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New benzopyranocarbazoles: synthesis and photochromic behaviour

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Abstract—The synthesis of three new benzopyranocarbazoles (=[indole]naphthopyrans) from hydroxybenzo[*a*]carbazoles is described. The photochromic properties of these novel compounds were investigated under flash photolysis and continuous irradiation. Compared to known [indole]benzopyrans these new compounds showed a significant bathochromic shift in the spectra of the open forms, an increase in colourabilities and slower ring closure kinetics. The photochromic behaviour of compound **4** has been further investigated. Continuous near-UV irradiation led to the formation of one photoisomer (TC) that was subsequently partially converted, to the other (TT). Thermal reversion of the preirradiated system to the original form was only partial and followed a monoexponential decay involving the back-conversion of the TC-isomer to the uncoloured closed form (CF). The thermally stable TT-isomer could only be photobleached with visible light. This process was shown to proceed through a fast photoconversion TT→TC followed by the thermal path TC→CF. Thermal relaxation of the activated system was also studied at various temperatures.

1. Introduction

Benzo- and naphthopyrans derivatives are one of the most studied and important class of photochromic molecules.[1,2] They were originally studied for their potential in offering complementary colours (yellow to orange) to the well known (blue) indolinospironaphthoxazines.[3] Nowadays, it is possible to obtain any colour using only naphthopyrans.[4] Owing to their good photochromic properties, associated with high fatigue resistance, this family of compounds has been used in recent years in the manufacture of photochromic lenses that darken in sunlight.[5]

Under UV irradiation these molecules, in solution or incorporated in polymer matrices, undergo a pyran-ring opening due to the breaking of the $C_{(sp}3)$–O bond leading to an equilibrium between the uncoloured closed form (CF) and a set of coloured stereoisomers of the open form (OF), having different stabilities (Scheme 1).[6] Usually the phenomenon is thermally reversible, although it is well known that in some cases it can be also photoinduced with visible light.

Typically, UV–Vis spectroscopy has been used to study this phenomenon and has resulted in the determination of intrinsic properties of the process which is responsible for the reversible change.[7–9] Normally, however, the UV spectroscopy only gives global information about the photochromic system and does not give individual information about each of the various forms obtained under irradiation.

Recently, the photochromic process has been deeply studied by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. This technique allowed the elucidation of important mechanistic and structural features along with the calculation of kinetic and thermodynamic parameters. From these studies, it is apparent that benzo- and naphthopyrans, under continuous UV irradiation, usually generate two major photoproducts, namely the *trans–cis* (TC) and the *trans–trans* (TT) forms. Both are responsible for the colour obtained after irradiation; however, usually, the latter isomer was found to be the most thermally stable.[10–12]

Benzo- and naphthopyrans containing a fused carbazolo or indolo group exhibit interesting photochromic properties and have been patented.[13–16] In previous works, we described the photochromic properties of indolo-fused benzopyrans.[17,18] These compounds showed some interesting properties such as a high photocolouration efficiency in the near-UV and two absorption bands in the visible range. Since naphthopyrans are more photochromic and less fatigue prone than benzopyrans (because they are activated

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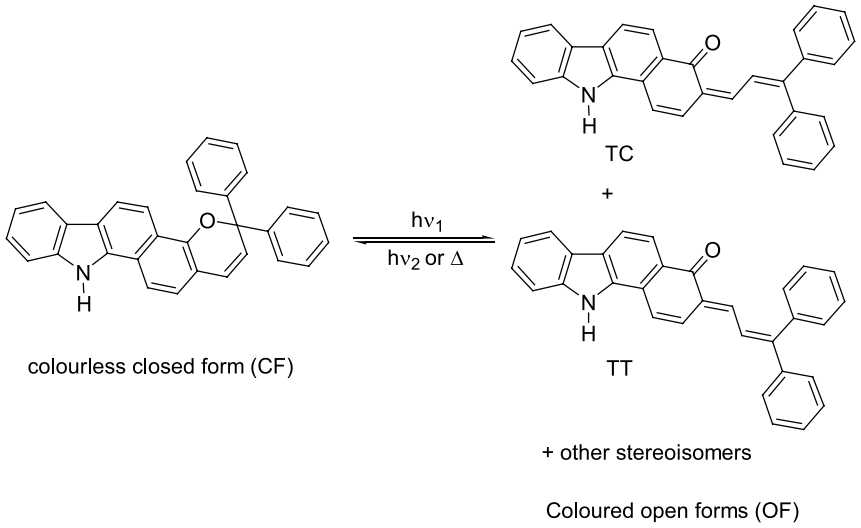


Scheme 1.

with less energetic light) and the photochromic properties can be dramatically changed by structural features[1,4,19] we decided to synthesise and study new indolo-fused naphthopyrans.

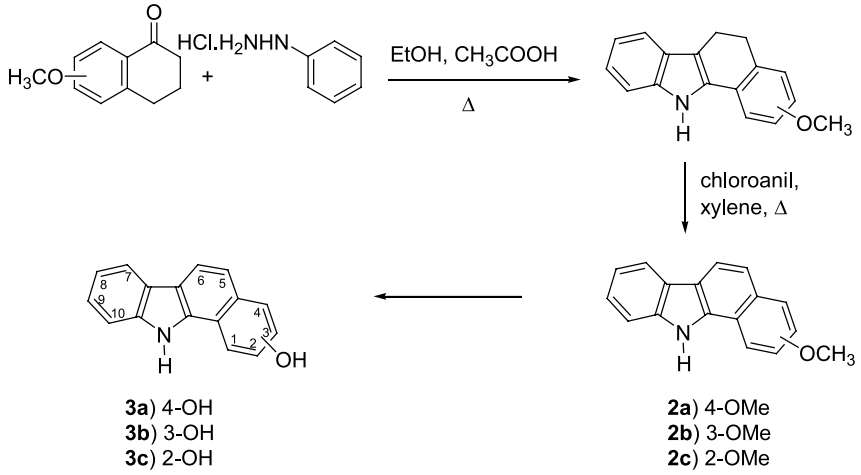
During the evaluation of spectrokinetic parameters, we have found that one of the compounds was particularly suitable to make further studies that allowed to elucidate some interesting features about the photochromic mechanism in the naphthopyrans family.

