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New halogenated diphenyl-2*H*-benzo[*h*]chromene derivatives: synthesis and optical properties

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Abstract

The synthesis and the optical properties of eleven new photochromic compounds of the diphenyl-chromene family containing different halogen substituents are reported. Kinetic studies under continuous irradiation indicate that for these compounds the bleaching of the merocyanines involves two first order processes. Fluoro-substitution of the phenyl ring(s) always leads to an increase in the fast rate constant, k_1, that is also found to increase on changing the halogen in the naphthalenic fragment from fluorine to chlorine and to bromine. ^{19}F NMR confirms the presence of isomers produced under irradiation. One of these isomers exhibits a great stability in solution. A single crystal X-ray diffraction study indicates that in 6-fluoro-2,2-bis(4′-fluorophenyl)-2*H*-benzo[*h*]chromene the two phenyl rings are orthogonal to each other and that the pyranic fragment deviates considerably from planarity.

Keywords: Chromene; Photochromism; Kinetic studies; Thermal bleaching rate constant; ^{19}F NMR

1. Introduction

Photochromic compounds are of great interest to industry. Indeed, although they have been exploited in a wide range of applications that spans from the manufacturing of optical lenses to colour printing and optical recording, many other promising utilisations are as yet to be put into practice [1]. In 1952, Fisher and Hirshberg [2] first defined as photochromic a chemical species capable of undergoing, under the influence of electromagnetic irradiation, a reversible isomerisation to a new species with a different absorption spectrum. In 1966, the photochromic properties of the [3*H*]naphthopyrans were described [3], and it was shown that they were due to a reversible light induced cleavage of the pyranic ring. The resulting photomerocyanines are usually red or yellow in colour in solution, their actual colour strongly depending on the substitution [4]. The chemistry of these compounds, as well as that of other photochromic families, their physiochemical behaviour and their biological applications have been recently reviewed [5].

In the course of our studies on fluorinated diphenyl-3*H*-benzo[*h*]chromene we have observed that some compounds exhibited a particular thermal back rate constant in solution by means of UV spectroscopy [6] and ^{19}F NMR spectroscopy [7,8]. So, we were prompted to extend our investigation to halogenated [2*H*]benzochromene. If the ^{19}F nucleus is used as a NMR molecular probe, the presence of halogen could be useful in the determination of the by-products formed after light exposure by comparison of the different mass spectra and bromo-compounds could be good precursors in organometallic coupling reaction. We here report about the synthesis using Boswell and Licause method [9] of some new halogenated diphenyl-2*H*-benzo[*h*]chromene and their particular photochromic behaviour.

2. Results and discussion

2.1. Synthesis

The investigated compounds **1**–**11** have the general structure **J** shown in Fig. 1.

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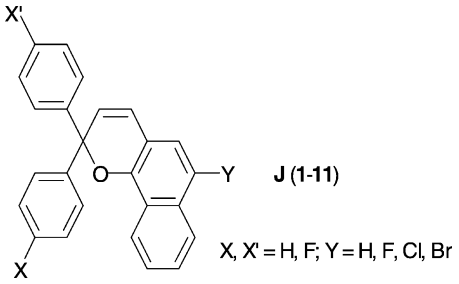


Fig. 1. General structure of the compounds **1**–**11**.

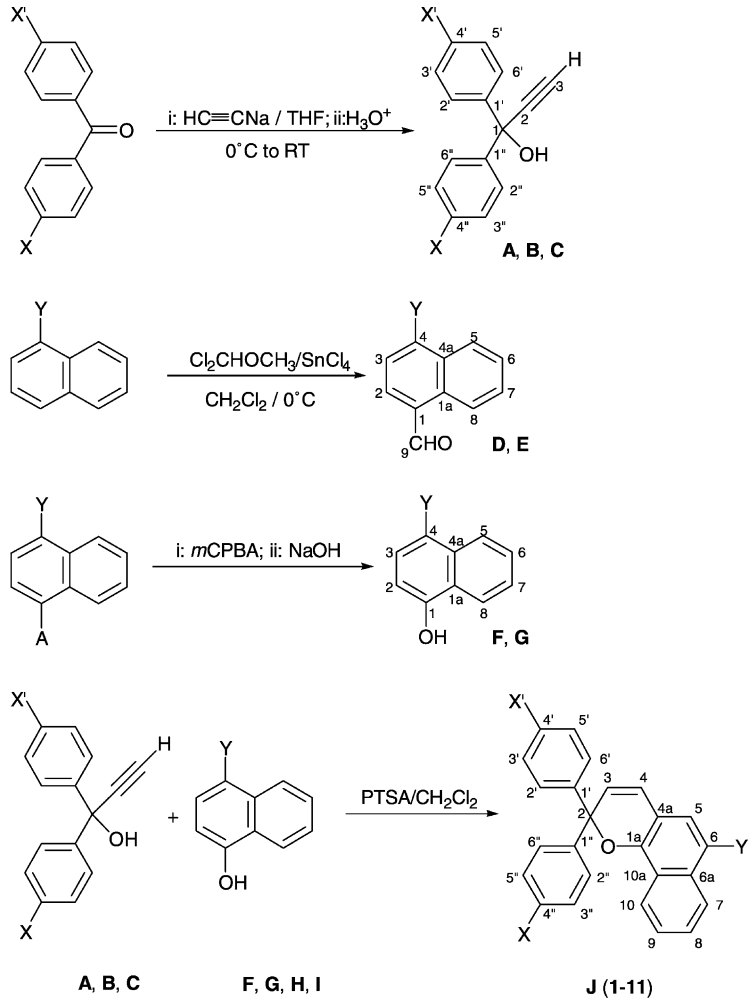
Compounds **1**–**11** all contain one or two 4-fluoro-substituted phenyl ring. The overall synthetic route to compounds **1**–**11** is outlined in Scheme 1.

We have followed the most convenient synthetic route to benzochromene, that is the one involving condensation between a propargyl alcohol and a substituted naphthol in methylene chloride in the presence of a catalytic amount of *p*-toluenesulphonic acid, whereas 4-fluoronaphthol, **F,** and 4-bromonaphthol, **G**, were obtained through the Boswell and Licause method [9], that is the carbonylation of the appropriate α-halonaphthalene followed by the formation of formate by Baeyer–Villiger transposition and hydrolysis of the resulting ester.

The chromenisation is strongly dependent on the nature of the Y substituent, being maximum for Y = Br and minimum for Y = H (see Section 3). Although we suggest that the chromatography stage may influence the yields and that some chromenes while in the column, could be restrained. It is probably the case concerning compounds **4** and **8** for which the retention time is expected to be the longest and which are obtained with the lower yields.

