

[2+2] Heterodimers of methyl phenanthrene-9-carboxylate and benzene

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Both *syn*- and *anti*-[2+2] heterodimers (**1** and **2**) of methyl phenanthrene-9-carboxylate (9-MP) and benzene were synthesized from 9-MP and cyclohexa-1,4-diene. Upon irradiation of 9-MP and excess methyl orthoformate of *cis*-cyclohexa-3,5-diene-1,2-diol followed by hydrolysis, the *syn*-[2+2] cycloadduct and also four cyclodimers of 9-MP were produced. Triplet-sensitized photocycloaddition followed by hydrolysis provided the *anti*-[2+2] cycloadduct. Dehydroxylation of the cycloadducts under mild conditions gave **1** and **2**. In contrast to the previous reports on [2+2] dibenzenes and [2+2] heterodimers of acenaphthylenes and benzene, kinetic analysis of the thermolyses of **1** and **2** indicated that **1** was kinetically less stable than **2**. Photodissociation of **1** and **2** were found to be adiabatic with efficiencies of 0.33 and 0.39. An explanation is provided for their thermoreversion and photoreversion.

Introduction

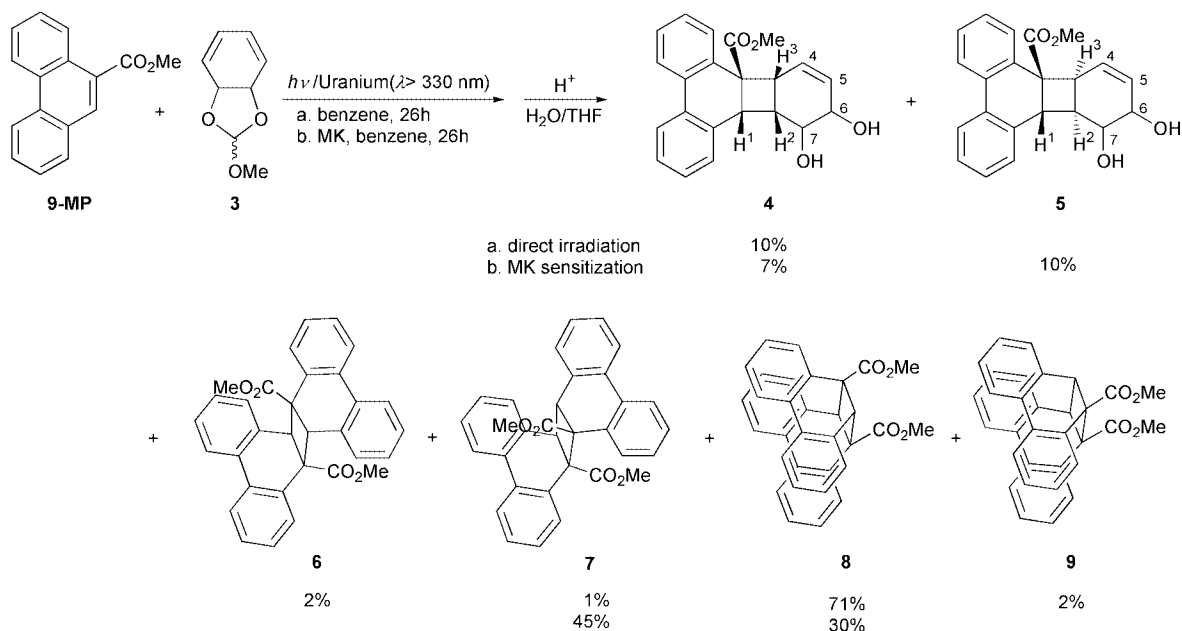
The chemistry of arene–arene dimers has been a subject of considerable interest due to their novel chemical and physical properties as well as their theoretical significance. The dimers are composed of rigid carbon skeletons with high strain energy. Therefore, they dissociate exoergically to their components by retrocycloaddition. Much progress has been made recently, especially on the synthesis of arene–benzene dimers and the discovery of their unusual chemical and physical properties such as adiabatic photodissociation^{1–6} and thermal dissociative chemiluminescence.^{3,7} Because of their unique topology, the dimers are also good models for studying the through-bond and through-space interactions between molecular orbital fragments.⁸ However, the unit components of the dimers studied thus far are rather limited. Most studies were carried out with the units of benzene,¹ furan,^{9,10} naphthalene^{2,4} and anthracene.^{3,4} We recently extended the unit components by synthesizing the *anti*-[2+2] heterodimers of 9-cyanophenanthrene and small arenes (benzene and furan)⁵ and the [2+2] heterodimers of acenaphthylenes and benzene.⁶ To the best of our knowledge, only two studies comparing the properties of *syn*- and *anti*-[2+2] dimers, dibenzenes¹ and acenaphthylenes–benzene heterodimers,⁶ have been reported. In these studies, *syn*-[2+2] dimers were kinetically more stable than their corresponding *anti*-[2+2] dimers, although the latter were thermodynamically more stable than the former. This was explained by the through-bond interaction between the two cyclohexa-1,3-diene units through the cyclobutyl ring in addition to the through-space interaction, and this explanation was supported by larger splittings between the buta-1,3-diene units of the *anti*-[2+2] dibenzene than of the *syn*-[2+2] dibenzene in photoelectron spectra.^{8c} In this paper, we report the syntheses of both *syn*- and *anti*-[2+2] heterodimers (**1** and **2**) of methyl phenanthrene-9-carboxylate (9-MP) and benzene and compare their thermolytic and photolytic behavior.

