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Photoreorganisation of some bischromones

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Abstract—Photoreorganisation of 2,2′-dithienyl/diphenyl-3,3′-polymethylene-dioxychromones is described. The product formation has been found to depend upon the length of the intervening alkyl chain. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

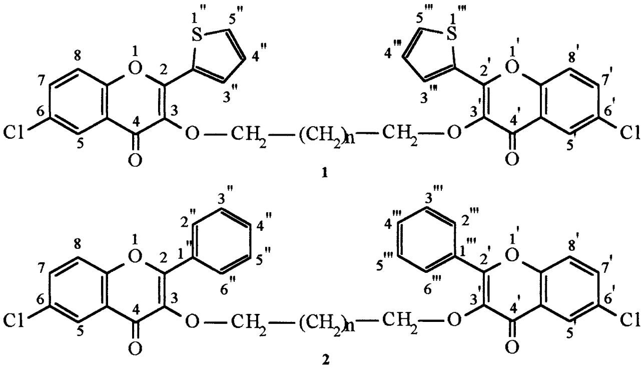
Bischromones, bichromophoric systems, are formed by joining two chromone nuclei through an alkyl chain of varying length and structure. In bichromophoric molecules, though individual chromophores have no important interactions among themselves in the ground state, they are known to exhibit different photochemical properties on excitation. Such behaviour could be the result of the formation of excited state complexes which lead to many deactivation processes coupled with the formation of some photoproducts.[1–3] In the studies on systems like bisanthracenes,[4,5] bisthymines,[6–8] biscoumarins[9–10] and bisfurocoumarins[11] and bispyrones,[12] it has been revealed that the photoproduct formation/distribution is profoundly affected by the length of the intervening carbon chain. In this communication, we report the results of our investigations pertaining to the photochemical transformations of 2,2′-dithienyl/diphenyl-3,3′-polymethylene-dioxychromones **1** and **2**.

Our interest in these molecules was manifold:

(a) The pyrone double bond could undergo intramolecular [2+2] photocycloaddition.
(b) H-abstractions from the 3-alkoxy group by the excited C═O could initiate the reaction.

2. Results

The bischromones **1** and **2** were synthesized by reacting 6-chloro-2-(2′-thienyl)[13] and 6-chloro-2-phenyl-3-hydroxy-4-oxo-4*H*-1-benzopyran[14] with an appropriate 1,ω-dibromoalkane in the presence of K_2CO_3/tetrabutylammonium iodide. The photolysis of bischromone **1a** (n=3) through pyrex filtered UV light furnished three products **3** (n=2), **4** (n=2) and **5** (n=1). The photolysis had to be abandoned after 45 min as the reaction solution acquired yellow colour that further intensified on longer exposure. Similarly, the photolysis of **2a** (n=3) produced **6** (n=2), **7** (n=2) and **8** (n=1). The *cis*-dispositions of H-11b, H-3a and H-4 in **3** and **5** were confirmed[13,15,16] from $J_{11b,3a}$=8 Hz and $J_{3a,4}$=10.0 Hz.



1a, 2a: n = 3; 1b, 2b: n = 2; 1c, 2c: n = 1; 1d, 2d: n = 0

In the photolysis of **1b** and **2b** (n=2), the products isolated were **3** (n=1), **4** (n=1), and **6** (n=1) and **7** (n=1), respectively. Similarly, **1c** and **2c** (n=1) on photolysis produced **3** (n=0), **4** (n=0), and **6** (n=0) and **7** (n=0). The bischromones **1d** and **2d** (n=0) remained unreacted under various conditions of photolysis (254/316 nm, CH_3CN, THF). Even the extended period of irradiation did not bring about any change and the starting bischromones were recovered as such. The fact that the photoproducts **4** and **7** are formed independently from **1** and **2** and are not the photodehydrogenated products of **3** and **6** was proved by the fact that the irradiation of **3** produced only polymeric products.[13]

Keywords: bischromones; photoreorganisation; alkyl chain.

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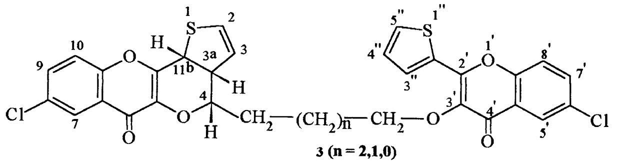
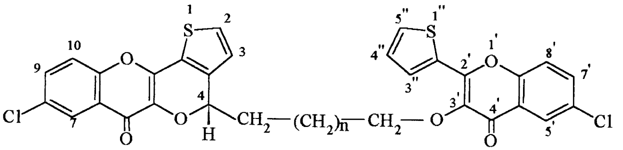


3 (n = 2,1,0)



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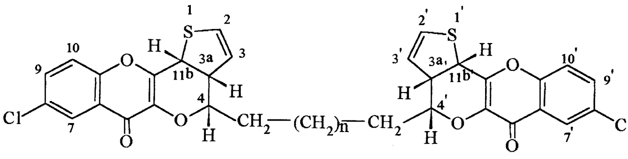
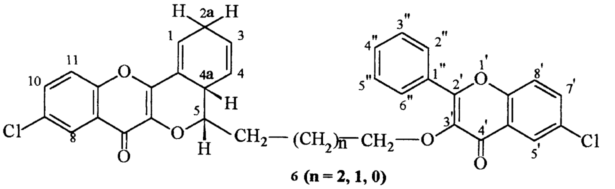


5 (n = 1)



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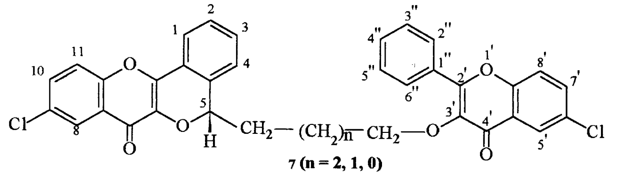