2.2. Optical properties

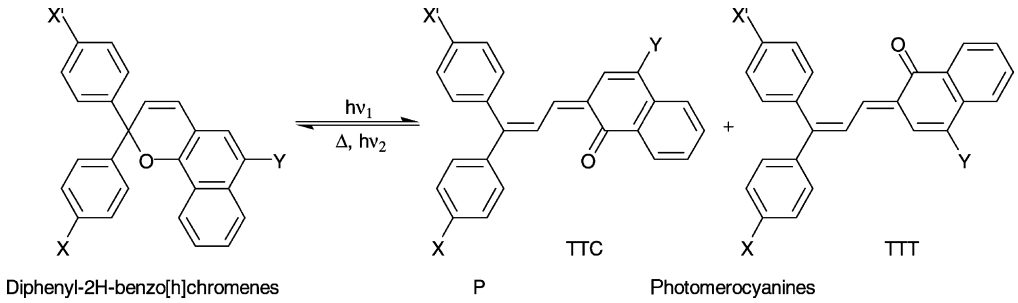
The photochromic behaviour of diphenyl-2*H*-benzochromene derivatives reflects the light-induced reversible opening of the pyranic ring as outlined in Scheme 2.



A: X = X' = H. **B**: X = H, X' = F. **C**: X = X' = F. **D**: Y =F. **E**: Y = Br. **F**: Y = F. **G**: Y = Br. **H**: Y = Cl. **I**: Y = H

mCPBA = *m*-Chloroperbenzoic acid; PTSA = *p*-toluenesulphonic acid

Scheme 1.



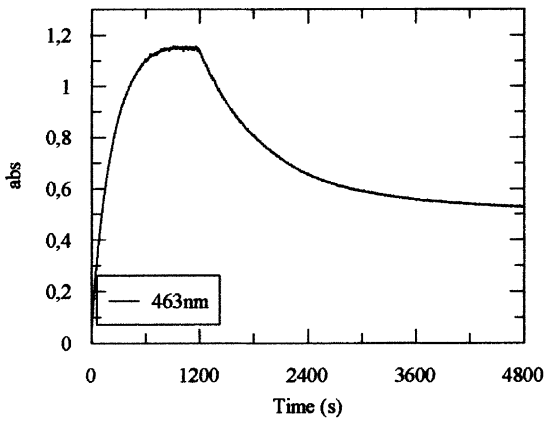
Scheme 2.

In principle, with $X \neq X'$, the open forms may exist in up to eight geometrical isomers due to the presence of the two exocyclic double bonds. Four of these isomers (CCT, CCC, TCT, TCC) are, however, too sterically hindered to have any real chance of existence. Of the remaining four isomers (CTT, CTC, TTT, TTC), that are known as photomerocyanines, only the TTC and the TTT with the longest lifetimes, are normally observed [8].

While the starting chromenes are very lightly coloured, the open forms are characterised by a deep orange to red colour, and from an application point of view, the most important feature of these compounds is their rate of bleaching. The ring closure consists of two distinct first order processes [6], a fast one that is responsible for the initial strong decrease of the coloration and a slower one that leads back to the starting compounds. The multikinetics of compounds **1**–**11** were followed at the open form maximum absorption wavelength, and calculated by using the model Eq. (1), where $A_{o_1} + A_{o_2} + \text{off}$ is the maximal absorbance at the photostationary state, k_1 is the fast rate constant, k_2 the slow rate constant and off the residual absorbance.

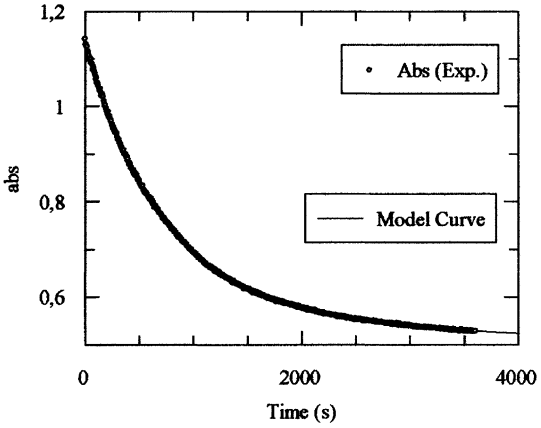
$$A(t) = A_{o_1} e^{-k_1 t} + A_{o_2} e^{-k_2 t} + \text{off} \quad (1)$$

A bleaching curve of compound **9** is plotted in Scheme 3(a) and the calculated multikinetics are shown in Scheme 3(b).



C = 10-4mol/L, T = 24°C, Flux = 220W/m2, CH3CN

(a)



Double Exponential Decay + Offset
Simple weighting
Reduced Chi squared = 3,143e-006

Variable	Value	Std. Err.
Offset	0,4646	0,0054
Initial 1	0,5636	0,0021
Rate 1	0,0014	0,0000
Initial 2	0,1099	0,0043
Rate 2	0,0002	0,0000

(b)

Scheme 3.

Table 1
Visible absorption maxima and ring-closure rate constants for the photomerocyanines from compounds **1**–**11** at 297 K

Compounds **J**	λ_{max} (ACN) (nm)	A_{o_1}	$k_1 \times 10^{-3}$ (s^{-1})	A_{o_2}	$k_2 \times 10^{-3}$ (s^{-1})	Off
Ref: X = X′ = H, Y = H	467	0.37	1.9	0.52	0.1	0.15
1, X = X′ = H, Y = F	464	0.57	1.1	0.22	0.4	0.48
2, X = X′ = H, Y = Cl	471	0.32	3.7	0.48	0.1	0.89
3, X = X′ = H, Y = Br	479	0.30	4.3	0.30	0.2	0.69
4, X = H, X′ = F, Y = H	467	0.38	1.9	0.55	0.1	0.17
5, X = H, X′ = F, Y = F	462	0.56	1.5	0.19	0.6	0.54
6, X = H, X′ = F, Y = Cl	472	0.48	4.4	0.21	0.4	0.27
7, X = H, X′ = F, Y = Br	476	0.27	5.1	0.37	0.1	0.62
8, X = X′ = F, Y = H	466	0.33	1.8	0.60	0.1	0.20
9, X = X′ = Y = F	463	0.56	1.4	0.11	0.2	0.46
10, X = X′ = F, Y = Cl	472	0.19	5.0	0.55	0.1	0.55
11, X = X′ = F, Y = Br	474	0.39	5.9	0.29	0.1	0.60

It is important to note that for all these compounds, the photostationary state is reached after more than 10 min of irradiation in these conditions.

Table 1 collects the values of the fading rate constants k_1 and k_2 (respective amplitudes, A_{o_1} and A_{o_2} and offset) that have been determined by analysing the time profile of the intensity of the absorption of the photomerocyanines (at the appropriate λ_{max}) in acetonitrile solution just after 20 min irradiation with a xenon lamp in order to reach the photostationary state. The data related to the unsubstituted diphenyl-2*H*-benzo[*h*]chromene are mentioned (ref. compound) in Table 1 for comparison.