2. Results and discussion

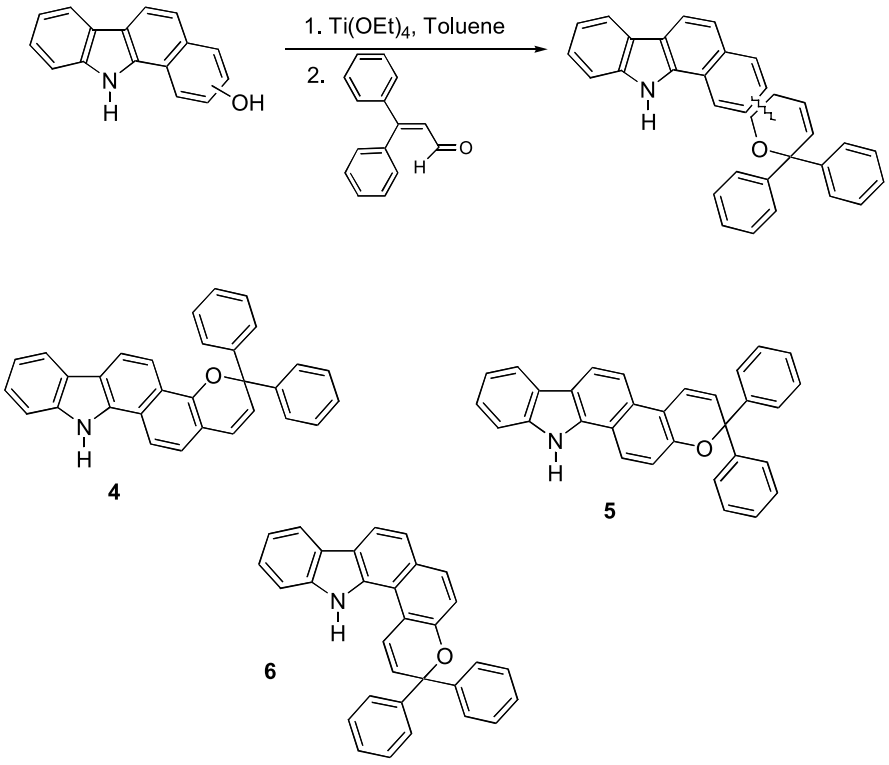
2.1. Synthesis

The new benzopyranocarbazoles **4–6** were prepared in four steps from methoxytetralones **1a–c** as outlined in Schemes 2 and 3. The 5-, 6- and 7-methoxytetralones **1a–c** were refluxed 1 h with phenylhydrazinium chloride in ethanol, in the presence of a few drops of acetic acid[20] and were then dehydrogenated with tetrachloro-1,4-benzoquinone (*p*-chloroanil) in xylene[21,22] affording methoxybenzo[*a*]-carbazoles **2a–c** in very good yields (80–96%). This two step procedure represents an easier route to prepare methoxybenzo[*a*]carbazoles over the Fischer–Borsche[16] method because it avoids bubbling the hydrazone intermediate with gaseous HCl. Demethylation of methoxyl groups using pyridine hydrochloride[21–23] afforded the hydroxybenzo[*a*]carbazoles **3a–c** in good yields (63–85%).

Naphthopyrans are usually prepared through reaction of naphthols with 1,1-diarylprop-2-yn-1-ol under acid catalysis. For basic naphthols, such as hydroxybenzo[*a*]-carbazoles **3a–c**, an alternative method involving the organotitanium mediated condensation with an α,β-unsaturated aldehyde is more adequate. The reaction of α-phenylcinnamaldehyde with a Ti^{IV} 'phenolate', obtained by adding $Ti(OEt)_4$ to the hydroxybenzo[*a*]carbazoles **3a–c** and separating the ethanol formed by azeotropic distillation, leads to C-alkylation in *ortho*-position that through a subsequent electrocyclisation yielded the naphthopyrans **4** (63%), **5** (24%) and **6** (77%) (Scheme 3).[24]



Scheme 2.



Scheme 3.

2.2. Photochromic properties

Although benzopyranocarbazoles with an indole moiety fused to the *f*-face (5,6-positions) of a 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran nucleus were already described in prior art,[16] the compounds **4**–**6**, 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran fused to the *i*-face and 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran fused to the *i*- and *k*- faces are now described for the first time. The new naphthopyrans exhibit photochromic behaviour at room temperature in toluene solutions. The relevant spectrokinetic parameters (activation wavelengths of closed forms, maxima wavelengths of the coloured forms, colourability and thermal bleaching rates) were evaluated under flash photolysis and continuous near-UV irradiation. Both methods are extensively used to quantify spectrokinetic parameters of organic photochromes, but the information obtained by the two methods can be very distinct because time scales of observation and light flux intensities applied are completely different. Methods employing continuous irradiation use a longer irradiation time and a lower intensity light flux and are usually well suited to the study of slow systems. Moreover they operate in experimental conditions quite comparable to those that are found in applications where sunlight activation is intended. The data obtained are summarized in Table 1 together with data obtained with the corresponding pyranocarbazoles (**Ref1**, **Ref3** and **Ref4**)[18] and the reference naphthopyrans (**Ref2** and **Ref5**)[25,26] for comparative purposes.

2.2.1. Activation wavelengths of uncoloured forms. Compared to the reference pyranocarbazoles, the introduction of an additional benzene ring, in the *f*- and *h*-faces (5,6- and 7,8-positions) of the 2*H*-1-benzopyran ring system, led to the apparition, in the closed forms, of strong UV absorption bands shifted further towards the visible (see Figure 1 for comparison of **Ref1** and compound **4**). This feature is important as the activation with less energetic radiation improves both the sensitiveness to solar light and also the fatigue resistance.[2]

2.2.2. Maxima wavelengths of coloured forms. Compared to the corresponding 2*H*- and 3*H*-naphthopyrans, the fusion of an indole ring to naphthopyrans led to a global bathochromic shift in the spectra of the open forms. This effect was already observed for 2*H*-1-benzopyrans fused to an indole moiety.[17,18] From a general point of view comparing the two sets of compounds with a fused indole moiety, both under flash photolysis and continuous irradiation, the introduction of an additional benzene ring led to the loss of the two band profile in the visible absorption spectra of the coloured forms. One exception was observed, under continuous irradiation, for the open form of compound **4** (2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran with the indole fused to 7,8 positions) that displays two significant absorption bands in the visible range (Fig. 1). The same was observed for 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran with the indole group fused to the 5,6 positions.[24] No clear electronic effect could be readily observed due to the presence of the indole nitrogen atom. Electron-donating substituents at the 7-position of diphenylnaphthopyrans have little effect on the maxima absorption wavelength of the open form and at the 10-position have not been reported.[2,4]