Results and discussion

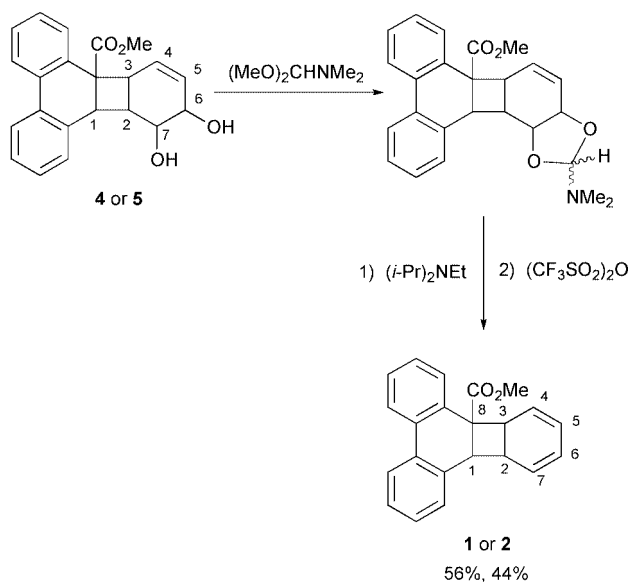
9-MP was prepared in 2 steps from 9-cyanophenanthrene.¹¹ Methyl orthoformate (**3**) of *cis*-cyclohexa-3,5-diene-1,2-diol was synthesized in 4 steps from cyclohexa-1,4-diene.^{3a,9b} Irradiation of a benzene solution of 9-MP and **3** through a uranium

filter for 26 h followed by the treatment of the resulting reaction mixture with aqueous HCl solution gave the *syn*-[2+2] cycloadduct (**4**) of 9-MP and *cis*-cyclohexa-3,5-diene-1,2-diol (Scheme 1). The isolated yield of **4** by silica gel chromatography was 10% based on the consumed 9-MP. In contrast to the reports of previous studies, in which a single cyclodimer (**8**) of 9-MP was formed in the photodimerization of 9-MP,^{12,13} four cyclodimers **6–9** were also found in the irradiated mixture. Cyclodimers **8** and **9** were isolated with consumed yields of 71 and 2%. A mixture of **6** and **7** could not be separated by conventional purification methods. The yields of **6** and **7**, on the basis of the consumed 9-MP, were estimated to be 2 and 1%. Photoexcitation of Michler's ketone (MK, $E_S = 70 \text{ kcal mol}^{-1}$, $E_T = 65 \text{ kcal mol}^{-1}$)¹⁴ through a uranium filter in the presence of 9-MP ($E_S = 80 \text{ kcal mol}^{-1}$,¹⁵ $E_T = 58 \text{ kcal mol}^{-1}$)¹⁶ and **3** ($E_T = \sim 52 \text{ kcal mol}^{-1}$)¹⁴ for 26 h afforded *anti*-[2+2] cycloadduct **5** in an isolated yield of 1%. Compounds **4**, **7** and **8** as well as the excess unreacted 9-MP were also isolated. Based on the consumed 9-MP, the isolated yields of **4**, **5**, **7** and **8** were 7, 10, 45 and 30%, respectively. In the triplet-sensitized reaction, the formation of **7** was found to increase but that of **8** decrease. Diols **4** and **5** were then converted to their corresponding 2-dimethylamino-1,3-dioxolanes by heating in the presence of excess *N,N*-dimethylformamide dimethyl acetal under anhydrous conditions (Scheme 2).¹⁷ Crude 2-dimethylamino-1,3-dioxolanes were treated with *N,N*-diisopropylethylamine and trifluoromethanesulfonic anhydride at room temperature to give their [2+2] heterodimers. The yields of the dehydroxylation steps for the preparation of **1** and **2** were 56 and 44%, respectively.