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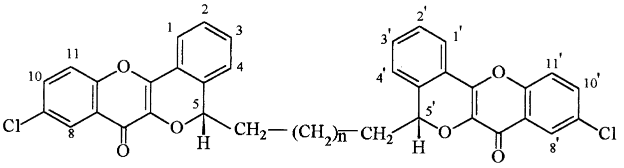
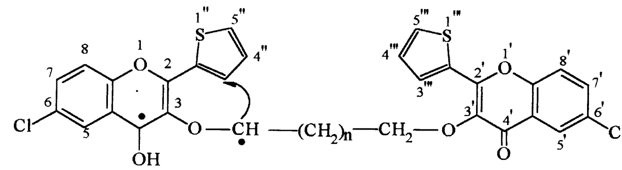


8 (n = 1)

3. Discussion

The photo-conversions described here can be rationalised to occur through the abstraction of the H atom from the 3–O–CH_2– by the excited C=O of the chromone moiety[13,16,17] to give 1,4-biradicals **9** and **10** that cyclise to provide the products **3**, **4** and **5**, respectively.



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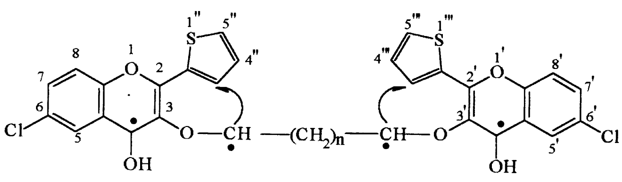

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Similarly, the formation of the photoproducts[14,17] **6–8** from bischromone **2** can be explained. The behaviour of these bischromones **1** and **2** towards photolysis seems to be dependent upon the length of the alkyl chain joining the two chromone-nuclei. That is, there is no reaction when $n=0$, reaction occurs only on one side when $n=1$ and 2, and involves both sides of the molecules in case of $n=3$. This may be rationalised on the basis of intramolecular complex formation between the two chromone-moieties in these molecules. Herein, the governing factor could be the lifetime of the excited states involved and the free energy change accompanying the reaction. The possibility of the formation of the intramolecular complex is limited by the probability of overlapping of the two nuclei bearing the chromophores in the lifetime of the excited states involved.[4] An intramolecular complex formation can lead to deactivation. An increase in the length of the intervening alkyl chain shall increase the number of rotamers. Consequently, this decreases the tendency of intramolecular complex formation and deactivation of the excited state in turn. This is corroborated by the observation that the recovery of the starting bischromones is more than 95% when $n=0$, ~60% when $n=1$ or 2 and only ~20% when $n=3$. Although the possibility of the formation of the photoproducts similar to **5** and **8** from bischromones **1** and **2** ($n=1$ and 2) cannot altogether be excluded, we were unable to isolate any such products however. In the investigations on the photolytic behaviour of the biscoumarins[9–10] and bisfurocoumarins,[11] the intramolecular cycloadditions involving the double bond of the pyrone/furan have been reported; however, in the present study, no such intramolecular [2+2] photocycloadditions have been observed and reaction occurred only through the H-abstractions. The intermolecular [2+2] photocycloadditions on 4-oxo-4*H*-pyrones is well documented.[18–21]

4. Conclusion

The bischromones studied here on photoirradiation yield the products through the H-abstractions and the products formed depend upon the length of the alkyl chain.

5. Experimental

IR spectra were recorded on a Perkin–Elmer 1000PL FT-IR 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 Me_4Si as internal standard. Melting points reported are uncorrected.

5.1. Typical procedure for the synthesis of bischromones 1 and 2

5.1.1. 1,5-Bis[6′-chloro-2′-(2″-thienyl)-4′-oxo-4′*H*-1-benzopyran-3-oxy]-pentane, 1a (n=3). A well stirred suspension of 6-chloro-3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (2.0 g, 0.0072 mol), 1,5-dibromopentane (0.8 g, 0.0036 mol), tetrabutylammonium iodide (2.0 g,) and freshly ignited K_2CO_3 (1.5 g) were refluxed in dry acetone

(25 mL) for 1 h. The colour of the reaction mixture changed from deep red to colourless. The reaction mixture after filtration and the distillation of acetone was poured into iced HCl to obtain a mixture of monochromone and bischromone. This mixture was then separated on a column of silica-gel (100–200 mesh) using benzene as eluent to obtain bischromone **1a** (crystallized from $CHCl_3$–MeOH).

Compound **1a**. Yield 60%, white needles; mp 201–203°C; [Found: C, 59.43; H, 3.60. $C_{31}H_{22}Cl_2O_6S_2$ requires C, 59.52; H, 3.52%]; ν_{max} (cm^{-1}) 1645 (C=O); λ_{max} THF (ε) 344 nm (17 500), 328 nm (18 000), 260 nm (14 000); δ_H ($CDCl_3$) 8.16 (2H, d, J_m=2.5 Hz, H-5,5′), 7.95 (2H, dd, $J_{3'',4''}$=3.7 Hz, $J_{3'',5''}$=1.2 Hz, H-3″,3‴), 7.62 (2H, dd, $J_{5'',4''}$=5.1 Hz, $J_{5'',3''}$=1.2 Hz, H-5″,5‴), 7.59 (2H, dd, $J_{m,o}$=2.5, 8.9 Hz, H-7,7′), 7.47 (2H, d, J_o=8.9 Hz, H-8,8′), 7.21 (2H, dd, $J_{4'',3''}$=3.7 Hz, $J_{4'',5''}$=5.1 Hz, H-4″,4‴), 4.32 (4H, t, J_{vic}=6.9 Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 2.02 (4H, quintet, J_{vic}=6.9 Hz, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}$ $\mathrm{CH_2O}$), 1.75 (2H, m, $\mathrm{OCH_2CH_2}\mathit{CH_2}\mathrm{CH_2CH_2O}$); *m/z* 625/627.