From an examination of the data collected in Table 1, it emerges that the introduction of one or two fluorine atoms in the *para* position of the phenyl ring(s) has very little effect, if any, on either the λ_{max} of the photomerocyanines or the rate contants k_1 and k_2 of their bleaching process. On the contrary, while the introduction of a fluorine atom in position 6 of the diphenyl-2*H*-benzo[*h*]chromene(s) is also ineffective, the introduction of a chlorine or of a bromine atom results in a three-fold (Cl) to four-fold (Br) increase of the k_1 value. The ring closure rate is faster with a weak electron-drawing susbstituent in position 6.

The value of k_2 is instead fairly insensitive to substitution. Moreover, 1 h after the end of the irradiation, the residual offset is quite important showing the presence of stable open forms in the solution. The chlorine or bromine substitution has also a slight bathochromic effect on the value of λ_{max}, whereas fluorine substitution has a minute ipsochromic effect. The greater bleaching rates found for compounds **2**, **3**, **6**, **7**, **10** and **11** with respect to the unsubstituted diphenyl-*2H*-benzo[*h*]chromenes and their fluorine substituted derivatives **1**, **4**, **5**, **8**, and **9** makes these compounds better candidates for practical applications.

At this temperature, the two observed kinetics may be consistent with the generation of different isomers. So, as we already reported on a neighbouring series [7,8], we have run an ^{19}F NMR experiment to confirm these observations.

2.3. ^{19}F NMR spectroscopy

In order to simplify the ^{19}F NMR spectra, we have chosen the compound **8** as an archetype of compounds **J** and run some experiments before and after UV irradiation of this compound. The ^{19}F NMR spectrum recorded before irradiation displayed well-known signals at $\delta = -114.80$ ppm for the *para*-fluorine atoms of the closed form. The ^{19}F NMR spectra after irradiation, are plotted and shown in Scheme 4. In this scheme, the spectral window does not show the signal at −114.80 ppm which is still predominant.

The spectrum (a) recorded just after irradiation illustrates the presence of the TC isomer of the ring opened form (4%) at $\delta = -111.05$ ppm and $\delta = -112.07$ ppm and TT isomer (16%) at $\delta = -111.0$ ppm and $\delta = -111.07$ ppm.

The spectrum (b) recorded 30 min after (a) indicates the disappearing of the TC isomer (<1%). Thirteen percent of the TT isomer is observed. The closed form is now present at 86%.

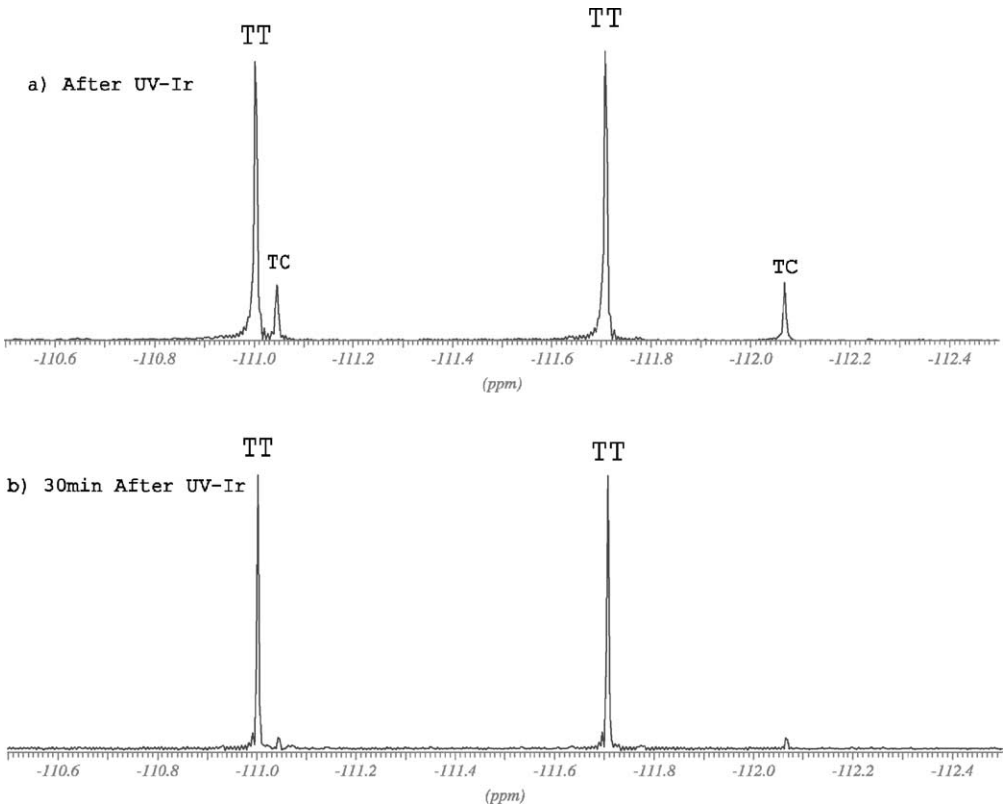
We have recorded the same spectrum 24 h after the irradiation at room temperature and it is important to note that the TT isomer of **8** is still persistent. These observations confirm that the k_1 rate can be correlated to the TC isomer. The residual offset is consistent with the singular persistence of the TT isomer.

2.4. X-ray diffractometry

6-Fluoro-2,2-bis(4′-fluorophenyl)-2*H*-benzo[*h*]chromene **9**, for which good quality single crystals could be grown, was subjected to X-ray diffractometry and its ORTEP plot is shown in Fig. 2, where also the 50% displacement ellipsoids are represented. Some selected bond distances and torsion angles are collected in Table 2.

The intramolecular bond lengths and angles are in line with the hybridisation expected for the atoms involved and in agreement with those found in the other benzo or pyrido-annulated [2*H*]chromenes studied earlier.

Reports of the structures of [*f*] [10–13] or [*h*] [13–15] chromenes condensed with other six-membered rings



Scheme 4.

are present in the literature. In all the molecules of [2*H*]chromenes the pyran ring has the same geometry and the distance from the oxygen and the sp^3 carbon atom in position 2 ranging around 1.46 Å, is longer than C–O bond in the six-membered heterocycles (1.41–1.43 Å) [16]. The C(2) atom has a distorted tetrahedral geometry with O–C–C(Ph) valence angles of 105.0(1) and 106.7(1)°, i.e. smaller with respect to the ideal value of 109.2°. The phenyl groups are quite orthogonal to one another, being the angle between their mean planes 89.5(1)°. The pyran ring is not planar and its deviation from planarity is considerable ($\chi^2 \approx 21{,}000$); the conformational analysis proposed by Cremer and Pople [17] indicates that this ring adopts a twist-boat conformation ($\phi = 147.7(5)°$] with C_2 symmetry [18], with a *pseudo* two-fold axis bisecting O(1)−C(2) bond and the out-of-plane of O(1) and C(2) with respect to the mean plane of the other four carbon atoms results of −0.177(1) and 0.226(2) Å, respectively; the bending along O(1)−C(3) and O(1)−C(4) vectors (25.4(2) and 18.1(1)°, respectively) are comparable with those found in the other chromenes reported in the literature. Packing is consistent with van der Waals interactions.