The structures of the products were determined unequivocally by spectroscopic data analyses and/or comparison with the reported data of known compounds. The isolated cycloadducts are 1 : 1 adducts of their unit components, based on the weak protonated molecular ion peak (M+1) at m/z 349 and the base peak of 9-MP in the chemical ionization mass spectra of **4** and **5**, and the ratio of 8 : 2 : 3 for the peak areas of aromatic, olefinic and cyclobutyl protons in their ¹H NMR spectra. The connectivity was established especially with their COSY spectra. For example, strong crosspeaks of H² (δ 2.84) \leftrightarrow H³ (δ 4.10) and H² \leftrightarrow H¹ (δ 4.32) in the COSY spectrum of **4** suggest the [2+2] structure (Fig. 1). The stereochemistry of **1**, **2**, **4** and **5** were determined by analyzing their



Scheme 1 Irradiation of 9-MP and 3.



Scheme 2 Dehydroxylation of 4 and 5.

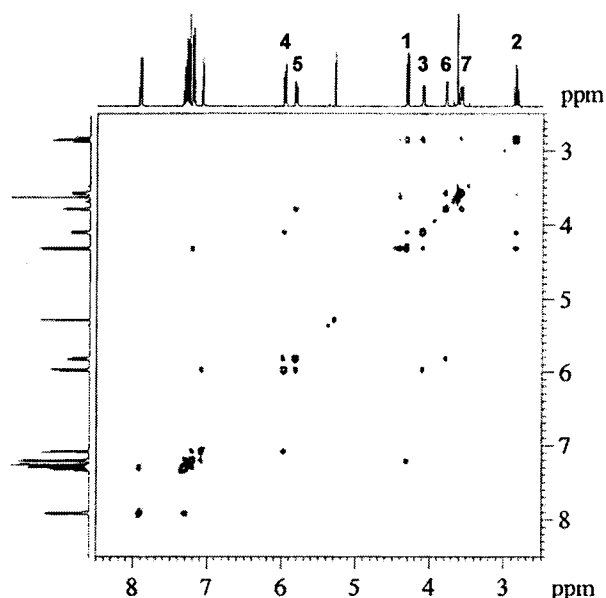


Fig. 2 NOESY spectrum of 4 in CDCl_3 .

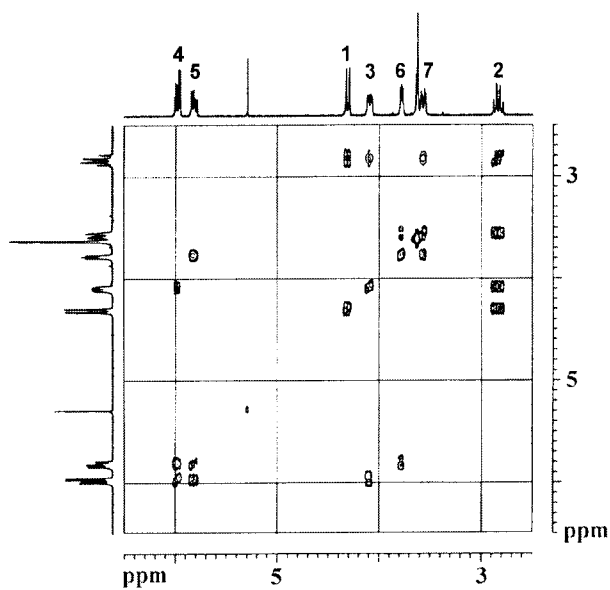


Fig. 1 COSY spectrum of 4 in CDCl_3 .

^1H NMR and NOESY spectra. Compound 4 displays more upfield chemical shifts (δ 5.98 and 5.83) for olefinic protons (H^4 and H^5) than 5 (δ 6.17 and 5.81), but more downfield shifts (δ 4.32, 4.10 and 2.84) for cyclobutyl protons than 5 (δ 3.63, 3.16 and 2.90), which suggest that 4 has a *syn* orientation and 5 has an *anti* orientation.¹⁸ Similar patterns were also found in the ^1H NMR spectra of 1 and 2. The stereochemistry was confirmed by the NOESY spectrum of 4 (Fig. 2), where the olefinic proton (H^4) displays an NOE with an aromatic proton. The assignment of their stereochemistry is also consistent with the irradiation results in which 5 was isolated in the MK-sensitized irradiation but not in direct irradiation.

