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Photolysis of xylylbischromones

Satish C. Gupta,* Mohamad Yusuf, Surinder Arora and Ramesh C. Kamboj

Department of Chemistry, Kurukshetra University, Kurukshetra 136119, India

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Abstract—Photoreorganisation of xylylbischromones occurring through 1,4-biradical is described. In these bischromones, the two chromophores have been found to behave independently. © 2003 Published by Elsevier Science Ltd.

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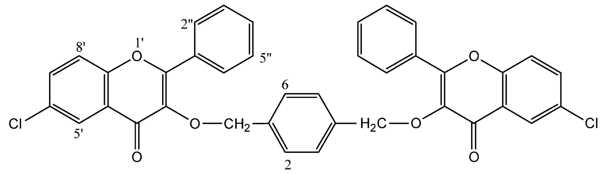
1. Introduction

Intramolecular bichromophoric interactions in bisthymines,[1] bisanthracenes,[2] biscoumarins,[3] bispyrones[4] and bisalkoxybenzophenones[5] have been the subject of considerable interest both to chemists and spectroscopists. In these molecules, photophysical and photochemical behaviour is revealed to be influenced by the length of the alkyl chain (spacer) linking the two chromophores. Recently, we have reported the results of our investigations[6] on the photolytic behaviour of some bischromones built around alkyl chains of varying lengths wherein the product formation has been found to be dependent upon the flexibility of the carbon chain—a consequence of the number of C-atoms in the chain. To examine further the role of the spacer in the product formation, we have synthesized the bischromones **1**,**2** in which the spacer is a xylyl moiety instead of a flexible alkyl chain.

2. Results

The bischromones **1** and **2** were obtained by reacting 2-aryl-3-hydroxychromones[7,8] **3** and **4** with α,α′-dibromo-*p*-xylene in the presence of $K_2CO_3/n\text{-}Bu_4N^+I^-$ in dry acetone. The photoirradiation of **1** dissolved in dry benzene with light from a 125 W Hg lamp, under anaerobic conditions, produced three photoproducts **5**–**7**. Similarly, the photoirradiation of **2** in benzene solution produced **8**–**10**. The structures of the photoproducts **5**–**10** could be confirmed by the comparison of their IR/^{1}H NMR spectra with those of **1** and **2** and the photoproducts obtained from the photoirradiation of **11**[7] and **12**.[8]



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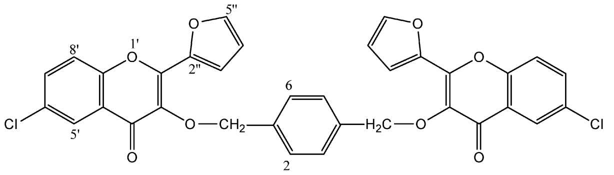

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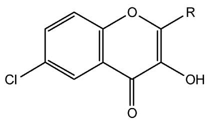

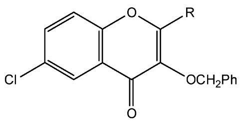

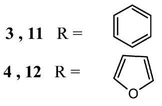

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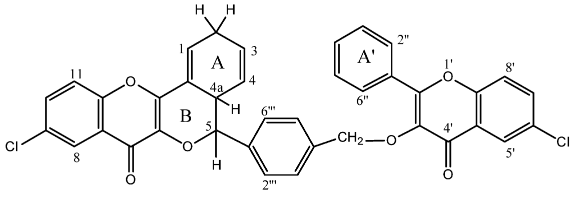

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Keywords: photoreorganisation; xylylbischromones.

* Corresponding author. Tel.: +91-1744-222203; fax: +91-1744-238277; e-mail: scguptaku@rediffmail.com

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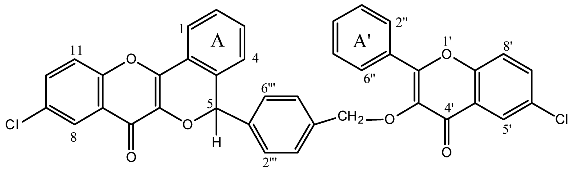

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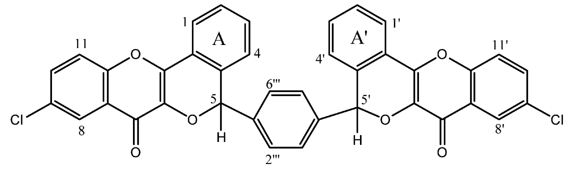

