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Solid State Photochemistry of Isocoumarins and Isothiocoumarins

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Abstract—1*H*-2-Benzothiopyran-1-ones (isothiocoumarins) and 1*H*-2-benzopyran-1-ones (isocoumarins) behave dissimilarly on solid state irradiation at room temperature as the former photocyclodimerize efficiently while the latter only undergo slow photodecomposition. Both 4*H*-naphtho[2,1-*c*]pyran-4-one and thiopyran-4-one turn out to be photostable under these same reaction conditions. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Despite the fact that the isocoumarin skeleton is found in a variety of natural products,[1] the photodimerization of isocoumarin (**1a**) itself and of derivatives with an unsubstituted olefinic double bond has not been investigated. The only relevant example in the literature[2] reports the photodimerization of 3-phenylisocoumarin—a molecule containing a fixed stilbene moiety—on sunlight irradiation. The parent isothiocoumarin (**2a**) has been found[3] to photodimerize efficiently on solid state irradiation. Here we report on the synthesis of novel isocoumarins and isothiocoumarins and on their comparative behaviour on solid state irradiations.

Results

Our synthetic approach (Scheme 1) to isocoumarins **1b–d** and isothiocoumarins **2b–d** includes pyranones **3** as common intermediate; compounds **3** are easily accessible from 2-arylethanols **4** via their MEM-derivatives **5**,[4] cyclization[5] to isochromans **6** and subsequent oxidation.[6] Conversion of **3** to isocoumarins **1** is achieved by a bromination/dehydrobromination sequence[7] without purification of the intermediate 4-bromoisochromanone. Treatment of **3** with the anion of α-mercaptotoluene[8] affords carboxylic acids **7** which on treatment with trifluoroacetic acid anhydride cyclize to thiopyranones **8**. Finally, bromination of **8** with NBS in boiling CCl_4 gives bromothiopyranones **9**, which after purification are then treated with triethylamine to give isothiocoumarins **2**. For comparative purpose the UV-absorption spectra of **1b** and **2b** in solution are also shown (Scheme 1). X-Ray structure analyses for naphthopyranone **1d** and naphthothiopyranone **2d** (Scheme 2) were performed.

Irradiation (350 nm) of **2b** as homogeneous solid film leads to the selective (94%) formation of the *HH-cis-cisoid-cis* photocyclodimer **10b** and traces (6%) of the *HT-cis-cisoid-cis* dimer **11b** (monitoring by ^{1}H NMR). Dimer **10b** was isolated and purified by chromatography. Similarly, irradiation of **2c** affords a 4:5 mixture of dimers **10c** and **11c** (Scheme 3) which were not separated. The structure assignment for these dimers stems from ^{1}H NMR analysis of the $AA'XX'$ signals of the cyclobutane protons.[9] Irradiation (300 nm) of either **1b** or **1c** as solid film leads to photodegradation of the starting material, only traces of dimers being detectable by ^{1}H NMR analysis. Finally, both naphtho-derivatives **1d** and **2d** turn out to be photostable under these conditions.

Discussion

To a certain extent the behaviour of isothiocoumarins **2a–c** on solid state photodimerization parallels that of both coumarins[10] and thiocoumarins.[9] For **2a** we have shown[3] that the selective formation of the *HH-cis-cisoid-cis* photocyclodimer proceeds according to well-established topochemical principles.[11] The fact that this same selectivity is observed for **2b** (with the methyl substituent located far away from the reactive C–C double bond) but not for **2c** (with the trifluoromethyl group in proximity of the reactive centre), might indicate that in addition to the role of packing in the crystal—a favourable arrangement of the olefin moieties allowing both photochemical dimerization modes—there is also a pronounced effect of the site of the substituent on the benzene ring on product formation. For **2d** X-ray structural data indicate that the distance

Keywords: isocoumarins; isothiocoumarins; photodimerization; cyclobutanes.