2.2.3. Colourability and thermal bleaching rate. All the new described compounds exhibit better colourabilities than the corresponding 2*H*-1-benzopyrans fused to an indole

Table 1. Maxima wavelengths of the coloured forms (λ_{max}, nm), colourability (A_0 and A_{eq}), fading rate (k_Δ,s^{-1}) of compounds **4–6** and five reference compounds in toluene solutions under flash photolysis (2.5×10^{-5} M at 25 °C) and continuous irradiation (1×10^{-4} M at 20 °C)

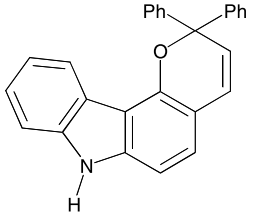
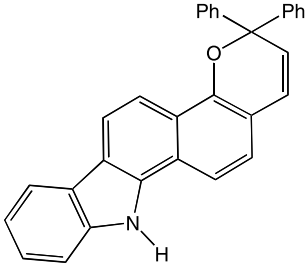
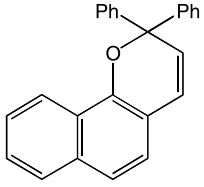
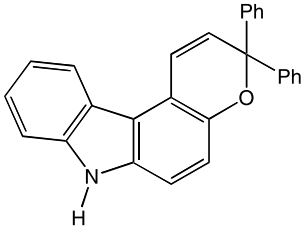
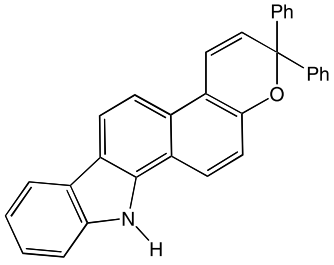
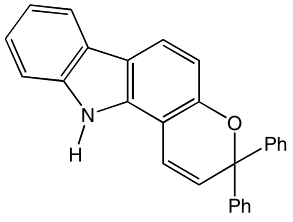
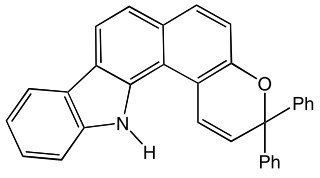
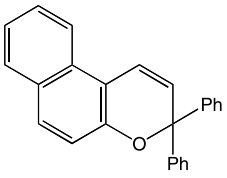
Compound		Flash photolysis open form			Continuous irradiation open form		
		λ_{max}	A_0	k_Δ (%)	λ_{max}	A_{eq}	k_Δ (%)
Ref1		415 542	1.8 0.26	1×10^{-2} (38) 4×10^{-3} (62)	415	2.22	4×10^{-3} (71) 2×10^{-3} (29)
4		531	1.1	1×10^{-3} (100)	414 517	1.34 1.38	1×10^{-3} (100) (414 and 517 nm)
Ref2		403 481	1.08 1.62	<0.01	469	0.72	6×10^{-4} (98) 3×10^{-4} (2)
Ref3		460 549	0.68 0.61	4×10^{-2} (100)	460	0.28	0.04 (100)
5		490	3.2	3×10^{-2} (100)	485	0.37	0.13 (100)
Ref4		443 590	1.1 0.29	0.17 (94) 2×10^{-2} (6)	443	0.15	0.10 (80) 6×10^{-3} (20)
6		474	1.9	4×10^{-2} (84) 9×10^{-3} (16)	467	0.61	3×10^{-2} (100)

Table 1 (*continued*)

Compound		Flash photolysis open form			Continuous irradiation open form		
		λ_{max}	A_0	k_Δ (%)	λ_{max}	A_{eq}	k_Δ (%)
Ref5		432	0.84	0.09	432	0.21	7×10^{-2} (80) 3×10^{-3} (20)

Ref1=2,2-diphenyl-2*H*-pyran[3,2-*c*]carbazole,[18] **Ref2**=2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran,[25] **Ref3**=2,2-diphenyl-2*H*-pyran[6,5-*c*]carbazole,[18] **Ref4**=2,2-diphenyl-2*H*-pyran[5,6-*a*]carbazole[18] and **Ref5**=3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.[26]

moiety, but slower thermal bleaching kinetics. This points to an increase in the thermal stability of the open forms, due to the extension of π-conjugation, and results in higher concentrations of coloured forms in the mixture obtained upon irradiation. The effect can be explained by the decrease of nonbonding interactions in the open forms, promoted by the spacing of the indole moiety imposed by the additional benzene ring.

As generally observed for photochromic naphthopyrans, compounds **5** and **6** (5,6 annellation) are less thermally stable than compound **4** (7,8 annellation). Compared to compounds **4** and **5**, under flash photolysis compound **6** exhibits a different bi-exponential bleaching kinetic. Observing the structures of the TT and TC open forms for compound **6** it is apparent, particularly for the TT-isomer, the possible existence of steric interactions, between the NH function and one ethylenic H-atom, that can affect the pyran ring opening/closing process, leading to two thermally unstable isomers with two observable kinetic constants.

After continuous irradiation, all the new compounds exhibited thermal bleaching kinetics that follow the monoexponential law $A=A_0e^{-kt}+R$ (R is the residual absorption of the solution) from which the kinetic constants were determined. Consequently, after the UV irradiation has ceased all the solutions were only partially bleached and, in the dark, a significant residual colour remained for a long time. This behaviour indicates the formation of two photoproducts that possess very similar absorption spectra, but one is thermally unstable and the other has a high thermal stability.[8] According to recent studies these photoproducts can be identified, as the *trans–cis* (TC) and *trans–trans* (TT) isomers (Scheme 1) and the fast fading phase, of higher amplitude, can usually be attributed to the TC-isomer.[11]

2.3. Mechanistic studies

2.3.1. The effect of different times of irradiation. The most interesting observed feature is that compounds **4** and **5**, under flash photolysis or continuous irradiation, follow a bleaching monoexponential model. Compound **6** exhibits a biexponential bleaching kinetic under flash photolysis, but follows a monoexponential model under continuous irradiation. This is indicative that, for this compound, there is a significant difference in the relative amounts of photoisomers in the mixture obtained after irradiation in both methods.

