Photochemical reactions of anthracene–naphthalene bichromophoric systems linked by a three-carbon chain

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Photochemical reactions of bichromophoric compounds having 9-anthryl and 1-naphthyl groups linked by a three-carbon chain have been investigated in solution and in the solid state. Direct photolysis of 1a–c,e–g in degassed benzene gave both cyclomers 2a–c,e–g and head-to-tail anthracene dimers 3a–c,e–g through intra- and inter-molecular [4 + 4] cycloaddition, respectively, while 1-acetoxy derivative 1d gave only cyclomer 2d. The reactivity for the cyclomerisation of 1a–g was lower than that of the bisanthracene system. The conjugated carbonyl group in 1e and 1f significantly retarded the reactions. On biacetyl sensitisation neither cyclomerisation nor dimerisation occurred, but alkene 1e underwent *cis–trans* isomerisation. In the solid state, (*E*)-1e gave dimer 3e in 22% yield, while the other compounds were photostable or gave the corresponding dimer in a lower yield. X-Ray structure analysis showed that in the crystal of (*E*)-1e adjacent anthracene rings related by an inversion centre were stacked with 3.45 Å separation, which was favourable for head-to-tail dimerisation.

Photochemistry of conjugatively or non-conjugatively linked bisanthracenes has been widely investigated.[1–5] A three-atom link facilitates formation of an intramolecular excimer due to possible sandwich-type overlap of two chromophores.[6] Propano-linked bisanthracenes showed no emission from the excimer,[3] but underwent intramolecular [4 + 4] cycloaddition (cyclomerisation) efficiently.[4,5] As for bichromophoric systems involving 9-anthryl and 1-naphthyl groups, 1-(9-anthryl)-3-(1-naphthyl)propane (**1a**)[7] and 9-(1-naphthylmethoxymethyl)anthracene ($AnCH_2OCH_2Nap$; An = 9-anthryl, Nap = 1-naphthyl)[8] were reported to undergo cyclomerisation in a dilute solution, while $AnCOOCH_2Nap$ underwent intermolecular [4 + 4] cycloaddition between the anthracene moieties (dimerisation).[7] These facts suggested that photochemical behaviour of the anthracene–naphthalene system should be sensitive to the structure of the linkage. As a part of the study on excited-state interactions between two aromatic chromophores in unsymmetrical bichromophoric systems, we have investigated photochemical reactions of **1a–i**. In this paper we discuss effects of the linkage structure on photochemical behaviour in solutions and in the solid state, especially selectivity between cyclomerisation and dimerisation. Furthermore, the reactivity is compared with that of bisanthracene or anthracene–phenyl systems containing a three-carbon link.

Results and discussion

Absorption and fluorescence spectra

The absorption spectra of **1a–g** in benzene or ethanol exhibited a structured absorption band in the range 330–390 nm due to an anthracene chromophore and a little broader structured band in the range 270–300 nm due to a naphthalene moiety or *ca.* 320 nm due to a naphthoyl moiety.

The fluorescence spectra of **1a–d** were quite similar to that of anthracene, which is characterised by distinct fine structure and a small Stokes shift ($\Delta\nu < 300$ cm^{-1}). It was reported that **1a** exhibited a weak exciplex emission,[8] but as for **1b–d**, exciplex fluorescence was too weak to be observed with a conventional fluorophotometer. When the naphthalene chromophore was excited, the fluorescence from the anthracene part was observed, indicating that the singlet energy transfer from the naphthalene to anthracene took place. The fluorescence spectra of (*E*)-**1e** and (*Z*)-**1e** were much broader than that of **1a–d**, and the Stokes shifts were larger [$\Delta\nu = 1250$ cm^{-1} for (*E*)-**1e**, 950 cm^{-1} for (*Z*)-**1e**]. A large Stokes shift is characteristic of vinylanthracene, which has a large dihedral angle between the vinyl group and the anthracene ring in the ground state and is flexible enough to cause geometrical change in the excited state.[4] The dihedral angle between the ethylene plane and the anthracene ring of (*E*)-**1e** in the crystal was 73(1)°, which was similar to that of (*Z*)-AnCH=CHPh (78.4°)[9] or (*Z*)-AnCH=CH-COPh (75.5°).[10] At room temperature **1f** did not fluoresce and it is likely that the excited singlet state of **1f** is deactivated by efficient intersystem crossing into the triplet state.† A cyclohexane solution of **1g** exhibited a weak fluorescence spectrum similar to that of **1a**, while in an ethanol solution **1g** did not fluoresce. The lack of fluorescence in the polar solvent was probably due to electron-transfer quenching by the aroyl chromophore, as was the case for $AnCH_2CH_2COPh$.[2]

Photochemical reactions in solutions

When a degassed benzene solution of **1a–g** was irradiated ($\lambda > 330$ nm), intramolecular [4 + 4] cycloaddition products (cyclomer) **2a–g** and intermolecular cycloaddition products (dimer) **3a–c,e–g** were obtained (Table 1, entry 1–8), as was reported for **1a**.[8] On dimerisation of **1b,c,e–g** only the head-to-tail dimer was obtained, while it was reported that 9-(arylmethoxymethyl)anthracenes gave both the head-to-head and the head-to-tail dimers.[12] The stereochemistry of the alkenic parts of **3e** was determined to be *trans* based on the coupling constant (17 Hz) between the alkenic protons. As for the cyclomers from **1b** and **1c**, two epimers can be formed. The ^1H NMR spectrum (in $CDCl_3$) of the cyclomer formed from **1b** indicated that it consisted of two epimers with a ratio of 5:1. When this mixture was acetylated, the methine proton adjacent to the OAc group in the major epimer resonated at a lower field (δ 5.95) than that in the minor one (δ 5.35), suggesting that the major isomer should be of the *exo*-form (**2c**). This assignment was confirmed by X-ray structure analysis (Fig. 1). In the case of **1c**, **2c** and **2c′** were formed in a ratio of 3.6:1. While **1c** having an acetoxy group in the γ-position to the anthryl group showed a slight preference of cyclomerisation over dimerisation,

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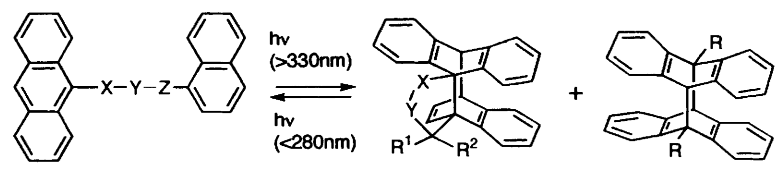
† In general, 9-anthryl ketones are non-fluorescent because of efficient intersystem crossing to the triplet state.[11]