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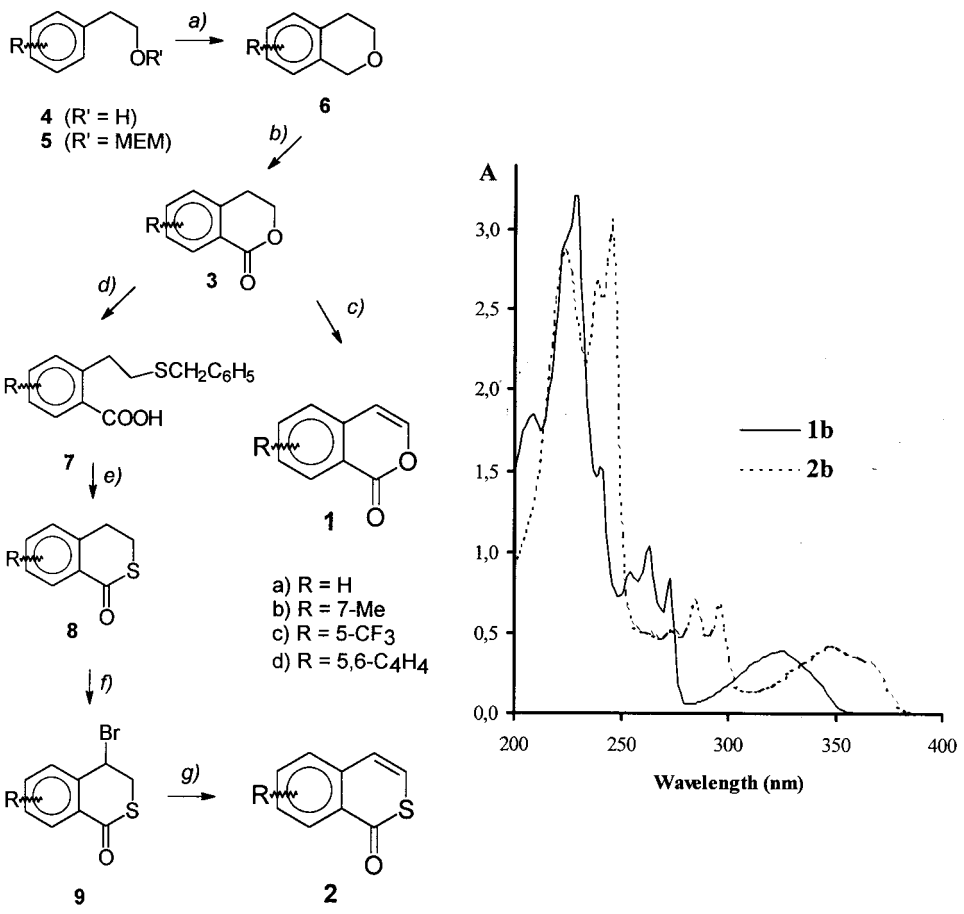
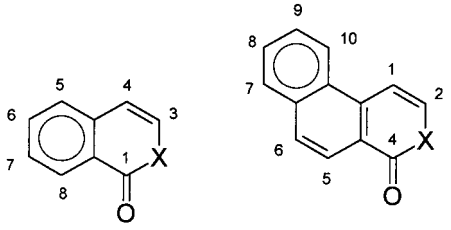


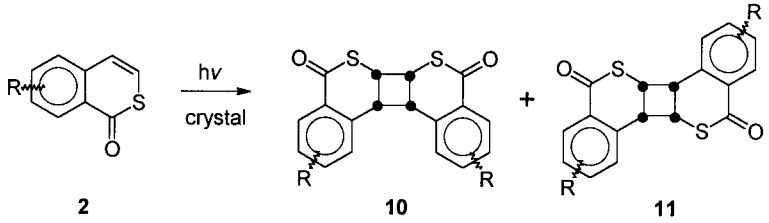
Scheme 1. Synthesis of isocoumarins **1** and isothiocoumarins **2** [(a) $TiCl_4$; (b) PCC; (c) NBS/Et_3N; (d) $C_6H_5CH_3S^-$; (e) TFAA; (f) NBS; (g) Et_3N] and UV-spectrum of **1b** and **2b** (0.1 mmol l^{-1} in CH_3CN)



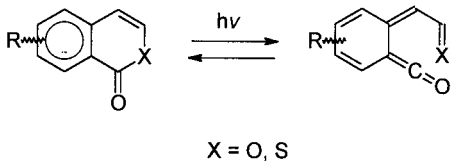
Scheme 2. Numbering of isocoumarins, isothiocoumarins, and naphthocompounds **1d** and **2d**.

between two C–C double bonds (>4.81 Å) is too large, thus preventing dimerization.