Compound **1b**. Yield 50%, white solid; mp 219–220°C; [Found: C, 58.75; H, 3.15. $C_{30}H_{20}Cl_2O_6S_2$ requires C, 58.91; H, 3.27%]; ν_{max} (cm^{-1}) 1643 (C=O); λ_{max} THF (ε) 344 nm (20 600), 328 nm (21 300), 260 nm (16 500); δ_H ($CDCl_3$) 8.17 (2H, d, J_m=2.7 Hz, H-5,5′), 7.96 (2H, dd, $J_{3'',5''}$=1.2 Hz, $J_{3'',4''}$=3.4 Hz, H-3″,3‴), 7.60 (4H, m, H-7,7′,5″,5‴), 7.48 (2H, d, J_o=9.0 Hz, H-8,8′), 7.20 (2H, dd, $J_{4'',3''}$=3.4 Hz, $J_{4'',5''}$=5.1 Hz, H-4″,4‴), 4.39 (4H, t, J_{vic}=5.8 Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 2.18 (4H, quintet, J_{vic}=5.8 Hz, $\mathrm{OCH_2}\mathit{CH_2CH_2}\mathrm{CH_2O}$); *m/z* 611/613.

Compound **1c**. Yield 55%, white needles; mp 196–198°C; [Found: C, 58.40; H, 3.10. $C_{29}H_{18}Cl_2O_6S_2$ requires C, 58.29; H, 3.01%]; ν_{max} (cm^{-1}) 1640 (C=O); λ_{max} THF (ε) 343 nm (19 700), 328 nm (20 000), 260 nm (15 300); δ_H ($CDCl_3$) 8.17 (2H, d, J_m=2.7 Hz, H-5,5′), 7.97 (2H, dd, $J_{3'',5''}$=1.2 Hz, $J_{3'',4''}$=3.8 Hz, H-3″,3‴), 7.60 (4H, m, H-5″,5‴, 7,7′), 7.47 (2H, d, J_o=8.9 Hz, H-8,8′), 7.20 (2H, dd, $J_{4'',3''}$=3.8 Hz, $J_{4'',5''}$=5.1 Hz, H-4″,4‴), 4.53 (4H, t, J_{vic}=6.6 Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}\mathrm{O}$), 2.58 (2H, quintet, J_{vic}=6.6 Hz, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2O}$); *m/z* 597/599.

Compound **1d**. Yield 50%, white needles; mp 150–152°C; [Found: C, 57.43; H, 2.65. $C_{28}H_{16}Cl_2O_6S_2$ requires C, 57.63; H, 2.74%]; ν_{max} (cm^{-1}) 1642 (C=O); λ_{max} THF (ε) 344 nm (20 500), 329 nm (20 600), 260 nm (17 800); δ_H ($CDCl_3$) 8.20 (2H, d, J_m=2.4 Hz, H-5,5′), 7.95 (2H, dd, $J_{3'',5''}$=1.0 Hz, $J_{3'',4''}$=3.7 Hz, H-3″,3‴), 7.65 (2H, dd, $J_{5'',3''}$=1.0 Hz, $J_{5'',4''}$=5.1 Hz, H-5″,5‴), 7.61 (2H, dd, $J_{m,o}$=2.4, 8.9 Hz, H-7,7′), 7.48 (2H, d, J_o=8.9 Hz, H-8,8′), 7.22 (2H, dd, $J_{4'',3''}$=3.7 Hz, $J_{4'',5''}$=5.1 Hz, H-4″,4‴), 4.80 (4H, s, $\mathrm{O}\mathit{CH_2CH_2}\mathrm{O}$); *m/z* 583/585.

Compound **2a**. Yield 55%, white solid; mp 158–160°C; [Found: C, 68.57; H, 4.30. $C_{35}H_{26}Cl_2O_6$ requires C, 68.51; H, 4.24%]; ν_{max} (cm^{-1}) 1642 (C=O); λ_{max} THF (ε) 302 nm (15 100), 247 nm (20 600); δ_H ($CDCl_3$) 8.19 (2H, d, J_m=2.7 Hz, H-5,5′), 8.10 (4H, m, H-2″,2‴,6″,6‴), 7.61 (2H, dd, $J_{m,o}$=1.6, 6.0 Hz, H-7,7′), 7.50 (8H, m, H-8,8′,3″,3‴,4″,4‴,5″,5‴), 4.02 (4H, t, J_{vic}=4.0 Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 1.74 (4H, m, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}$-$\mathrm{CH_2O}$), 1.44 (2H, m, $\mathrm{OCH_2CH_2}\mathit{CH_2}\mathrm{CH_2CH_2O}$); *m/z* 613/615.

Compound **2b**. Yield 60%, white solid; mp 170–171°C; [Found: C, 68.07; H, 4.06. $C_{34}H_{24}Cl_2O_6$ requires C, 68.11; H, 4.00%]; ν_{max} (cm^{-1}) 1641 (C=O); λ_{max} THF (ε) 301 nm (16 700), 247 nm (22 500); δ_H ($CDCl_3$) 8.19 (2H, d, J_m=2.4 Hz, H-5,5′), 8.05 (4H, m, H-2″,2‴,6″,6‴), 7.60 (2H, dd, $J_{m,o}$=2.4, 8.8 Hz, H-7,7′), 7.48 (8H, m, H-8,8′,3″,3‴,4″,4‴,5″,5‴), 4.01 (4H, t, J_{vic}=5.6 Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 1.78 (4H, quintet, J_{vic}=5.6 Hz, $\mathrm{OCH_2}\mathit{CH_2CH_2}\mathrm{CH_2O}$); *m/z* 599/601.