1a–i **2a–g** **3a–c, e–g**

	X-Y-Z		X-Y	R^1	R^2		R
1a:	$CH_2CH_2CH_2$	**2a**:	CH_2CH_2	H	H	**3a**:	$CH_2CH_2CH_2$Nap
1b:	$CH_2CH_2CH(OH)$	**2b**:	CH_2CH_2	OH	H	**3b**:	$CH_2CH_2CH(OH)$Nap
		2b':	CH_2CH_2	H	OH		
1c:	$CH_2CH_2CH(OAc)$	**2c**:	CH_2CH_2	OAc	H	**3c**:	$CH_2CH_2CH(OAc)$Nap
		2c':	CH_2CH_2	H	OAc		
1d:	$CH(OAc)CH_2CH_2$	**2d**:	$CH(OAc)CH_2$	H	H	**3d**:	$CH(OAc)CH_2CH_2$Nap
1e:	$CH{=}CHCH_2$	**2e**:	$CH{=}CH$	H	H	**3e**:	$CH{=}CHCH_2$Nap
1f:	$COCH_2CH_2$	**2f**:	$COCH_2$	H	H	**3f**:	$COCH_2CH_2$Nap
1g:	CH_2CH_2CO	**2g**:	CH_2CH_2	=O		**3g**:	CH_2CH_2CONap
1h:	CH=CHCO (See Scheme 2)						(Nap=1-naphthyl)
1i:	COCH=CH						

Scheme 1

Table 1 Product yields of photochemical reactions of **1a–h** in a benzene solution and in the solid state

Entry	Comp.	Conc./mol dm^{-3}	Time/h	Conv. (%)	Products [yield (%)][a]	
1[b]	**1a**	2.0×10^{-3}	5	100	**2a** (56)	**3a** (44)[c]
2[b]	**1b**	1.9×10^{-3}	5	100	**2b** (36) + **2b'** (7)	**3b** (57)[c]
3[b]	**1c**	2.0×10^{-3}	6	100	**2c** (58) + **2c'** (16)	**3c** (21)[c]
4[b]	**1d**	1.8×10^{-3}	6	100	**2d** (>97)[d]	
5[b]	(*E*)-**1e**	2.1×10^{-3}	5	100	**2e** (54)	**3e** (40)[e]
6[b]	(*Z*)-**1e**	2.2×10^{-3}	5	100	**2e** (80)	**3e** (20)[d]
7[b]	**1f**	1.9×10^{-3}	6	44	**2f** (80)	**3f** (20)[d]
8[b]	**1g**	2.0×10^{-3}	6	44	**2g** (85)	**3g** (15)[d]
9[f]	**1b**	8.3×10^{-3}	0.5	57	**2b** (6) + **2b'** (1)	**3b** (68)[d]
10[f]	**1b**	8.3×10^{-3}	2	100	**2b** (16) + **2b'** (3)	**3b** (61)[d]
11[f]	**1d**	8.2×10^{-3}	2	100	**2d** (>97)[d]	
12[f]	**1f**	8.4×10^{-3}	22	64	**2f** (54)	**3f** (27)[d]
13[f]	**1g**	8.3×10^{-3}	3	34	**2g** (62)	**3g** (35)[d]
14[f]	**1g**	8.3×10^{-3}	14	100	**2g** (53)	**3g** (19)[d,g]
15[f]	$AnCO(CH_2)_2An$	8.0×10^{-3}	0.3	100	cyclomer (>97)[d]	
16	**1a**	Solid	41	13		**3a** (>97)[d]
17	**1b**	Solid	35	12		**3b** (>97)[c]
18	**1c**	Solid	55	0[d]	—	
19	**1d**	Solid	38	<5	**2d** (trace)	**3d** (trace)[c]
20	(*E*)-**1e**	Solid	41	22		**3e** (>97)[d]
21	**1f**	Solid	41	<5		**3f** (trace)[c]
22	(*E*)-**1h**	Solid	26	69	**4** (>97)[c]	

[a] Based on the consumed starting material. [b] 3 cm^3 of a sample solution was irradiated in a stoppered Pyrex test tube. [c] Determined by ^1H NMR integration ratio measured in $CDCl_3$. [d] Determined by ^1H NMR integration ratio measured in C_6D_6. [e] Isolated yields. [f] 0.6 cm^3 of a C_6D_6 solution was irradiated in a sealed NMR tube. [g] **3g** was partially decomposed during photolysis.

the α-acetoxy derivative **1d** exclusively gave cyclomer **2d** and the corresponding dimer was not detected by TLC or ^1H NMR spectroscopy even in a higher concentration (Table 1, entry 11). **2d** was a mixture of two epimers in a ratio of *ca.* 2 : 1, although the stereochemistry of each isomer could not be determined. Since $AnCH(OAc)CH_2CH_3$ gave the head-to-tail dimer in degassed benzene solution,[14] the presence of an α-acetoxy group in **1d** will not inhibit dimerisation. The selective formation of **2d** may be due to high population of a conformer favourable for cyclomerisation.

On monitoring the reaction of (*E*)-**1e** by NMR spectroscopy, no signal assigned to the *cis* isomer was detected, although **2e** was formed by cyclomerisation of (*Z*)-**1e**. This result is similar to that of (*E*)-$AnCH{=}CHCH_2An$, which gave the corresponding cyclomer without any spectroscopic evidence for intermediacy of the *cis* isomer.[4] (*Z*)-**1e**, separately prepared, also afforded **2e** and **3e** (Table 1, entry 6), and no dimers containing a *cis*-alkene were obtained. Rapid isomerisation from (*Z*)-**1e** to (*E*)-**1e** was confirmed in a dilute C_6D_6 solution ($< 1 \times 10^{-3}$ mol dm^{-3}) by ^1H NMR spectroscopy. Although the quantum efficiency for cyclomerisation of (*Z*)-**1e** might be much lower than that of (*Z*)-$AnCH{=}CHCH_2An$, it is likely that the isomerisation from (*Z*)-**1e** to (*E*)-**1e** took place more rapidly than the reverse isomerisation. As a result, when (*E*)-**1e** was irradiated, the concentration of (*Z*)-**1e** in the solution was considered too low to be detected by NMR spectroscopy.