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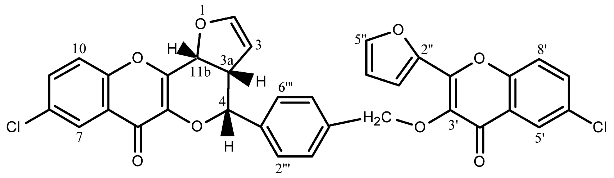

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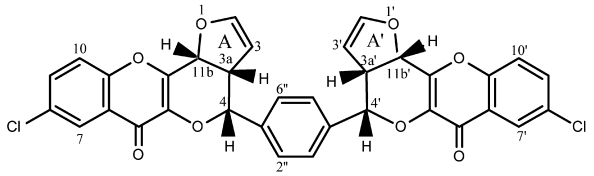

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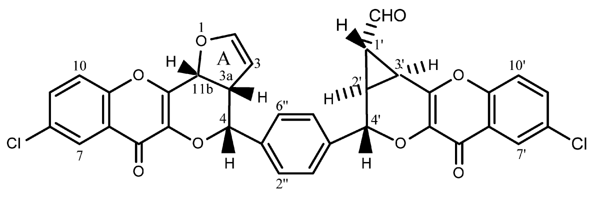

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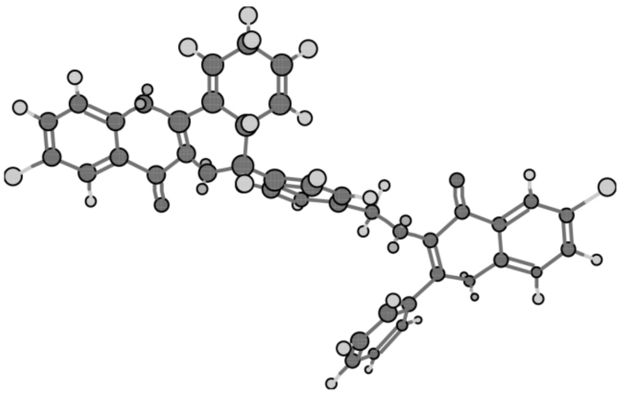
3. Discussion

The *cis*-disposition of H-11b, H-3a and H-4 in **8**–**10** is based upon the observation that $J_{11b,3a}$ and $J_{3a,4}$ are 8.1 Hz and 11.0 Hz respectively; the heavier group (phenyl) at C-4 is present in the preferred ψ-equatorial conformation and ring B in the half chair form. In **10**, the cyclopropane protons H-2′ and H-3′ are *cis* to each other and H-1′ is *trans* to both H-2′ and 3′; the −CHO group is *exo* to pyrone.[8] It may be significant to mention here that H-4′ (δ 5.77) in **10** has been observed as a sharp singlet, inferring that the planes containing H-2′ and H-4′ possess ϕ tending to 90°.

The energy minimized structures **13**–**15** (of compounds **5**, **8** and **10**) generated through molecular mechanics calculations (MM2) show that H-4 (δ 5.10) in **5** and H-3 (δ ~4.87) in **8**–**10** fall in the shielding zone of the phenyl group at C-5 and C-4, respectively. This observation is supported by the fact that similar protons, in the compounds where an alkyl chain replaces phenyl,[6] appeared at δ 5.95 and 5.12.



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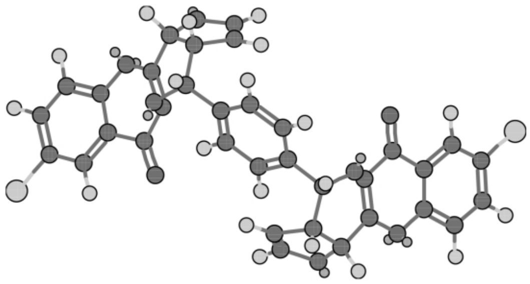

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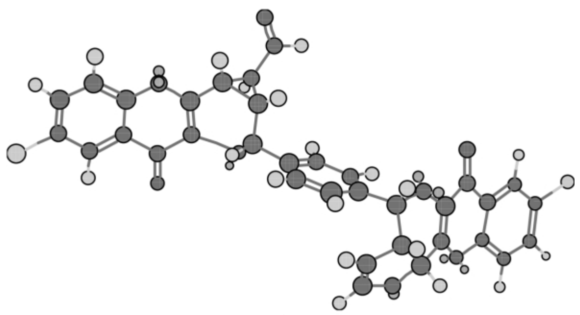