Compound **2c**. Yield 50%, white needles; mp 153–155°C; [Found: C, 67.80; H, 3.60. $C_{33}H_{22}Cl_2O_6$ requires C, 67.69; H, 3.76%]; ν_{max} (cm^{-1}) 1649 (C=O); λ_{max} THF (ε) 301 nm (17 900), 244 nm (27 500); δ_H ($CDCl_3$) 8.17 (2H, d, J_m=2.4 Hz, H-5,5′), 7.98 (4H, m, H-2″,2‴,6″,6‴), 7.61 (2H, dd, $J_{m,o}$=2.4, 8.9 Hz, H-7,7′), 7.48 (2H, d, J_o=8.9 Hz, H-8,8′), 7.40 (6H, m, H-3″,3‴,4″,4‴,5″,5‴), 4.10 (4H, t, J_{vic}=6.2 Hz, $\mathrm{O}\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}\mathrm{O}$), 2.08 (2H, quintet, J_{vic}=6.2 Hz, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2O}$); *m/z* 585/587.

Compound **2d**. Yield 45%, white solid; mp 148–150°C; [Found: C, 67.23; H, 3.60. $C_{32}H_{20}Cl_2O_6$ requires C, 67.25; H, 3.50%]; ν_{max} (cm^{-1}) 1642 (C=O); λ_{max} THF (ε) 301 nm (16 700), 242 nm (28 200); δ_H ($CDCl_3$) 8.22 (2H, d, J_m=2.3 Hz, H-5,5′), 8.10 (4H, m, H-2″,2‴,6″,6‴), 7.61 (2H, dd, $J_{m,o}$=2.3, 8.9 Hz, H-7,7′), 7.54 (6H, m, H-3″,3‴, 4″,4‴,5″,5‴), 7.48 (2H, d, J_o=8.9 Hz, H-8,8′), 4.40 (4H, s, $\mathrm{O}\mathit{CH_2CH_2}\mathrm{O}$); *m/z* 571/573.

5.2. Typical procedure for the synthesis of bischromones 1 and 2

5.2.1. Photolysis of 1,5-bis[6′-chloro-2′-(2″-thienyl)-4′-oxo-4′*H*-1-benzopyran-3-oxy]-pentane, 1a (*n*=3). A benzene solution (100 mL) of **1a** (100 mg, 0.00015 mol) was irradiated with the light from 125 W mercury lamp in a pyrex reactor under nitrogen for 45 min. The reaction mixture developed an intense yellow colour and the photolysis for longer duration did not show any further reaction (tlc). The solvent was distilled off and the photolysate was chromatographed over a column of silica-gel (100–200 mesh) packed in benzene. Elution of column with (benzene–EtOAc, 8:2) provided starting compound **1a** (20 mg, co-tlc & mmp), **3** (*n*=2), **4** (*n*=2) and **5** (*n*=1).

Compound **3** (*n*=2). Yield (10 mg, 10%); pale yellow solid; mp 146–148°C; [Found: C, 59.65; H, 3.40. $C_{31}H_{22}Cl_2O_6S_2$ requires C, 59.52; H, 3.52%]; ν_{max} (cm^{-1}) 1656 (C=O), 1638 (C=O); λ_{max} THF (ε) 350 nm (19 500), 325 nm (19 000), 260 nm (20 000); δ_H ($CDCl_3$) 8.20 (1H, d, J_m=2.4 Hz, H-7), 8.16 (1H, d, J_m=2.4 Hz, H-5′), 7.95 (1H, dd, $J_{3'',4''}$=3.6 Hz, $J_{3'',5''}$=1.2 Hz, H-3″), 7.65 (1H, dd, $J_{5'',4''}$=5.0 Hz, $J_{5'',3''}$=1.2 Hz, H-5″), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7′), 7.56 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.47 (1H, d, J_o=9.0 Hz, H-8′), 7.38 (1H, d, J_o=9.0 Hz, H-10), 7.21 (1H, dd, $J_{4'',5''}$=5.0 Hz, $J_{4'',3''}$=3.6 Hz, H-4″), 6.38 (1H, d, $J_{2,3}$=5.7 Hz, H-2), 5.68 (1H, dd, $J_{3,2}$=5.7 Hz, $J_{3,3a}$=3.2 Hz, H-3), 4.97 (1H, d, $J_{11b,3a}$=8.0 Hz, H-11b), 4.28 (2H, dd, *J*=5.1, 8.1 Hz, $\mathrm{CH_2CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 3.97 (1H, m, H-4), 3.27 (1H, d{dd}, $J_{3a,3}$=3.2 Hz, $J_{3a,11b}$=8.0 Hz, $J_{3a,4}$=10.0 Hz, H-3a), 2.07 (2H, m, $\mathrm{CH_2CH_2}\mathit{CH_2}\mathrm{CH_2O}$), 1.90 (2H, m, $\mathit{CH_2}\mathrm{CH_2CH_2CH_2O}$), 1.76 (2H, m, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2CH_2O}$); *m/z* 625/627 ($M^+$).

Compound **4** (*n*=2). Yield (14 mg, 14%); pale yellow solid; mp 160–162°C; [Found: C, 59.65; H, 3.26. $C_{31}H_{20}Cl_2O_6S_2$ requires C, 59.71; H, 3.21%]; ν_{max} (cm^{-1}) 1645 (C=O), 1638 (C=O); λ_{max} THF (ε) 346 nm (19 000), 327 nm (18 600), 229 nm (23 000); δ_H ($CDCl_3$) 8.22 (1H, d, J_m=2.4 Hz, H-7), 8.10 (1H, d, J_m=2.4 Hz, H-5′), 7.93 (1H, dd, $J_{3'',4''}$=3.7 Hz, $J_{3'',5''}$=1.2 Hz, H-3″), 7.63 (1H, d, $J_{2,3}$=5.3 Hz, H-2), 7.60 (1H, dd, $J_{5'',4''}$=5.5 Hz, $J_{5'',3''}$=1.2 Hz, H-5″), 7.55 (2H, dd, $J_{m,o}$=2.4, 8.9 Hz, H-9,7′), 7.47 (1H, d, J_o=8.9 Hz, H-8′), 7.44 (1H, d, J_o=8.9 Hz, H-10), 7.21 (1H, dd, $J_{4'',5''}$=5.5 Hz, $J_{4'',3''}$=3.7 Hz, H-4″), 7.00 (1H, d, $J_{3,2}$=4.7 Hz, H-3), 5.61 (1H, dd, J_{vic}=4.7, 7.2 Hz, H-4), 4.25 (2H, m, $CH_2CH_2CH_2\mathit{CH_2}O$), 2.26 (1H, m, $\mathit{CH}HCH_2CH_2CH_2O$), 2.05 (3H, m, $CH\mathit{H}CH_2\mathit{CH_2}CH_2O$), 1.78 (2H, m, $CH_2\mathit{CH_2}CH_2CH_2O$); *m*/*z* 623/625 ($M^+$).

