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Synthesis and photochromic behaviour under flash photolysis and continuous irradiation of novel 2*H*-chromenes derived from hydroxydibenzothiophenes

M. Manuel Oliveira,[a,*] Corinne Moustrou,[b] Luis M. Carvalho,[a] José A. C. Silva,[a] André Samat,[b] Robert Guglielmetti,[b] Roger Dubest,[c] Jean Aubard[c] and Ana M. F. Oliveira-Campos[d]

[a]*Dept. de Química, Universidade de Trás-os-Montes e Alto Douro, 5000 Vila Real, Portugal*
[b]*LCMOM, ESA 6114 CNRS, Université de la Méditerranée, 13288 Marseille cedex 9, France*
[c]*ITODYS, Université Denis Diderot Paris 7, 75005 Paris, France*
[d]*Centro de Química, IBQF, Universidade do Minho, 4710 Braga, Portugal*

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Abstract—The synthesis and photochromic properties, under flash photolysis and continuous irradiation, of new 2,2-diphenyl-2*H*-1-benzopyrans including a dibenzothiophene nucleus are described. Under flash photolysis, all compounds exhibit photochromic behaviour in solution at room temperature, but under continuous irradiation the same was not perceived. Compared to reference compounds, a general bathochromic shift and the existence of two absorption bands in the Vis spectra of the open forms, leading to a boardening in the absorption range, is observed. The heteroannellation effects on the spectrokinetic parameters are variable and depend on the position and geometry of the fused benzothiophene moiety. The effect of electron-withdrawing substituents in C(6) of the 2*H*-1-benzopyran skeleton, with the benzothiophene nucleus fused at the 7,8 positions, are analyzed. © 2002 Published by Elsevier Science Ltd.

1. Introduction

In the last decades photochromic molecules became an important field of research in organic chemistry due to the large number of their practical and potential applications. All these applications, based on the reversibility, configure the fascinating ability of modulating given physical properties through an external stimulation, namely upon light irradiation. Variable transmission materials, optical switches and memories[1–5] are among the most interesting.

These chemical species undergo a reversible structural photo-transformation, leading to states with different absorption spectra and different physical and chemical properties, as a result of the structural change involved. Generally, the back reaction occurs predominantly through a thermal pathway, which can be accompanied by a photochemical process, although often not important. In some systems, however, the bleaching time can be significantly accelerated by irradiation with visible light and this can become the main process to return to the original state.

Since the early 1990s, the applications in the field of photochromic plastic ophthalmic lenses[6–8] became the major commercial success of these unique organic chemicals. Important families, such as spiropyrans and spirooxazines have been extensively developed and studied. More recently 2*H*-1-benzopyrans (=2*H*-chromenes) have been the subject of intense research efforts in order to obtain a greater basic understanding of the photochromic behaviour and to achieve an improvement of the photochromic properties.

The photochromic behaviour of 2*H*-1-benzopyrans is based on a reversible pyran ring opening, induced by light, that converts a colourless form (usually named the 'closed form') in a set of photoisomers where the pyran ring is opened (the 'open form') (Scheme 1).[9,10] Due to the quasi planarity of the open forms structures, an extension of the π-electrons conjugation is achieved, leading to distinct absorption, usually in the visible range, after irradiation.

The photochromic properties looked for are mainly dependent on the application. In the field of photochromic lenses the ideal targets are molecules that can be photo stimulated by sunlight (heliochromism), developing rapidly an intense neutral colouration (absorption covering as much as possible the visible spectrum) and returning to the original state (bleaching) predominantly through a thermal process with a reasonable kinetic (not too fast, nor too slow). Furthermore they should be fatigue resistant, allowing the occurrence of many colouring–decolouring cycles.

Keywords: photochromism; 2*H*-chromenes; flash photolysis; continuous irradiation; dibenzothiophene.

* Corresponding author. Tel.: +351-259-350259; fax: +351-259-350480; e-mail: moliveir@utad.pt

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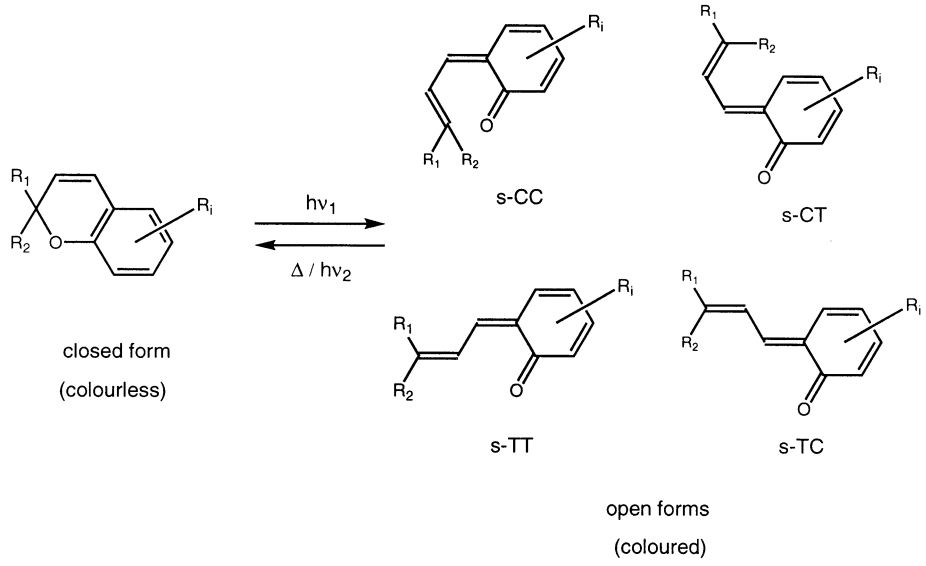
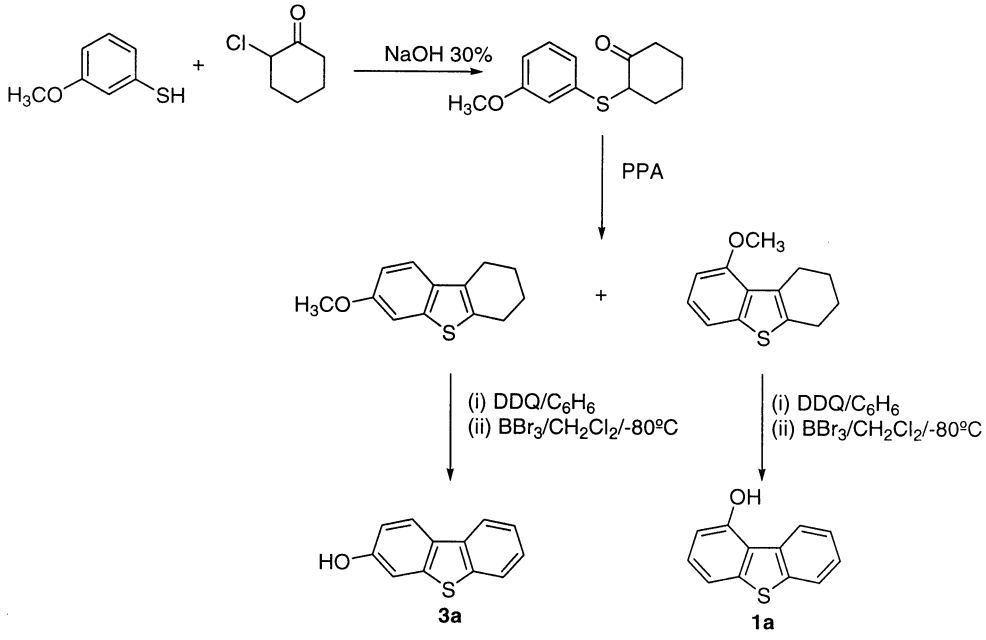


Scheme 1. Photochromic equilibrium for 2*H*-chromenes.