In contrast, the reluctance of isocoumarins **1a–c** to photodimerize is surprising. A comparison of X-ray structural parameters for **1** and **2** shows the expected longer bond lengths for the C–S (174 ppm) vs C–O (136 ppm) bonds and smaller bond angles for the C–S–C (104°) vs C–O–C (121°) group, but the bond length for the olefinic double bond (133.3 pm) is identical for both heterocycles. It is well known[12] that the structural parameters mentioned above have important effects on *intramolecular* photochemical reactions and therefore the different tendencies of undergoing photodimerization of **1a–c** and **2a–c** could be due to a more efficient *monomolecular* side reaction of excited **1**. One such possibility would be a—reversible—electrocyclic ring opening/closure (Scheme 4), wherein the



Scheme 3. Photodimerization of **2b** and **2c**.



Scheme 4. Electrocyclic ring opening of isocoumarins and isothiocoumarins.

relative stability of the ring open product should be greater for X=O due to the much higher bond energy of a C=O bond as compared to a C=S double bond. The fact that isocoumarins also undergo slow photodegradation in solution while, again in solution—isothiocoumarins undergo bimolecular photoreactions efficiently tends to support this interpretation. Further studies aimed at trapping the proposed ketene intermediates are in progress.

Experimental

General

Photolyses were performed in a *Rayonet RPR-100* photoreactor equipped with either 300 or 350-nm lamps. Chromatographic purification was accomplished with 230–400 mesh silica gel. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 and 125.8 MHz, resp.; chemical shifts in ppm rel. to TMS (=0 ppm), coupling constants J in Hz. UV spectra (nm, log ϵ) were obtained on a *Perkin–Elmer Lambda20* spectrometer in CH_3CN as solvent. Mass spectra (m/z) were measured at 70 eV. X-Ray analyses were run on a *Enraf-Nonius-CAD-4* four circle diffractometer at 293 K with CuK_α radiation (λ=1.54178 Å).

Procedure for the preparation of benzopyranones 3

The respective 2-arylethanols **4** are converted to their MEM-ethers **5** by treatment with MEM-Cl and ethyldiisopropylamine in dichloromethane for 24 h at rt;[4] cyclization to isochromanes **6** is achieved by reacting **5** with $TiCl_4$ in dichloromethane at −40° for 6 h[5] and oxidation to **3** with PCC in boiling dichloromethane[6] followed by purification by chromatography using dichloromethane as eluent.

7-Methyl-3,4-dihydro-1*H*-2-benzopyran-1-one (3b). 61%, mp cf.[13] ^{1}H NMR: δ=7.87 (d, J=1.02 Hz), 7.34 (dd, J=1.02 and 7.63 Hz), 7.15 (d, J=7.63 Hz), 4.49 and 3.00 ($AA'XX'$, 4H), 2.37 (s, 3H). ^{13}C NMR: δ=165.3, 137.4, 136.7, 134.5, 130.4, 125.0, 127.5, 67.5, 27.4, 21.0.

5-Trifluoromethyl-3,4-dihydro-1*H*-2-benzopyran-1-one (3c). 34%, mp 58°. ^{1}H NMR: δ=8.33 (d, J=8.10 Hz), 7.88 (d, J=7.63 Hz), 7.54 (dd, J=7.63 and 8.10 Hz), 4.57 and 3.25 ($AA'XX'$, 4H). ^{13}C NMR: δ=163.8, 138.2, 130.7 (q, J=5.1 Hz), 128.0 (q, J=31.5 Hz), 127.6, 127.2, 123.7 (q, J=273.7 Hz), 66.5, 25.0 (q, J=2.0 Hz).

