Novel photochromism of differently-linked bis-benzopyrans†

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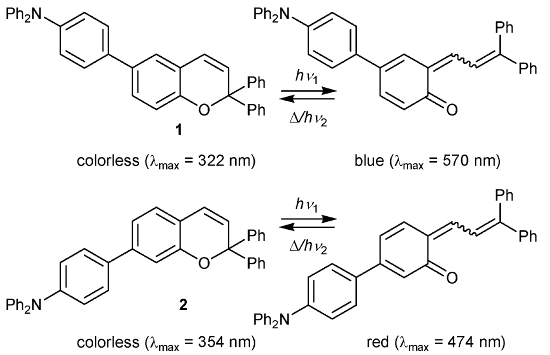
Received 5th February 2007, Accepted 13th March 2007
First published as an Advance Article on the web 26th March 2007
DOI: 10.1039/b701706e

The unique photochromic bis-chromene 5 incorporates the structural attributes of both 3 and 4. UV–vis irradiation of 5 leads to a dark brown colour, which is formed by mixing the purple and red colours observed for the photolysates of 3 and 4, respectively.

Organic photochromic compounds have significant implications in a number of applications that include optical data storage and switching, imaging devices, smart windows, *etc.*[1] In particular, benzo- and naphthopyran derivatives have emerged as an important class of photochromic materials due to their practical applications in variable optical transmission glasses and optoelectronic devices.[2] As compared to benzopyrans, naphthopyrans have been extensively investigated due to their high colourability, fast thermal bleaching and high fatigue resistance—the attributes of a good photochromic material;[2] the studies on the former have largely been limited to mechanistic insights.[3] In our recent investigations, we discovered that simple 6-/7-arylbenzopyrans, which may be accessed in a facile manner *via* Suzuki coupling protocols, lend themselves to remarkable photochromic properties that parallel those of the naphthopyrans.[4] Further, we uncovered a significant difference (*ca.* 100 nm) in the absorption maxima of 6- and 7-arylchromenes **1** and **2**, respectively (Scheme 1). A wide window in the absorption maxima of these closely related analogues spurred us to explore the biphotochromic systems such as bis-chromenes **3–5** (Fig. 1).



Scheme 1 Photochromism of aryl-substituted chromenes **1** and **2** *via* π-conjugation.

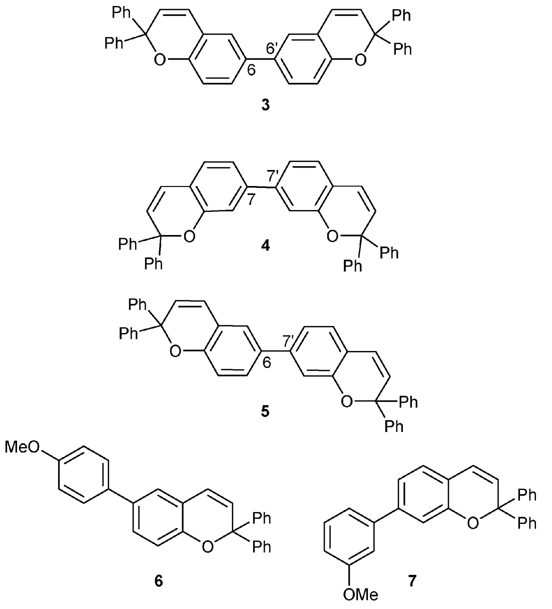


Fig. 1 The structures of chromenes investigated in the present study.