In order to determine the spin multiplicity of the excited state involved in the reactions, photolysis of **1a**,**b**,**e**–**g** was carried out in the presence of biacetyl as a triplet sensitiser in degassed benzene solution with light $\lambda > 400$ nm.‡ Neither cyclomer (**2a**,**b**,**e**–**g**) nor dimer (**3a**,**b**,**e**–**g**) was formed and **1a**,**f**,**g** were completely recovered, while **1b** was partly decomposed. In the case of (*E*)-**1e** or (*Z*)-**1e** a photostationary mixture of the alkenes was obtained with a *Z*/*E* ratio of 1 : 1.6. These results indicated that both the cyclomerisation and the dimerisation of **1a**–**g** took place from the excited singlet state. The low reactivity of **1f** (Table 1, entries 7 and 12) is explained by efficient

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‡ The T_1 state of the anthracene (E_T 175 kJ mol^{-1}) is selectively generated, because E_T of the naphthalene moiety (250 kJ mol^{-1} for 1-methylnaphthalene) or naphthoyl (240 kJ mol^{-1} for 1-acetylnaphthalene) is higher than that of biacetyl (235 kJ mol^{-1}).[15]

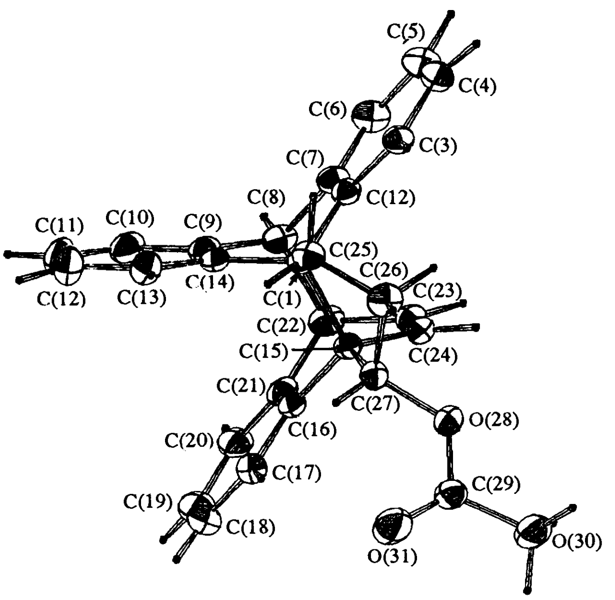


Fig. 1 ORTEP[13] diagram of **2c**. The anisotropic ellipsoids for non-H atoms enclose 30% probability.

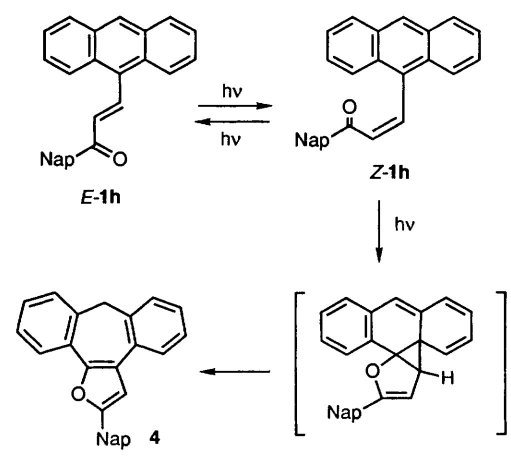
intersystem crossing to the unreactive triplet state. It was reported that three-atom linked bisanthracenes cyclised from either singlet or triplet excited state depending on the structure of the linkage.[4,5] The high reactivity for cyclomerisation of AnCOCH$_2$CH$_2$An in the triplet state ($\Phi = 0.65$)[4] is in contrast to the case of **1f**.

Thus, the photochemical behaviour of the anthracene–naphthalene bichromophoric compounds is rather different from that of the bisanthracene systems. Bouas-Laurent *et al.* pointed out that the rate constant of cyclomerisation from the intramolecular exciplex of AnCH$_2$OCH$_2$Nap was much smaller than that of AnCH$_2$OCH$_2$An.[1] The low reactivity towards cyclomerisation of **1a–g** in comparison with AnCOCH$_2$CH$_2$An (Table 1, entry 9–14 *vs.* 15) is probably attributable to the low rate of the cyclomerisation and competitive thermal deactivation to the ground state from the intramolecular exciplexes. Under irradiation with shorter wavelength light ($\lambda < 280$ nm) the cyclomer **2a–g** and dimer **3a–c,e–g** underwent cycloreversion to regenerate the starting monomer **1a–g**.

Enone **1h** rapidly underwent *cis–trans* isomerisation to give a photostationary mixture with the $Z:E$ ratio of 3.3 : 1 in benzene. (*Z*)-**1h** did not give a cyclomer, but instead furan-fused dibenzocycloheptene **4** was obtained as a sole product. Neither (*E*)-**1h** nor (*Z*)-**1h** gave a dimer even at a relatively high concentration (1.8×10^{-2} mol dm^{-3}). The reaction was not affected by the presence of oxygen, suggesting that both the *cis–trans* isomerisation and the formation of **4** should take place from the excited singlet state. The rearrangement from (*Z*)-**1h** to **4** can be explained by [4 + 2] cycloaddition and subsequent hydrogen shift (Scheme 2). This photochemical behaviour of **1h** is very similar to that of AnCH=CHCOPh,[16] but not AnCH=CHCOAn, which exclusively took place by [4 + 4] cyclomerisation.[4] The regioisomer of **1h**, (*E*)-**1i**, did not undergo any photoreaction in degassed benzene solution.

Photochemical reactions in the solid state

Some anthracene derivatives were known to undergo photochemical dimerisation in the crystalline state[17,18] and therefore dimer **3** might be obtained selectively in the solid state. Solid samples of **1a–h** were irradiated ($\lambda > 330$ nm) and the products were analysed by ^{1}H NMR spectroscopy (Table 1, entry 16–22). (*E*)-**1e** showed higher reactivity for dimerisation than **1a** or **1b**, which was in contrast to the result that these compounds afforded the dimer in a similar yield in benzene. The ^{1}H NMR spectrum of the photolytic mixture from **1d** exhibited singlet signals at δ 2.58 and 4.16 assignable to the acetoxy and the bridgehead protons of dimer **3d**, respectively, although it could not be isolated. In the case of (*E*)-**1h**, (*Z*)-**1h** was not detected in the photolysate. Isomerisation from (*E*)-**1h** to (*Z*)-**1h** will disorganize regular crystal packing around the isomerised molecule, which will facilitate the transformation into **4**, as was suggested for (*E*)-AnCH=CHCOPh.[10]



Scheme 2

In order to clarify factors controlling the solid-state photoreactivity of these compounds, X-ray structure analyses of **1a**, **1c** and (*E*)-**1e** were carried out. It was reported for anthracene derivatives that deviation of the aromatic π-system from planarity precluded photochemical dimerisation.[19] In **1a**, **1c** and (*E*)-**1e**, the dihedral angles between the two benzene rings of the anthracene were 2.1(2), 4.3(2) and 2.7(4)°, respectively, suggesting that distortion of the anthracene π-system was too small to have a large influence on photochemical behaviour. In the crystal of **1a**, the adjacent naphthalenes, which were related by a centre of symmetry, were stacked with an interplane distance of 3.6 Å, while adjacent anthracenes were separated by 6.0 Å [Fig. 2(*a*)]. When dimerisation of the anthracenes takes place, large movement of the molecules is required, and it is suggested that the dimerisation proceeded mainly in defects and/or at the surface rather than in the bulk of the crystal. Since in the conformation observed in the crystal, the two chromophores were rather distant from each other, the cyclomerisation was unlikely to occur. As for (*E*)-**1e**, two anthracene groups related by a centre of symmetry were stacked at a distance of 3.45 Å, and the interatomic distance of C(9)–C(10^i) ($i = 1 - x, 1 - y, 1 - z$) where a new bond was formed on dimerisation, was 4.05 Å [Fig. 2(*b*)]. This molecular packing seems suitable for dimerisation. **1c** crystallised in a non-centrosymmetrical space group ($P2_1$), indicating that spontaneous resolution occurred on crystallisation. The mutual orientation of the adjacent anthracenes is unfavourable for dimerisation [Fig. 2(*c*)].