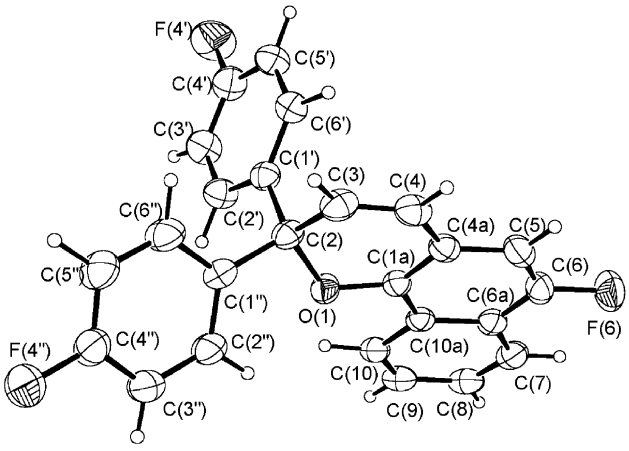


Fig. 2. ORTEP plot of compound **9** showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radii.

3. Experimental

3.1. Materials

Compounds **J** were synthesised according to Scheme 1. All reagents were obtained from Aldrich™ and were used as supplied. Reaction solvents were pre-dried and distilled immediately prior to use: dichloromethane was distilled from phosphorous pentoxide and tetrahydrofuran (THF) was pre-dried over potassium hydroxide and distilled from sodium/benzophenone. Flash column chromatography was carried out using Merck 60 silica gel (0.063–0.200 nm),

Table 2
Selected bond distances (Å), angles (°) and torsion angles (°) with esd's in parentheses for compound **9**

O(1)–C(1a)	1.366(2)	O(1)–C(1a)–C(4a)	121.8(2)	O(1)–C(1a)–C(10a)–C(6a)	−6.3(2)
O(1)–C(2)	1.459(2)	O(1)–C(2)–C(3)	110.4(2)	O(1)–C(1a)–C(4a)–C(4)	−3.0(3)
C(1a)–C(4a)	1.376(3)	O(1)–C(2)–C(1′)	106.7(1)	O(1)–C(2)–C(3)–C(4)	22.4(3)
C(1a)–C(10a)	1.414(2)	O(1)–C(2)–C(1″)	105.0(1)	O(1)–C(2)–C(1′)–C(2′)	−116.4(2)
C(2)–C(3)	1.513(4)	C(1a)–O(1)–C(2)	119.9(1)	O(1)–C(2)–C(1″)–C(2″)	5.3(3)
C(2)–C(1′)	1.533(3)	C(1a)–C(4a)–C(4)	117.1(2)	C(1a)–C(4a)–C(4)–C(3)	−8.0(3)
C(2)–C(1″)	1.524(3)	C(2)–C(3)–C(4)	121.5(2)	C(3)–C(2)–C(1′)–C(2′)	4.5(3)
C(3)–C(4)	1.317(4)	C(3)–C(2)–C(1′)	112.1(2)	C(3)–C(2)–C(1″)–C(2″)	−113.8(2)
C(4)–C(4a)	1.454(3)	C(3)–C(2)–C(1″)	110.7(2)	C(4a)–C(4)–C(3)–C(2)	−3.1(4)
		C(1′)–C(2)–C(1″)	111.7(2)		
		C(3)–C(4)–C(4a)	121.5(2)		

solvents were used as supplied. Compounds **H** and **I** were commercially available.

3.2. Instrumentation

The compounds were characterised by MS and NMR spectra. The GC–MS (6890 HP GC system and 5973 MS detector) apparatus was equipped with a short column (optima 0.2 μm, 12 m × 0.2 mm). The mass spectra were obtained under electronic impact (EI = 70 eV). All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 NMR spectrometer in $CDCl_3$ solutions, using tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer in $CDCl_3$. The compound **8** was irradiated with a Xe lamp (350 W) (Oriel) at 297 K. After 20 min irradiation, the 5 mm tube was transferred into the QNP probe of the spectrometer. Melting points were measured using an Electrothermal 9100 apparatus. The visible absorption spectra of photomerocyanines were recorded in acetonitrile with a DAD Beckman DU 7500 diode array spectrophotometer (400 W/m^2 measured between 315 and 400 nm). The new compounds were characterised by elemental analyses.

3.3. Synthetic procedures

Propargyl alcohols **A**, **B** and **C** were prepared as outlined in Scheme 1. To a solution of sodium acetylide (solution in xylenes, 30 ml (10 eq.)) in freshly distilled THF (250 ml) at −10 °C was added dropwise a solution of the ketone (11.0 mmol) in THF (100 ml). On completion of addition, the mixture was allowed to warm to room temperature. The reaction mixture was poured into ice/water and the two phases separated. The organic phase was washed with saturated aqueous ammonium chloride solution (100 ml). The aqueous phase was further extracted with ether (3 × 100 ml) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated under vacuum. The xylenes were removed by azeotropic distillation of a methanol–xylene mixture. Chromatography (0–5% ether in pentane) afforded the alcohol **A** as a white powder (88% yield), mp 48.9–50.7 °C. **B** and **C** were obtained as a yellow oil, respectively, in 70 and 75% yields.

3.3.1. 1,1-Di(4′-fluorophenyl)-2-propyn-1-ol, *C*

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 2.71 (s, 1H, H-3), 6.83 (dd, 4H, $^{3}J_{H–F}$ = 8.7 Hz, $^{3}J_{H–F}$ = 8.7 Hz, H-3′, 3″, 5′ and 5″), 7.37 (dd, 4H, $^{4}J_{H–F}$ = 5.4 Hz, $^{3}J_{H–F}$ = 8.5 Hz, H-2′, 2″, 6′ and 6″). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 73.44 (s, 1C, C-1), 76.02 (s, 1C, C-3), 86.07 (s, 1C, C-2), 115.22 (d, 4C, $^{2}J_{C–F}$ = 21.6 Hz, C-3′, 3″, 5′ and 5″), 127.93 (d, 4C, $^{3}J_{C–F}$ = 8.3 Hz, C-2′, 2″, 6′ and 6″), 140.26 (d, 2C, $^{4}J_{C–F}$ = 3.0 Hz, C-1′ and 1″), 162.42 (d, 2C, $^{1}J_{C–F}$ = 247 Hz, C-4′ and 4″).