1,2-Dihydro-4*H*-naphtho[2,1-*c*]pyran-4-one (3d). 74%, mp cf.[13] ^{1}H NMR: δ=8.11 (d, J=8.65 Hz), 8.02 (dd, J=6.61 and 2.80 Hz), 7.90 (dd, J=6.61 and 2.80 Hz), 7.83 (d, J=8.65 Hz), 7.63 (m, 2H), 4.66 and 3.43 ($AA'XX'$, 4H). ^{13}C NMR: δ=165.5, 138.5, 135.6, 129.8, 128.9, 128.7, 127.7, 127.2, 125.2, 124.4, 122.4, 66.7, 24.2.

Procedure for the preparation of isocoumarins 1

A mixture of 0.01 mol **3**, 0.12 mol *N*-bromosuccinimide and 20 mg AIBN in 25 ml CCl_4 was refluxed for 2 h, then cooled to rt and filtered. After evaporation of the solvent, triethylamine (25 ml) was added, the mixture refluxed for 1 h and the excess triethylamine evaporated. Ether (25 ml) and 2N HCl (5 ml) were added, the ethereal layer then separated, washed with saturated aq. NaCl and dried over $MgSO_4$. Purification was achieved by flash chromatography using ether/pentane 1:1 as eluent.

7-Methyl-1*H*-2-benzopyran-1-one (1b). 48%, mp 95°. ^{1}H NMR: δ=8.10 (d, J=1.0 Hz), 7.53 (dd, J=7.63 and 1.02 Hz), 7.33 (d, J=7.63 Hz), 7.23 (d, J=5.60 Hz), 6.47 (d, J=5.60 Hz), 2.47 (s, 3H). ^{13}C NMR: δ=162.4, 143.9, 138.1, 136.0, 134.0, 129.4, 125.5, 121.8, 106.9, 21.4. MS: 160 (M+., 80), 132 (100). UV: 324 (3.59), 273 (3.93), 263 (4.02), 254 (4.94), 241 (4.19), 229 (4.51), 208 (4.26). Anal. Calcd for $C_{10}H_8O_2$: C, 75.00; H, 5.03. Found: C, 74.98; H, 5.01.

5-Trifluoromethyl-1*H*-2-benzopyran-1-one (1c). 42%, mp 53°. ^{1}H NMR: δ=8.52 (d, J=7.88 Hz), 8.05 (d, J=7.88 Hz), 7.62 (dd, J=7.88 and 7.88 Hz), 7.38 (d, J=5.99 Hz), 6.80 (d, J=5.99 Hz). ^{13}C NMR: δ=160.9, 146.2, 134.1, 133.7, 132.1 (q, J=5 Hz), 127.9, 125.5 (q, J=31 Hz), 123.3 (q, J=274 Hz), 123.2, 103.0 (q, J=2.5 Hz). MS: 214 (M+., 70), 186 (100). UV: 317 (3.79), 279 (4.14), 270 (4.26), 260 (4.14), 238 (4.51), 230 (4.60), 225 (4.60), 200 (4.80). Anal. Calcd for $C_{10}H_5O_2F_3$: C, 56.09; H, 2.35. Found: C, 56.04; H, 2.34.

4*H*-Naphtho[2,1-*c*]pyran-4-one (1d). 90%, mp ^{1}H and ^{13}C NMR, MS, cf.[14] UV: 360 (3.68), 344 (3.70), 313 (3.93), 299 (3.87), 288 (3.69), 250 (4.65), 247 (4.68), 244 (4.65), 242 (4.63), 239 (4.62), 203 (4.26). Anal. Calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11. Found: C, 79.61; H, 4.04.

Procedure for the preparation of arenecarboxylic acids 7

Ring opening of pyranones **3** (0.03 mol) with the anion of α-mercaptotoluene and subsequent work-up according to[8] afforded the crude carboxylic acids **7** which were then recrystallized from ether.

2-(2′-Benzylthioethyl)-5-methylbenzenecarboxylic acid (7b). 99%, mp 98°. ^{1}H NMR: δ=7.87 (d, J=1.5 Hz), 7.35–7.18 (m, 6H), 7.14 (d, J=7.63 Hz), 3.73 (s, 2H), 3.25 and 2.72 ($AA'XX'$, 4H), 2.36 (s, 3H). ^{13}C NMR: δ=172.8, 140.3, 138.7, 136.4, 133.9, 132.3, 131.7, 128.9, 128.5, 127.7, 126.9, 36.4, 34.6, 32.9, 20.6.