For compound **4** it was observed a noteworthy agreement between the bleaching kinetic obtained in both under flash photolysis and continuous irradiation. This may indicate a close similarity between the photoproducts formed in the two methods. A series of experiments was performed with compound **4**, in the dark at 293 K, evaluating the bleaching kinetics after different times of continuous irradiation

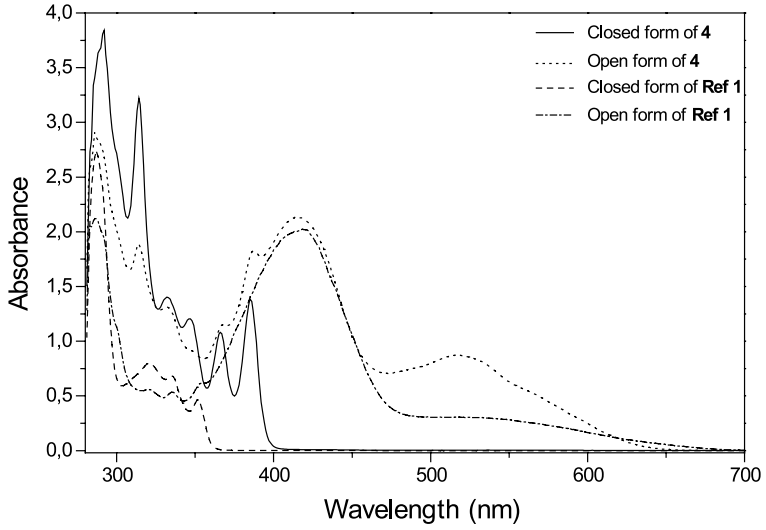


Figure 1. Absorbance spectra of compound **4** and **Ref1** before and after UV–Vis irradiation.

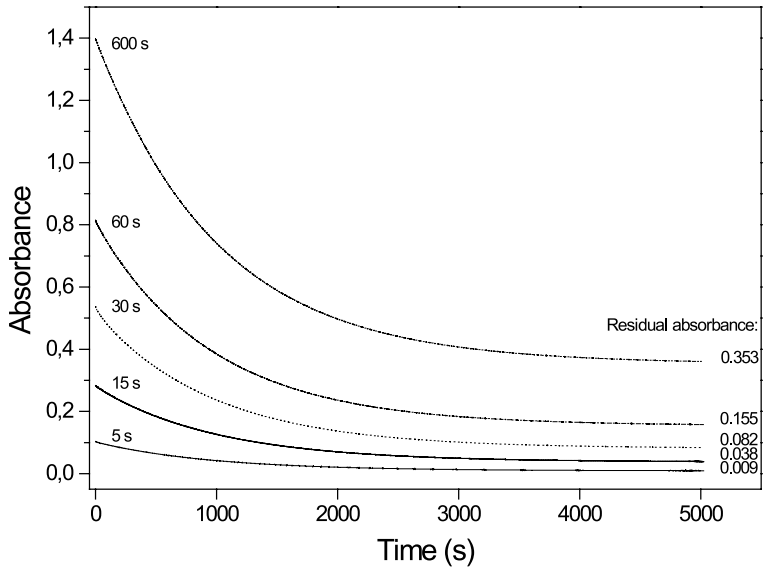


Figure 2. Absorbance decrease at 517 nm after different times of irradiation (toluene solution 1×10^{-4} M of compound **4** at 293 K). Residual absorbances were measured after the system has reached an apparent constant value.

during the colouration process. The results are depicted in Figure 2.

In all experiments the system exhibited the same kinetic behaviour. However, as the time of irradiation became longer, the residual colour of the solution increased. The residual colour can be attributed to the presence of slow decaying coloured species and/or to the formation of coloured photodegradation products. The last assumption was not considered because degradation was estimated to be less than 3%, based on the colourabilities obtained in successive colouration/decolouration cycles. The residual coloured system, on irradiating with visible light (>420 nm), returned to the uncoloured state and recovered almost the same photochromic behaviour as before. From these observations, it is apparent that the residual colour should be attributed to the presence of a thermally stable isomer.

These results suggest that, in this system, the faster decaying isomer (TC) is first produced and, subsequently, partially converted, through light absorption, to the slower decaying isomer (TT). This is in accordance with the expected different energies required to produce each isomer. After the C–O cleavage, promoted by UV irradiation, a one-bond rotation is required to produce the TC-isomer, whereas the TT-isomer requires a subsequent *E*–*Z* isomerisation of a double bond also induced by light. The same was already observed for photochromic 2*H*-chromenes investigated by spectrophotometric methods[8] and ^{19}F NMR spectroscopy.[10]

2.3.2. Visible irradiation and temperature effects. The bleaching was complete only by irradiating with visible light (>420 nm). A series of experiments was performed in order to study the effect of visible light irradiation on the kinetic behaviour of the system at different temperatures. The results are summarized in Table 2.

A monoexponential model could be considered for all the bleaching processes, and examination of the results in Table 2 shows that all the bleaching processes were significantly accelerated by temperature increase (this acceleration was accompanied by an expected decrease in the colourability) (Fig. 3).