Halonaphtaldehydes **D**, **E** were prepared as outlined in Scheme 1. To a solution of 1,1-dichloromethylmethylether (2.19 ml, 24.0 mmol) in dichloromethane (10 ml) at 0 °C was added dropwise in tetrachloride (2.83 ml, 24.0 mmol) and the mixture stirred for 1 h. A solution of the halonaphthalene (19.0 mmol) in dichloromethane was added dropwise and the reaction was allowed to warm to room temperature overnight. The reaction mixture was poured into ice/water and the phases separated. The organic phase was washed with water (3 × 20 ml), dried (Na_2SO_4), filtered and concentrated under vacuum. **D** and **E** were obtained, respectively, in 93% yield, mp 76.4–78.8 °C; and 50% yield, mp 77.8–79.0 °C.

3.3.2. 4-Fluoronaphthalenecarbaldehyde, *D* [9]

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 7.16 (dd, 1H, $^{3}J_{H–F}$ = 9.6 Hz, $^{3}J_{H–H}$ = 7.9 Hz, H-3), 7.54 (dd, 1H, $^{3}J_{H–H}$ = 7.5 Hz, $^{3}J_{H–H}$ = 7.19 Hz, H-6), 7.64 (ddd, 1H, $^{3}J_{H–H}$ = 7.0 Hz, $^{3}J_{H–F}$ = 8.5 Hz, $^{4}J_{H–H}$ = 1.1 Hz, H-7), δ 7.85 (dd, 1H, $^{3}J_{H–H}$ = 7.9 Hz, $^{4}J_{H–F}$ = 5.6 Hz, H-2), δ 8.06 (d, 1H, $^{3}J_{H–H}$ = 8.3 Hz, H-5), δ 9.19 (d, 1H, $^{3}J_{H–H}$ = 8.6, H-8), δ 10.19 (s, 1H, H-9). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 108.99 (d, 1C, $^{2}J_{C–F}$ = 21.4 Hz, C-3), 120.95 (d, 1C, $^{3}J_{C–F}$ = 6.3 Hz, C-5), 123.78 (d, 1C, $^{2}J_{C–F}$ = 15.9 Hz, C-4a), 124.90 (d, 1C, $^{4}J_{C–F}$ = 2.5 Hz, C-8), 127.33 (d, 1C, $^{4}J_{C–F}$ = 1.9 Hz, C-6), 128.06 (d, 1C, $^{4}J_{C–F}$ = 3.8 Hz, C-1), 130.08 (s, 1C, C-7), 132.36 (d, 1C, $^{3}J_{C–F}$ = 6.0 Hz, C-1a), 137.87 (d, 1C,

$^3J_{C-F}$ = 10.9 Hz, C-2), 162.69 (d, 1C, $^1J_{C-F}$ = 263.7 Hz, C-4), 192.10 (s, 1C, C-9).

*3.3.3. 4-Bromonaphthalenecarbaldehyde, **E***

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 7.61 (m, 2H, H-6 and 7), 7.68 (d, 1H, $^3J_{H-H}$ = 7.6 Hz, H-2), 7.85 (d, 1H, $^3J_{H-H}$ = 7.6 Hz, H-3), 8.24 (dd, 1H, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 2.3 Hz, H-5), 9.17 (dd, 1H, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 2.2 Hz, H-8), 10.25 (s, 1H, H-9). MS: *m/z* (E.I.): M^+ = 236/234 (formula weight: 235.07).

Halonaphtols **F**, **G** were prepared as outlined in Scheme 1. Halonaphthaldehyde (8.30 mmol) and 3-chloroperbenzoic acid (4.10 g, 16.6 mmol) were dissolved in dichloromethane (60 ml) and the mixture was left overnight. Aqueous sodium thiosulfate solution (20%, 20 ml) was added and the mixture stirred for 45 min before being poured into more aqueous sodium thiosulfate solution (20%, 80 ml). The phases were separated and the aqueous phase was extracted with dichloromethane (60 ml). The combined organic phases were washed with further aqueous sodium thiosulfate solution (20%, 80 ml) and then with saturated brine (80 ml). The organic layer was concentrated, diluted in a 1:1 methanol:THF mixture (40 ml) and cooled to 0 °C. To this solution was rapidly added a solution of potassium hydroxide (1.25 g) in methanol (10 ml) and the mixture stirred for 15 min. The solution was acidified to pH = 1 with concentrated hydrochloric acid, then diluted with water (ca. 50 ml) and stirred for 1 h. The aqueous phase was extracted with dichloromethane (2 × 25 ml) and the combined organic phases were dried (Na_2SO_4), filtered concentrated under vacuum. Chromatography (25–75% dichloromethane/pentane) yielded the desired halonaphthol **F** (79% yield), mp 131.1–136.9 °C and **G** (91% yield), mp 128.8–129.6 °C.

*3.3.4. 4-Fluoronapht-1-ol, **F** [9]*

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 5.71 (s, 1H, –OH), 6.59 (dd, 1H, $^4J_{H-F}$ = 4.0 Hz, $^3J_{H-H}$ = 8.2 Hz, H-2), 6.87 (dd, 1H, $^3J_{H-F}$ = 10.2 Hz, $^3J_{H-H}$ = 8.2 Hz, H-3), 7.45 (m, 2H, H-6 and 7), 7.95 (m, 1H, H-5), 8.08 (m, 1H, H-8). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 107.46 (d, 1C, $^3J_{C-F}$ = 7.9 Hz, C-2), 108.80 (d, 1C, $^2J_{C-F}$ = 21.8 Hz, C-3), 120.55 (d, 1C, $^3J_{C-F}$ = 4.5 Hz, C-5), 121.91 (s, 1C, C-8), 124.45 (d, 1C, $^2J_{C-F}$ = 20 Hz, C-4a), 125.2 (d, 1C, $^3J_{C-F}$ = 4 Hz, C-1a), 126.17 (s, 1C, C-6), 126.72 (s, 1C, C-7), 147.61 (s, 1C, C-1), 153 (d, 1C, $^1J_{C-F}$ = 250 Hz, C-4).

Halobenzochromenes **J** from **1** to **11** were prepared as outlined in Scheme 1. A 7 mmol amount of propargyl alcohol was dissolved in methylene chloride at 25 °C and then a catalytic amount of *p*-toluenesulphonic acid was added. After 10 min, a 10 mmol of substituted naphthol dissolved in methylene chloride was added dropwise. After 2 h, the solvent was evaporated and the organic residue was purified by flash chromatography on silica with pentane diethyl ether as eluant (with a gradient from 0 to 5% Et_2O). After evaporation of the eluate and pentane recrystallisation, pure chromene was obtained as a "white-yellow" powder.