2-(2′-Benzylthioethyl)-3-trifluoromethylbenzenecarboxylic acid (7c). 91%, mp 112°. ^{1}H NMR: δ=11.42 (s), 8.17 (d, J=8.1 Hz), 7.85 (d, J=8.1 Hz), 7.42 (dd, J=8.0 and 8.1 Hz), 7.37–7.23 (m, 5H), 3.80 (s, 2H), 3.49 and 2.72 ($AA'XX'$, 4H). ^{13}C NMR: δ=172.4, 141.7, 138.6, 135.1, 131.2, 130.7

(q, J=6.1 Hz), 128.8, 128.5, 128.4 (q, J=32.6 Hz), 126.9, 126.7, 124.2 (q, J=274.0 Hz), 36.5, 33.0, 30.7.

1-(2′-Benzylthioethyl)-napthalene-2-carboxylic acid (7d). 81%, mp 148°. ^{1}H NMR: δ=8.04 (d, J=8.6 Hz), 8.00 (d, J=8.6 Hz), 7.87 (dd, J=1.0 and 8.1 Hz), 7.78 (d, J=8.6 Hz), 7.56 (m, 2H), 7.39 (d, J=7.1 Hz), 7.32 (m, 2H), 3.86 (s, 2H), 3.78 and 2.86 ($AA'XX'$, 4H).

Procedure for the preparation of benzothiopyranones 8

Treatment of carboxylic acids **7** with trifluoroacetic acid anhydride and work-up according to[8] gave crude thiolactones **8** which were then purified by flash-chromatography using ether/pentane 1:1 as eluent.

7-Methyl-3,4-dihydro-1*H*-2-benzothiopyran-1-one (8b). 61%, mp 57°. ^{1}H NMR: δ=7.75 (d, J=1.40 Hz), 7.29 (dd, J=7.60 and 1.40 Hz), 7.13 (d, J=7.60 Hz), 3.25 and 3.18 ($AA'XX'$, 4H), 3.37 (s, 3H). ^{13}C NMR: δ=191.3, 138.1, 137.4, 134.0, 132.0, 129.9, 126.9, 30.0, 28.9, 20.9.

5-Trifluoromethyl-3,4-dihydro-1*H*-2-benzothiopyran-1-one (8c). 34%, mp 38°. ^{1}H NMR: δ=8.16 (d, J=7.90 Hz), 7.85 (d, J=7.50 Hz), 7.50 (dd, J=7.90 and 7.50 Hz), 3.41 and 3.30 ($AA'XX'$, 4H). ^{13}C NMR: δ=190.0, 139.6, 134.0, 130.5, 130.3 (q, J=6.1 Hz), 128.7 (q, J=30.0 Hz), 127.3, 123.8 (q, J=274.2 Hz), 27.7, 26.2 (q, J=2.0 Hz).

1,2-Dihydro-4*H*-naphtho[2,1-*c*]thiopyran-4-one (8d). 74%, mp 142°. ^{1}H NMR: δ=8.16 (m, 1H), 8.06 (d, J=8.50 Hz), 7.89 (m, 1H), 7.82 (d, J=8.50 Hz), 7.62 (m, 2H), 3.70 and 3.40 ($AA'XX'$, 4H). ^{13}C NMR: δ=191.4, 139.6, 135.5, 130.8, 129.8, 128.9, 128.4, 127.5, 127.1, 124.6, 122.8, 27.9, 25.1.

Procedure for preparation of bromothiopyranones 9

A mixture of thiopyranone **8** (0.01 mol), NBS (0.015 mol) and 20 mg AIBN in CCl_4 (20 ml) was refluxed for 2 h, then cooled to rt and filtered. After evaporation of the solvent the residue was purified by flash-chromatography using ether/pentane 1:1 as eluent.