Experimental

UV and fluorescence spectra were recorded on a Shimadzu UV2200 spectrophotometer and a Shimadzu RF510 spectrofluorophotometer, respectively. IR spectra were recorded as KBr disks on a JASCO A-3 spectrometer. ^{1}H (270 or 400 MHz) and ^{13}C (67.8 MHz) NMR spectra were obtained on a JEOL JNM-GSX270 or JNM-GSX400 spectrometer with tetramethylsilane as internal standard. *J* Values are given in Hz. The ^{1}H NMR signals of **2b–g** were assigned by means of ^{1}H–^{1}H COSY experiments. Mass spectra (EI, 70 eV) were recorded on a JEOL DX-300 mass spectrometer. Purity of samples for high resolution mass spectrometry was checked by TLC on Kieselgel 60 F$_{254}$ (Merck) with benzene–hexane (1 : 1) as eluent. Mps were obtained with a Yanagimoto micro apparatus and are uncorrected. Cyclohexane and benzene were spectroscopic

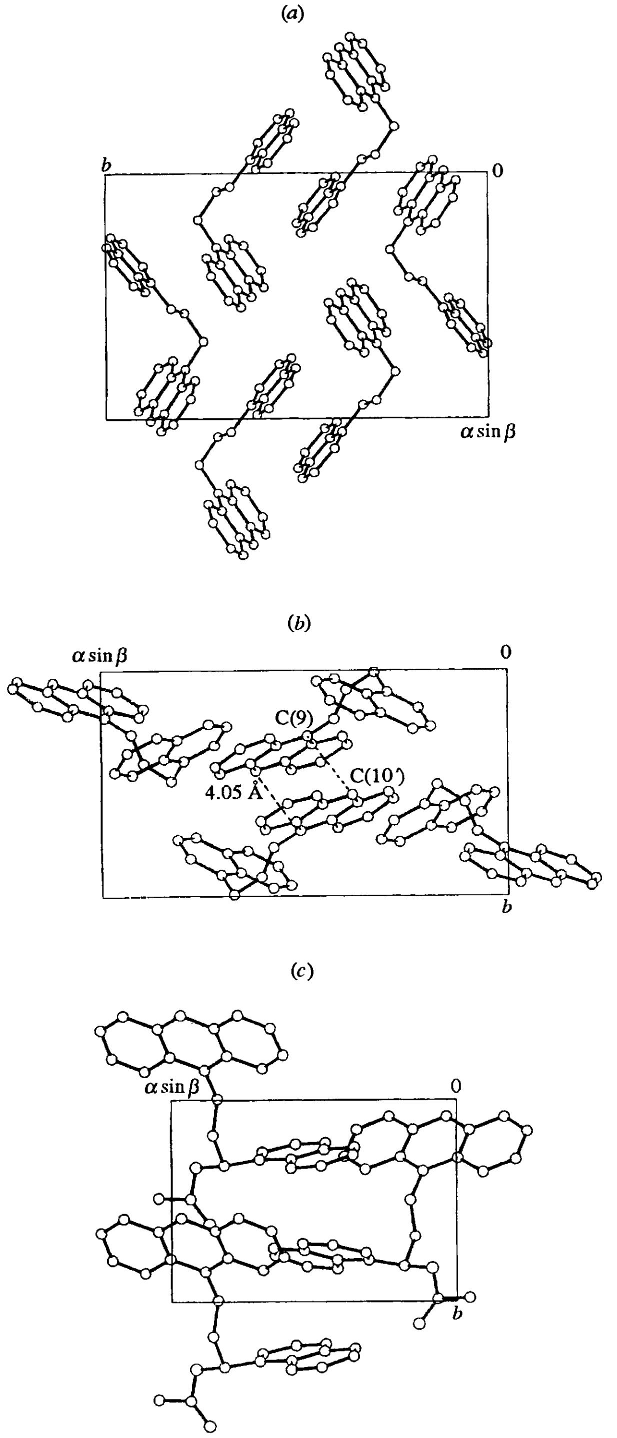


Fig. 2 Crystal structures viewed along the *c* axis. (*a*) **1a**, (*b*) (*E*)-**1e**, (*c*) **1c**. The chirality of **1c** may be the mirror image of this figure.

grade and used without further purification. Photochemical reactions were carried out at room temperature with a 400 W high-pressure mercury lamp through 1 mol dm^{-3} KNO_3 aqueous solution (λ > 330 nm) using a Riko RH-400-10 W merry-go-round apparatus unless otherwise noted.

(*E*)-3-(9-Anthryl)-1-(1-naphthyl)prop-2-en-1-one (*E*)-1h

This compound was prepared from 9-anthraldehyde and 1-acetylnaphthalene by the method of Russel and Happoldt.[20] Yield 47%. Yellow plates; mp 134–135 °C (EtOH) (Found: C, 90.5; H, 5.25. $C_{27}H_{18}O$ requires C, 90.5; H, 5.1%); ν_{max}/cm^{-1} 1640 (C=O); δ_H($CDCl_3$) 7.34 (1 H, d, *J* 16, =C*H*CO), 7.5–8.1 (12 H, m), 8.26 (2 H, m), 8.46 (1 H, s, 10'-H), 8.58 (1 H, d, *J* 8) and 8.63 (1 H, d, *J* 16, AnC*H*=); *m*/*z* 358 (M$^+$, 61%), 203 (31), 202 (36) and 155 (100) (Found: *m*/*z* 358.1383. Calc. for $C_{27}H_{18}O$: *M*, 358.1357).

(*Z*)-3-(9-Anthryl)-1-(1-naphthyl)prop-2-en-1-one (*Z*)-1h

An ethanol solution of (*E*)-**1h** was irradiated with sunlight for 2 days. After removal of the solvent, chromatographic separation of the residue (silica gel, benzene–hexane 2:1) gave (*Z*)-**1h** as yellow fine crystals. Mp 108–110 °C (Found: C, 89.6; H, 5.2. $C_{27}H_{18}O$ requires C, 90.5; H, 5.1%); ν_{max}/cm^{-1} 1660 (C=O); δ_H($CDCl_3$) 6.69 (1 H, dd, *J* 8, 7), 7.1–7.5 (10 H, m), 7.70 (2 H, d, *J* 8), 7.80 (1 H, d, *J* 8) and 7.9–8.1 (4 H, m).