*3.3.5. 6-Fluoro-2,2-bis-phenyl-2H-benzo[h]chromene, **1***

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.15 (d, 1H, $^3J_{H-H}$ = 9.72 Hz, H-3), 6.59 (d, 1H, $^3J_{H-H}$ = 9.72 Hz, H-4), 6.77 (d, 1H, $^3J_{H-F}$ = 10.36 Hz, H-5), 7.19 (m, 6H, H-3′, 3″, 4′, 4″, 5′ et 5″), 7.42 (m, 6H, H-2′, 2″, 6′, 6″, 8 et 9), 7.87 (m, 1H, H-7), 8.26 (m, 1H, H-10). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 83 (s, 1C, C-2), 107.65 (d, 1C, $^2J_{C-F}$ = 22.20 Hz, C-5), 120.76 (d, 1C, $^3J_{C-F}$ = 6.3 Hz, C-7), 122.21 (d, 1C, $^4J_{C-F}$ = 3 Hz, C-10), 123.66 (d, 1C, $^4J_{C-F}$ = 2 Hz, C-4), 124, 124.5, 125.5, 126.72 (s, 2C, C-8 and 9), 127.01 (s, 4C, C-2′,2″,6′ and 6″), 127.77 (s, 2C, C-4′ and 4″), 128.35 (s, 4C, C-3′, 3″, 5′ and 5″), 128.61 (s, 1C, C-3), 145.01 (s, 2C, C-1′ and 1″), 153 (d, 1C, $^1J_{C-F}$ = 250 Hz, C-6). Yield: 26%, mp: 135.5–137.0 °C. Elemental analyses: formula $C_{25}H_{17}OF$ requires 85.21% C, 4.86% H, found: 85.16% C, 4.88% H—MS: *m/z* (E.I.): M^+ = 352 (formula weight: 352.40).

*3.3.6. 6-Chloro-2,2-bis-phenyl-2H-benzo[h]chromene, **2** [19]*

Yield: 51%, mp: 158.0–160.7 °C. Elemental analyses: formula $C_{25}H_{17}OCl$ requires 81.41% C, 4.65% H, 9.61% Cl; found: 81.48% C, 4.61% H, 9.59% Cl—MS: *m/z* (E.I.): M^+ = 368 (formula weight: 368.86).

*3.3.7. 6-Bromo-2,2-bis-phenyl-2H-benzo[h]chromene, **3** [19]*

Elemental analyses: formula $C_{25}H_{17}OBr$ requires 72.65% C, 4.15% H, 19.33% Br; found: 72.70% C, 4.11% H, 19.31% Br—MS: *m/z* (E.I.): M^+ = 414/412 (formula weight: 413.31).

*3.3.8. 2-(4′-Fluorophenyl)-2-phenyl-2H-benzo[h]-chromene, **4***

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.03 (d, 1H, $^3J_{H-H}$ = 9.68 Hz, H-3), 6.65 (d, 1H, H-4), 6.87 (dd, 2H, H-3′ et 5′), 7.04 (d, 1H, H-6), 7.18 (m, 3H, H-3″, 4″, 5″), δ 7.36 (m, 6H, H-2′, 2″, 6′, 6″, 8 and 9), δ 7.61 (dd, 1H, $^3J_{H-H}$ = 6.93 Hz, $^4J_{H-H}$ = 2.13 Hz, H-7), δ 8.29 (dd, 1H, $^3J_{H-H}$ = 7.3 Hz, H-10). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 83.03 (s, 1C, C-2), 115.25 (d, 2C, $^2J_{C-F}$ = 21.5 Hz, C-3′ and 5′), 115.68, 120.91, 122.15, 124.33, 124.74, 124.92, 125.93, 126.65, 126.99 (s, 2C, C-2″ and 6″), 127.33, 127.91 (d, 2C, $^3J_{C-F}$ = 7.7 Hz, C-2′ and 6′), 128.49 (s, 2C, C-3″ and 5″), 128.97, 129.10, 134.95, 141.23, 145.24, 147.81, 161.9 (d, 1C, $^1J_{C-F}$ = 234 Hz, C-4′). Yield: 6%, mp: 115.4–116.8 °C. MS: *m/z* (E.I.): M^+ = 352 (formula weight: 352.40).

*3.3.9. 6-Fluoro-2-(4′-fluorophenyl)-2-phenyl-2H-benzo[h]-chromene, **5***

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.22 (d, 1H, $^3J_{H-H}$ = 9.70 Hz, H-3), 6.72 (d, 1H, $^3J_{H-H}$ =

9.7 Hz, H-4), 6.90 (d, 1H, $^3J_{H-F} = 10.3$ Hz, H-5), 7.02 (dd, 2H, H-3′ and 5′), 7.33 (m), 7.54 (m), 8.01 (m, 1H, H-7), 8.34 (m, 1H, H-10). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 83 (s, 1C, C-2), 107.37 (d, 1C, $^2J_{C-F} = 22.2$ Hz, C-5), 114.97 (d, 2C, $^2J_{C-F} = 21.5$ Hz, C-3′ and 5′), 120.54 (d, 1C, $^3J_{C-F} = 4.6$ Hz, C-7), 121.8 (d, 1C, $^3J_{C-F} = 2$ Hz, C-10), 123.58 (s, 1C, C-4), 124, 126 (d), 126.6 (2C, C-2″ and 6″), 127.63, 128.16 (2C, C-3″ and 5″), 128.69 (d, 2C, $^3J_{C-F} = 8.2$ Hz, C-2′ and 6′), 141 (d, 1C, C-1′), 144.55 (s, 1C, C-1a), 152.5 (d, 1C, $^1J_{C-F} = 250.1$ Hz, C-6), 161.5 (d, 1C, Hz, C-4′). Yield: 24%, mp: 115.1–118.6 °C. Elemental analyses: formula $C_{25}H_{16}OF_2$ requires 81.07% C, 4.35% H, found: 81.14% C, 4.29% H—MS: *m*/*z* (E.I.): $M^+ = 370$ (formula weight: 370.39).

3.3.10. 6-Chloro-2-(4′-fluorophenyl)-2-phenyl-2H-benzo[h]chromene, **6**

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.08 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-3), 6.55 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-4), 6.87 (dd, 2H, $^3J_{H-H} = 8.6$ Hz, $^3J_{H-F} = 8.6$ Hz, H-3′ and 5′), 7.17 (m, 4H, H-5, 3″, 4″and 5″), 7.38 (m, 6H, H-8,9,2′, 2″, 6′ and 6″), 8.01 (m, 1H, H-7), 8.23 (m, 1H, H-10). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 83.26 (s, 1C, C-2), 115.30 (d, 2C, $^2J_{C-F} = 21.4$ Hz, H-3′ and 5′), 116.02 (s, 1C, C-4a), 122.44 (s, 1C, C-10), 123.42 (s, 1C, C-4),123.85 (s, 1C, C-6), 124.45, 124.72, 125.97 (s, 1C, C-10a), 126.64, 126.92 (s, 2C, C-2″ and 6″), 127.65, 127.98, 128.23, 128.52 (s, 2C, C-3″ and 5″), 128.99 (d, 2C, $^3J_{C-F} = 8.2$ Hz, C-2′ and 6′), 131.58 (s, 1C, C-6a), 140.69 (s,1C, C-1′), 144.71 (s, 1C, C-1″), 146.82 (s, 1C, C-1a), 162.5 (d, 1C, $^1J_{C-F} = 250.1$ Hz, C-4′). Yield: 8%, mp: 132.9–134.2 °C. Elemental analyses: formula $C_{25}H_{16}OClF$ requires 72.62% C, 4.19% H, 9.16% Cl, found: 72.70% C, 4.13% H, 9.15% Cl—MS: *m*/*z* (E.I.): $M^+ = 386$ (formula weight: 386.85).