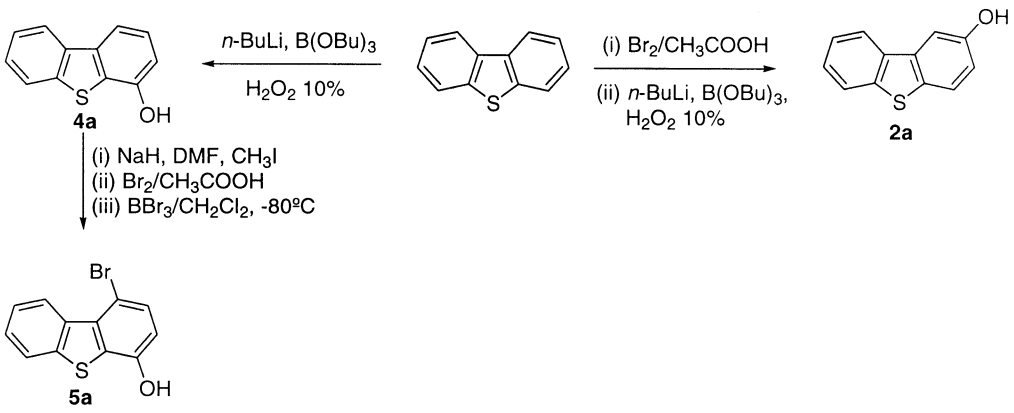
The evaluation of the photochromic behaviour of molecules involves the knowledge of some relevant parameters, related to the kinetic and spectral properties, through a kinetic analysis performed by photolysis under flash or continuous irradiation. The information obtained by the two methods can be very distinct since the time scales of observation are completely different.

The main strategies to improve the photochromic properties of these molecules involve the modification of the 2*H*-1-benzopyrans structures through fusion of five or six-membered heteroaromatic rings and the appropriate substitution on the molecule, namely the introduction of substituents, to the sp^3 carbon of the pyran ring, such as phenyl or spirofluorene allowing extension of the conjugation[11,12]

The presence of a thiophene moiety in 2*H*-chromene molecules seems to give rise to interesting photochromic properties.[13–16] Molecules of 2*H*-chromene including dibenzothiophene nuclei are not described in the literature and so we decided to investigate the photochromic behaviour of these novel systems. In this paper, we report the synthesis and the spectrokinetic properties in solution, under flash and continuous irradiation, of a variety of 2,2-diphenyl-2*H*-chromenes in which the position and geometry of a fused benzothiophene group was varied.



Scheme 2. General synthesis of compounds **1a** and **3a**.



Scheme 3. General synthesis of compounds **2a**, **4a** and **5a**.

2. Results and discussion

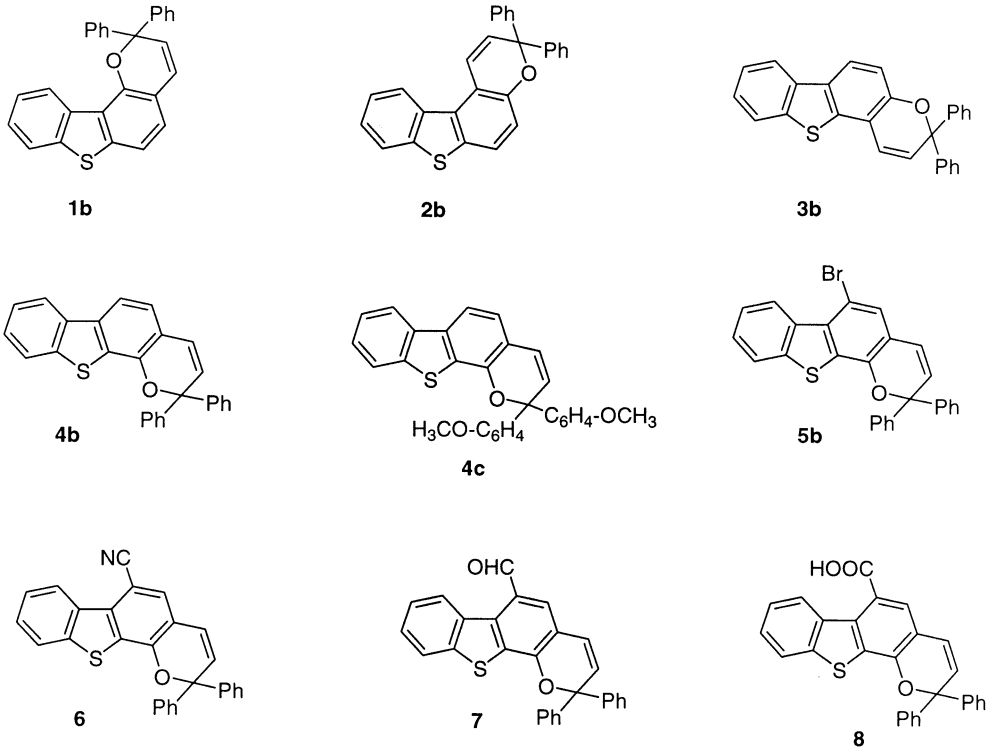
2.1. Synthesis

Compounds **1a** and **3a** were prepared by known methods from coupling of 3-methoxybenzenethiol with 2-chlorocyclohexanone in presence of NaOH 30% followed by cyclisation with PPA at 150°C to yield a mixture of both tetrahydrodibenzothiophenes (1-OMe 22% and 3-OMe 53%).[17,18] After separation by column chromatography they were aromatized with DDQ in benzene[19] and demethylated with BBr_3 in CH_2Cl_2 at $-80°C$[20] with an overall yield of 56% (3-OMe) and 74% (1-OMe) (Scheme 2).

Compounds **2a**, **4a** and **5a** were obtained from dibenzothiophene[21–23] accordingly to Scheme 3 in 69, 59 and 72% yields, respectively. These known compounds showed melting points and spectral characteristics in accordance with literature values.

Among several methods available to obtain heteroannellated 2,2-diaryl-2*H*-chromenes[24] two synthetic approaches were considered, both involving the transformation of the corresponding heterocyclic phenols through a 'one-pot reaction'.