3-(9-Anthryl)-1-(1-naphthyl)propan-1-one 1g

(*E*)-**1h** (1.392 g, 3.9 mmol) was hydrogenated in ethyl acetate (75 cm^3) in the presence of 10% Pd–C (240 mg) at room temperature for 11 h. After the catalyst was filtered off, the solvent was removed with a rotary evaporator and the residue was crystallised from ethanol to give **1g** in 81% yield. Pale yellow needles; mp 110–111 °C (Found: C, 90.15; H, 5.9. $C_{27}H_{20}O$ requires C, 90.0; H, 5.6%); ν_{max}/cm^{-1} 1680 (C=O); δ_H($CDCl_3$) 3.55 (2 H, m), 4.15 (2 H, m), 7.4–7.7 (7 H, m), 7.8–8.1 (5 H, m), 8.31 (2 H, d, *J* 8.7), 8.39 (1 H, s) and 8.79 (1 H, d, *J* 8); *m*/*z* 360 (M$^+$, 45%), 191 (100) and 155 (16) (HRMS Found: *m*/*z* 360.1495. Calc. for $C_{27}H_{20}O$: *M*, 360.1514).

3-(9-Anthryl)-1-(1-naphthyl)propan-1-ol 1b

To an ethanol solution (20 cm^3) of **1g** (488 mg, 1.35 mmol) $NaBH_4$ (117 mg, 3.1 mmol) was added. The solution was stirred for 30 min and then diluted with 10 cm^3 of water. The precipitate was collected, washed with water and dried *in vacuo*. Yield 86%; mp 153–154 °C (Found: C, 89.0; H, 6.1. $C_{27}H_{22}O$ requires C, 89.45; H, 6.1%); ν_{max}/cm^{-1} 3300 (O–H); δ_H($CDCl_3$) 2.09 (1 H, d, *J* 3, OH), 2.45 (2 H, m, 2-H), 3.85 (2 H, t, *J* 8, 3-H), 5.63 (1 H, m, 1-H), 7.3–7.9 (11 H, m), 8.0 (2 H, m), 8.2 (2 H, m) and 8.34 (1 H, s, 10'-H).

3-(9-Anthryl)-1-(1-naphthyl)propyl acetate 1c

Alcohol **1b** (0.36 g, 1.0 mmol) was dissolved in a mixture of acetic anhydride (12 cm^3) and pyridine (3 cm^3). The solution was stirred at room temperature for 1 h and then 6 cm^3 of ethanol was added. The solvent was removed under reduced pressure and the residue was dissolved in benzene, washed with water and brine, dried (Na_2SO_4) and concentrated. The resultant oil was chromatographed on silica gel with benzene as eluent to give **1c**. Yield 76%; colourless prisms; mp 146–148 °C (benzene–hexane) (Found: C, 86.2; H, 6.1. $C_{29}H_{24}O_2$ requires C, 86.1; H, 6.0%); ν_{max}/cm^{-1} 1745 (C=O); δ_H($CDCl_3$) 2.18 (3 H, s, COMe), 2.55 (2 H, m, 2-H), 3.5–3.8 (2 H, m, 3-H), 7.3–7.6 (7 H, m), 7.68 (1 H, d), 7.8–8.2 (7 H, m) and 8.32 (1 H, s, 10'-H); *m*/*z* 404 (M$^+$, 5%) and 344 (73, M − AcOH).

(*E*)-1-(9-Anthryl)-3-(1-naphthyl)prop-2-en-1-one (*E*)-1i

9-Acetylanthracene and 1-naphthaldehyde reacted by the method of Becker and Andersson.[4] Yield 44%; yellow plates, mp 143.5–145 °C (Found: C, 90.7; H, 5.4. $C_{27}H_{18}O$ requires C, 90.5; H, 5.1%); ν_{max}/cm^{-1} 1640 (C=O); δ_H($CDCl_3$) 7.3–7.7 (9 H, m), 7.8–7.9 (3 H, m), 8.02 (2 H, m), 8.09 (2 H, m), 8.18 (1 H, d, *J* 16, =C*H*-Nap) and 8.59 (1 H, s, 10'-H); *m*/*z* 358 (M$^+$, 100%), 205 (39) and 177 (38) (HRMS Found: *m*/*z* 358.1359. Calc. for $C_{27}H_{18}O$: *M*, 358.1357).

[1-(9-Anthryl)-3-(1-naphthyl)propyl] acetate 1d

Reduction of (*E*)-**1i** with $NaBH_4$ gave 1-(9-anthryl)-3-(1-

naphthyl)propan-1-ol[21] and this alcohol was acetylated by a similar procedure to the preparation of **1c**. Yield 61%; pale yellow plates; mp 114–115 °C (EtOH) (Found: C, 86.2; H, 6.1. $C_{29}H_{24}O_2$ requires C, 86.1; H, 6.0%); ν_{max}/cm^{-1} 1740 (C=O); δ_H(CDCl$_3$) 2.10 (3 H, s, COMe), 2.65 (1 H, m), 2.95 (2 H, m), 3.3 (1 H, m), 7.2–7.9 (12 H, m), 8.00 (2 H, d, *J* 8), 8.42 (1 H, s, 10′-H) and 8.5 (2 H, br s, 1′-H, 8′-H); *m*/*z* 344 (10%, M − AcOH) and 208 (100).

(*E*)-1-(9-Anthryl)-3-(1-naphthyl)prop-1-ene (*E*)-1e

This compound was prepared from **1d** by similar procedures reported for 1,3-bis(9-anthryl)propene.[4] Pale yellow plates; mp 132 °C (EtOH) (Found: C, 94.15; H, 6.0. $C_{27}H_{20}$ requires C, 94.15; H, 5.85%); ν_{max}/cm^{-1} 1620 (C=C); δ_H(C_6D_6) 3.88 (2 H, d, *J* 6, CH$_2$), 6.10 (1 H, dt, $J_{1.2}$ 16, $J_{2.3}$ 6, =C*H*CH$_2$), 6.96 (1 H, d, *J* 16, AnC*H*=), 7.2–7.9 (12 H, m) and 8.1–8.3 (4 H, m).

(*Z*)-1-(9-Anthryl)-3-(1-naphthyl)prop-1-ene (*Z*)-1e

2e was kept at 210 °C for 5 min under vacuum in the dark. ^{1}H NMR spectral analysis showed quantitative conversion into (*Z*)-**1e**. Colourless plates; mp 122–123.5 °C (benzene–hexane); δ_H(CDCl$_3$) 3.54 (2 H, dd, $J_{2.3}$ 7, $J_{1.3}$ 1.5, CH$_2$), 6.49 (1 H, dt, $J_{1.2}$ 11, $J_{2.3}$ 7, =C*H*CH$_2$), 7.1–7.4 (5 H, m), 7.5 (4 H, m), 7.64 (2 H, t, *J* 8), 7.77 (1 H, d, *J* 8), 8.06 (2 H, m), 8.27 (2 H, m) and 8.48 (1 H, s, 10′-H).