The structure of cyclodimer 8 was previously assigned and confirmed by X-ray structure analysis.¹² The structure of 9 was established from its ^1H NMR spectrum, which is similar to that of its hydrolyzed product, the *syn*-head-to-head cyclodimer of phenanthrene-9-carboxylic acid, given in the literature.¹⁹ The downfield shifts (δ 8.16–6.55) of aromatic protons (anisotropic effect) in the ^1H NMR spectra of 6 and 7 and higher *R* values in TLC indicate that the cyclodimers are in the *anti* orientation. The downfield shift of the cyclobutyl proton (δ 4.84, two

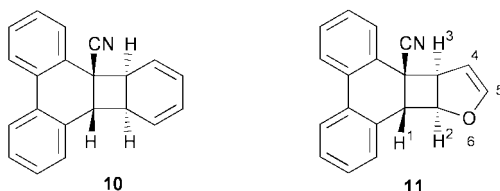
Table 1 Activation parameters for the thermolysis of **1**, **2** and **10** in DMF

	E_a / kcal mol ⁻¹	ΔH^\ddagger / kcal mol ⁻¹	ΔS^\ddagger /e.u. ^a	ΔG^\ddagger / kcal mol ^{-1b}
1	29.36 ± 0.72	28.77 ± 0.72	1.92 ± 4.84	28.20 ± 2.16
2	31.94 ± 0.70	31.35 ± 0.70	4.77 ± 4.71	29.93 ± 2.11
10 ^c	25.72 ± 0.36	25.13 ± 0.36	-0.15 ± 2.42	25.17 ± 1.08

^a 1 e.u. = 4.184 J K⁻¹ mol⁻¹. ^b At 298.15 K. ^c Taken from ref. 5.

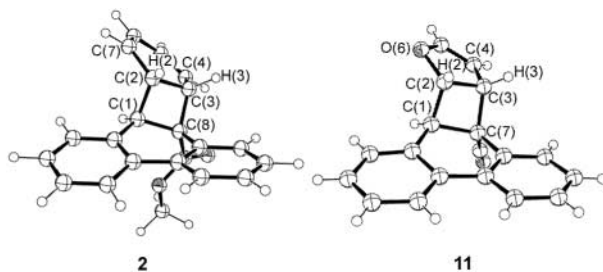
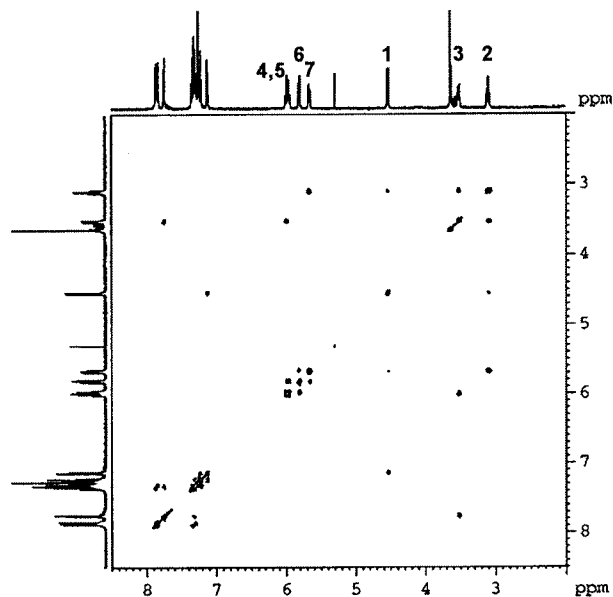
electron-withdrawing groups) and the upfield shift of the methoxy proton (δ 3.24) of **6** compared to those (δ 4.21 and 3.50) of **7** suggested that **6** is an *anti*-head-to-tail cyclodimer and **7** is an *anti*-head-to-head cyclodimer. These interpretations are also consistent with results in which the isolated yield of **7** increased but that of **8** decreased by adding MK in the photodimerization of 9-MP.

Heating a solution of **1** or **2** causes clean cycloreversion to 9-MP and benzene. The thermal dissociation of **1** and **2** in DMF at five different temperatures was followed by UV spectroscopy to determine the activation parameters. Kinetic plots gave the first-order rate constants. The activation parameters, obtained from transition state theory,²⁰ are summarized in Table 1, and compared with those for the *anti*-[2+2] heterodimer (**10**) of 9-cyanophenanthrene and benzene.⁵ High activation enthalpies and little or no activation entropies for **1** and **2**, as usually found in a highly exoergic process,¹ indicate that they undergo the thermoreversion in a stepwise mechanism. As expected, **1** and **2** were found to be more stable than **10**. For example, the activation enthalpy for **2** (half life at 70 °C = 227 h) is 31.35 kcal mol⁻¹, which is about 6 kcal mol⁻¹ higher than that (25.13 kcal mol⁻¹) for **10** (half life at 70 °C = 0.3 h). The cyano group of **10** more effectively stabilizes the biradical transition state probably due to its cylindrically symmetric shape compared with the planar carboxy group of **2**, and was previously observed in the thermolysis of some dimers.^{2g,3c,7a}