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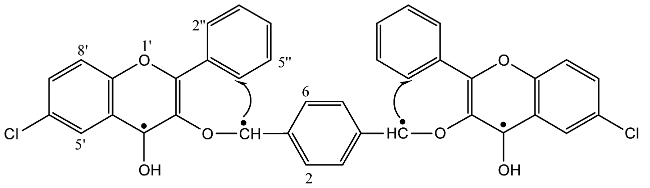
The phototransformations of **1** and **2** can be visualized as having occurred through an initial H-abstraction from the 3-OCH$_2$− group by the excited carbonyl group of the pyrone moiety to produce 1,4-biradical followed by bond formation between −OĊH− and carbon atom of aryl ring at C-2. The dihydro-aromatic compound **5** and aromatic compound **6** are formed independently from a common 1,4-biradical intermediate.[7] The photoirradiation of **1**, in addition to the products **5**–**7**, could have furnished two more products similar to **7**—one where both the rings A and A′ are dihydro (as in **5**) and the other product where one of the two rings (A/A′) is aromatic and other is dihydro.



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In the photoirradiation of **2**, compound **10** is produced by the further photolysis of compound **9** where dihydrofuran ring A undergoes ring contraction and ring expansion mechanism to provide the cyclopropylaldehyde moiety.[8] That **10** is formed from **9** was corroborated by the fact that the latter on irradiation gave former along with some other products that could not be isolated. Similarly, the dihydrofuran rings in **8** and **10** and both the dihydrofuran rings in **9** could have transformed themselves into cyclopropylaldehydes to give two more compounds. These additional products in the photolysis of both **1** and **2** could not be isolated probably due to their extremely low yields.

4. Conclusion

It may thus be concluded that in bischromones **1** and **2**, the inclusion of the rigid spacer like benzenoid moiety makes the two chromophores behave independently of each other and no intrachromophoric interactions are observed.

5. Experimental

5.1. General

IR spectra were recorded on a Buck Scientific 500 spectrophotometer using KBr pellets and UV spectra on U-2000 Hitachi-Spectrophotometer. ^{1}H NMR spectra were recorded on a 300 MHz Bruker spectrometer using TMS as internal standard. Melting points reported are uncorrected.

5.1.1. Synthesis of 1,4-bis[6′-chloro-2′-phenyl-4′-oxo-4′*H*-1′-benzopyran-3′-oxy]dimethylbenzene 1. The 3-hydroxychromone[7] **3** (2.88 g, 0.01 mol) was refluxed with α,α′-dibromo-*p*-xylene (1.3 g, 0.005 mol) in the presence of $Bu_4N^+I^-$ (1.0 g), K_2CO_3 (1.5 g) in acetone for 1 h. The reaction mixture was filtered, evaporated and the residue was chromatographed to obtain **1**.

Yield (60%); colourless solid; mp 215–217°C; [Found: C, 70.60; H, 3.89. $C_{38}H_{24}O_6Cl_2$ requires C, 70.49; H, 3.74]; ν_{max} (cm^{-1}) 1642 (C=O); λ_{max} THF (ε) 302 nm (16400), 247 nm (25100), 214 nm (28200); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.24 (2H, d, J_m=2.7 Hz, H-5′), 7.94 (4H, t{d}, J=1.5, 3.0, 6.5 Hz, H-2″,6″), 7.62 (2H, dd, $J_{m,o}$=2.7, 9.0 Hz, H-7′), 7.46 (6H, m, H-3″,4″,5″), 7.42 (2H, d, J_o=9.0 Hz, H-8′), 7.15 (4H, s, H-2,3,5,6), 5.09 (4H, s, OCH$_2$).

5.1.2. Synthesis of 1,4-bis[6′-chloro-2′-(2″-furyl)-4′-oxo-4′*H*-1′-benzopyran-3′-oxy]dimethylbenzene 2. The bischromone[8] **2** was prepared by the alkylation of 6-chloro-3-hydroxy-2-(2′-furyl)-4-oxo-4*H*-1-benzopyran[2] **4** (2.6 g, 0.01 mol) with α,α′-dibromo-*p*-xylene (1.3 g, 0.005 mol) following the same procedure as used for **1**.