Method A is based on the organotitanium-mediated condensation of α,β-unsaturated aldehydes with phenols. It involves the titanium(IV) salt of the phenol, obtained with $Ti(OEt)_4$ on azeotropic distillation of formed EtOH and leads to the C-alkylation in a *ortho*-position, that through a subsequent electrocyclization yields the chromene moiety.[25,26] Method B is based on the thermal condensation of a suitable alkynol and the phenol in an apolar solvent



Scheme 4. 2*H*-Chromenes derived from dibenzothiophene nuclei.

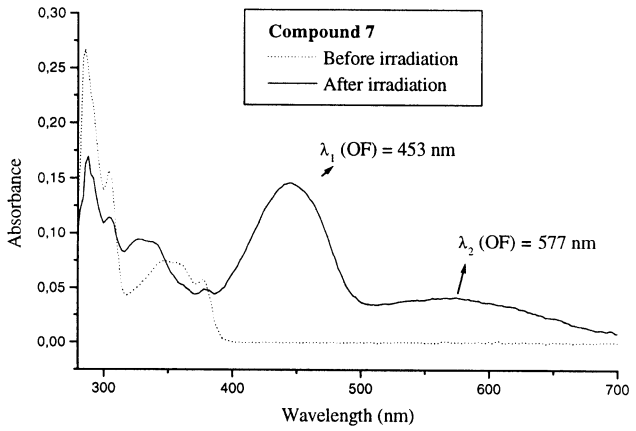


Figure 1. UV/Vis absorption spectra of uncoloured (CF) (···) and coloured species (—) of compound **7** in toluene.

under acid catalysis (*p*-toluenesulphonic acid or pyridinium *p*-toluenesulfonate). The reaction proceeds via a Claisen-like [3,3]-sigmatropic rearrangement of the resulting propargyl aryl ether and a subsequent [1,5]-sigmatropic shift and electrocyclisation leading to the chromene.[26–28]

Although we often obtain better yields with method B, for compounds **1b** and **3b**, very complex mixtures that are very difficult to purify were obtained, thus we decided to apply method A that affords good results 28 and 32%, respectively. To observe the effect of electron-withdrawing groups on the photochromic behaviour, derivatives **5b**, **6**–**8** were also synthesised (Scheme 4).

Chromene **6** was obtained in 30% yield by treatment of **5b** with $Zn(CN)_2$ in DMF with dppf and $Pd(dba)_3$,[29] and the IR band at 2213 cm^{-1} was conclusive. The formyl derivative **7** was prepared in 40% yield by lithiation (*n*-BuLi) followed by treatment with DMF.[23] Its identification was first confirmed by the IR band due to the carbonyl group at 1670 cm^{-1} and the aldehyde proton that appears at 10.51 ppm in its ^1H NMR spectrum. The carboxylation of **5b** to obtain **8** was also effected by lithiation and dry ice quenching[30] in 48% yield, which was confirmed by IR bands at 3058 cm^{-1} (–OH) and 1677 cm^{-1} (C=O) and by a signal at 169 ppm in the ^{13}C NMR spectrum due to the carboxylic acid group.

All the synthesised chromenes were fully characterised by spectroscopic methods and elemental analysis.

2.2. Photochromic properties

All the closed forms of the 2*H*-1-benzopyrans synthesised including a dibenzothiophene nucleus (Scheme 4) show absorption bands in the near-UV (see Section 4 and, for example, Fig. 1) and can, in principle, be activated by sunlight (heliochromism).

Spectrokinetic studies under flash photolysis—Under flash photolysis the compounds described exhibit photochromic behaviour, at room temperature in toluene solutions. The usual comparative spectrokinetic parameters (maxima wavelengths of the coloured form, colourability and rate constant of thermal bleaching) are summarized in Table 1 in which we included two reference naphthopyrans (Ref 1 and Ref 2) for comparison.[31,32]

The effects of the heteroannellation and the introduction of some groups in the molecule on the photoactivity of these compounds can be evaluated and discussed through the comparison to values obtained for reference compounds and similar compounds with a thiophene moiety.[15,32,33]

2.2.1. Annellation effects. Comparing to the reference naphthopyrans, the introduction of a fused benzothiophene group led to a global bathochromic shift in the spectra of the open forms. Moreover, an interesting broadening in the visible absorption spectra of all the open forms can be observed, due to the presence of two absorption bands, located at 430–460 and 510–580 nm (see, for example, Fig. 1). Two bands in the visible absorption spectrum of the open forms are also observed with the reference 7,8-annellated naphthopyran (Ref 2), although they are located at shorter wavelengths. The reference naphthopyran with a 5,6-annellation (Ref 1) is distinctly different displaying only one single absorption band culminating at 432 nm. Another general characteristic in chromenes with a fused thiophene

Table 1. Maxima wavelengths of the coloured forms (λ_1OF, λ_2OF), colourability (A_{01}, A_{02} and A_{eq}), fading rate ($k_{\Delta f}$ and $k_{\Delta c}$) of the described 2*H*-chromenes and two 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). *S* position is relative to the 2*H*-1-benzopyran moiety. Ref 1=3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran; Ref 2=2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran (from Ref. 32)

Compound	Annellation	Flash photolysis					Continuous irradiation	
		λ_1OF	A_{01}	λ_2OF	A_{02}	$k_{\Delta f}$ (amplitude %)	A_{eq}	$k_{\Delta c}$ (amplitude %)
3b	5,6 S–(C5)	459	0.64	557	0.28	0.68 (89), 0.16 (11)	Not heliochromic	
2b	5,6 S–(C6)	449	0.88	513	0.59	2.23 (97), 0.05 (3)	Not heliochromic	
1b	7,8 S–(C7)	436	1.2	513	0.3	0.04 (67), 0.01 (33)	0.6	0.02 (82), <0.01 (18)
4b	7,8 S–(C8)	440	2.3	544	0.51	0.06 (94), 0.01 (6)	0.45	0.05 (65), 0.02 (35)
4c	7,8 S–(C8)	457	1.3	551	0.75	0.31 (96), 0.007 (4)	0.13	0.23 (78), <0.01 (22)
5b	7,8 S–(C8)	454	1.3	558	0.57	0.16 (87), 0.02 (13)	0.35	0.04 (96), <0.01 (4)
6	7,8 S–(C8)	454	1.7	578	0.62	1.34 (96), 0.02 (4)	0.07	0.11 (63), 0.01 (37)
7	7,8 S–(C8)	453	3.9	577	0.84	0.82 (68), 0.01 (32)	Bistable system	
8	7,8 S–(C8)	446	2.8	570	0.69	0.59 (95), <0.01 (5)	0.24	0.05[a]
Ref 1	5,6	432	0.84	–	–	0.09	0.21	0.07 (80), 0.003 (20)
Ref 2	7,8	403	1.08	481	1.62	<0.01	–	–

[a] 30 min after the end of the irradiation the solution remained with a residual yellowish colour corresponding to about 0.1 absorbance units, at the wavelength of the measurement.

or benzothiophene group, is observed: the existence of two phases, of variable amplitudes, in the fading kinetics, whereas for the reference compounds only one is observed.[15] The slow fading rate phase is usually attributed to the most stable *s-trans*-isomer.