4-Bromo-7-methyl-3,4-dihydro-1*H*-2-benzothiopyran-1-one (9b). 36%, mp 45° (dec.). ^{1}H NMR: δ=7.82 (d, J=0.95 Hz), 7.37 (d, J=7.88 and 0.95 Hz), 7.32 (*d*, J=7.88 Hz), 4.57 (dd, J=2.84 and 4.41 Hz), 3.93 (dd, J=2.84 and 14.03 Hz), 3.47 (dd, J=4.41 and 14.03 Hz), 2.39 (*s*, 3H).

4-Bromo-5-trifluoromethyl-3,4-dihydro-1*H*-2-benzothiopyran-1-one (9c). 34%, mp 52°(dec.). ^{1}H NMR: δ=8.21 (d, J=7.35 Hz), 7.91 (d, J=8.4 Hz), 7.63 (dd, J=8.4 and 7.35 Hz), 5.99 (dd, J=3.06 and 4.06), 3.93 (dd, J=3.06 and 14.25 Hz), 3.54 (dd, J=4.06 and 14.25 Hz). ^{13}C NMR: δ=188.2, 139.0, 132.5, 131.4, 130.8 (q, J=5.6 Hz), 129.8, 127.1 (q, J=30.5 Hz), 123.4 (q, J=274.7 Hz), 39.1 (q, J=2.5 Hz), 36.8.

1-Bromo-1,2-dihydro-4*H*-naphtho[2,1-c]thiopyran-4-one (9d). 32%, mp 70° (dec.). ^{1}H NMR: δ=8.25 (d, J=8.70 Hz), 8.09 (d, J=8.70 Hz), 7.94 (m, 2H), 7.71 (m, 2H), 6.36 (dd, J=2.54 and 3.56 Hz), 4.05 (dd, J=2.54 and 14.75 Hz), 3.60 (dd, J=3.56 and 14.75 Hz). ^{13}C NMR: δ=189.3, 137.7, 135.8, 130.2, 129.0, 128.9, 128.1, 128.0, 127.9, 124.1, 122.7, 40.5, 37.1.

Procedure for the preparation of isothiocoumarins 2

A solution of bromothiolactone **9** (0.003 mol) in triethylamine (5 ml) was refluxed for 1 h and the excess triethylamine evaporated. Ether (10 ml) and 2N HCl (2 ml) were added, the ethereal layer then separated, washed with saturated aq. NaCl and dried over $MgSO_4$. Purification was achieved by flash chromatography using ether/pentane 1:1 as eluent.

7-Methyl-1*H*-2-benzothiopyran-1-one (2b). 78%, mp 54°. ^{1}H NMR: δ=8.12 (d, J=1.52 Hz), 7.54 (dd, J=7.89 and 1.52 Hz), 7.47 (d, J=7.89 Hz), 7.14 (d, J=9.92 Hz), 7.03 (d, J=9.92 Hz), 2.49 (s, 3H). ^{13}C NMR: δ=186.7, 139.3, 135.6, 135.0, 130.1, 128.9, 125.5, 124.0, 121.7, 21.5. MS: 176.2 (M+., 100), 147.2 (90). UV: 349 (3.63), 296 (3.83), 284 (3.84), 274 (3.72), 245 (4.49), 238 (443), 223 (4.46). Anal. Calcd for $C_{10}H_8OS$: C, 68.15; H, 4.58; S, 18.19. Found: C, 68.12; H, 4.58; S, 18.21.

5-Trifluoromethyl-1*H*-2-benzothiopyran-1-one (2c). 87%, mp 82°. ^{1}H NMR: δ=8.56 (d, J=8.14 Hz), 8.08 (d, J=7.63 Hz), 7.65 (dd, J=8.14 and 7.63 Hz), 7.54 (d, J=10.17 Hz), 7.30 (d, J=10.17 Hz). ^{13}C NMR: δ=185.2, 135.0, 131.4 (q, J=5 Hz), 130.1, 130.0, 127.9, 127.8, 127.7 (q, J=31 Hz), 123.8 (q, J=275 Hz), 117.0 (q, J=3 Hz). MS: 230 (M+., 99), 202 (100). UV: 343 (3.52), 306 (3.81), 2.95 (3.83), 264 (3.68), 256 (3.65), 242 (4.22), 236 (4.20), 219 (4.55). Anal. Calcd for $C_{10}H_5OF_3S$: C, 52.17; H, 2.19; S, 13.93. Found: C, 52.16; H, 2.18; S, 13.86.