A remarkable feature in the results is that, for the same temperature, the observed kinetic constants remained at the same order of magnitude whether or not visible light was on. The visible light, although promoting the complete bleaching of solutions, has a minor effect on the values of kinetic constants whatever the path considered: photostationary state→residual colour, photostationary state→uncoloured state or residual colour→uncoloured state. These results suggest that, for this particular system, the return to the closed uncoloured form (CF) is essentially thermal and corresponds predominantly with a TC→CF pathway. The TT-isomer does not proceed directly to CF but undergoes a

Table 2. Bleaching rate constants for compound **4** at different temperatures considering various paths

Path	Temperature (K)	Visible light (>420 nm)	k (s^{-1})
Photostationary state→residual colour	283	Off	2.6×10^{-4}
Residual colour→uncoloured state	283	On	2.5×10^{-4}
Photostationary state→uncoloured state	283	On	2.6×10^{-4}
Photostationary state→residual colour	293	Off	1.0×10^{-3}
Residual colour→uncoloured state	293	On	8.1×10^{-4}
Photostationary state→uncoloured state	293	On	7.9×10^{-4}
Photostationary state→residual colour	313	Off	8.6×10^{-3}
Photostationary state→residual colour	323	Off	2.3×10^{-2}

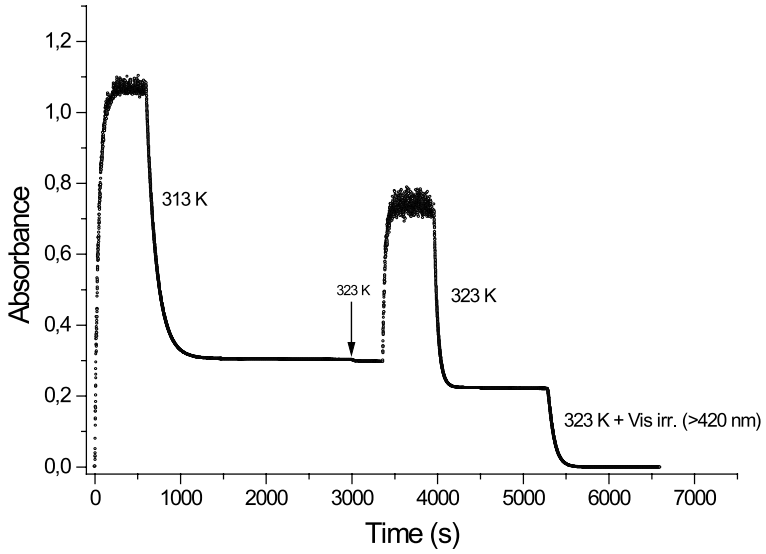


Figure 3. Kinetic behaviour of compound **4** at two different temperatures.

fast photoisomerization TT→TC, induced by visible irradiation. Complete bleaching is then achieved through the slow rate determining thermal process TC→CF. This suggestion is further confirmed with additional experiments irradiating the system with visible light for short time periods, after the first thermal fading. It was observed that it was unnecessary to irradiate with visible light during the whole decolouration process to decolourize the solution completely. With our irradiating device, 180 s of visible irradiation was enough for the system to proceed to the complete bleaching in the dark (Fig. 4).

Based on these informations, the major processes occurring during a photocolouration/decolouration cycle are depicted in Figure 5.

2.3.3. Activation energies. The experiments carried out at different temperatures allowed us to evaluate the standard entropy and enthalpy of activation, for the TC→CF process, using a Eyring plot (Fig. 6): $\Delta H^{\ddagger}=82.2\pm 3.4$ kJ mol^{-1} and $\Delta S^{\ddagger}=-22.3\pm 5.6$ J mol^{-1} K^{-1}. The enthalpy of activation value agrees with those referred for photochromic compounds (40–120 kJ mol^{-1}).[11] The negative value obtained for $\Delta S^{\ddagger}$ points to an expected loss of freedom in the recyclization into the original closed form but is difficult to interpret as it includes an unknown contribution from the rearrangement of the solvent (toluene).

3. Conclusion

The inclusion of an additional benzene ring in pyranocarbazoles yielded three new photochromic benzopyranocarbazoles. All the compounds described exhibited strong absorption bands in the range 370–390 nm which made them readily activated with solar light and potentially less prone to photodegradation. The fusion of an indole moiety

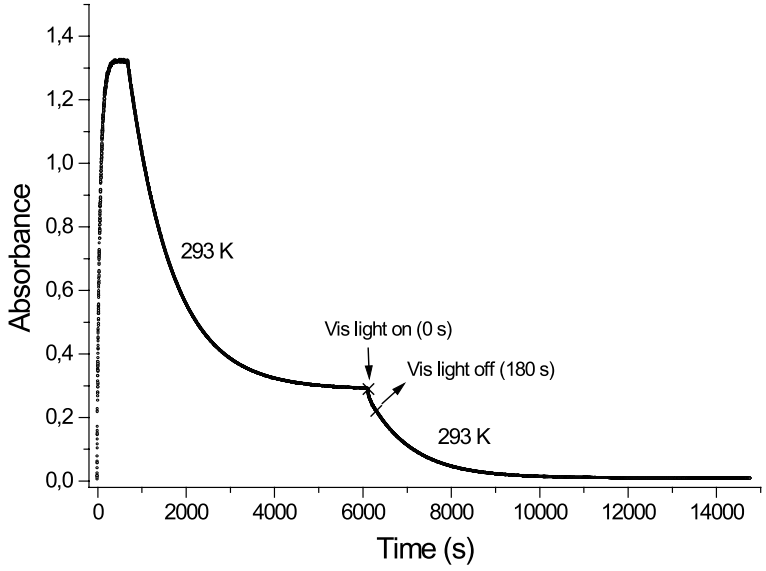


Figure 4. Thermal and photochemical bleaching for compound **4** at 293 K (toluene solution 1×10^{-4} M; visible light >420 nm).

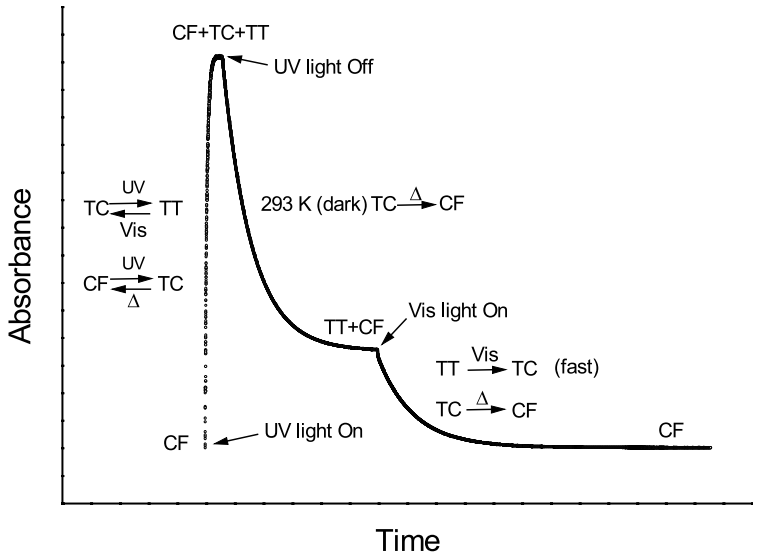


Figure 5. Isomerization processes occurring during a photocolouration/decolouration cycle for compound **4**.