-5,6-Annellation: taking into account the 2*H*-1-benzopyran moiety, two structural types may be considered: one where the sulphur atom is bound to C(5) (**3b**) and the other one with the sulphur atom bound to C(6) (**2b**). Table 1 shows that the position of the sulphur atom has a marked influence in the photochromic behaviour of these compounds. Compound **2b** (S–C(6)) exhibits a less pronounced bathochromic shift than **3b** (S–(C5)) but displays an enhanced photocolouration efficiency (colourability) and a faster kinetics of ring closure (higher thermal instability). Qualitatively the same conclusions can be drawn from the literature data for 2*H*-chromenes with a fused dimethylthiophene nucleus in the same positions, although poorer colourabilities and slower fading rates are apparent.[15]

-7,8-Annellation: again, considering the 2*H*-1-benzopyran moiety, two structural types may be considered, one where the sulphur atom is bound to C(7) (**1b**) and others with the sulphur atom bound to C(8) (**4b** and the substituted derivatives **4c**, **5b**, **6**–**8**). As it is usually observed the compounds without substituents and with a 7,8-annellation, exhibit a very slow thermal bleaching rate which can be explained by the less important nonbonding interactions in the open forms.[26] It can be observed here that there are differences in the spectrokinetic parameters when the geometry of the fused benzothiophene moiety is reversed. The sulphur atom in C(8) led to a more pronounced bathochromic shift and to a significant colourability exaltation. The ring closure kinetics is not much affected but the amplitude of the second phase is quite different in both compounds. In compound **1b** (S–(C7)) the second kinetic phase is about one third of the total bleaching process, meaning that this compound persists with a residual colour for a much longer time than **4b** after the flash irradiation.

2.2.2. Substituent effects. Due to the interesting photochromic properties of **4b** we tried to improve the slow kinetics of ring closure, maintaining a good colourability and an extended absorption range in the visible spectra. The introduction of some moderately to weak electron-withdrawing substituents in the C(7) position is known to produce this kind of modifications in 2,2-diphenylnaphthopyrans annellated in the 5,6-positions.[30] So, we decided to introduce in C(6) the bromo, formyl, cyano and carboxylic groups (compounds **5b**, **7**, **6** and **8**, respectively) to evaluate their influence on the photochromic behaviour of this novel structure. This approach is also interesting as it opens the possibility of further modifications in the molecule.

The values show that this kind of substitution led to a global acceleration of the bleaching process and a bathochromic shift as observed before with equally substituted naphthopyrans.[30]

Comparatively to the molecule without substituents (**4b**) the effects of the formyl, cyano and carboxylic groups (**7**, **6** and **8**, respectively) are similar, a bathochromic shift of about +14 nm in the absorption band at lower wavelengths, a larger bathochromic shift (about +30 nm) of the absorption band at higher wavelengths and a decrease in the stability of the open forms, leading to an acceleration of the fading processes. This indicates that the presence of electron-withdrawing groups in that part of the molecule promotes the unstability of the open forms, as it was already observed with photochromic naphthopyrans annellated in the 5,6-positions. It is noteworthy that the interesting kinetic phase amplitudes of **6** (with the cyano group), which is not observed in **7** (with the formyl group), that exhibits a slower kinetic phase too long. Compound **8** exhibits an interesting amplitude of the first kinetic phase, but the fading process becomes so slow that it is difficult to calculate its value. The effects of these groups in the colourability are modest indicating that this kind of substitution may not contribute to an enhancement of the quantum yield for photocolouration.

The induced modifications achieved with the bromo group, although in the same direction, are not as pronounced, what is in agreement with its weaker electron withdrawing characteristics through inductive effect. The greater bathochromic shifts observed for **6**–**8** can be, in part, explained by the greater extension conjugation of the additional π-electrons of the substituents.

In compound **4c** one methoxy group was introduced, in the *para* position, in each phenyl group attached to the sp^3 carbon of the pyran ring. Relatively to **4b** the effects observed due to the presence of this electron-donor group, were a global bathochromic shift with relevance to the absorption band located at lower wavelengths (+17 nm) and a faster fading process, with a magnitude that can be interesting for applications in the field of variable optical transmission materials. The observed effects on the colouration efficiency are not relevant.

Spectrokinetic studies under continuous irradiation—methods employing continuous irradiation operate in experimental conditions quite comparable to those that are found in the normal uses of photochromic lenses. A solution containing the photochromic molecule is exposed to an adequate light until a photochemical and thermal equilibrium (photostationary state) is reached. The kinetics of decolouration can then be studied in the absence of light (thermal process) or, if wanted, under irradiation with a different light (photochemical process).

In comparison with the flash photolysis method a longer irradiation time and a lower intensity light flux is used. During irradiation, the open forms are formed, but only the photoisomers with the longest lifetimes will accumulate and will be observed. The spectrokinetic analysis is based on considering the photostationary state or on the reaction progress. The method is particularly well suited for the study of slow photochromic systems such as those used in ophthalmic lenses that are coloured in the sun and colourless in the dark.

The spectrokinetic parameters (A_{eq} and the rate constants of thermal bleaching, $k_{\Delta c}$) obtained under continuous irradiation are summarized in Table 1 in which we included a corresponding naphthopyran (Ref 1) as a reference

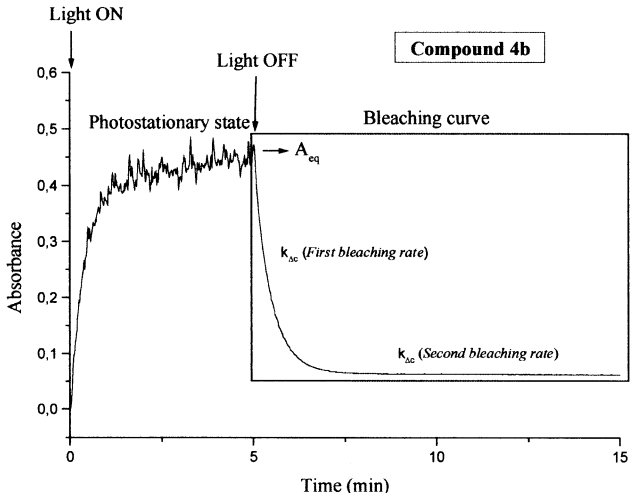


Figure 2. Photoinduced absorbance change under continuous irradiation of compound **4b** showing the kinetics of the biexponential thermal relaxation at 440 nm.

compound for comparison. Absorbance measurements were made at the maximum wavelength of the first absorption band of the open forms (see, for example, Fig. 2).

An analysis of these data allows some conclusions about the results of both methods: in some cases the fading kinetics observed under flash irradiation ($k_{\Delta f}$) can be correlated with the one ($k_{\Delta c}$) observed under continuous irradiation; the absorbance attained under continuous irradiation is always lower than the colourability under flash irradiation; compounds **2b** and **3b**, annellated in the 5,6-positions could not be activated under the conditions used for continuous irradiation (see, for example, Fig. 3).