Yield (50%); colourless solid; mp 258–260°C; [Found: C, 65.15; H, 3.33. $C_{34}H_{20}O_8Cl_2$ requires C, 65.09; H, 3.21]; ν_{max} (cm^{-1}) 1640 (C=O); λ_{max} THF (ε) 324 nm (20100), 256 nm (17500), 219 nm (22100); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.20 (2H, d, J_m=2.6 Hz, H-5′), 7.65 (2H, d, $J_{5'',4''}$=1.8 Hz, H-5″), 7.61 (2H, dd, $J_{m,o}$=2.6, 9.0 Hz, H-7′), 7.50 (2H, d, J_o=9.0 Hz, H-8′), 7.47 (4H, s, H-2,3,5,6), 7.27 (2H, d, $J_{3'',4''}$=3.6 Hz, H-3″), 6.56 (2H, dd, $J_{4'',5''}$=1.8 Hz, $J_{4'',3''}$=3.6 Hz, H-4″), 5.32 (4H, s, OCH$_2$).

5.1.3. Photolysis of 1,4-bis[6′-chloro-2′-phenyl-4′-oxo-4′*H*-1′-benzopyran-3′-oxy]dimethylbenzene 1. A benzene solution of **1** (100 mg, 0.00015 mol) was irradiated with light from a 125 W mercury lamp, in a pyrex reactor under N$_2$ atmosphere. The photolysate was chromatographed over a column of silica gel (100–200 mesh) to yield **1** (50%, mmp), **5**, **6** and **7**.

Compound **5**. Yield (10%); pale yellow solid; mp 205–207°C; [Found: C, 70.68; H, 3.84. $C_{38}H_{24}O_6Cl_2$ requires C, 70.49; H, 3.74]; ν_{max} (cm^{-1}) 1647 (C=O), 1642 (C=O); λ_{max} THF (ε) 310 nm (14000), 223 nm (26500); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.23 (1H, d, J_m=2.4 Hz, H-8), 8.20 (1H, d, J_m=2.4 Hz, H-5′), 7.99 (2H, d{dd}, J=1.5, 3.5, 6.3 Hz, H-2″,6″), 7.61 (1H, dd, $J_{m,o}$=2.4, 8.9 Hz, H-10), 7.59 (1H, dd, $J_{m,o}$=2.4, 8.9 Hz, H-7′), 7.51 (3H, m, H-3″,4″,5″), 7.42 (2H, d, J_o=8.9 Hz, H-11,8′), 7.30 (4H, br s, H-2‴,3‴,5‴,6‴), 6.75 (1H, br s, H-1), 5.80 (1H, dd, $J_{3,2a}$=1.0 Hz, $J_{3,4}$=10.0 Hz, H-3), 5.18 (2H, s, OCH$_2$), 5.10 (1H, dd, $J_{4,4a}$=1.9 Hz, $J_{4,3}$=10.0 Hz, H-4), 4.61 (1H, d, $J_{5,4a}$=11.0 Hz, H-5), 3.30 (1H, m, H-4a), 2.98 (2H, m, H-2a); *m*/*z* 646 (M$^+$).

Compound **6**. Yield (12%); pale yellow solid; mp 215–218°C; [Found: C, 70.87; H, 3.50. $C_{38}H_{22}O_6Cl_2$ requires C, 70.71; H, 3.44]; ν_{max} (cm^{-1}) 1644 (C=O), 1635 (C=O); λ_{max} THF (ε) 314 nm (16000), 216 nm (24500); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.26 (1H, d, J_m=2.4 Hz, H-8), 8.21 (1H, d, J_o=2.4 Hz, H-5′), 7.92 (3H, m, H-1,2″,6″), 7.61 (2H, m H-10,7′), 7.50 (7H, m, H-2,3,11,8′,3″,4″,5″), 7.23 (4H, br s, H-2‴,3‴,4‴,5‴), 7.05 (1H, dd, J=1.8 Hz, 6.3 Hz, H-4), 6.32 (1H, s, H-5), 5.07 (2H, s, OCH$_2$); *m*/*z* 644 (M$^+$).

Compound **7**. Yield (7%); pale yellow solid; mp 238–240°C; [Found: C, 71.10; H, 3.18. $C_{38}H_{20}O_6Cl_2$ requires C, 70.93; H, 3.13]; ν_{max} (cm^{-1}) 1639 (C=O); λ_{max} THF (ε) 310 nm (12000), 220 nm (24500); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.25 (2H, d, J_m=2.5 Hz, H-8,8′), 7.93 (2H, m, H-1,1′), 7.60 (2H, dd, $J_{m,o}$=2.5 Hz, 9.0 Hz, H-10,10′), 7.50 (2H, d, J_o=9.0 Hz, H-11,11′), 7.42 (4H, m, H-2,3,2′,3′), 7.30 (4H, br s, H-2″,3″,5″,6″), 7.12 (2H, dd, J=2.4 Hz, 8.5 Hz, H-4,4′), 6.32 (2H, s, H-5,5′); *m*/*z* 642 (M$^+$).