4*H*-Naphtho[2,1-*c*]thiopyran-4-one (2d). 92%, mp 148°. ^{1}H NMR: δ=8.49 (m, 1H), 8.34 (d, J=9.16 Hz), 8.13 (d, J=10.17 Hz), 7.94 (m, 2H), 7.70 (m, 2H), 7.43 (d, J=10.17 Hz). ^{13}C NMR: δ=186.2, 136.0, 135.5, 130.0, 129.4, 129.1, 129.0, 127.5, 127.4, 123.0, 124.2, 121.5, 116.4. MS: 212.1 (M^+., 85), 184 (100). UV: 385 (3.67), 367 (3.72), 325 (3.82), 311 (3.80), 298 (3.73), 265 (4.78), 261 (4.64), 257 (4.69), 254 (4.78), 222 (4.13), 213 (4.30), 208 (4.30). Anal. Calcd for $C_{13}H_8OS$: C, 73.56; H, 3.79; S, 15.11. Found: C, 73.63; H, 3.78; S, 15.04.

Crystal structure determination of 1d. Pale yellow transparent blocks (0.40×0.60×0.70 mm^3) from dichloromethane, $C_{13}H_8O_2$, M=196.20, monoclinic, $P2_1/n$, Z=4, a=7.1881(17), b=7.8160(16), c=16.183(4) Å, β=95.87(2)°, V=904.4(4) Å^3, D_x=1.4410(6) g cm^{-3}, F(000)=408, μ=0.79 mm^{-1}. The cell parameters were determined by least-square refinement against the setting angles of 25 reflections, Θ=22.6–42.8°. Of the 1899 independent reflections (Θ_{max}=76.4°), 1851 were considered to be observed [$I>2(I)$]. Final R value for all reflections R=0.0818 ($\omega R2$=0.2395).†

† Crystallographic data were deposited (CCDC 139670 for **1d**/CCDC 139671 for **2d**) with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

Crystal structure determination of 2d. Pale yellow transparent blocks ($0.35\times0.70\times0.80\ mm^3$) from dichloromethane, $C_{13}H_8OS$, M=212.26, monoclinic, $P2_1/c$, Z=4, a=10.3305(15), b=8.590(2), c=11.757(3) Å, β=109.016(17)°, V=986.4(4) Å^3, D_x=1.429 g cm^{-3}, $F(000)$=440, μ=2.61 mm^{-1}. The cell parameters were determined by least-square refinement against the setting angles of 25 reflections, Θ=23.4–43.1°. Of the 2067 independent reflections (Θ_{max}=76.4°), 1869 were considered to be observed[$I>2(I)$]. Final R value for all reflections R=0.0853 ($\omega R2$=0.2288).†

Photodimerization experiments. Solutions of 0.1 mmol of **1** or **2** in dichloromethane (1 ml) in a 5 ml tapered flask were slowly evaporated to produce a homogeneous solid film. The flask was then purged with Ar and irradiated (**1** with λ=300 nm, **2** with λ=350 nm) for 12 h, the progress of the reaction being monitored by ^{1}H NMR spectroscopy. In this period isocoumarins **1b** and **1c** underwent slow degradation to non-dimeric material and the naphtho-derivatives **1d** and **2d** remained unaltered. For **2b** and **2c** the solid residue was separated by preparative thin layer chromatography using ether/pentane 1:1 as eluent. *Irradiation of* ***2b***. ^{1}H NMR indicates the formation of two dimers **10b** and **11b** in a 94:6 ratio, the degree of conversion of **2b** reaching a constant level at 80%. Chromatography afforded 10.5 mg (75%) of *6aα,6bα,12bα,12cα-3,10-dimethyl-tetrahydrocyclobuta[1,2-*c*;4,3-*c′*]bis([2]benzothiopyran)-5,8-dione* (**10b**). Mp 178–183°, ^{1}H NMR δ=7.72 (*s*, 2H), 7.08 (d, J=7.9 Hz, 2H), 6.62 (d, J=7.9 Hz, 2H), 4.81 and 4.48 ($AA'XX'$, $J_{AA'}$=8.5 Hz, J_{AX}=8.3 Hz, $J_{AX'}$=1.5 Hz, $J_{XX'}$=−5.5 Hz, 4H), 2.30 (s, 6H). ^{13}C NMR δ=188, 139, 134, 132, 128, 127, 46.9, 43.0, 20.3. The corresponding ^{1}H NMR data for the cyclobutane hydrogens of **11b** are: 4.82 and 4.44 ($AA'XX'$, J_{AX}=J_{AX}=8.05 Hz, $J_{AA'}$=$J_{XX'}$=0 Hz, 4H).