It is interesting to note that **1** is kinetically less stable than **2**. In the thermolysis of dibenzenes¹ and the heterodimers of acenaphthylene and benzene,⁶ *syn*-[2+2] dimers were found to be kinetically more stable than their corresponding *anti*-[2+2] dimers. This comparison may imply that the through-bond interaction between the buta-1,3-diene unit and the biphenyl unit through the cyclobutyl ring (Walsh type orbitals)⁸ is not effective in the cases of **1** and **2**. Therefore, steric repulsion between the two units is the major factor in the thermodynamic and kinetic stabilities of the heterodimers. Since the magnitude of through-bond interaction depends significantly on the orientation of π -systems, their inefficient through-bond interaction may be due to the distorted structure of the [2+2] heterodimers of 9-MP and benzene. In a simple calculation (MM2) for the structure of **2** (Fig. 3), a significant difference was calculated for the dihedral angles of the cyclobutyl ring and the two carbon atoms linked to it (94.794° for C(1)–C(2)–C(3)–C(4) and 138.504° for C(8)–C(3)–C(2)–C(7)). Geometrical distortions for the *anti*-[2+2] heterodimer (**11**) of 9-cyanophenanthrene and furan⁵ and **8**^{12b} (**11**: 102.960° for C(1)–C(2)–C(3)–C(4) and 134.749° for C(7)–C(3)–C(2)–O(6)) have also been shown.

The experimental evidences for the distorted structure can be found in the ¹H NMR and NOESY spectra of **2**. The signals

**Fig. 3** Distorted structures of **2** calculated by MM2 and **11** obtained from X-ray crystallography.**Fig. 4** NOESY spectrum of **2** in CDCl₃.

due to H¹ and H² show a coupling constant of 9.8 Hz, which is relatively large in spite of its *anti*-[2+2] structure. While no NOE between H² and aromatic protons was found in the NOESY spectrum of **2**, a strong crosspeak between H³ and an aromatic proton was observed (Fig. 4). This indicates that H³ is closer to the aromatic ring than H². In agreement with this interpretation, a crosspeak between H³ and an aromatic proton, but no crosspeak between H² and aromatic protons in the NOESY spectrum of the *anti*-[2+2] heterodimer (**11**) of 9-cyanophenanthrene and furan⁵ was previously reported, for which a distorted structure had been shown by X-ray crystallography (Fig. 3). Other evidence can be also found in their UV absorption spectra. The UV spectra of **1** and **2** in ethanol are characterized by the onset of absorption at around 340 nm and by a maximum at around 270 nm. The similar shape of the two UV spectra indicates that the through-bond interaction, which is known to be much larger than the through-space interaction,⁸ is not effective for the heterodimers.

As was observed in the thermal reaction of **1** and **2**, the irradiation of **1** and **2** in aerated or degassed solution through a pyrex filter was found to yield 9-MP and benzene. The emission spectra of **1** and **2** in cyclohexane upon excitation at 280 nm showed fluorescence of 9-MP (Fig. 5). In addition, the excitation spectra of **1** and **2** monitored at 380 nm are the same as their UV absorption spectra. These results mean that the excited 9-MP is derived from the excited **1** and **2**. The efficiencies for the photodissociation of **1** and **2** were determined to be 0.33 and 0.40 by potassium ferrioxalate actinometry,¹⁴ and the efficiencies for the formation of the excited 9-MP are 0.33 and 0.39 by comparison of the emission spectra of **1** and **2** with that of 9-MP (Table 2). The efficiencies for the photoreversion of **1** and **2** are similar within experimental error. In contrast to their thermolytic behavior, the photolytic behavior of **2** and **10** is not

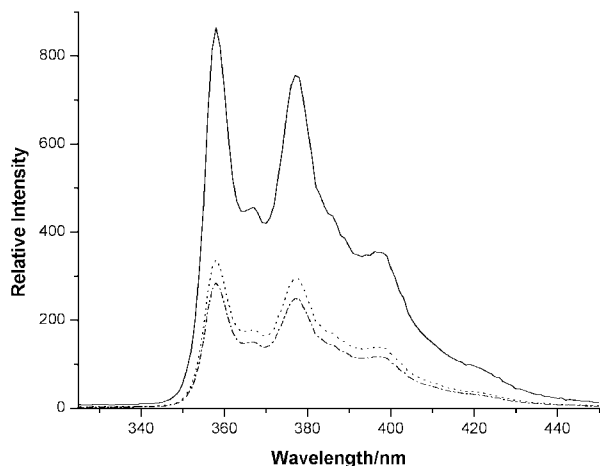


Fig. 5 Emission spectra of 9-MP (—), **1** (---) and **2** (·····) in cyclohexane. The spectra are observed by irradiation with UV light at 280 nm with the same absorbance at that wavelength.