1-(9-Anthryl)-3-(1-naphthyl)propan-1-one 1f

An ethyl acetate (50 cm^3) solution of (*E*)-**1i** (0.714 g, 2.0 mmol) was stirred in the presence of 10% Pd–C (96 mg) under H$_2$ until an equimolar amount of hydrogen was consumed. After the catalyst was filtered off, the solvent was evaporated and the oily residue was chromatographed on silica gel eluting with hexane–benzene (1 : 1–1 : 2) to give **1f** (0.43 g, 60%). Pale yellow needles; mp 125–126 °C (EtOH) (Found: C, 89.8; H, 5.7. $C_{27}H_{20}O$ requires C, 90.0; H, 5.6%); ν_{max}/cm^{-1} 1690 (C=O); δ_H(CDCl$_3$) 3.50 (2 H, t, *J* 8), 3.74 (2 H, t, *J* 8) and 7.3–8.1 (15 H, m); *m*/*z* 360 (M$^+$, 30%), 205 (100) and 178 (58) (HRMS Found: *m*/*z* 360.1517. Calc. for $C_{27}H_{20}O$: *M*, 360.1514).

General procedures for preparative photolysis

A benzene solution of each sample was degassed and sealed in a Pyrex tube and irradiated. After photolysis the solution was concentrated and products were isolated by silica gel column chromatography.

2,3,8,9-Tetrahydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]cyclopenta[*c*]cyclooctene 2a. δ_H(CDCl$_3$) 1.8 (1 H, m), 2.25 (2 H, m), 2.5–2.8 (3 H, m), 4.00 (1 H, ddd, $J_{8.9}$ 11, $J_{9.15}$ 7, $J_{9.14}$ 1, 9-H), 4.38 (1 H, d, *J* 11, 8-H), 5.69 (1 H, dd, $J_{14.15}$ 8, $J_{9,14}$ 1, 14-H), 6.03 (1 H, dd, $J_{14.15}$ 8, $J_{9.15}$ 7, 15-H) and 6.6–7.4 (12 H, m) [lit.,[22] δ_H(CDCl$_3$) 1.8–2.8 (6 H, m), 3.95 (1 H, ddd, *J* 11, 7, 1), 4.36 (1 H, d, *J* 11), 5.66 (1 H, dd, *J* 8, 1), 6.00 (1 H, dd, *J* 8, 7) and 6.6–7.5 (12 H, m)].

Photodimer 3a. Mp 206–208 °C (decomp) [lit.,[23] 219–220 °C (decomp)]; δ_H(CDCl$_3$) 1.84 (2 H, m, C*H*$_2$CH$_2$Nap), 2.87 (2 H, m, C*H*$_2$CH$_2$CH$_2$Nap), 3.28 (2 H, br t, C*H*$_2$Nap), 3.80 (1 H, s), 6.6–6.9 (8 H, m) and 7.4–8.1 (7 H, m) [lit.,[23] δ_H(CDCl$_3$), 2.0–2.8 (4 H, m), 3.26 (2 H, t) and 3.72 (1 H, s)].

***exo*-2,3,8,9-Tetrahydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]cyclopenta[*c*]cycloocten-1-ol 2b.** δ_H(CDCl$_3$) 2.3–2.8 (4 H, m, 2- and 3-H), 4.01 (1 H, ddd, $J_{8.9}$ 10, $J_{9.15}$ 7, $J_{9.14}$ 1, 9-H), 4.39 (1 H, d, *J* 10, 8-H), 4.99 (1 H, m, 1-H), 6.08 (1 H, dd, $J_{14.15}$ 8.5, $J_{9,15}$ 7, 15-H), 6.20 (1 H, dd, $J_{14.15}$ 8.5, $J_{9.14}$ 1, 14-H), 6.7–7.2 (11 H, m) and 7.44 (1 H, d, *J* 8). Most of the ^{1}H NMR signals of the *endo*-isomer **2b′** overlapped with the corresponding signals of **2b** and only two signals were assigned: δ_H(CDCl$_3$) 5.77 (1 H, dd, $J_{14.15}$ 8.5, $J_{9.14}$ 1, 14-H) and 6.18 (1 H, m, 15-H).

Photodimer 3b. Mp 206–207.5 °C (Found: C, 89.4; H, 6.4. $C_{54}H_{44}O_2$ requires C, 89.5; H, 6.1%); ν_{max}/cm^{-1} 3550 (OH); δ_H(CDCl$_3$) 1.99 [2 H, m, C*H*$_2$CH(OH)], 2.04 (1 H, s, OH), 2.8–3.1 [2 H, m, C*H*$_2$CH$_2$CH(OH)], 3.84 (1 H, s, 10′-H), 5.70 [1 H, m, C*H*(OH)], 6.7–7.0 (8 H, m), 7.5 (3 H, m), 7.6–7.9 (3 H, m) and 8.10 (1 H, m).

***exo*-2,3,8,9-Tetrahydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]cyclopenta[*c*]cycloocten-1-yl acetate 2c.** Colourless plates; mp 197–199 °C (benzene–hexane); ν_{max}/cm^{-1} 1730 (C=O); δ_H(CDCl$_3$) 2.01 (3 H, s, COMe), 2.3–2.4 (1 H, m, 2-H), 2.5–2.8 (3 H, m, 2-H and 3-H), 4.0 (1 H, m, 9-H), 4.39 (1 H, d, *J* 11, 8-H), 5.95 (1 H, m, 1-H), 6.1 (2 H, m, 14- and 15-H), 6.7–6.9 (6 H, m), 7.0 (2 H, m) and 7.1–7.4 (4 H, m); δ_C(CDCl$_3$) 21.2 (q), 27.8 (t), 31.3 (t), 47.8 (d), 54.4 (d), 62.7 (s), 63.3 (s), 76.1 (d) and 170.6(s).

***endo*-2,3,8,9-Tetrahydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]cyclopenta[*c*]cycloocten-1-yl acetate 2c′.** This compound could not be isolated in pure form. δ_H(CDCl$_3$) 1.86 (3 H, s, COMe), 5.35 (1 H, dd, *J* 12, 6, 1-H) and 5.71 (1 H, d, *J* 9, 14-H). Other proton signals were overlapped by the corresponding signals of **2c**. δ_C(CDCl$_3$) 21.4 (q), 26.9 (t), 30.8 (t), 48.2 (d), 54.5 (d), 62.5 (s), 81.1 (d) and 170.8 (s).

Photodimer 3c. δ_H(CDCl$_3$) 2.0–2.1 [2 H, m, C*H*$_2$CH(OAc)], 2.22 (3 H, s, COMe), 2.6–2.9 [2 H, m, C*H*$_2$CH$_2$CH(OAc)], 3.75 (1 H, s, 10′-H), 6.6–6.9 (9 H, m), 7.4–7.6 (4 H, m), 7.8 (2 H, m) and 8.15 (1 H, m); δ_C(CDCl$_3$) 21.4 (q), 31.2 (t), 33.1 (t), 56.0 (d), 64.6 (d), 74.2 (s) and 170.5 (s).