The biphotochromic compounds have assumed considerable significance at the present time in the development of complex single molecular systems that integrate several switchable functions.[5] Such multi-addressable photochromic compounds are believed to be of great utility in the development of optical memory media capable of processing two pieces of information at the same storage site.[6] In principle, three different types of biphotochromic compounds may be conceived, as described by Guglielmetti *et al.*; the two photochromic entities are separated by a non-interactive spacer in the first category, annulated in the second category and are linked through a spacer that results in effective conjugation between the two in the last category.[7] Thus, the bis-chromenes **3–5** in which the two entities responsible for photochromism are directly linked may correspond to a new type. Herein, we have inquired specifically into the photobehaviour of 6,7′-bischromene **5** *vis-à-vis* 6,6′- and 7,7′-bischromenes, **3** and **4**, respectively. With each of the chromene rings viewed as an aryl ring, the mono-opened forms in the case of **3** and **4** were expected *a priori* to exhibit the photochromic properties akin to those of the simple aryl analogues **6** and **7**. However, the cross-linked bis-chromene **5** was anticipated to be an interesting and extraordinary case due to the fact that the heterolysis may lead to the formation of two optically-distinct species, *cf.* Scheme 2. Thus, the investigation of the photobehaviour of **5** as compared to **3** and **4** was deemed very appealing.

The bis-chromenes **3–5** were synthesized following the protocol shown in Scheme 3. Accordingly, the required bis-phenols were synthesized *via* Suzuki coupling followed by demethylation with BBr_3. Condensation of the phenols with 1,1-diphenyl-2-propynol in the presence of pyridinium *p*-toluenesulfonate as a catalyst

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† Electronic supplementary information (ESI) available: Experimental procedure and characterization data for the compounds. See DOI: 10.1039/b701706e

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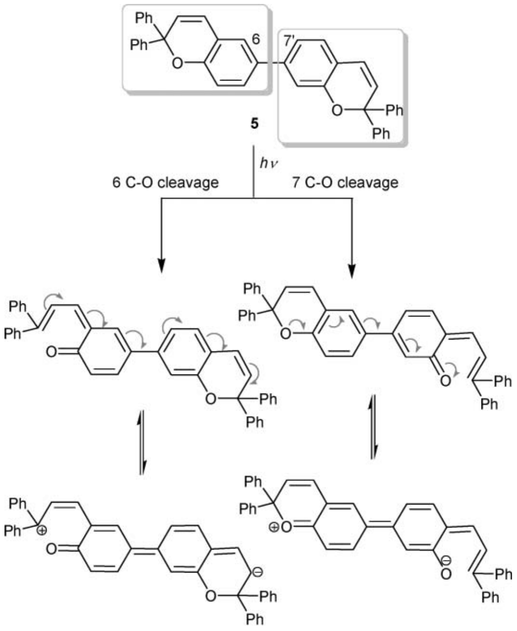
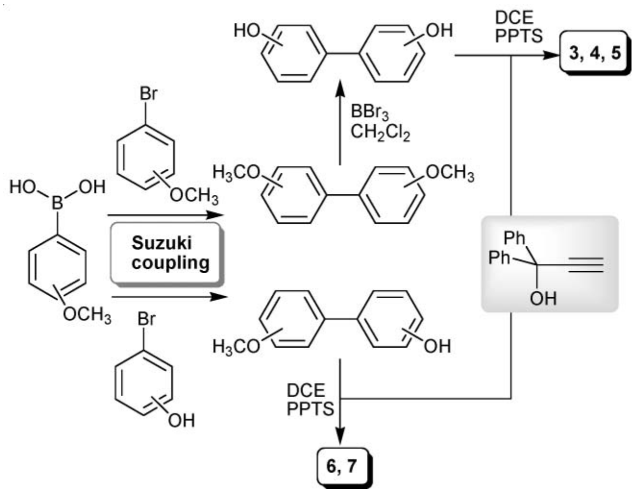


Scheme 2 Possible pathways of cleavage upon photolysis of **5**.



Scheme 3 Synthetic protocol for the preparation of chromenes **3–7**.

in 1,2-dichloroethane led to **3–5** in 24–64% isolated yields. The bis-chromenes **3–5** were fully characterized by IR, ^{1}H, and ^{13}C NMR spectroscopic techniques. In a similar manner the model compounds **6** and **7** were prepared and characterized.

The UV–vis absorption spectra of the bis-chromenes **3–5** in toluene are shown in Fig. 2. Clearly, all three analogues exhibit very distinct absorption profiles. This, in conjunction with the absorption maximum for the parent unsubstituted 2,2-diphenyl-2*H*-1-benzopyran (λ_{max} *ca.* 312 nm), attests to the fact that there exists significant π-conjugation between the two chromene moieties in all of the bis-chromenes **3–5**. The absorption in the case of 6,6′-bis-chromene **3** is highly blue-shifted relative to that of the 6,7′-bis-chromene **5**, while that of the 7,7′-analogue **4** is tremendously red-shifted. As Fig. 2 reveals, all three bis-chromenes **3–5** exhibit respectable absorption at *ca.* 300 nm.