In both methods the bleaching kinetics is biexponential (except for **8**) and it seems that there is some correlation between the values of the calculated constants by the two methods for **1b**, **4b** and **4c**, indicating a similar nature of the stable photoisomers in the mixture obtained after irradiation in both methods. However, for compounds **5b** and **7** there is no correlation in the calculated constants, even the slower ones, what may signify that for those compounds there is a

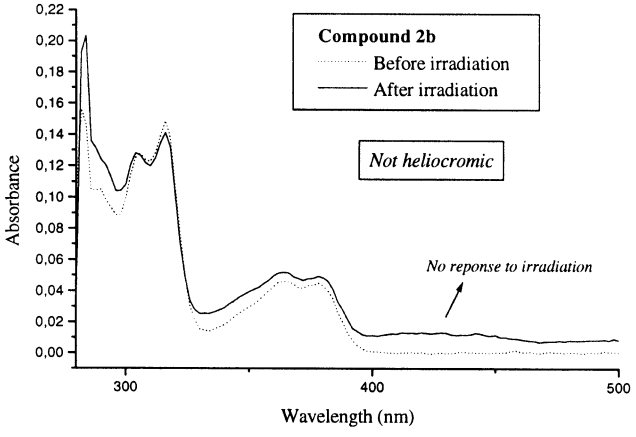


Figure 3. UV/Vis absorption spectra of a solution of compound **2b** in toluene.

significative difference between the stable photoisomers produced in both methods. Compound **8** seems to have a different fading process with only one kinetic phase. This may not be correct because a relevant residual yellowish colour at the end of the measurement is observed that may be attributed to a very stable open form (second kinetic constant very low) or to degradation products that masked the second kinetic phase, avoiding its evaluation.

Some correlation can be observed in the colourabilities obtained through both methods (A_0 and A_{eq}), although the observed colourabilities under continuous irradiation are always much lower. These differences in the colourability observed in both methods can be explained: A_0 is dependent on the quantum yield of the photochemical colouration and on the absorptivity of the open forms; A_{eq} is dependent on the absorptivity of the coloured forms, the rate coefficient of the photochemical colouring reaction and the rate coefficient of thermal bleaching reaction. A fast thermal decolouration means a lower A_{eq} and this may be the case of all the compounds described.

Compounds **3b** and **2b** may constitute fast photochromic systems that cannot be studied under continuous irradiation. The lifetime of the coloured forms must be more than about 0.1 s for the photoisomer to accumulate under the continuous irradiation conditions.

Under continuous irradiation the open form of compound **7** has a high thermal stability and could only be photochemically bleached, thus constituting a bistable system (Fig. 4).

3. Conclusion

The synthesis of benzothiophene-fused 2*H*-1-benzopyrans was achieved by the usual methods. All compounds exhibited photochromic activity, in solution at room temperature, under flash photolysis. Studies made under continuous irradiation were not in total agreement particularly with compounds with the benzothiophene moiety fused at the 5,6 position. The observed spectrokinetic parameters are dependent on the relative position and geometry of the annellation. From a general point of view the heteroannellation led to a global bathochromic shift and a broadening of the visible absorption range. The presence of electron-withdrawing substituents in C(6) of the 2*H*-1-benzopyran skeleton, with the benzothiophene nucleus fused at the 7,8 positions, led to a global acceleration of the thermal bleaching process. The presence of the formyl group led to a bistable system under continuous irradiation, with interesting colouration efficiency and visible spectrum coverage, that can be important to applications where the transformations can be photoinduced, in both directions, using light of different wavelengths.

4. Experimental

4.1. Materials and methods

Solvents (Riedel–Haën and Merck) were used without

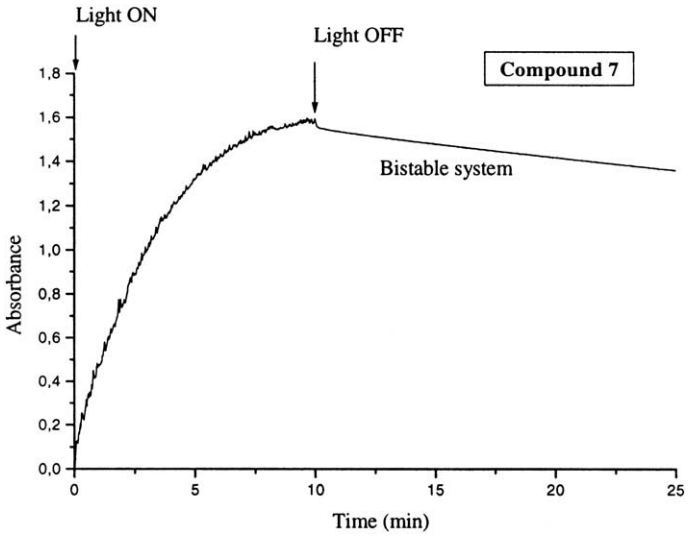


Figure 4. Kinetics of thermal relaxation at 453 nm of compound **7** after irradiation.

further purification other than drying over sodium (Et_2O) and over anhydrous calcium chloride (CH_2Cl_2). Column chromatography was performed on silica gel Merck 60 (70–230 mesh). ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus (300 and 75.4 MHz, respectively) and on a Bruker BM 250 (250 and 62.9 MHz, respectively) using tetramethylsilane as internal standard. 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^{-5} M toluene solutions. Maxima wavelengths (λ_{max}) are given in nm and molar absorption coefficients of closed forms (ε) are given in $l\,mol^{-1}\,cm^{-1}$. Elemental analysis was performed on a LECO-932-CNS analyser and mass spectra on a AutoSpecE spectrometer. Melting points (°C), measured in capillary tubes on a Büchi 535 apparatus, are uncorrected.

4.2. Spectrokinetic measurements

For the determination of λ_1 and λ_2, A_{01} and A_{02}, and $k_{\Delta f}$, 5×10^{-5} mol dm^{-3} toluene solutions were used. The flash photolysis apparatus was 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).[31,34] 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 GC400 high-pass filter.

For the determination of absorption spectra of closed form and open form 1×10^{-5} mol dm^{-3} toluene solutions were used. Determination of λ_{max} were made with a light flux of 400 W m^{-2}. For measurements of A_{eq}, and $k_{\Delta c}$ under continuous irradiation, 1×10^{-4} mol dm^{-3} toluene solutions were used. The apparatus was monitored by a CARY 50 Varian spectrometer (2.0 nm spectral band pass) with a Xenon lamp (Ushio type UXL-150SO/Oriel instruments). For measurements, thermostated (20°C) 10 mm cells were used. The irradiation was carried out in the spectrophotometer holder at the right angle to the monitoring beam, using a fiber-optic system.

The relaxation kinetics for both methods were calculated using Origin 5.0 Professional program.

4.3. General method for the synthesis of pyranodibenzothiophenes 1b and 3b

A solution of the hydroxydibenzothiophene (10 mmol) in dry toluene (50 ml), under Ar, was stirred until all the dibenzothiophene was dissolved. A solution of titanium(IV) ethoxide (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 at rt and a solution of β-phenylcinnamaldehyde (10 mmol in 40 ml of dry toluene) was added dropwise. The mixture was refluxed for a period of 2–6 h, cooled to rt, quenched with 40 ml of 2 M aq. NaOH, and extracted with CH_2Cl_2 (3×40 ml). The combined org. extracts were dried ($MgSO_4$), evaporated to dryness and the residue was purified by CC on silica gel.