Table 2 Quantum yields for the photoreversion of **1**, **2** and **10** in cyclohexane

	1 ^a	2 ^a	10 ^b
ϕ_{phen}	0.33 ± 0.05	0.40 ± 0.07	0.40 ± 0.08
ϕ_{phen}^*	0.33 ± 0.03	0.39 ± 0.03	0.33 ± 0.02

^a Numbers reported are the average of at least 3 measurements. ^b Taken from ref. 5.

significantly different, suggesting that thermodynamic factors such as internal energy,²¹ singlet energy, and triplet energy for the two compounds are similar.^{15,16,18b} Since the difference in the exothermicity between *syn*- and *anti*-[2+2] dimers of arenes is expected to be less than about 1–4 kcal mol⁻¹,²¹ the energy surfaces around the pericyclic minima in the photochemical retrocycloaddition of **1** and **2** should be similar.

Experimental

9-MP was prepared from 9-cyanophenanthrene in 56% overall yield following the literature method,¹¹ and recrystallized from methanol three times before use. Compound **3** was prepared from cyclohexa-1,4-diene in 36% overall yield,^{3a,9b} and distilled under reduced pressure before use. Most reagents and solvents were purified following procedures in the literature.²²

Melting points were determined on a MEL-TEMP II melting point apparatus, and are reported uncorrected. UV spectra were recorded on a Cary 300 Bio UV/VIS spectrophotometer. IR spectra were obtained using a Perkin-Elmer Spectrum 2000 Explorer FT-IR spectrometer or a JASCO IR-810 spectrometer. ¹H and ¹³C NMR spectra were routinely recorded at 300 MHz and/or 500 MHz on AMX Bruker spectrometers. Chemical shifts (δ) are reported in ppm downfield from TMS, and coupling constants (*J*) are given in Hz. Mass spectra (MS) were obtained on a Hewlett-Packard 5890-JMS AX505WA. Peaks are reported as *m/z* (% intensity relative to a base peak). Fluorescence spectra were taken on an Aminco-Bowman series 2 luminescence spectrometer.

Irradiation of 9-MP and **3**

A solution of 9-MP (2.50 g, 10.6 mmol) and **3** (7.50 g, 49.3 mmol) in benzene (120 mL) under a nitrogen atmosphere was irradiated with a 450-watt Hanovia medium-pressure mercury lamp through a cylindrical uranium filter for 26 h. The reaction mixture was concentrated, and the resulting oily residue was dissolved in 100 mL THF. After treatment with 100 mL aqueous 0.5 M HCl overnight at room temperature, the reaction mixture was neutralized with aqueous 1 M NaOH, and

extracted with dichloromethane (4 × 100 mL). Combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated. Silica gel column chromatography, eluting with *n*-hexane–dichloromethane–ethyl acetate mixtures of increasing polarity, afforded 113 mg (5%) of unreacted 9-MP, 359 mg (10% based on consumed 9-MP) of **4**, 1.68 g (71%) of **8**, and 44.8 mg (2%) of **9**. Compounds **6** and **7** could not be separated by column chromatography, recrystallization and preparative HPLC. The yields, on the basis of consumed 9-MP, were estimated to be 2 and 1% from a ¹H NMR spectrum of the mixture.