Compound **5** (*n*=1): Yield (7 mg, 7%); pale yellow solid; mp 188–190°C; [Found: C, 59.46; H, 3.64. $C_{31}H_{22}Cl_2O_6S_2$ requires C, 59.52; H, 3.52%]; ν_{max} (cm^{-1}) 1652 (C=O); λ_{max} THF (ε) 324 nm (14 600), 284 nm (12 800), 233 nm (22 000); δ_H ($CDCl_3$) 8.17 (2H, d, J_m=2.6 Hz, H-7,7′), 7.56 (2H, dd, $J_{m,o}$=2.6, 8.9 Hz, H-9,9′), 7.38 (2H, d, J_o=8.9 Hz, H-10,10′), 6.41 (2H, d, $J_{2,3}$=6.2 Hz, H-2,2′), 5.67 (1H, dd, $J_{3,2}$=6.2 Hz, $J_{3,3a}$=3.2 Hz, H-3,3′), 4.98 (2H, d, $J_{11b,3a}$=8.0 Hz, H-11b,11b′), 3.95 (2H, m, H-4,4′), 3.27 (2H, d{dd}, $J_{3a,3}$=3.2 Hz, $J_{3a,11b}$=8.0 Hz, $J_{3a,4}$=10.0 Hz, H-3a,3a′), 1.88 (6H, m, $\mathit{CH_2CH_2CH_2}$); *m*/*z* 625/627 (M^+).

5.2.2. Photolysis of 1,4-bis[6′-chloro-2′-(2″-thienyl)-4′-oxo-4′*H*-1-benzopyran-3-oxy]-butane, 1b (*n*=2).

A benzene solution (100 mL) of **1b** (100 mg, 0.00016 mol) was irradiated for 45 min under the similar conditions as employed earlier for **1d**. The photolysate on chromatographic separation over a column silica-gel (100–200 mesh) furnished starting compound **1b** (60 mg, co-tlc & mmp), **3** (*n*=1) and **4** (*n*=1).

Compound **3** (*n*=1). Yield (10 mg, 10%); pale yellow solid; mp 202–204°C; [Found: C, 58.85; H, 3.32. $C_{30}H_{20}Cl_2O_6S_2$ requires C, 58.91; H, 3.27%]; ν_{max} (cm^{-1}) 1653 (C=O), 1634 (C=O); λ_{max} THF (ε) 326 nm (20 000), 258 nm (23 000), 245 nm (25 600); δ_H ($CDCl_3$) 8.20 (1H, d, J_m=2.6 Hz, H-7), 8.15 (1H, d, J_m=2.7 Hz, H-5′), 7.95 (1H, dd, $J_{3'',4''}$=3.6 Hz, $J_{3'',5''}$=1.1 Hz, H-3″), 7.60 (3H, m, H-9,7′,5″), 7.48 (1H, d, J_o=8.9 Hz, H-8′), 7.38 (1H, d, J_o=8.0 Hz, H-10), 7.20 (1H, dd, $J_{4'',5''}$=4.6 Hz, $J_{4'',3''}$=3.6 Hz, H-4″), 6.40 (1H, d, $J_{2,3}$=6.0 Hz, H-2), 5.68 (1H, dd, $J_{3,2}$=6.0 Hz, $J_{3,3a}$=3.0 Hz, H-3), 4.99 (1H, d, $J_{11b,3a}$=8.2 Hz, H-11b), 4.30 (2H, m, $CH_2CH_2\mathit{CH_2}O$), 4.07 (1H, t{d}, *J*=2.7, 9.0 Hz, H-4), 3.30 (1H, d{dd}, $J_{3a,3}$=3.0 Hz, $J_{3a,11b}$=8.3 Hz, $J_{3a,4}$=11.0 Hz, H-3a), 2.18 (1H, m, $\mathit{CH}HCH_2CH_2O$), 2.09 (3H, m, $CH\mathit{HCH_2}CH_2O$); *m*/*z* 611/613 (M^+).

Compound *4* (*n*=1). Yield (12 mg, 12%); pale yellow solid; mp 210–213°C; [Found: C, 59.18; H, 2.99. $C_{30}H_{18}Cl_2O_6S_2$ requires C, 59.11; H, 2.95%]; ν_{max} (cm^{-1}) 1644 (C=O), 1635 (C=O); λ_{max} THF (ε) 348 nm (20 900), 324 nm (21 100), 259 nm (23 000); δ_H ($CDCl_3$) 8.25 (1H, d, J_m=2.4 Hz, H-7), 8.11 (1H, d, J_m=2.4 Hz, H-5′), 7.90 (1H, dd, $J_{3'',4''}$=3.6 Hz, $J_{3'',5''}$=1.0 Hz, H-3″), 7.60 (4H, m, H-2,9,7′,5″), 7.48 (1H, d, J_o=8.9 Hz, H-10), 7.45 (1H, d, J_o=8.9 Hz, H-8′), 7.20 (1H, dd, $J_{4'',3''}$=3.6 Hz, $J_{4'',5''}$=5.1 Hz, H-4″), 7.06 (1H, d, $J_{3,2}$=4.9 Hz, H-3), 5.77 (1H, dd, *J*=3.9, 8.4 Hz, H-4), 4.35 (1H, m, $CH_2CH_2CH\mathit{H}O$), 4.26 (1H, m, $CH_2CH_2\mathit{CH}HO$), 2.32 (2H, m, $\mathit{CH_2}CH_2CH_2O$), 2.19 (2H, m, $CH_2\mathit{CH_2}CH_2O$); *m*/*z* 609/611 (M^+).