4.3.1. 2,2-Diphenyl-[2*H*]-pyran[6,5-*a*]dibenzothiophene (1b). 3 h reflux, 28% yield, purification by column chromathography, eluent CH_2Cl_2/pentane (1:5) gave a white solid, mp 117–119. IR: 3057, 3023, 1631, 1594, 1486, 1444, 1419, 1305, 1226, 1105, 1062, 1051, 989, 950, 808, 755, 746, 730, 696. UV/Vis (closed form): 316 (ε 6230), 336 (ε 6310), 352 (ε 8730). ^1H NMR ($CDCl_3$): 6.28 (1H, d, J=9.8 Hz, H-3); 6.88 (1H, d, J=9.8 Hz, H-4); 7.24 (1H, d, J=8 Hz, H-6); 7.38–7.49 (7H, m, H-5, 3′, 4′, 5′, 3″, 4″ and 5″); 7.53–7.57 (2H, m, H-9 and 10); 7.65–7.69 (4H, m, H-2′, 6′, 2″ and 6″); 7.91–7.95 (1H, m, H-8); 8.89–8.92 (1H, m, H-11). ^{13}C NMR ($CDCl_3$): 83.9 (s); 115.0 (d); 116.7 (s); 122.2 (d); 123.5 (d); 123.9 (s); 124.6 (d); 125.2 (d); 125.9 (d); 126.9 (d); 127.0 (4C, C-2′, 6′, 2″ and 6″); 127.6 (2C, C-4′ and 4″); 128.2 (4C, C-3′, 5′, 3″ and 5″); 134.8 (s); 139.0 (s); 141.0 (s); 144.9 (2C, C-1′ and 1″); 149.7 (s). MS: 390 (100, $M^{+\cdot}$), 313 (72), 284 (15), 191

(19), 165 (9). Anal. calcd for $C_{27}H_{18}OS$: C 83.05, H 4.65, S 8.21; found C 83.16, H 4.90, S 8.04.

4.3.2. 2,2-Diphenyl-[2*H*]-pyran[6,5-*c*]dibenzothiophene (3b). 4 h 30 min reflux, 32% yield, purification by column chromatography, eluent CH_2Cl_2/pentane (1:4), gave a white solid, mp 191–194. IR: 3058, 3024, 1633, 1577, 1490, 1444, 1251, 1220, 1170, 1049, 1000, 943, 914, 817, 752, 696. UV/Vis (closed form): 310 (ε 6360), 324 (ε 4500), 350 (ε 1650). ^{1}H NMR ($CDCl_3$): 6.25 (1H, d, J=9.8 Hz, H-3); 6.78 (1H, d, J=9.8 Hz, H-4); 7.02 (1H, d, J=8.5 Hz, H-11); 7.22–7.31 (8H, m, H-7, 8, 3′, 4′, 5′, 3″, 4″ and 5″); 7.39–7.42 (4H, m, H-2′, 6′, 2″ and 6″); 7.71–7.75 (1H, m, H-6); 7.82 (1H, d, J=8.5 Hz, H-10); 7.90–7.93 (1H, m, H-9). ^{13}C NMR ($CDCl_3$): 80.1 (s); 111.6 (d); 112.2 (s); 117.7 (d); 117.8 (d); 119.0 (d); 119.7 (d); 121.5 (d); 122.6 (d); 124.0 (4C, C-2′, 6′, 2″ and 6″); 124.6 (s); 124.7 (2C, C-4′ and 4″); 125.2 (4C, C-3′, 5′, 3″ and 5″); 126.2 (d); 126.9 (s); 132.8 (s); 135.2 (s); 141.5 (2C, C-1′ and 1″); 148.4 (s). MS: 390 (100, $M^{+\cdot}$), 313 (73), 284 (20), 191 (26), 178 (13), 165 (10). Anal. calcd for $C_{27}H_{18}SO$: C 83.05, H 4.65, S 8.21; found C 82.96, H 4.69, S 8.24.

4.4. General method for the synthesis of pyranodibenzothiophenes 2b, 4b and 5b

To a stirred mixture of the hydroxydibenzothiophene (10 mmol) and 1,1-diphenyl-2-propyn-1-ol (11 mmol) in dry CH_2Cl_2 (10–25 ml), under Ar, a catalytic amount of *p*-toluenesulfonic acid (APTS) was added. The mixture was kept at rt or heated to reflux, according to TLC analysis.

4.4.1. 2,2-Diphenyl-[2*H*]-pyran[5,6-*a*]dibenzothiophene (2b). 70 min rt, 54% yield, purification by column chromatography, eluent CH_2Cl_2/pentane (15:85), gave a yellow solid, mp 138–140. IR: 3058, 1631, 1571, 1444, 1411, 1255, 1205, 1110, 989, 944, 759, 725, 698. UV/Vis (closed form): 306 (ε 12,700), 316 (ε 14,850), 364 (ε 4590), 378 (ε 4500). ^{1}H NMR ($CDCl_3$): 6.39 (1H, d, J=9.9 Hz, H-3); 7.16 (1H, d, J=8.5 Hz, H-11); 7.22–7.28 (2H, m, H-4′ and 4″); 7.30–7.35 (4H, m, H-3′, 5′, 3″ and 5″); 7.40–7.42 (1H, m, H-7); 7.42–7.44 (1H, m, H-6); 7.49–7,53 (4H, m, H-2′, 6′, 2″ and 6″); 7.59 (1H, d, J=8.5 Hz, H-10); 7.67 (1H, d, J=9.9 Hz, H-4); 7.80–7.83 (1H, m, H-8); 8.31–8.35 (1H, m, H-5). ^{13}C NMR ($CDCl_3$): 81.5 (s); 116.9 (d); 118.0 (s); 121.2 (d); 123.0 (d); 123.3 (d); 124.1 (d); 124.6 (d); 129.0 (d); 127.1 (4C, C-2′, 6′, 2″ and 6″); 127.6 (2C, C-4′ and 4″); 128.1 (4C, C-3′, 5′, 3″ and 5″); 129.9 (d); 131.0 (s); 132.5 (s); 135.7 (s); 140.9 (s); 144.4 (2C, C-1′ and 1″); 150.6 (s). MS 390 (100, $M^{+\cdot}$); 313 (96); 284 (9); 191 (9); 165 (11). Anal. calcd for $C_{27}H_{18}OS$: C 83,05; H 4,65; S 8,21%; found C 82.95, H 4.60, S 8.10.