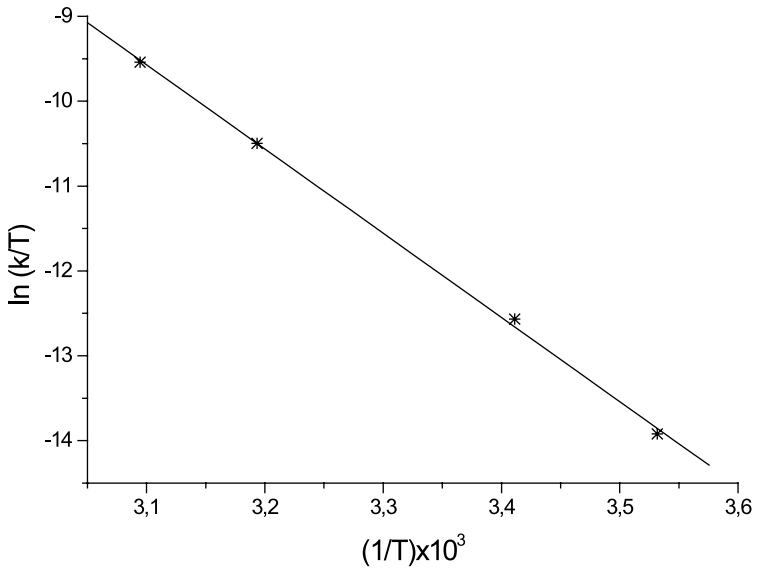
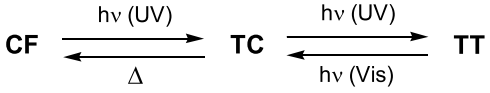


Figure 6. Eyring plot for the thermal relaxation process TC→CF.

at the *i*-face of 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran or *i*- and *k*- faces of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran induced some thermal instability to the open forms. However, it is apparent that electronic effects are modest and no relevant additional steric strain is promoted in open forms. Compared to pyranocarbazoles, no relevant enhancement in the colourabilities was observed, and the effects seem to be related to the increase in the thermal stabilities of the open forms due to the extension of conjugation. In the dark, all the UV-irradiated solutions exhibited a partial monoexponential thermal bleaching and a persistent relevant residual colour, which could be removed only through the irradiation with visible light. This points to a three-component system with an original uncoloured compound (CF) giving, upon UV-irradiation, two coloured photoisomers (TC and TT) with very different thermal stabilities.

The photochromic mechanism was investigated for compound **4** and, based on the results, the following plausible reaction mechanism could be proposed (Scheme 4).

In solution, UV irradiation induces the opening of the pyran ring through the C–O bond breakage followed by a one-bond rotation leading to the TC-isomer. Subsequently, this isomer is partially converted to the TT-isomer through a *E–Z* isomerisation of a double bond, also induced by UV light. At the photostationary state, the coloured mixture includes CF, TC and TT and, when the light was turned off,



Scheme 4.

the thermal bleaching observed is mainly due to the process TC→CF, and a thermal process TT→CF can be excluded. Irradiation with visible light promotes the disappearance of the persistent residual colour through the fast back-conversion TT→TC followed by the thermal conversion TC→CF.

4. Experimental

4.1. General remarks

Solvents (Riedel–Haën and Merck) were used without further purification other than drying over sodium (Et_2O) or anhydrous calcium chloride (CH_2Cl_2). Column chromatography (CC) was performed on silica gel Merck 60 (70–230 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX (400 and 100.5 MHz, respectively) using tetramethylsilane as internal standard in acetone-d_6 or DMSO-d_6, respectively. Chemical shifts are given in ppm and coupling constants in Hz. IR spectra were recorded on a Perkin–Elmer-FTIR-1600 spectrophotometer using KBr disks and wavenumbers are given in cm^{-1}. UV–Vis spectra were recorded on a CARY 50 Varian spectrophotometer using 1×10^{-4} M toluene solutions. Maxima 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 a AutoSpecE spectrometer. Melting points (°C), measured in capillary tubes on a Büchi 535 apparatus, are uncorrected. All new compounds were determined to be >95% pure by ^1H NMR spectroscopy. ta=apparent triplet; sl=large singlet; dl=large duplet.

4.2. Spectrokinetic measurements

4.2.1. Spectrokinetic studies under flash photolysis. For the determination of λ_{max}, A_0, and k_Δ, 5×10^{-5} mol dm^{-3} toluene solutions were used. The flash photolysis experiments were monitored by a Warner and Swasey rapid spectrometer, allowing to record visible absorption spectra of coloured forms in the 400–700 nm range (acquisition time 1 ms, repetitivity 1.25 ms).[27,28] Flashes (duration 50 μs) were generated by two xenon tubes with a quartz envelope. The energy of the flashes was 60 J for the whole polychromatic emission spectrum. For measurements, thermostated (25 °C) 100 mm cells were used. The light from the analysis lamp (50 W, quartz–iodide) was filtered using a Schott GC 400 high-pass filter.

4.2.2. Spectrokinetic studies under continuous irradiation. For measurements of λ_{max}, A_{eq} and k_Δ under continuous irradiation, 1×10^{-4} M toluene solutions were used. Irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150 W ozone free xenon lamp (6255 Oriel Instruments). 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 a fiber-optic system (77654 Oriel Instruments). A light flux of 40 W m^{-2}, measured with a Goldilux Photometer with a UV-A probe was used. Visible irradiation experiments were performed using a long-pass filter, Schott GG 420 (Oriel 59480). A thermostated (10, 20, 40 and 50 °C) 10 mm quartz cell, containing the sample solution (3.5 mL), equipped with magnetic stirring was used. In a preliminary experiment, the visible absorption spectrum of the closed form and the λ_{max} of the open form were determined. In a second experiment the absorbance at photostationary equilibrium, A_{eq}, was measured at λ_{max} and then the decrease in the absorbance with the time was monitored. The rate constants were calculated using mono and multiexponential models.

