (C-8), 120.5 (C-10), 120.8 (C-9), 122.8 (C-7), 123.9 (C-2), 125.4 (C-2″ and 6″), 125.9 (C-5), 127.0 (C-2‴, 3‴, 4‴, 5‴ and 6‴), 127.1 (C-11), 128.3 (C-3″ and 5″), 128.6 (C-4″), 129.3 (C-1a), 136.1 (C-1‴), 138.8 (C-12b), 138.9 (C-1), 141.0 (C-1′), 143.4 (C-6), 144.6 (C-12a), 152.7 (C-3), 189.1 (C=O).

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References

[1] H. Durr, H. Bouas-Laurent (Eds.), Photochromism—Molecules and Systems, Elsevier, Amsterdam, 1990.
[2] H. Bouas-Laurent, H. Durr, Pure Appl. Chem. 73 (2001) 639–665.
[3] B.L. Feringa (Ed.), Molecular Switches, Wiley–VCH, Weinheim, 2001.
[4] B. Van Gemert, in: J.C. Crano, R.J. Guglielmetti (Eds.), Organic Photochromic and Thermochromic Compounds, vol. 1, Kluwer Academic/Plenum Publishers, New York, 1999, pp. 111–140.
[5] B. Van Gemert, Mol. Cryst. Liquid Cryst. 344 (2000) 57–62.
[6] S. Delbaere, J.C. Micheau, G. Vermeersch, J. Org. Chem. 68 (2003) 8968–8973.
[7] X. Sallenave, S. Delbaere, G. Vermeersch, A. Saleh, J.-L. Pozzo, Tetrahedron Lett. 46 (2005) 3257–3259.
[8] (a) M. Irie, Chem. Rev. 100 (2000) 1685–1716;
(b) Y. Yokoyama, Chem. Rev. 100 (2000) 1717–1739.
[9] K. Matsuda, M. Irie, J. Photochem. Photobiol. C: Photochem. Rev. 5 (2004) 169–182.
[10] M. Frigoli, V. Pimienta, C. Moustrou, A. Samat, R. Guglielmetti, J. Aubard, F. Maurel, J.-C. Micheau, Photochem. Photobiol. Sci. 2 (2003) 888–892.
[11] J.-L. Pozzo, V.A. Lokshin, R. Guglielmetti, J. Chem. Soc., Perkin Trans. 1 (1994) 2591–2595.
[12] H. Nishi, H. Kohno, T. Kano, Bull. Chem. Soc. Jpn. 54 (1981) 1897–1899.
[13] M.M. Oliveira, M.A. Salvador, P.J. Coelho, L.M. Carvalho, Tetrahedron 61 (2005) 1681–1691.
[14] S. Delbaere, J.-C. Micheau, J. Berthet, G. Vermeersch, Int. J. Photoenergy 6 (2004) 151–158.
[15] S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon, G. Vermeersch, J. Chem. Soc., Perkin Trans. 2 (1998) 1153–1157.
[16] (a) G. Ottavi, G. Favaro, V. Malatesta, J. Photochem. Photobiol. A: Chem. 115 (1998) 123–128;
(b) G. Favaro, D. Levi, F. Ortica, A. Samat, R. Guglielmetti, U. Mazzucato, J. Photochem. Photobiol. A: Chem. 149 (2002) 91–100.
[17] D. Venec, S. Delbaere, J.-C. Micheau, M. Frigoli, C. Moustrou, A. Samat, G. Vermeersch, J. Photochem. Photobiol. A: Chem. 181 (2006) 174–179.
[18] B.M. Barclay, N. Campbell, J. Chem. Soc. (1945) 530–533.
[19] N.P. Buu-Hoï, N. Hoan, N.H. Khôi, J. Org. Chem. 14 (1949) 492–497.
[20] N.P. Buu-Hoï, F. Périn, P. Jacquignon, Bull. Chim. Soc. Fr. (1966) 584–586.
[21] D.A. Patrick, D.W. Boykin, W.D. Wilson, F.A. Tanious, J. Spychala, B.C. Bender, J.E. Hall, C.C. Dykstra, K.A. Ohemeng, R.R. Tidwell, Eur. J. Med. Chem. 32 (1997) 781–793.
[22] N.P. Buu-Hoï, N. Hoan, N.H. Khôi, N.D. Xuong, J. Org. Chem. 15 (1950) 962–965.