4.4.2. 2,2-Diphenyl-[2*H*]-pyran[6,5-*a*]dibenzothiophene (4b). 1 h 45 min reflux, 43% yield, purification by column chromatography, eluent CH_2Cl_2/pentane (1:4), gave a yellow solid, mp 134–135. IR: 3056, 3023, 2921, 1602, 1479, 1444, 1405, 1214, 1056, 1000, 960, 902, 813, 767, 742, 698. UV/Vis (closed form): 304 (ε 17,190), 318 (ε 23,020), 347 (ε 4370), 362 (ε 4430). ^{1}H NMR ($CDCl_3$): 6.27 (1H, d, J=9.8 Hz, H-3); 6.77 (1H, d, J=9.8 Hz, H-4); 7.13 (1H, d, J=7.9 Hz, H-5); 7.26–7.79 (2H, m, H-4′ and 4″); 7.30–7.35 (4H, m, H-3′, 5′, 3″ and 5″); 7.41–7.43 (1H, m, H-9); 7.41–7.44 (1H, m, H-8); 7.51–7.54 (4H, m, H-2′, 6′, 2″ and 6″); 7.66 (1H, d, J=7.9, H-6); 7.83–7.86 (1H, m, H-10); 8.04–8.08 (1H, m, H-7). ^{13}C NMR ($CDCl_3$): 83.4 (s); 114.3 (d); 118.3 (s); 121.6 (d); 123.0 (d); 123.3 (d); 123.4 (d); 124.3 (d); 126,6 (d); 126.7 (4C, C-2′, 6′, 2″ and 6″); 126.8 (s); 127.5 (2C, C-4′ and 4″); 128.1 (4C, C-3′, 5′, 3″ and 5″); 128.5 (d); 135.7 (s); 137,5 (s); 140.1 (s); 144.6 (2C, C-1′ and 1″); 147.2 (s). MS: 390 (100, $M^{+\cdot}$); 371 (8); 313 (87); 284 (20); 191 (21); 178 (8); 165 (11); 77 (8). Anal. calcd for $C_{27}H_{18}OS$: C 83.05; H 4.65; S 8.21%; found C 83.25, H 4.82, S 8.02.

4.4.3. 6-Bromo-2,2-diphenyl-[2*H*]-pyran[6,5-*a*]dibenzothiophene (5b). 3 h 30 min reflux, 86% yield, purification by column chromatography, eluent CH_2Cl_2/pentane (3:7), gave an off-white solid, mp 217–219. IR: 3058, 3023, 1637, 1594, 1486, 1469, 1438, 1392, 1346, 1251, 1214, 1170, 1062, 997, 948, 904, 769, 728, 698. UV/Vis (closed form): 304 (ε 20,290), 318 (ε 27,310), 346 (ε 5500), 362 (ε 5700). ^{1}H NMR ($CDCl_3$): 6.33 (1H, d, J=10 Hz, H-3); 6.73 (1H, d, J=10 Hz, H-4); 7.25–7.30 (2H, m, H-4′ and 4″); 7.32 (1H, s, H-5); 7.33–7.37 (4H, m, H-3′, 5′, 3″ and 5″); 7.48–7.53 (6H, m, H-8, 9, 2′, 6′, 2″ and 6″); 7.85–7.89 (1H, m, H-10); 9.10–9.13 (1H, m, H-7). ^{13}C NMR ($CDCl_3$): 83.8 (s); 108.8 (s); 118.7 (s); 122.1 (d); 122.8 (d); 124.0 (d); 125.1 (d); 126.7 (4C, C-2′, 6′, 2″ and 6″); 127.0 (d); 127.8 (2C, C-4′ and 4″); 127.9 (d); 128.2 (4C, C-3′, 5′, 3″ and 5″); 129.3 (s); 130.0 (d); 133.9 (s); 135.5 (s); 140.5 (s); 144.2 (2C, C-1′ and 1″); 146.3 (s). MS: 470 ($M^{+\ 81}$Br, 100); 468 ($M^{+\ 79}$Br, 100); 393 (37); 371 (10); 311 (16); 284 (12); 239 (5); 191 (12); 178 (14); 165 (11); 105 (5); 77(6). Anal. calcd for $C_{27}H_{17}BrOS$: C 69.09; H 3.65; S 6.83; found C 69.02, H 3.72, S 7.06.

4.5. General method for the synthesis of pyranodibenzothiophene 4c

To a stirred mixture of the hydroxydibenzothiophene **4a** (10 mmol) and 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol (11 mmol) in dry CH_2Cl_2 (10–25 ml), under Ar, a catalytic amount of of pyridinium *p*-toluenesulfonate (PPTS) was added. The mixture was kept at rt or heated to reflux, according to TLC analysis.

4.5.1. 2,2-Bis(4-methoxyphenyl)-[2*H*]-pyran[5,6-*c*]dibenzothiophene (4c). 2 h 15 min reflux, 56% yield, purification by column chromatography, eluent CH_2Cl_2/pentane (2–1:3–1), gave an off-white solid, mp 184–185. IR: 3048, 2954, 2904, 2834, 1606, 1511, 1442, 1401, 1371, 1297, 1247, 1174, 1031, 829, 752, 705, 626. UV/Vis (closed form): 304 (ε 19,150), 318 (ε 26,130), 356 (ε 5400), 372 (ε 5570). ^{1}H NMR ($CDCl_3$): 3.78 (6H, s, 2×OCH_3); 6.21 (1H, d, J=9.9 Hz, H-3); 6.74 (1H, d, J=9.9 Hz, H-4); 6.83–6.88 (4H, m, H-3′, 5′, 3″ and 5″); 7.14 (1H, d, J=8 Hz, H-5); 7.41–7.46 (6H, m, H-8, 9, 2′, 6′, 2″ and 6″); 7.66 (1H, d, J=8 Hz, H-6); 7.84–7.87 (1H, m, H-10); 8.06–8,08 (1H, m, H-7). ^{13}C NMR ($CDCl_3$): 55.2 (2C, q); 83.2 (s); 113.4 (4C, C-3′, 5′, 3″ and 5″); 114.3 (d); 118.4 (s); 121.7 (d); 122.9 (d); 123.0 (d); 123.4 (d); 124.3 (d); 126.6 (d); 126.9 (s); 128.1 (4C, C-2′, 6′, 2″ and 6″); 128.9 (d); 135.8 (s); 137.1 (2C, C-1′ and 1″); 137.5 (s); 140.2 (s); 147.4 (s); 158.9 (2C, C-4′ and 4″). MS: 450 (100, $M^{+\cdot}$); 343 (46); 300 (6); 271

(5); 251 (5); 225 (7). Anal. calcd for $C_{29}H_{22}O_3S$: C 77.33; H 4.89; S 7.11; found C 77.17, H 4.90, S 7.11.