3.3.11. 6-Bromo-2-(4′-fluorophenyl)-2-phenyl-2H-benzo[h]chromene, **7**

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.06 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-3), 6.59 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-4), 6.90 (dd, 2H, $^3J_{H-F} = 8.7$ Hz, $^3J_{H-F} = 8.7$ Hz, H-3′ and 5′), 7.20 (m, 4H, H-5, 3″, 4″ and 5″), 7.40 (m, 6H, H-2′, 2″, 6′, 6″, 8 and 9), 8.00 (m, 1H, H-7), 8.24 (m, 1H, H-10). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 83.31 (s, 1C, C-2), 113.90 (s, 1C, C-6), 115.31 (d, 2C, $^2J_{C-F} = 21.5$ Hz, C-3′ and 5′), 116.66 (s, 1C, C-4a),122.46 (s, 1C, C-10), 123.29 (s, 1C, C-4), 126.15, 126.65,126.92 (s, 2C, C-2″ and 6″), 127.37, 127.94, 128.00, 128.07, 128.21, 128.52 (s, 2C, C-3″ and 5″), 129.01 (d, 2C, $^3J_{C-F} = 8.2$ Hz, C-2′ and 6′), 132.75 (s, 1C, C-6a), 140.66 (s, 1C, C-1′), 144.69 (s, 1C, C-1″), 147.51 (s, 1C, C-1a), 162.02 (d, 1C, $^1J_{C-F} = 250.1$ Hz, C-4′). Yield: 24%, mp: 156.0–157.3 °C. Elemental analyses: formula $C_{25}H_{16}OBrF$ requires 69.62% C, 3.74% H; 18.53% Br, found: 69.69% C, 3.68% H, 18.54% Br—MS: *m*/*z* (E.I.): $M^+ = 432/430$ (formula weight: 431.40).

3.3.12. 2,2-bis(4′-Fluorophenyl)-2H-benzo[h]chromene, **8**

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.02 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-3), 6.68 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-4), 6.92 (dd, 4H, $^3J_{H-F} = 8.7$ Hz, $^3J_{H-F} = 8.7$ Hz, H-3′, 3″, 5′ and 5″), δ 7.24 (m, 5, 6, 8, 9, 2′, 2″, 6′ and 6″), 7.64 (m, 1H, H-7), 8.19 (m, 1H, H-10). Yield: 2%, mp: 115.2–116.4 °C.

3.3.13. 6-Fluoro-2,2-bis(4′-fluorophenyl)-2H-benzo[h]-chromene, **9**

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.03 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-3), 6.58 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-4), 6.76 (d, 1H, $^3J_{H-F} = 10.33$ Hz, H-5), 6.90 (dd, 4H, $^3J_{H-F} = 8.5$ Hz, $^3J_{H-F} = 8.5$ Hz, H-3′, 3″, 5′ and 5″), 7.38 (m, 6H, H-2′, 2″, 6′, 6″, 8 and 9), 7.88 (d, 1H, $^3J_{H-H} = 8.6$ Hz, H-7), 8.18 (d, 1H, $^3J_{H-H} = 9.0$ Hz, H-10). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 82.53 (s, 1C, C-2), 107.60 (d, 1C, $^2J_{H-F} = 22.3$ Hz, C-5), 115.02, 115.33 (d, 4C, $^2J_{H-F} = 21.5$ Hz, C-3′, 3″, 5′ et 5″), 120.86 (d, 1C, $^3J_{C-F} = 4.6$ Hz, C-7), 121.94 (d, 1C, $^4J_{C-F} = 2.4$ Hz, C-10), 124.03 (s, 1C, C-4), 124.66, 125.68, 126.93 (s, 2C, C-8 and 9), 128.18 (s, 1C, C-3), 128.85 (d, 4C, $^3J_{C-F} = 8.2$ Hz, C-2′, 2″, 6′ and 6″), 140.58 (s, 2C, C-1′ and 1″), 144 (s, 1C, C-1a), 153.50 (d, 1C, $^1J_{C-F} = 180$ Hz, C-6), 162.39 (d, 2C, $^1J_{C-F} = 247.1$ Hz, C-4′ and 4″). Yield 20%, mp: 111.2–112.8 °C. Elemental analyses: formula $C_{25}H_{15}OF_3$ requires 77.31% C, 3.89% H, found: 77.27% C, 3.91% H—MS: *m*/*z* (E.I.): $M^+ = 388$ (formula weight: 388.38).

3.3.14. 6-Chloro-2,2-bis(4′-fluorophenyl)-2H-benzo[h]-chromene, **10**

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 6.03 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-3), 6.60 (d, 1H, $^3J_{H-H} = 9.7$ Hz, H-4), 6.91 (dd, 4H, $^3J_{H-F} = 8.7$ Hz, $^3J_{H-F} = 8.7$ Hz, H-3′, 3″, 5′ and 5″), 7.19 (s, 1H, H-5), 7.35 (m, 4H, H-2′, 2″, 6′ and 6″), 7.46 (m, 2H, H-8 and 9), 8.05 (m, 1H, H-7), 8.22 (m, 1H, H-10). ^{13}C NMR (63 MHz, $CDCl_3$) δ_C (ppm from TMS): 83 (s, 1C, C-2), 115.40 (d, 4C, $^2J_{C-F} = 21.6$ Hz, C3′, 3″, 5′ and 5″), 115.9 (s, 1C, C-4a), 122.33 (s, 1C, C-10), 123.63 (s, 1C, C-4), 124.0 (s, 1C, C-6), 124.41 (s, 1C, C-7), 124.79 (s, 1C, C-5), 126.0 (s, 1C, C-10a), 126.73 (s, 1C, C-9), 127.75 (s, 1C, C-8), 128.03 (s, 1C, C-3), 128.89 (d, 4C, $^3J_{C-F} = 8.2$ Hz, C-2′,2″,6′ and 6″), 132 (s, 1C, C-6a), 141 (s, 2C, C-1′ and 1″), 147 (s, 1C, C-1a), 163 (d, 2C, $^1J_{C-F} = 240$ Hz, C-4′ and 4″). Yield: 60%, mp: 140.8–143.6 °C. Elemental analyses: formula $C_{25}H_{15}OClF_2$ requires 74.17% C, 3.73% H, 8.76% Cl, found: 74.15% C, 3.73% H, 8.80% Cl—MS: *m*/*z* (E.I.): $M^+ = 404$ (formula weight: 404.84).