Compound **4**: mp 205.0–206.0 °C (from dichloromethane and *n*-hexane); λ_{max} (EtOH)/nm 215 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 32 800), 237 (15 000), 245 (13 200) and 277 (10 900); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3687, 3019, 1724, 1227 and 1206; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.92 (2H, m, ArH), 7.36–7.19 (5H, m, ArH), 7.08 (1H, dd, *J* 7.8, 1.4, ArH), 5.99 (1H, dd, *J* 9.9, 4.0, H⁴), 5.83 (1H, ddd, *J* 9.9, 6.0, 1.9, H⁵), 4.32 (1H, d, *J* 9.0, H¹), 4.10 (1H, ddd, *J* 8.9, 4.0, 1.9, H²), 3.80 (1H, m, H⁶), 3.63 (3H, s, OMe), 3.58 (1H, m, H⁷) and 2.85 (1H, ddd, *J* 10.2, 9.0, 8.9, H³); δ_{C} (75 MHz; CDCl₃; Me₄Si) 175.02, 132.83, 132.14, 131.19, 131.07, 130.47, 130.27, 129.06, 128.91, 128.48, 128.19, 127.93, 127.58, 123.52, 123.50, 68.28, 65.09, 52.54, 52.34, 44.81, 40.34 and 38.51; *m/z* (CI) 349 (MH⁺, 7%), 237 (100), 236 (23), 205 (13) and 95 (11); HRMS calcd for C₂₂H₂₁O₄ (MH⁺), *m/z* 349.1440, found 349.1435. Compound **6**: δ_{H} (300 MHz; CDCl₃; Me₄Si) 8.00–6.55 (16H, m, ArH), 4.84 (2H, s, cyclobutyl H) and 3.24 (6H, s, OMe). Compound **9**: mp 178.0–180.0 °C (from dichloromethane and *n*-hexane); λ_{max} (EtOH)/nm 277 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 22 000) and 269 (21 000); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3040, 3010, 2950, 1720, 1430 and 1220; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.41–6.73 (16H, m, ArH), 4.51 (2H, s, cyclobutyl H) and 3.78 (6H, s, OMe); *m/z* (FAB) 473 (MH⁺, 4%), 307 (25), 236 (38), 205 (31), 154 (100) and 136 (66).

Irradiation of 9-MP and **3** with MK

A solution of 9-MP (1.75 g, 7.42 mmol), **3** (6.00 g, 39.5 mmol) and MK (215 mg, 0.801 mmol) in benzene (120 mL) was irradiated through a uranium filter for 26 h under a nitrogen atmosphere. After hydrolysis with HCl, the resulting reaction mixture was separated by silica gel chromatography, eluting with *n*-hexane–dichloromethane–ethyl acetate, to yield 1.50 g (86%) of the unreacted 9-MP, 24.8 mg (7% based on consumed 9-MP) of **4**, 37.0 mg (10% based on consumed 9-MP) of **5**, 112.4 mg (45% based on consumed 9-MP) of **7**, and 74.6 mg (30% based on consumed 9-MP) of **8**.

Compound **5**: λ_{max} (EtOH)/nm 214 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 36 000), 236 (16 800), 243 (15 400) and 276 (11 800); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3687, 3564, 3018, 1726 and 1215; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.88 (2H, m, ArH), 7.79 (1H, m, ArH), 7.39–7.21 (4H, m, ArH), 7.05 (1H, dd, *J* 7.4, 1.2, ArH), 6.17 (1H, ddd, *J* 10.5, 2.9, 2.9, H⁴), 5.81 (1H, dd, *J* 10.5, 1.5, H⁵), 4.55 (1H, m, H⁶), 4.06 (1H, m, H⁷), 3.60 (3H, s, OMe), 3.63 (1H, d, *J* 10.3, H¹), 3.16 (1H, m, H²) and 2.90 (1H, ddd, *J* 10.3, 6.8, 3.4, H³); δ_{C} (75 MHz; CDCl₃; Me₄Si) 172.24, 134.26, 133.58, 132.86, 131.29, 130.03, 129.84, 128.46, 128.26, 128.20, 127.96, 127.81, 123.74, 123.32, 66.00, 65.50, 52.18, 52.04, 45.58, 40.82 and 40.11; *m/z* (CI) 349 (MH⁺, 1%), 237 (100), 236 (22), 205 (15) and 95 (65). Compound **7**: mp 110.0–112.0 °C (from dichloromethane and *n*-hexane); λ_{max} (EtOH)/nm 273 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 23 000) and 267 (22 000); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3061, 3022, 2950, 1726, 1431 and 1222; δ_{H} (300 MHz; CDCl₃; Me₄Si) 8.16–6.79 (16H, m, ArH), 4.21 (2H, s, cyclobutyl H) and 3.50 (6H, s, OMe); *m/z* (FAB) 473 (MH⁺, 8%), 307 (15), 236 (100), 205 (66), 154 (66) and 136 (42).

Synthesis of **1**

Diol **4** (160 mg, 0.460 mmol) in 3 mL of *N,N*-dimethylformamide dimethyl acetal was stirred at 55 °C overnight, and the solution was then evaporated to afford a yellow oily residue

which was further dried under vacuum. The resulting crude 2-dimethylamino-1,3-dioxolane of **4** and *N,N*-diisopropylethylamine (180 mg, 1.39 mmol) were dissolved in 15 mL dry dichloromethane. To this, at 0 °C, a solution of trifluoromethanesulfonic anhydride (156 mg, 0.553 mmol) in dichloromethane (5 mL) was added dropwise over a period of 3 min. After 30 min of additional stirring, the reaction mixture was washed with saturated sodium bicarbonate solution and brine, and dried over anhydrous sodium sulfate. Evaporization of the solvent under reduced pressure afforded a yellow solid residue. This was passed through a short silica gel column eluting with *n*-hexane and dichloromethane to yield 81 mg (56%) of **1**.