4.6. Synthesis of pyranodibenzothiophenes 6[24], 7[23] and 8[8]

4.6.1. 6-Cyano-2,2-diphenyl-[2*H*]-pyran[5,6-*c*]dibenzothiophene (6). To a solution of **5a** (0.567 g; 1.20 mmol) in DMF (9 ml), 1,1′-bis(diphenylphosphin) ferrocene (dppf) (0.133 g, 0.240 mmol) and $Pd_2(dba)_3$ (0.055 g, 0.060 mmol) were added. When the reaction mixture reached 90°C, $Zn(CN)_2$ (0.169 g, 1.44 mmol) was added over a 2 h period and heating continued for 3 h. The mixture was cooled to rt, filtered through Celite 545, washed with CH_2Cl_2 and the solvent was evaporated. The residue was poured into water and extracted with a saturated solution of NaCl. The org. layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2/pentane 1:4) yielding the product as a white solid (0.130 g, 30%). Mp 212–214. IR: 3064, 3031, 2213 (CN), 1643, 1598, 1544, 1473, 1444, 1261, 1153, 1002, 944, 908, 736, 700. UV/Vis (closed form): 318 (ε 8966), 331 (ε 11,300), 351 (ε 4626), 367 (ε 4415). ^{1}H NMR ($CDCl_3$): 6.36 (1H, d, J=10 Hz, H-3); 6.77 (1H, d, J=10 Hz, H-4); 7.27–7.33 (2H, m, H-4′ and 4″); 7.34–7.40 (4H, m, H-3′, 5′, 3″ and 5″); 7.47–7.52 (5H, m, H-9, 2′, 6′, 2″ and 6″); 7.53 (1H, s, H-5); 7.54–7.57 (1H, m, H-8); 7.89–7.92 (1H, m, H-10); 8.86–8.89 (1H, m, H-7). ^{13}C NMR ($CDCl_3$): 84.8 (s); 98.3 (s); 117.5 (s); 118.7 (s); 121.6 (d); 123.0 (d); 123.8 (d); 125.1 (d); 126,7 (4C, C-2′, 6′, 2″ and 6″); 128.0 (2C, C-4′ and 4″); 128.1 (d); 128,4 (4C, C-3′, 5′, 3″ and 5″); 129.6 (d); 129.8 (d); 133.8 (s); 137.0 (s); 140.8 (s); 143.8 (2C, C-1′ and 1″); 150.8 (s), the C-6b signal was not detected. MS: 415 (100, $M^{+\cdot}$); 338 (53); 309 (9); 208 (6); 191 (14); 165 (8); 77 (5). Anal. calcd for $C_{28}H_{17}SNO$: C 80.94; H 4.12; N 3.37, S 7.72; found C 80.63, H 4.20, N 3.13, S 7.46.

4.6.2. 6-Formyl-2,2-diphenyl-[2*H*]-pyran[5,6-*c*]dibenzothiophene (7). *n*-Butyllithium (1.6 M in hexanes, 1.28 mmol) was added to a solution of **5a** (0.546 g, 1.16 mmol) in sodium dried ether under an atmosphere of Ar. The solution was stirred for 15 min, *N*,*N*-dimethylformamide (3.49 mmol) was added and the mixture was refluxed for 2 h 30 min. The reaction mixture was poured into ice (35 g) and ether was added to dissolve the solid formed. The ether phase was separated and the aqueous layer was extracted with ether (3×25 ml). The residue was purified by column chromatography, eluent CH_2Cl_2/pentane (4:1), to give an off-white solid (0.190 g, 40%). Mp 164–165. IR: 3062, 2915, 2848, 1670 (C=O), 1594, 1446, 1294, 1255, 1149, 1068, 1002, 946, 910, 757, 730, 701. UV/Vis (closed form): 304 (ε 15,700), 351 (ε 7242), 377 (ε 5692). ^{1}H NMR (Acetone): 6.36 (1H, d, J=10 Hz, H-3); 6.85 (1H, d, J=10 Hz, H-4); 7.29–7.39 (7H, m, H-9, 3′, 4′, 5′, 3″, 4″ and 5″); 7.48–7.54 (5H, m, H-8, 2′, 6′, 2″ and 6″); 7.75 (1H, s, H-5); 7.89–7.92 (1H, m, H-10); 9.04–9.07 (1H, m, H-7); 10.51 (1H, s, –CHO). ^{13}C NMR (acetone): 84.9 (s); 116.7 (s); 121.9 (d); 122.9 (d); 124.8 (d); 126.7 (4C, C-2′, 6′, 2″ and 6″); 127.5 (d); 127.6 (d); 127.6 (d); 128.0 (2C, C-4′ and 4″); 128.4 (4C, C-3′, 5′, 3″ and 5″); 129.0 (s); 129.3 (d); 130.9 (d); 135.2 (s); 137.1 (s); 141.0 (s); 144.0 (2C, C-1′ and 1″); 151.7 (s); 190.1 (s). MS: 420 (100, $M^{+\cdot}$); 404 (7); 389 (13); 371 (6); 343 (59); 313 (7); 284 (7); 191 19); 165 (7). Anal. calcd for $C_{28}H_{18}O_2S$: C 80.36; H 4.33; S 7.66; found C 80.01, H 4.41, S 7.41.

4.6.3. 6-Carboxy-2,2-diphenyl-[2*H*]-pyran[5,6-*c*]dibenzothiophene (8). To a solution of **6** (0.400 g, 0.85 mmol) in dry ether (20 ml), *n*-BuLi (1.6 M in hexanes, 0.85 mmol) was added dropwise with stirring and under Ar. The mixture was left at rt for 1 h and an excess of dry ice was added and left stirring for 30 min. The mixture was hydrolysed with cold water (40 ml), washed with NaOH 5% (3×50 ml) and acidified with HCl 2N. The solid was filtered and recrystallised from pentane to give a white solid (0.160 g, 48%). Mp 241–242. IR: 3058 (OH), 2998, 2881, 2672, 2561, 1677 (C=O), 1536, 1444, 1419, 1284, 1220, 1174, 1068, 1002, 732, 698. UV/Vis (closed form): 325 (ε 10,160), 352 (ε 4752), 369 (ε 3869). ^{1}H NMR (acetone): 6.33 (1H, d, J=9.6 Hz, H-3); 6.79 (1H, d, J=9.6 Hz, H-4); 7.28–7.38 (7H, m, H-9, 3′, 4′, 5′, 3″, 4″ and 5″); 7.45 (1H, t, J^1=J^2=7.8 Hz, H-8); 7.83 (1H, s, H-5); 7.87 (1H, ld, J=7.8 Hz, H-10); 8.83 (1H, ld, J=7.8 Hz, H-7), the COOH proton was not observed. ^{13}C NMR (Acetone): 85.1 (s); 118.0 (s); 123.1 (d); 123.3 (s); 123.8 (d); 125.3 (d); 127.3 (4C, C-2′, 6′, 2″ and 6″); 127.4 (d); 127.5 (d); 128.3 (d); 128.7 (2C, C-4′ and 4″); 129.0 (s); 129.2 (4C, C-3′, 5′, 3″ and 5″); 130.7 (d); 135.5 (s); 136.0 (s); 141.2 (s); 145.3 (2C, C-1′ and 1″); 150.1 (s); 169.1 (s). MS: 420 (100, $M^{+\cdot}$); 390 (12); 371 (5); 357 (53); 313 (9); 284 (6); 191 (11); 165 (7). Anal. calcd for $C_{28}H_{18}O_3S$: C 77.40; H 4.18; S 7.38; found C 72.62, H 4.02, S 7.25.

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