Irradiation of 2c. ^{1}H NMR indicates the formation of two dimers **10c** and **11c** in a 45:55 ratio, the degree of conversion of **2c** reaching a constant level at 65%. Chromatography afforded 11 mg (80%) of a 1:1 mixture of *6aα,6bα,12bα,12cα-1,12-(bis)trifluoromethyl-tetrahydrocyclobuta[1,2-*c*;4,3-*c′*]bis([2]benzothiopyran)-5,8-dione* (**10c**), ^{1}H NMR δ=8.37 (d, J=7.9 Hz, 2H), 7.97 (d, J=7.8 Hz, 2H), 7.60 (dd, J=7.8 and 7.9 Hz, 2H), 5.10 and 4.90 ($AA'XX'$, $J_{AA'}$=8.5 Hz, J_{AX}=8.3 Hz, $J_{AX'}$=1.5 Hz, $J_{XX'}$=−5.5 Hz, 4H) and of *6aα,6bα,12aα,12bα-1,7-(bis)trifluoromethyl-tetrahydrocyclobuta[1,2-*c*;3,4-*c′*]bis-([2]benzothiopyran)-5,11-dione* (**11c**), ^{1}H NMR δ=8.09 (d, J=7.9 Hz, 2H), 7.65 (d, J=7.9 Hz, 2H), 7.44 (dd, J=7.8 and 7.9 Hz, 2H), 5.10 and 4.90 ($AA'XX'$, J_{AX}=$J_{AX'}$=7.8 Hz, $J_{AA'}$=$J_{XX'}$=0 Hz, 4H).

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References

1. Hill, R. A. *Naturally Occuring Isocoumarins*. In *Progress in the Chemistry of Natural Compounds*; 1986; Vol. 49, p 1.
2. Schoenberg, A.; Latif, N.; Moubasher, R.; Awad, W. I. *J. Chem. Soc.* **1950**, 374.
3. Bethke, J.; Margaretha, P.; Kopf, J.; Pignon, B.; Dupont, L.; Christiaens, L. *Helv. Chim. Acta* **1997**, *80*, 1865.
4. Corey, E. J.; Gras, J. L.; Ulrich, P. *Tetrahedron Lett.* **1976**, *17*, 809.
5. Mohler, D. L.; Thompson, D. W. *Tetrahedron Lett.* **1987**, *28*, 2567.
6. Bonadies, F.; Di Fabio, R. *J. Org. Chem.* **1984**, *49*, 1647.
7. Sristava, J. N.; Chaudhury, D. N. *J. Org. Chem.* **1962**, *27*, 4337.
8. Lumma, W. C.; Dutra, G. A.; Voeker, C. A. *J. Org. Chem.* **1970**, *35*, 3442.
9. Klaus, C. P.; Thiemann, C.; Kopf, J.; Margaretha, P. *Helv. Chim. Acta* **1995**, *78*, 1079.
10. Gnanaguru, K.; Ramasubbu, N.; Venkatesan, K.; Ramamurthy, V. *J. Org. Chem.* **1985**, *50*, 2337.
11. Venkatesan, K.; Ramamurthy, V. *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991, p 133.
12. Margaretha, P. In *Molecular and Supramolecular Photochemistry*, Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 1997; Vol. 1, p 85.
13. Colonge, J.; Boisde, P. *Bull. Soc. Chim. Fr.* **1956**, 1337.
14. Stara, I. G.; Stary, I.; Kollarovic, A.; Teply, F.; Saman, D.; Fiedler, P. *Tetrahedron* **1998**, *54*, 11209.