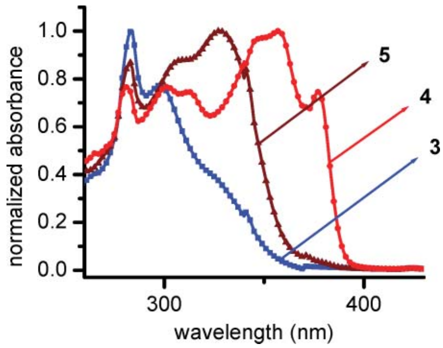


Fig. 2 Normalized UV–vis absorption spectra of **3–5**.

Steady-state photolysis of the solutions of **3–5** as well as the model chromenes **6** and **7** in toluene (5 × 10^{-5} M) led to readily observable colour changes. In Fig. 3 are shown the attendant colour changes when the solutions were briefly (90 s) exposed to ultraviolet radiation (λ_{max} *ca.* 300/350 nm) in a Luzchem photoreactor. As can be seen, the species responsible for the colour in the case of 6,6′-bis-chromene **3** exhibits absorption with a maximum at *ca.* 550 nm leading to a visible purple colour, whereas those of 7,7′- and 6,7′-bis-chromenes (**4** and **5**) exhibit highly blue-shifted absorptions with their λ_{max} at *ca.* 430 nm; a shoulder in the absorption in the region between 500–600 nm is also noteworthy for both cases. The model arylchromenes **6** and **7** are found to exhibit photochromism similar to those of bis-chromenes **3** and **4**, respectively, see ESI.†Thus, the bis-chromenes **3** and **4** truly behave as those of the simple aryl analogues. What is remarkable is the subtle difference in the absorption profiles for **4** and **5**. It may be readily discerned from Fig. 3 that the absorption in the region between 500–600 nm is considerably higher for the cross-linked

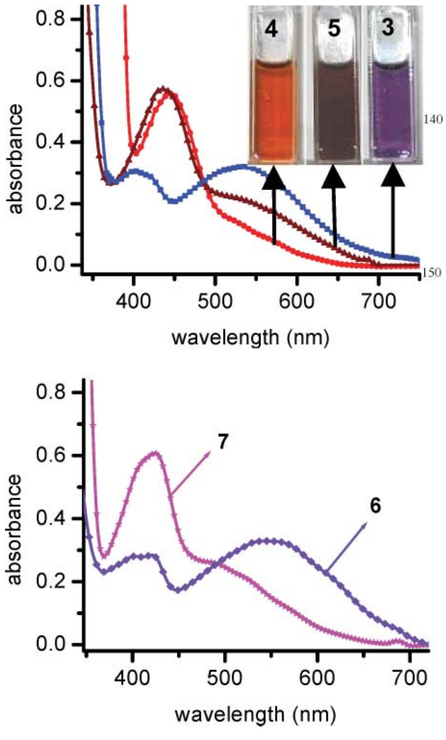


Fig. 3 UV–vis absorption spectra of the photolysates of **3–7**.

bis-chromene **5** as compared to that for **4**. This *subtle difference in the spectral distribution* evidently causes dramatic change in the way the photolysates exhibit colour; while the photolyzed solution in the case of **4** looks orange-red, that in the case of **5** appears dark brown (Fig. 3). Further, **5** was found to exhibit a considerable temperature-dependent absorption feature for the coloured species formed subsequent to photoirradiation. That is, the ratio $[\mathrm{Abs}]_{550\,\mathrm{nm}}/[\mathrm{Abs}]_{430\,\mathrm{nm}}$ was found to increase with a decrease in temperature (Fig. 4). In contrast, no such temperature-dependent absorption features were observed for the photolysates of bis-chromenes **3** and **4**. Also, the bis-chromenes **3–5** exhibited wavelength-independent transient absorption behaviour.