5.2.3. Photolysis of 1,3-bis[6′-chloro-2′-(2″-thienyl)-4′-oxo-4′*H*-1-benzopyran-3-oxy]-propane, 1c (*n*=2).

A benzene solution (100 mL) of **1c** (100 mg, 0.00017 mol) was irradiated for 45 min under the similar conditions as employed earlier for **1d**. The photolysate on chromatographic separation over a column silica-gel (100–200 mesh) yielded starting compound **1c** (62 mg, co-tlc & mmp), **3** (*n*=0) and **4** (*n*=0).

Compound **3** (*n*=0). Yield (10 mg, 10%); pale yellow solid; mp 208–211°C; [Found: C, 58.34; H, 3.07. $C_{29}H_{18}Cl_2O_6S_2$ requires C, 58.29; H, 3.01%]; ν_{max} (cm^{-1}) 1650 (C=O), 1643 (C=O); λ_{max} THF (ε) 326 nm (22 000), 285 nm (11 500), 242 nm (26 500); δ_H ($CDCl_3$) 8.06 (1H, d, J_m=2.6 Hz, H-7), 8.00 (1H, d, J_m=2.9 Hz, H-5′), 7.92 (1H, dd, $J_{3'',4''}$=3.7 Hz, $J_{3'',5''}$=1.2 Hz, H-3″), 7.69 (1H, dd, $J_{5'',4''}$=4.8 Hz, $J_{5'',3''}$=1.2 Hz, H-5″), 7.65 (2H, m, H-9,7′), 7.54 (2H, d, J_o=8.9 Hz, H-10,8′), 7.24 (1H, dd, $J_{4'',3''}$=3.7 Hz, $J_{4'',5''}$=4.8 Hz, H-4″), 6.31 (1H, dd, *J*=6.2, 2.8 Hz, H-2), 5.79 (1H, dd, $J_{3,2}$=6.1 Hz, $J_{3,3a}$=2.0 Hz, H-3), 4.99 (1H, d, $J_{11b,3a}$=8.9 Hz, H-11b), 4.45 (2H, m, $CH_2\mathit{CH_2}O$), 4.16 (1H, d{t}, J_{vic}=5.2 Hz, $J_{4,3a}$=9.2 Hz, H-4), 3.30 (1H, m, H-3a), 2.54 (2H, m, $\mathit{CH_2}CH_2O$); *m*/*z* 597/599 (M^+).

Compound **4** (*n*=0). Yield (15 mg, 15%); pale yellow solid; mp 230–232°C; [Found: C, 58.55; H, 2.77. $C_{29}H_{16}Cl_2O_6S_2$ requires C, 58.49; H, 2.69%]; ν_{max} (cm^{-1}) 1648 (C=O), 1636 (C=O); λ_{max} THF (ε) 348 nm (24 000), 325 nm (24 200), 260 nm (23 800); δ_H ($CDCl_3$) 8.26 (1H, d, J_m=2.7 Hz, H-7), 8.18 (1H, d, J_m=2.7 Hz, H-5′), 7.98 (1H, dd, $J_{3'',4''}$=3.7 Hz, $J_{3'',5''}$=1.1 Hz, H-3″), 7.65 (1H, d, $J_{2,3}$=4.9 Hz, H-2), 7.64 (1H, dd, $J_{5'',4''}$=5.0 Hz, $J_{5'',3''}$=1.1 Hz, H-5″), 7.60 (2H, dd, $J_{m,o}$=2.7, 8.9 Hz, H-9,7′), 7.50 (1H, d, J_o=8.9 Hz, H-10), 7.47 (1H, d, J_o=9.0 Hz, H-8′), 7.37 (1H, d, $J_{3,2}$=4.9 Hz, H-3), 7.22 (1H, dd, $J_{4'',5''}$=5.0 Hz, $J_{4'',3''}$=3.7 Hz, H-4″), 6.00 (1H, t, J_{vic}=6.6 Hz, H-4), 4.48 (1H, m, $CH_2\mathit{CH}HO$), 4.37 (1H, m, $CH_2CH\mathit{H}O$), 2.71 (1H, m, $\mathit{CH}HCH_2O$), 2.56 (1H, m, $CH\mathit{H}CH_2O$); *m*/*z* 595/597 (M^+).

5.2.4. Photolysis of 1,5-bis[6′-chloro-2′-phenyl-4′-oxo-4′*H*-1-benzopyran-3-oxy]-pentane, 2a (*n*=3).

A benzene solution (100 mL) of **2a** (100 mg, 0.00016 mol) was irradiated for 45 min under the similar conditions as employed earlier for **1d**. The photolysate on chromatographic separation over a column silica-gel (100–200 mesh) gave starting compound **2a** (25 mg, co-tlc & mmp), **6** (*n*=2), **7** (*n*=2) and **8** (*n*=1).