4.3. General method for the synthesis of compounds 2a–c

A mixture of the appropriate methoxytetralone **1a–c** (1.8 g, 10 mmol), phenylhydrazinium chloride (1.1 g, 7.6 mmol) and a few drops of acetic acid was refluxed in ethanol (15 mL) for 1 h. After cooling, the solid formed was filtered, washed with water (2×20 mL) and dissolved with dichloromethane (10 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated to dryness. To the crude (dihydrobenzocarbazoles), chloroanil (tetrachloro-1,4-benzoquinone) (1.4 equiv) and dry xylene (50 mL) were added and the mixture was refluxed for 2 h, under Ar. After cooling the tetrachlorohydroquinone was filtered off by suction and washed with Et_2O. The filtrate was washed with NaOH (10%), water and dried (Na_2SO_4). After solvent evaporation Et_2O was added and a precipitate was formed that corresponded to 5-methoxy-, 6-methoxy- and 7-methoxybenzo[*a*]carbazole in each case.

4.3.1. 4-Methoxybenzo[*a*]carbazole 2a. Light brown powder. Yield 90%. Mp 166–168 (lit[20] 168). ^1H NMR (acetone-d_6): 4.11 (3H, s, –OC*H*$_3$), 7.08 (1H, dl, *J*=8.4 Hz, H-3), 7.29 (1H, dt, *J*=7.6, 1.2 Hz, H-8), 7.44 (1H, dt, *J*=7.6, 1.2 Hz, H-9), 7.58 (1H, t, *J*=8.4 Hz, H-2), 7.66 (1H, dd, *J*=7.6, 1.2 Hz, H-10), 8.06–8.09 (m, 2H), 8.22–8.25 (m, 2H), 10.25 (1H, sl, –N*H*).

4.3.2. 3-Methoxybenzo[*a*]carbazole 2b. Light brown powder. Yield 80%. Mp 243–244 (lit[23] 245).^1H NMR (acetone-d_6): 4.00 (3H, s, –OC*H*$_3$), 7.24–7.31 (2H, m, H-2 and H-8), 7.40 (1H, dt, *J*=8.0, 1.0 Hz, H-9), 7.52 (1H, d, *J*=2.0 Hz, H-4), 7.62–7.64 (2H, m, H-5 and H-10), 8.17 (1H, dd, *J*=8.0 Hz, 1.0, H-7), 8.20 (1H, d, *J*=8.7 Hz, H-6), 8.42 (1H, d, *J*=9.0 Hz, H-2), 11.20 (1H, sl, –N*H*).

4.3.3. 2-Methoxybenzo[*a*]carbazole 2c. Brown powder. Yield 96%. Mp 186–187 (lit[23] 190).^1H NMR (acetone-d_6): 4.03 (3H, s, –OC*H*$_3$), 7.22 (1H, dd, *J*=9.0, 2.4 Hz, H-3), 7.27 (1H, dt, *J*=7.5, 1.0 Hz, H-8), 7.43 (1H, dt, *J*=7.5, 1.0 Hz, H-9), 7.63–7.67 (2H, m, H-5 and H-10), 7.95 (1H, d, *J*=2.4 Hz, H-1), 7.99 (1H, d, *J*=9.0 Hz, H-4), 8.10 (1H, d, *J*=8.4 Hz, H-6), 8.20 (1H, dd, *J*=7.5 Hz, 1.0, H-7), 11.25 (1H, sl, –N*H*).

4.4. General method for the synthesis of compounds 3a–c

A mixture of methoxybenzo[*a*]carbazole 2a–c (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 hydroxybenzo-[*a*]carbazoles.

4.4.1. 4-Hydroxybenzo[*a*]carbazole 3a. Light brown powder. Yield 94%. Mp >250 (lit[20] 266). ^{1}H NMR (acetone-d_6): 6.92 (1H, dd, J=7.5, 2.3 Hz), 7.13–7.17 (1H, m), 7.28–7.35 (2H, m), 7.52 (1H, d, J=7.8 Hz, 7.86 (1H, d, J=8.2 Hz), 7.96 (1H, d, J=9.0 Hz), 8.06–8.09 (2H, m), 9.00 (1H, s, –O*H*), 11.00 (1H, sl, –N*H*).

4.4.2. 3-Hydroxybenzo[*a*]carbazole 3b. Light brown powder. Yield 94%. Mp >250 (lit[23] 265).^{1}H NMR (acetone-d_6): 7.22–7.29 (2H, m, H-2 and H-8), 7.38 (1H, dt, J=7.5, 1.2 Hz, H-9), 7.42 (1H, d, J=2.4 Hz, H-4), 7.51 (1H, d, J=8.7 Hz, H-5), 7.62 (1H, dl, J=8.1 Hz, H-10), 8.13–8.16 (2H, m, H-6 and H-7), 8.38 (1H, d, J=9.0 Hz, H-1), 8.67 (1H, s, –O*H*).

4.4.3. 2-Hydroxybenzo[*a*]carbazole 3c. Light brown powder. Yield 65%. Mp 237–239 (lit[23] 246). ^{1}H NMR (acetone-d_6): 7.10–7.17 (2H, m), 7.30 (1H, ta, J=7.7 Hz, H-9), 7.49–7.53 (2H, m), 7.71 (1H, sl, H-1), 7.84 (1H, dd, J=7.7 Hz, 1.1), 7.92 (1H, dd, J=8.5 Hz, 1.3), 8.06 (1H, d, J=7.9 Hz), 8.68 (1H, s, –O*H*).

4.5. General method for the synthesis of compounds 4–6

A suspension of hydroxybenzo[*a*]carbazole **3a–c**, (2.33 g, 10 mmol) in dry toluene (50 ml), under Ar, was stirred until all the hydroxybenzocarbazole was dissolved. A solution of titanium (IV) ethoxide (2.28 g, 10 mmol) in dry toluene (40 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 (2.08 g, 10 mmol) in 40 ml of dry toluene was added dropwise. The mixture was refluxed for a period of 2–6 h, cooled to r.t., quenched with NaOH (2M aq, 40 mL), and extracted with CH_2Cl_2 (3×40 ml). The combined organic extracts were dried ($MgSO_4$), evaporated to dryness and the residue was purified by CC on silica gel.