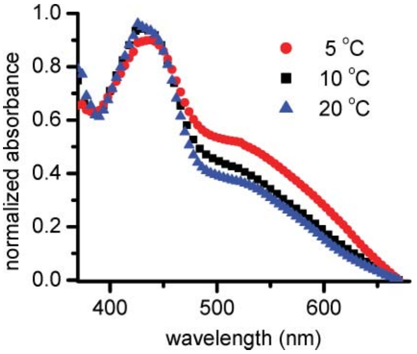
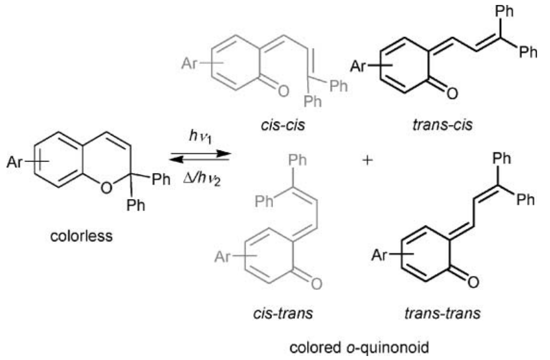


Fig. 4 The absorption spectra (normalized at 450 nm) of bis-chromene **5** at different temperatures.

The species responsible for the observation of colour in **3–7** upon photolysis are attributed to the mono-opened *o*-quinonoid intermediates of the kind shown in Scheme 4.[8,9] The initially formed *trans–cis* conformer may undergo, under steady-state conditions, further light-induced isomerization to the *trans–trans* form such that the decay of the coloured species is, in essence, a composite of the decays of the two isomers, *vide infra*.



Scheme 4 Structures of the four possible isomeric *o*-quinonoid intermediates, which may result from the photolysis of an arylchromene.

How can the unique absorption feature as well as the temperature-dependent behaviour of **5** be reconciled? As mentioned at the outset, the bis-chromene **5** may, in principle, undergo heterolysis in two different ways to generate the *o*-quinonoid intermediates that differ significantly in their absorption properties, *cf.* Scheme 2. Thus, the 6 C–O and 7 C–O cleavages may lead to the *o*-quinonoid intermediates, whose absorptions may be readily compared to those of the intermediates derived from **3**/**6** and **4**/**7**. A comparison of the spectral features in Fig. 3 suggests that both of the intermediates derived *via* 6 C–O as well as 7 C–O heterolyses exhibit absorptions at 430 and 550 nm, but the absorbance at 550 nm is higher as compared to that at 430 nm for the intermediate of 6 C–O heterolysis and *vice versa* for the intermediate of 7 C–O heterolysis. Thus, a significant increase in the absorbance at 550 nm relative to that at 430 nm for bis-chromene **5** indicates unequivocally the formation of the intermediates of both 6 C–O as well as 7 C–O heterolyses. The visible dark brown colour for the photolysate of **5** suggests the occurrence of two possible cleavages that lead to varying ratios of the respective *o*-quinonoid intermediates (Scheme 2); indeed, the visible dark brown colour can be generated by mixing the complementary purple and orange colours, which are observed for the photolysis of **3** and **4**, respectively. The temperature-dependent absorption spectra in Fig. 4 for irradiation at 300 nm show that the absorption at *ca.* 550 nm decreases with increasing temperature relative to that at 430 nm, which implies the fact that i) the overall transient absorption is a superposition of varying proportions of the *o*-quinonoid intermediates of 6 C–O and 7 C–O heterolyses and ii) a certain population of the intermediates of 6 C–O heterolysis decays rapidly as compared to that of 7 C–O heterolysis.