2,3,8,9-Tetrahydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]cyclopenta[*c*]cycloocten-3-yl acetate 2d. Cyclomer **2d** was obtained as an inseparable mixture of two epimers with a ratio of 2 : 1. δ_H(CDCl$_3$) 2.0–2.1 (1 H, m, 1-H), 2.03, 2.04 (3 H, s, COMe), 2.6–2.8 (3 H, m, 1-H and 2-H), 3.95–4.05 (1 H, m, 9-H), 4.35, 4.39 (1 H, d, 8-H), 5.63, 5.70 (1 H, dd, 14-H), 6.0–6.1 (1 H, m, 15-H), 6.0 and 6.32 (1 H, m, 3-H).

8,9-Dihydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]-cyclopenta[*c*]cyclooctene 2e. Mp 154–155 °C; δ_H(CDCl$_3$) 2.77 (1 H, dt, J_{gem} 18, $J_{1.2}$ 2.5, 1-H), 3.51 (1 H, dt, J_{gem} 18, $J_{1,2}$ 2.5, 1-H), 4.01 (1 H, dd, $J_{8.9}$ 10, $J_{9,15}$ 7.5, 9-H), 4.38 (1 H, d, *J* 10, 8-H), 5.74 (1 H, dd, $J_{14.15}$ 8, $J_{9.14}$ 1, 14-H), 5.85 (1 H, dt, $J_{2.3}$ 6, $J_{1,2}$ 2.5, 2-H), 6.06 (1 H, dd, $J_{14.15}$ 8, $J_{9.15}$ 7.5, 15-H), 6.39 (1 H, dt, $J_{2.3}$ 6, $J_{1.3}$ 2.5, 3-H), 6.6–6.9 (9 H, m) and 7.1–7.3 (3 H, m); *m*/*z* 344 (M$^+$, 41%), 215 (19) and 203 (100).

Photodimer 3e. δ_H(CDCl$_3$) 4.32 (2 H, d, *J* 6, CH$_2$), 4.83 (1 H, s, 10′-H), 6.05 (1 H, d, *J* 17, C*H*=CHCH$_2$), 6.7–8.0 (8 H, m) and 8.31 (1 H, d, *J* 8); δ_C(CDCl$_3$) 29.8, 36.7 and 55.0.

2,3,8,9-Tetrahydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]cyclopenta[*c*]cycloocten-3-one 2f. Mp 186–189 °C (decomp.); ν_{max}/cm^{-1} 1735 (C=O); δ_H(CDCl$_3$) 2.26 (1 H, m), 2.9–3.1 (3 H, m), 4.03 (1 H, dd, $J_{8.9}$ 11, $J_{9.15}$ 7, 9-H), 4.44 (1 H, d, *J* 11, 8-H), 5.70 (1 H, d, *J* 8, 14-H), 6.09 (1 H, dd, $J_{14.15}$ 8, $J_{9.15}$ 7, 15-H), 6.50 (1 H, d, *J* 7) and 6.6–7.3 (11 H, m); *m*/*z* 360 (M$^+$, 29%), 208 (59), 205 (100) and 178 (57).

Photodimer 3f. Mp 220–222 °C (decomp.); ν_{max}/cm^{-1} 1710 (C=O); δ_H(CDCl$_3$) 2.83 (2 H, t, *J* 8), 3.57 (2 H, t, *J* 8), 5.82 (1 H, s, 10′-H), 6.42 (2 H, d, *J* 8), 6.68 (2 H, td, *J* 8, 2), 6.82 (2 H, td, *J* 8, 1), 6.98 (2 H, d, *J* 7), 7.2–7.4 (4 H, m), 7.63 (1 H, m), 7.77 (1 H, m) and 7.90 (1 H, m).

Table 2 Crystal data and details for data collection and structure refinements

Comp.	**1a**	**1c**	(*E*)-**1e**	**2c**
Formula	$C_{27}H_{22}$	$C_{29}H_{24}O_2$	$C_{27}H_{20}$	$C_{29}H_{24}O_2$
FW	346.4	404.5	344.4	404.5
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$	$P2_1/n$	$C2/c$
a/Å	11.866(2)	13.111(1)	16.390(9)	26.209(3)
b/Å	17.211(2)	7.680(1)	9.047(2)	10.374(2)
c/Å	9.848(2)	11.090(2)	13.165(7)	15.791(2)
β/°	109.84(1)	103.961(8)	105.26(4)	99.92(1)
V/Å^3	1891.7(6)	1083.6(2)	1879.9(15)	4229.5(11)
D_x/g cm^{-3}	1.216	1.240	1.217	1.270
Z	4	2	4	8
λ/Å	1.541 84	1.541 84	0.710 68	1.541 84
μ/cm^{-1}	5.26	5.61	0.64	5.80
F(000)	736	428	728	1712
Scan width/°	$1.0 + 0.15 \tan \theta$	$1.3 + 0.3 \tan \theta$	$1.0 + 0.35 \tan \theta$	$1.84 + 0.4 \tan \theta$
$2\theta_{max}$/°	120.0	120.0	50.0	120.0
Absorption correction	ψ Scan	None	None	ψ Scan
No. of reflections				
measured	3110	1850	3459	3428
unique (R_{int})	2923 (0.053)	1713 (0.011)	2387 (0.015)	3344 (0.036)
observed	1852	1660	1282	2346
criterion for obsd.	$> 3\sigma(F_o)$	$> 2\sigma(F_o)$	$> 2\sigma(F_o)$	$> 3\sigma(I)$
No. of parameters	329	366	305	372
Final R	0.060	0.034	0.087	0.051
wR	0.051	0.040	0.092	0.026
Weighting scheme	$1/\sigma(F)^2$	$1/(\sigma^2 + 0.001F^2)$	$1/(\sigma^2 + 0.004F^2)$	$1/\sigma(F)^2$
$(\Delta/\sigma)_{max}$	0.38	0.8	0.40	0.17
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.14/0.16	−0.12/0.09	−0.24/0.26	−0.31/0.25

2,3,8,9-Tetrahydro-3a,8[1,2]benzeno-9,13b-etheno-1*H*-dibenzo[*a*,*e*]cyclopenta[*c*]cycloocten-1-one 2g. Mp 169–172 °C (decomp.); ν_{max}/cm^{-1} 1740 (C=O); δ_H($CDCl_3$) 2.8–3.1 (4 H, m, 2- and 3-H), 4.09 (1 H, ddd, $J_{8,9}$ 11, $J_{9,15}$ 7, $J_{9,14}$ 1, 9-H), 4.47 (1 H, d, J 11, 8-H), 5.75 (1 H, dd, $J_{14,15}$ 8.5, $J_{9,14}$ 1, 14-H), 6.20 (1 H, dd, $J_{14,15}$ 8.5, $J_{9,15}$ 7, 15-H), 6.62 (1 H, m), 6.8 (6 H, m), 7.02 (1 H, m) and 7.1–7.4 (4 H, m).