Compound **6** (*n*=2). Yield (5 mg, 5%); pale yellow solid; mp 115–118°C; [Found: C, 68.61; H, 4.28. $C_{35}H_{26}Cl_2O_6$ requires C, 68.51; H, 4.24%]; ν_{max} (cm^{-1}) 1653 (C=O), 1648 (C=O); λ_{max} THF (ε) 316 nm (16 800), 248 nm (27 700); δ_H ($CDCl_3$) 8.23 (1H, d, J_m=2.6 Hz, H-5′), 8.20 (1H, d, J_m=2.6 Hz, H-8), 8.07 (2H, m, H-2″,6″), 7.61 (1H, dd, $J_{m,o}$=2.6, 8.9 Hz, H-7′), 7.57 (1H, dd, $J_{m,o}$=2.6, 8.9 Hz, H-10), 7.49 (3H, m, H-3″,4″,5″), 7.38 (2H, d, J_o=8.9 Hz, H-11,8′), 6.67 (1H, br s, H-1), 5.95 (1H, dd, $J_{3,2a}$=2.0 Hz,

$J_{3,4}$=11.1 Hz, H-3), 5.75 (1H, d, $J_{4,3}$=11.1 Hz, H-4), 4.13 (1H, m, CH$_2$CH$_2$CH$_2$*CH*HO), 4.00 (1H, m, CH$_2$CH$_2$CH$_2$CH*H*O), 3.77 (1H, m, H-5), 3.20 (1H, br s, H-4a), 2.96 (2H, m, H-2a), 2.10 (3H, m, *CH*HCH$_2$*CH$_2$*CH$_2$O), 1.95 (3H, m, CH*HCH$_2$*CH$_2$CH$_2$O); *m*/*z* 613/615 (M$^+$).

Compound **7** (*n*=2). Yield (12 mg, 12%); pale yellow solid; mp 131–33°C; [Found: C, 68.65; H, 3.85. C$_{35}$H$_{24}$Cl$_2$O$_6$ requires C, 68.74; H, 3.93%]; $\nu_{\max}$ (cm^{-1}) 1646 (C=O), 1642 (C=O); $\lambda_{\max}$ THF (ε) 349 nm (15 000), 315 nm (16 500), 246 nm (26 000); δ_H (CDCl$_3$) 8.22 (1H, d, J_m=2.4 Hz, H-8), 8.13 (1H, d, J_m=2.4 Hz, H-5′), 8.05 (2H, m, H-2″,6″), 7.85 (1H, dd, *J*=2.0, 7.5 Hz, H-1), 7.61 (1H, dd, $J_\mathrm{m,o}$=2.4, 8.6 Hz, H-10), 7.57 (1H, dd, $J_\mathrm{m,o}$=2.4, 9.0 Hz, H-7′), 7.48 (7H, m, H-11, 8′,2,3,3″,4″,5″), 7.15 (1H, dd, *J*=2.7, 6.0 Hz, H-4), 5.30 (1H, dd, *J*=3.9, 8.1 Hz, H-5), 4.06 (1H, m, CH$_2$CH$_2$CH$_2$*CH*HO), 3.97 (1H, m, CH$_2$CH$_2$CH$_2$CH*H*O), 2.10 (1H, m, *CH*H–CH$_2$CH$_2$CH$_2$O), 1.75 (5H, m, CH*HCH$_2$CH$_2$*CH$_2$O); *m*/*z* 611/613 (M$^+$).

Compound **8** (*n*=1). Yield (12 mg, 12%); yellow solid; mp 145–148°C; [Found: C, 69.02; H, 3.57. C$_{35}$H$_{22}$Cl$_2$O$_6$ requires C, 68.96; H, 3.61%]; $\nu_{\max}$ (cm^{-1}) 1648 (C=O); 1611 $\lambda_{\max}$ THF (ε) 352 nm (19 400), 317 nm (19 000), 246 nm (25 000); δ_H (CDCl$_3$) 8.24 (1H, d, J_m=2.2 Hz, H-8), 8.20 (1H, d, J_m=2.2 Hz, H-8′), 7.86 (1H, dd, *J*=1.8, 7.5 Hz, H-1), 7.81 (1H, dd, *J*=1.2, 7.5 Hz, H-1′), 7.63 (1H, dd, $J_\mathrm{m,o}$=2.2, 9.0 Hz, H-10), 7.61 (1H, dd, $J_\mathrm{m,o}$=2.1, 9.0 Hz, H-10′), 7.49 (6H, m, H-2,2′,3,3′,11,11′), 7.22 (1H, dd, *J*=2.2, 6.6 Hz, H-4), 7.17 (1H, dd, *J*=2.2, 6.6 Hz, H-4′), 5.36 (1H, dd, *J*=4.0, 8.8 Hz, H-5), 5.31 (1H, dd, *J*=4.0, 8.3 Hz, H-5′), 2.10 (2H, m, *CH*H–CH$_2$*CH*H), 1.85 (4H, m, CH*HCH$_2$*CH*H*); *m*/*z* 609/611 (M$^+$).

5.2.5. Photolysis of 1,4-bis[6′-chloro-2′-phenyl-4′-oxo-4′*H*-1-benzopyran-3-oxy]-butane, 2b (*n*=2). A benzene solution (100 mL) of **2b** (100 mg, 0.00017 mol) was irradiated for 45 min under the similar conditions as employed earlier for **1d**. The photolysate on chromatographic separation over a column silica-gel (100–200 mesh) provided starting compound **2b** (60 mg, co-tlc & mmp), **6** (*n*=1) and **7** (*n*=1).

Compound **6** (*n*=1). Yield (5 mg, 5%); pale yellow solid; mp 125–127°C; [Found: C, 68.17; H, 4.07. C$_{34}$H$_{24}$Cl$_2$O$_6$ requires C, 68.11; H, 4.00%]; $\nu_{\max}$ (cm^{-1}) 1656 (C=O), 1649 (C=O); $\lambda_{\max}$ THF (ε) 315 nm (20 000), 306 nm (19 700), 248 nm (26 000); δ_H (CDCl$_3$) 8.23 (1H, d, J_m=2.7 Hz, H-8), 8.19 (1H, d, J_m=2.7 Hz, H-5′), 8.01 (2H, dd, *J*=2.1, 7.8 Hz, H-2″,6″), 7.62 (2H, dd, $J_\mathrm{m,o}$=2.7, 8.9 Hz, H-10,7′), 7.51 (3H, m, H-3″,4″,5″), 7.38 (2H, d, J_o=8.9 Hz, H-11,8′), 6.67 (1H, d, $J_{1,2\mathrm{a}}$=1.5 Hz, H-1), 5.96 (1H, dd, $J_{3,2\mathrm{a}}$=2.0 Hz, $J_{3,4}$=11.8 Hz, H-3), 5.75 (1H, d, $J_{4,3}$=11.8 Hz, H-4), 4.13 (2H, m, CH$_2$CH$_2$*CH$_2$*O), 3.77 (1H, m, H-5), 3.10 (1H, m, H-4a), 3.01 (2H, m, H-2a), 2.20 (2H, m, *CH$_2$*CH$_2$CH$_2$O), 1.95 (2H, m, CH$_2$*CH$_2$*CH$_2$O); *m*/*z* 599/601 (M$^+$).