3.3.15. 6-Bromo-2,2-bis(4′-fluorophenyl)-2H-benzo[h]-chromene, **11**

^{1}H NMR (250 MHz, $CDCl_3$), δ_H (ppm from TMS): 5.91 (d, 1H, $^3J_{H-H} = 9.68$ Hz, H-3), δ 6.49 (d, $^3J_{H-H} = 9.71$ Hz, H-4), δ 6.81 (dd, 4H, $^3J_{H-H} \approx 8.7$ Hz, $^3J_{H-F} = 8.7$ Hz, H-3′, 3″, 5′ et 5″), δ 7.25 (m), δ 7.34 (m), δ 7.91 (m, 1H, H-7), δ 8.12 (m, 1H, H-10). ^{13}C NMR (63 MHz, $CDCl_3$)

δ_C (ppm from TMS): 82.83 (s, 1C, C-2), 113.99 (s, 1C, C-6), 115.31 (d, 4C, $^2J_{C-F} = 21.5$ Hz, C-3′, 3″, 5′ and 5″), 116.52 (s, 1C, C-4a), 122.25 (s, 1C, C-10), 123.39 (s, 1C, C-4), 126.01, 126.66, 127.34, 127.94 (s, 2C, C-8 and 9), 128.79 (d, 4C, $^3J_{C-F} = 8.2$ Hz, H-2′, 2″, 6′ and 6″), 132.69 (s, 1C, C-6a), 140.38 (d, 2C, $^4J_{C-F} = 3.1$ Hz, C-1′ and 1″), 147.24 (s, 1C, C-1a), 162.34 (d, 2C, $^1J_{C-F} = 247.2$ Hz, C-4′ and 4″). Yield: 76%, mp: 154.0–154.6 °C. Elemental analyses: formula $C_{25}H_{15}OBrF_2$ requires 66.83% C, 3.37% H, 17.78% Br, found: 66.89% C, 3.31% H, 17.76% Br. MS: *m/z* (E.I.): $M^+ = 450/448$ (formula weight: 449.29).

Table 3
Experimental data for the X-ray diffraction studies on crystalline compound **9**

Formula	$C_{25}H_{15}F_3O$
Cryst. Habit	Prism
Cryst. Colour	Colourless
F_w; F(0 0 0)	388.4; 800
Cryst. Syst.	Monoclinic
Space group	$P2_1/c$
Cell parameters at 295 K	[a]
a (Å)	14.531(4)
b (Å)	11.182(2)
c (Å)	12.012(2)
α (°)	90
β (°)	100.47(2)
γ (°)	90
V (Å^3)	1919.3(7)
Z	4
d_{calc} (g cm^{-3})	1.34
Cryst. Dimension (mm^3)	0.14 × 0.32 × 0.58
Linear abs. coeff., cm^{-1}	8.4
Diffractometer	Enraf Nonius Cad4
Scan type	ω–2θ
Scan width (°)	[b]
Radiation	[c]
2θ range collection (°)	6–140
hkl range	$\pm h, k, l$
Unique total data	3978
Criterion of obs.	$I > 2\sigma(I)$
Unique obs. data (NO)	2975
No. of refined par (NV)	322
Overdetermination ratio (NO/NV)	9.2
Absorption	[d]
Solution	[e]
H atoms	[f]
R	0.046
R_w	0.044
GOF	1.357
Largest shift (esd)	0.490
Largest peak (eÅ^{-3})	0.232
Programs	[g]

$R = \sum|\Delta F|/\sum|F_o|$; $R_w = \left[\sum w(\Delta F^2)^2/\sum w(F_o^2)^2\right]^{1/2}$; GOF $= \left[\sum w|\Delta F|^2/(\mathrm{NO}-\mathrm{NV})\right]^{1/2}$.

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centered reflections chosen from diverse regions of reciprocal space.

[b] From $(\theta - 0.6)°$ to $[\theta + (0.6 + \Delta\theta)]°$; $\Delta\theta = [(\lambda\alpha_2 - \lambda\alpha_1)/\lambda]\tan\theta$.

[c] Ni-filtered Cu Kα $\lambda = 1.54178$ Å.

[d] No correction applied.

[e] Direct methods.

[f] Located in ΔF map and isotropically refined.

[g] SIR97 [22], SHELX76 [23], PARST [24].

3.4. Optical measurements

The photochromic compounds were dissolved in acetonitrile (sample concentration: 10^{-4} M). Irradiation was derived from an ozone-free Oriel xenon 150 W lamp equipped with diaphragm and aqueous solution, which removed most of the infrared radiation. Polychromatic light intensity was determined by an Oriel quantum photoradiometer (400 W/m^2 measured between 315 and 400 nm). The quartz analysis cell was enclosed in a thermostated copper block placed inside the sample chamber of the spectrophotometer. The temperature was controlled with a Bioblock Scientific thermocouple. The cell had an optical path length of 1 cm. The aerated solutions were stirred continuously using a mechanical stirrer. Spectra of photostationary mixtures were measured and the decay of the open form was followed at the maximum absorption wavelength, at $T = 297$ K, flux $= 220$ W/m^2.

3.5. X-ray diffractometry

Table 3 shows the experimental and crystallographic data. The intensities I_{hkl} were determined by analysing the reflection profiles by the Lehmann and Larsen [20] procedure. Corrections for Lorentz and polarisation effects were performed; there were no corrections for absorption effects.

Atomic scattering factors were from the International Tables for X-ray Crystallography [21]. Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220. Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: teched@chemcrys.cam.ac.uk).

4. Conclusion

New photochromic compounds of the diphenyl-chromene family containing halogen substituents have been prepared. Kinetic studies under continuous irradiation indicate that fluoro-substitution of the phenyl ring(s) always leads to a slight increase in the fast rate constant, k_1, while the introduction in position 6 of the diphenyl-2*H*-benzo[*h*]chromene(s) of a chlorine or of a bromine atom results in a three-fold (Cl) to four-fold (Br) increase of the k_1 value. Concerning the bromine compounds, these rate constant observations are consistent with the

recent results published by Coelho et al. [25]. These diphenyl-2*H*-benzo[*h*]chromene derivatives exhibit a particular behaviour in solution showing a very stable open form being observed in ^{19}F NMR. Some kinetics experiments are in progress in order to follow the interdependence of isomers and their thermal stability.

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