Photodimer 3g. δ_H(C_6D_6) 2.98 (2 H, t, J 7.5), 3.28 (2 H, t, J 7.5) and 4.00 (1 H, s, 10′-H).

2-(1-Naphthyl)-8*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*b*]furan 4. δ_H(CD_2Cl_2) 3.88 (2 H, s, 8-H), 7.27 (1 H, s, 3-H), 7.3–7.7 (10 H, m), 7.8–8.0 (4 H, m) and 8.63 (1 H, d, J 8); δ_C(CD_2Cl_2) 42.0, 110.4.

Acetylation of 2b and 2b′

A mixture (*ca.* 4 mg) of **2b** and **2b′** was dissolved into 2 cm^3 of pyridine and an excess of acetic anhydride was added. The solution was stirred at room temperature for 1 h, poured into water and extracted with benzene. The organic layer was washed with 10% HCl and brine, dried (Na_2SO_4) and evaporated. The ^{1}H NMR spectrum of the residue was recorded in $CDCl_3$ solution.

Following photochemical reactions by NMR spectroscopy

A C_6D_6 solution (0.6 cm^3) of **1a–h** containing *ca.* 3 μl (1 μl = 1 mm^3) of cyclohexane as internal standard was degassed and sealed in a Pyrex NMR tube. During photolysis the variation in the ^{1}H NMR spectrum was recorded at appropriate time intervals. Product yields were determined on the basis of the integration ratio.

Sensitized photolysis

A degassed benzene solution (*ca.* 2 × 10^{-3} mol dm^{-3}, 3 cm^3) of each sample containing 20 μl of biacetyl was irradiated with a 400 W high-pressure mercury lamp through 2 mol dm^{-3} $NaNO_2$ aqueous solution (λ > 400 nm). After irradiation for 5 h, the solution was evaporated, the residue was dissolved into $CDCl_3$ or C_6D_6 and the ^{1}H NMR spectrum was recorded.

Cycloreversion of 2 and 3

An argon-purged solution of each photoproduct in cyclohexane or ethanol was irradiated with 254 nm light from a low pressure mercury lamp in a 1 cm quartz cuvette. Regeneration of **1a–g** was detected by UV–VIS spectroscopy.

Solid-state photochemical reactions

KBr pellets (2% w/w) of each solid sample were placed between two glass plates and irradiated in a Pyrex test tube under vacuum. The products were extracted with $CDCl_3$ or C_6D_6 from the pellets and the yields were determined based on the ^{1}H NMR integration ratio.

X-Ray structure analyses of 1a, 1c, (*E*)-1e and 2c

Each single crystal was mounted on a Rigaku AFC-5 [for (*E*)-**1e**] or AFC-7R (for others) four-circle diffractometer. Data collection was performed at 298 K with graphite-monochromated Cu-Kα or Mo-Kα radiation using the $\omega - 2\theta$ scan technique. Three standard reflections were monitored every 50 reflections and no significant variation in intensity was observed. The structures were solved by direct methods using SHELXS86[24] or MULTAN78[25] and refined by full matrix least-squares on F with SHELX76[26] or TEXSAN system.[27] The methyl group in **1c** was treated as a rigid group. As for (*E*)-**1e** alkenic H atoms were located on a difference map and refined isotropically and other H atoms were treated as riding on the C atoms. In the other cases all the H atoms were located on difference maps and refined isotropically. Crystal data and details for data collection and refinement are summarized in Table 2.§ The absolute stereochemistry of **1c** was not determined. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[28]

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§ The lists of final atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC scheme see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, issue 1.

References

1 H. Bouas-Laurent, J.-P. Desvergne and A. Castellan, *Pure Appl. Chem.*, 1980, **52**, 2633.
2 H.-D. Becker, *Chem. Rev.*, 1993, **93**, 145.
3 H.-D. Becker, *Advances in Photochemistry*, ed. D. H. Volman, G. S. Hammond and K. Gollnick, Wiley Interscience, New York, 1990, vol. 15, pp. 139–227.
4 H.-D. Becker and K. Andersson, *J. Org. Chem.*, 1983, **48**, 4542.
5 H.-D. Becker and K. A. Amin, *J. Org. Chem.*, 1989, **54**, 3182.
6 F. Hirayama, *J. Chem. Phys.*, 1965, **42**, 3163.
7 E. A. Chandross and A. H. Schiebel, *J. Am. Chem. Soc.*, 1973, **95**, 611.
8 J.-P. Desvergne, N. Bitit, A. Castellan and H. Bouas-Laurent, *J. Chem. Soc., Perkin Trans. 2*, 1983, 109.
9 H.-D. Becker, V. A. Patrick and A. H. White, *Aust. J. Chem.*, 1984, **37**, 2215.
10 Y. Mori and K. Maeda, *Acta Crystallogr., Sect. B*, 1994, **50**, 106.
11 S. Harayama, *J. Chem. Soc., Faraday Trans. 1*, 1982, 2411.
12 J.-P. Desvergne, A. Castellan and H. Bouas-Laurent, *Tetrahedron Lett.*, 1981, **22**, 3529.
13 C. K. Johnson, *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, USA, 1965.
14 Y. Mori and K. Maeda, unpublished results.
15 S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973.
16 H.-D. Becker, H.-C. Becker, K. Sandros and K. Andersson, *Tetrahedron Lett.*, 1985, **26**, 1589.
17 J. C. J. Bart and G. M. Schmidt, *J. Isr. Chem.*, 1971, **9**, 429; E. Heller and G. M. Schmidt, *J. Isr. Chem.*, 1971, **9**, 449.
18 D. P. Craig and P. Sarti-Fantoni, *J. Chem. Soc., Chem. Commun.*, 1966, 742.
19 H.-D. Becker and V. Langer, *J. Org. Chem.*, 1993, **58**, 4703.
20 A. Russel and W. B. Happoldt, Jr., *J. Am. Chem. Soc.*, 1942, **64**, 1101.
21 K. Itoh, T. Ikeda, S. Tazuke and T. Shibata, *J. Phys. Chem.*, 1992, **96**, 5759.
22 J. Ferguson, A. W-H. Mau and M. Puza, *Mol. Phys.*, 1974, **28**, 1457.
23 J. Ferguson and A. W-H. Mau, *Mol. Phys.*, 1974, **28**, 1467.
24 G. M. Sheldrick, *SHELXS86*, program for crystal structure determination, University of Cambridge, England, 1986.
25 P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, *MULTAN78*, a System of Computer Programs for Automatic Solution of Crystal Structures from X-Ray Diffraction Data, Universities of York, England and Louvain, Belgium, 1978.
26 G. M. Sheldrick, *SHELX76*, program for crystal structure determination, University of Cambridge, England, 1976.
27 TEXSAN: Crystal Structure Analysis Package, Molecular Science Corporation, 1985.
28 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, vol. IV, 1974.

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