We have followed the kinetics for the disappearance of the transient intermediates of **3–5** at the photostationary state, the necessary durations of irradiation to reach the equilibrium conditions were determined from their respective colouration plots, see ESI.†The decays of the intermediates of **4** and **5** (Fig. 5) could be fitted to a biexponential function. The slow-decaying component of the intermediate of **3** was virtually negligible leading to a monoexponential fit.[10] The decay rate constants (s^{-1}) thus extracted from curve-fitting analyses are as follows: $k(\mathbf{3}) = 0.034$; $k_1(\mathbf{4}) = 0.043$, $k_2(\mathbf{4}) = 0.006$ and $k_1(\mathbf{5}) = 0.024$, $k_2(\mathbf{5}) = 0.006$. As can be seen, the fast-decaying species exhibit comparable lifetimes for all of the bis-chromenes **3–5**. In general, the fast- and slow-decaying components are believed to be *trans–cis* and *trans–trans* species, *cf.* Scheme 4; the *cis–cis* isomer is known to decay quite readily, while the *cis–trans* isomer can only be formed with difficulty.[8] Most remarkable is the finding that the bis-chromenes **3–5** exhibit ready photochromism in comparison to their parent monomer benzopyran, for which the photochromic property is observable only with difficulty at low temperatures.[11]

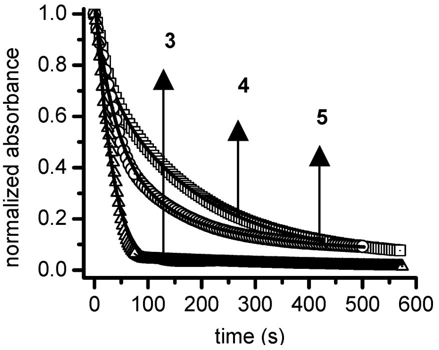


Fig. 5 The normalized thermal decay profiles of **3–5**. The decays were monitored at 550 (for **3**) and 450 nm (for **4** and **5**).

In conclusion, we have explored the photochromism in a unique set of directly-linked bis-chromenes **3–5**. Upon photolysis, the bis-chromenes **3** and **4** undergo mono-heterolysis leading to *o*-quinonoid intermediates, whose absorption properties parallel those of the model aryl analogues **6** and **7**, respectively. Whereas the intermediate derived from **3** was found to exhibit an absorption maximum at 550 nm (purple), the absorption of the *o*-quinonoid intermediate derived from **4** was found be highly blue-shifted with $\lambda_{\max}$ *ca.* 430 nm (orange-red). The cross-linked and substitutionally-biased bis-chromene **5**, which may be viewed as a 6-(7-chromenyl)chromene as well as 7-(6-chromenyl)chromene, lends itself to novel photobehaviour in that the irradiation leads to differing proportions (depending on the temperature) of the intermediates of 6 C–O and 7 C–O heterolysis. The unique absorption spectral distribution arising from the formation of two *o*-quinonoid intermediates derived from 6 C–O and 7 C–O heterolyses gives a dark brown colour to the solutions of irradiated **5**. In other words, the photobehaviour of **5** is equivalent to a composite of that observed for **3** as well as **4**. In view of the fact that naphthopyrans with a neutral grey colour are important for applications in conjunction with spiro-oxazines for the development of ophthalmic plastic lenses and that there exists tremendous interest currently in the development of multi-addressable photoswitchable systems, the bis-chromenes with novel photochromism represent a new class of molecular systems. We are presently exploring the behaviour of analogous bis-naphthopyrans toward bis-photochromic materials.

Acknowledgements

We are thankful to DST, India for finanical support. PV and SS are grateful to CSIR for their research fellowships.

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9 (*a*) The C–O bond heterolysis of both pyran rings synergistically to yield highly conjugated bis-opened forms does not appear to occur in **3–5** as reflected from the absorption spectra of the intermediates, which closely resemble those of the intermediates of the model analogs **6** and **7**. In general, considerable shifts in the absorption maxima have been observed for bis-opened forms relative to those of the mono-opened forms, see: W. Zhao and E. M. Carreira, *J. Am. Chem. Soc.*, 2002, **124**, 1582; (*b*) W. Zhao and E. M. Carreira, *Org. Lett.*, 2006, **8**, 99.

10 It is intriguing that the decay of the *o*-quinonoid intermediate of **3** follows an almost monoexponential function as compared to the behaviour observed for those of **4** and **5**. We believe that the electronic factors intrinsic to the aryl rings are transmitted differently in 6- and 7-arylchromenes.

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