Compound **7** (*n*=1). Yield (25 mg, 25%); pale yellow solid; mp 142–143°C; [Found: C, 68.40; H, 3.73. C$_{34}$H$_{22}$Cl$_2$O$_6$ requires C, 68.34; H, 3.68%]; $\nu_{\max}$ (cm^{-1}) 1646 (C=O), 1640 (C=O); $\lambda_{\max}$ THF (ε) 348 nm (17 600), 313 nm (16 400), 247 nm (25 000); δ_H (CDCl$_3$) 8.23 (1H, d, J_m=2.3 Hz, H-8), 8.13 (1H, d, J_m=2.3 Hz, H-5′), 8.01 (2H, m, H-2″,6″), 7.84 (1H, dd, *J*=2.0, 7.4 Hz, H-1), 7.61 (1H, dd, $J_\mathrm{m,o}$=2.3, 8.9 Hz, H-10), 7.58 (1H, dd, $J_\mathrm{m,o}$=2.3, 8.9 Hz, H-7′), 7.49 (5H, m, H-2,3,3″,4″,5″), 7.45 (2H, d, J_o=8.9 Hz, H-8′,11), 7.21 (1H, dd, *J*=2.4, 6.6 Hz, H-4), 5.42 (1H, dd, *J*=3.7, 9.5 Hz, H-5), 4.13 (1H, m, CH$_2$CH$_2$*CH*HO), 3.99 (1H, m, CH$_2$CH$_2$CH*H*O), 2.17 (1H, m, *CH*HCH$_2$CH$_2$O), 1.95 (3H, m, CH*HCH$_2$*CH$_2$O); *m*/*z* 597/599 (M$^+$).

5.2.6. Photolysis of 1,3-bis[6′-chloro-2′-phenyl-4′-oxo-4′*H*-1-benzopyran-3-oxy]-propane, 2c (*n*=1). A benzene solution (100 mL) of **2c** (100 mg, 0.00017 mol) was irradiated for 45 min under the similar conditions as employed earlier for **1d**. The photolysate on chromatographic separation over a column silica-gel (100–200 mesh) furnished starting compound **2c** (63 mg, co-tlc & mmp), **6** (*n*=0) and **7** (*n*=0).

Compound **6** (*n*=0). Yield (5 mg, 5%); pale yellow solid; mp 150–153°C; [Found: C, 67.61; H, 3.83. C$_{33}$H$_{22}$Cl$_2$O$_6$ requires C, 67.69; H, 3.76%]; $\nu_{\max}$ (cm^{-1}) 1653 (C=O); 1648 (C=O), $\lambda_{\max}$ THF (ε) 315 nm (16 200), 308 nm (18 700), 247 nm (23 800); δ_H (CDCl$_3$) 8.24 (1H, d, J_m=2.6 Hz, H-5′), 8.19 (1H, d, J_m=2.5 Hz, H-8), 8.01 (2H, m, H-2″,6″), 7.60 (2H, dd, $J_\mathrm{m,o}$=2.5, 8.9 Hz, H-10,7′), 7.52 (3H, m, H-3″,4″,5″), 7.38 (2H, d, J_o=8.9 Hz, H-11,8′), 6.60 (1H, br s, H-1), 5.95 (1H, dd, $J_{3,2\mathrm{a}}$=1.2 Hz, $J_{3,4}$=11.6 Hz, H-3), 5.73 (1H, d, $J_{4,3}$=11.6 Hz, H-4), 4.12 (2H, m, CH$_2$*CH$_2$*O), 3.76 (1H, dd, *J*=7.5, 7.9 Hz, H-5), 2.98 (1H, m, H-4a), 2.17 (2H, m, H-2a), 1.82 (2H, m, *CH$_2$*CH$_2$O); *m*/*z* 585/587 (M$^+$).

Compound **7** (*n*=0). Yield (25 mg, 25%); pale yellow solid; mp 202–204°C; [Found: C, 67.85; H, 3.52. C$_{33}$H$_{20}$Cl$_2$O$_6$ requires C, 67.92; H, 3.43%]; $\nu_{\max}$ (cm^{-1}) 1648 (C=O), 1644 (C=O); $\lambda_{\max}$ THF (ε) 349 nm (18 900), 316 nm (19 300), 247 nm (29 500); δ_H (CDCl$_3$) 8.22 (1H, d, J_m=2.4 Hz, H-8), 8.20 (1H, d, J_m=2.4 Hz, H-5′), 8.07 (2H, dd, *J*=1.5, 8.1 Hz, H-2″,6″), 7.84 (1H, dd, *J*=2.0, 6.0 Hz, H-1), 7.62 (2H, m, H-10,7′), 7.50 (5H, m, H-2,3,3″,4″,5″), 7.44 (2H, m, H-11,8′), 7.24 (1H, dd, *J*=1.8, 6.9 Hz, H-4), 5.55 (1H, dd, *J*=5.5, 8.4 Hz, H-5), 4.25 (2H, t, J_{vic}=6.0 Hz, CH$_2$*CH$_2$*O), 2.40 (1H, m, *CH*HCH$_2$O), 2.19 (1H, m, CH*H*CH$_2$O)); *m*/*z* 583/585 (M$^+$).

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