5.1.4. Photolysis of 1,4-bis[6′-chloro-2(2″-furyl)-4′-oxo-4′*H*-1′-benzo-pyran-3′-oxy]dimethylbenzene 2. A deoxygenated benzene solution of **2** (100 mg, 0.00015 mol) was irradiated as **1** to yield **2** (40%, mmp) and three new compounds **8**, **9** and **10**.

Compound **8**. Yield (10%); pale yellow solid; mp 215–218°C; [Found: C, 65.27; H, 3.28. $C_{34}H_{20}O_8Cl_2$ requires C, 65.09; H, 3.21]; ν_{max} (cm^{-1}) 1658 (C═O), 1641 (C═O); λ_{max} THF (ε) 320 nm (12400), 219 nm (25600) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (1H, d, J_m=2.5 Hz, H-7), 8.22 (1H, d, J_m=2.5 Hz, H-5′), 7.69 (1H, d, $J_{5'',4''}$=1.8 Hz, H-5″), 7.63 (2H, m, H-9,7′), 7.54 (4H, m, H-2‴,3‴,5‴,6‴), 7.50 (1H, d, J_o=8.9 Hz, H-10), 7.40 (1H, d, J_o=8.9 Hz, H-8′), 7.30 (1H, d, $J_{3'',4''}$=3.6 Hz, H-3″), 6.62 (1H, dd, $J_{4'',5''}$=1.8 Hz, $J_{4'',3''}$=3.6 Hz, H-4″), 6.59 (1H, d, $J_{2,3}$=2.7 Hz, H-2), 5.36 (2H, s, CH_2O), 5.25 (1H, d, $J_{11b,3a}$=8.1 Hz, H-11b), 4.87 (1H, dd, $J_{3,2}$=2.7 Hz, $J_{3,3a}$=1.0 Hz, H-3), 4.38 (1H, d, $J_{4,3a}$=11.0 Hz, H-4), 3.23 (1H, m, H-3a); *m/z* 626 (M^+).

Compound **9**. Yield (15%); pale yellow solid; mp 225–228°C; [Found: C, 65.29; H, 3.25. $C_{34}H_{20}O_8Cl_2$ requires C, 65.09; H, 3.21]; ν_{max} (cm^{-1}) 1648 (C═O); λ_{max} THF (ε) 322 nm (11800), 223 nm (24500); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (2H, d, J_m=2.5 Hz, H-7,7′), 7.63 (2H, dd, $J_{m,o}$=2.5 Hz, 9.0 Hz, H-9,9′), 7.52 (2H, d, J_o=9.0 Hz, H-10,10′), 7.46 (4H, s, H-2″,3″,5″,6″), 6.61 (2H, d, $J_{2,3}$=2.7 Hz, H-2,2′), 5.27 (2H, d, $J_{11b,3a}$=8.2 Hz, H-11b,11b′), 4.90 (2H, m, H-3,3′), 4.42 (2H, d, $J_{4,3a}$=10.5 Hz, H-4,4′), 3.48 (2H, m, H-3a,3a′); *m/z* 626 (M^+).

Compound **10**. Yield (8%); pale yellow solid; mp 205–208°C; [Found: C, 65.17; H, 3.26. $C_{34}H_{20}O_8Cl_2$ requires C, 65.09; H, 3.21]; ν_{max} (cm^{-1}) 1713 (C═O), 1657 (C═O); λ_{max} THF (ε) 322 nm (12200), 221 nm (24000); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (1H, d, J=2.4 Hz, CHO), 8.21 (1H, d, J_m=2.5 Hz, H-7), 8.16 (1H, d, J_m=2.5 Hz, H-7′), 7.60 (2H, dd, $J_{m,o}$=2.5 Hz, 8.9 Hz, H-9,9′), 7.52 (2H, m, H-10,10′), 7.40 (4H, m, H-2″,3″,5″,6″), 6.57 (1H, br s, H-2), 5.77 (1H, s, H-4′), 5.21 (1H, d, $J_{11b,3a}$=8.1 Hz, H-11b), 4.85 (1H, m, H-3), 4.32 (1H, d, $J_{4,3a}$=11.0 Hz, H-4), 3.20 (2H, m, H-3a,1′), 2.90 (1H, m, H-2′), 2.56 (1H, m, H-3′); *m/z* 626 (M^+).

Acknowledgements

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