4.5.1. 5,13-Dihydro-5,5-diphenyl-1-benzopyran[7,8-*a*]carbazole 4. Light brown solid. Yield 63%. Mp 230.5–231.5. IR: 3424 (NH), 3056, 1517, 1490,1457, 1398, 1232, 821, 746, 700. UV–Vis (closed form): 314 (32210), 332 (14020), 347 (12040), 366 (10810), 385 (13860). ^{1}H NMR: 6.46 (1H, d, J=9.7 Hz, H-4), 6.91 (1H, d, J=9.7 Hz, H-3), 7.22–7.27 (3H, m, H-4′, 4″ and H-12), 7.32–7.42 (6H, m, H-3′, 3′, 5′, 5″, H-10 and H-11), 7.61–7.63 (4H, m, H-2′, 2″, 6′ and 6″), 7.66 (1H, d, J=8.3 Hz, H-1), 8.03 (1H, d, J=8.3 Hz, H-2), 8.18 (1H, d, J=7.8 Hz, H-9), 8.22 (1H, d, J=8.8 Hz, H-7) and 8.27 (1H, d, J=8.8 Hz, H-8) AB system, 11.30 (1H, sl, N–H). ^{13}C NMR: 83.8 (C-5), 112.2 (d), 113.9 (d), 115.4 (d), 116.9 (d), 119.4 (s), 120.0(d), 120.3 (d), 120.5 (d), 123.5 (s), 123.8 (s), 124.6 (s), 124.9 (d), 125.6 (d), 127.4 (4C, C-2′, 2″, 6′ and 6″), 128.3 (2C, C-4′ and 4″), 128.5 (d), 129.4 (4C, C-3′, 3″, 5′ and 5″), 136.4 (s), 140.3 (s), 146.3 (2C, C-1′ and 1″), 149.4 (s). MS: *m*/*z* (%): 423 (100), 346 (43), 317 (6), 212 (7), 191 (7), 165 (6). Exact mass for $C_{31}H_{21}NO$: 423.1623. Found 423.1635.

4.5.2. 4,13-Dihydro-4,4-diphenyl-1-benzopyran[6,5-*a*]carbazole 5. White solid. Yield 24%. Mp > 250. IR: 3429 (NH), 1633, 1448, 1384, 1259, 1209, 1058, 809, 750, 698. UV–Vis (closed form): 333.0 (6180), 350.0 (5770), 368.0 (6270), 386.0 (7090). ^{1}H NMR: 6.53 (1H, d J=10.0 Hz, H-3), 7.07 (1H, t, J=7,5 Hz), 7.11–7.14 (m, 2H), 7.20–7.26 (m, 5H), 7.30 (1H, d, J=8.9 Hz), 7.39–7.41 (4H, m, H-2′, 2″, 6′ and 6″), 7.45 (1H, d J=10.0 Hz, H-4), 7.46 (1H, d, J=8.0 Hz), 7.69 (1H, d, J=8.9 Hz), 8.00 (1H, d, J=7.8 Hz), 8.07 (1H, d, J=8.8 Hz), 8.26 (1H, d, J=8.9 Hz), 11.2 (1H, sl, NH). ^{13}C NMR: 82.3 (C-4), 111.7 (d), 113.4 (d), 115.6 (s), 116.8 (s), 117.2 (d), 117.4 (s), 119.6 (d), 119.9 (d), 120.4 (d), 120.9 (d), 123.9 (s), 124.2 (d), 124.7 (d), 126.9 (4C, C-2′, 2″, 6′ and 6″), 127.8 (2C, C-4′ and 4″), 128.6 (4C, C-3′, 3″, 5′ and 5″), 128.8 (s), 128.9 (d), 136.7 (s), 139.5 (s), 145.4 (2C, C-1′ and 1″), 150.4 (s). MS: *m*/*z* (%): 423 (100), 346 (81), 315 (5), 257 (6), 211 (7), 173 (15), 165 (9). Exact mass for $C_{31}H_{21}NO$: 423.1623. Found 423.1639.

4.5.3. 3,13-Dihydro-3,3-diphenyl-1-benzopyran[5,6-*a*]carbazole 6. White solid. Yield 77%. Mp 217.3–218.4. IR: 3425 (NH), 3056, 1450, 1390, 1240, 809, 746, 699. UV–Vis (closed form): 335.0 (7540), 351.1 (6950), 371.0 (5750), 390.1 (6350). ^{1}H NMR: 6.51 (1H, d, J=9.8 Hz, H-2), 7.23–7.30 (3H, m, H-10 or H-11, H-4′ and 4″), 7.32–7.36 (5H, m, H-3′, 3″, 5′, 5″ and H-7), 7.43 (1H, dt, J=8.0, 1.2 Hz, H-11 or H-10), 7.59 (1H, d, J=8.5 Hz, H-5), 7.61–7.64 (4H, m, H-2′, 2″, 6′, 6″), 7.71 (1H, d, J=8.0 Hz, H-12), 7.91 (1H, d, J=8.8 Hz, H-8), 7.99 (1H, d, J=9.8 Hz, H-1), 8.09 (1H, d, J=8.5 Hz, H-6), 8.18 (1H d, J=8.0 Hz, H-9), 10.82 (1H, sl, N–H). ^{13}C NMR: 82.2 (C-3), 112.6 (d), 115.3 (s), 117.6 (d), 118.0 (d), 119.8 (s), 120.4 (d), 120.5 (d), 121.5 (s), 121.7 (d), 123.7 (d), 124.1 (s), 125.7 (d), 127.7 (4C, C-2′, 2″, 6′ and 6″), 128.3 (2C, C-4′ and 4″), 128.9 (4C, C-3′, 3″, 5′, 5″), 129.0 (d), 129.9 (s), 132.1 (d), 135.1 (d), 140.8 (d), 145.7 (2C, C-1′ and 1″), 151.9 (s). MS: *m*/*z* (%): 423 (100), 346 (40), 315 (5), 257 (9), 228 (6), 212 (7), 191 (6), 173 (8), 165 (11), 77 (5). Exact mass for $C_{31}H_{21}NO$: 423.1623. Found 423.1610.

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