Compound **1**: mp 122.5–123.5 °C (from dichloromethane and *n*-hexane); λ_{max} (EtOH)/nm 217 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 34 700), 247 (12 400), 270 (12 800) and 309 (2 950); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3019, 1721, 1435 and 1211; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.88 (2H, m, ArH), 7.33–7.22 (3H, m, ArH), 7.15 (1H, m, ArH), 7.09 (1H, m, ArH), 7.02 (1H, dd, *J* 7.7, 1.5, ArH), 5.52 (2H, m, H⁴, H⁵), 5.21 (1H, m, H⁶), 5.06 (1H, dd, *J* 10.1, 3.4, H⁷), 4.51 (1H, d, *J* 9.4, H¹), 4.06 (1H, m, H²), 3.60 (3H, s, OMe) and 3.46 (1H, m, H³); δ_{C} (75 MHz; CDCl₃; Me₄Si) 175.00, 133.08, 132.12, 131.20, 130.59, 130.49, 128.91, 127.92, 127.75, 127.40, 126.78, 126.10, 125.40, 123.96, 123.06, 122.74, 121.74, 55.77, 52.29, 47.98, 42.43 and 37.88; *m/z* (CI) 313 (M – 1, 2%), 237 (100), 236 (32), 205 (36) and 79 (20); HRMS calcd for C₂₂H₁₇O₂ (M – 1), *m/z* 313.1229, found 313.1234.

Synthesis of **2**

Diol **5** (45 mg, 0.13 mmol) was treated with 3 mL of *N,N*-dimethylformamide dimethyl acetal to give the corresponding *N,N*-dimethylformamide acetal, which was then treated with *N,N*-diisopropylethylamine (37 mg, 0.29 mmol) and trifluoromethanesulfonic anhydride (44 mg, 0.15 mmol) at room temperature. The isolated yield was 44% (18 mg, 0.057 mmol).

Compound **2**: λ_{max} (cyclohexane)/nm 215 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 27 000), 245 (13 000), 257 (11 000), 268 (12 000), 275 (12 000) and 311 (2 600); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3022, 1723, 1435 and 1213; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.86 (2H, m, ArH), 7.74 (1H, m, ArH), 7.36–7.19 (4H, m, ArH), 7.12 (1H, dd, *J* 7.3, 1.4, ArH), 5.97 (2H, m, H⁴, H⁵), 5.80 (1H, ddd, *J* 9.5, 4.6, 0.7, H⁶), 5.66 (1H, ddd, *J* 9.5, 5.8, 1.0, H⁷), 4.54 (1H, d, *J* 9.8, H¹), 3.63 (3H, s, OMe), 3.52 (1H, m, H³) and 3.09 (1H, ddd, *J* 9.8, 9.8, 5.8, H²); δ_{C} (75 MHz; CDCl₃; Me₄Si) 172.23, 135.80, 134.18, 132.62, 131.33, 129.94, 128.30, 128.17, 128.09, 128.04, 127.68, 126.14, 125.41, 124.67, 123.44, 123.33, 122.92, 57.21, 51.90, 50.09, 48.90 and 36.16; *m/z* (CI) 313 (M – 1, 2%), 237 (100), 236 (80), 205 (68) and 79 (21); HRMS calcd for C₂₂H₁₇O₂ (M – 1), *m/z* 313.1229, found 313.1229.

Kinetic studies for the thermolysis of **1** and **2**

A 1.02×10^{-4} M solution of **1** in DMF was divided into several degassing tubes with 1.5 mL in each. Each tube was deaerated with nitrogen by five freeze–pump–thaw cycles at 0.1 mmHg. The studies were conducted in the temperature range of 80.1–109.9 °C (± 0.3 °C). The amounts of **1** and 9-MP were estimated by UV spectrophotometry. The data were analyzed by the first order reaction rate law. Using the data for five kinetic measurements, the activation energy of the reaction was determined. By the least squares method, the data for the thermolysis of **1** were fitted to eqn. (1).

$$\ln k = 31.43 - 14776 (\pm 363)/T \quad R^2 = 0.998 \quad (1)$$

In the thermolysis of **2**, a 1.02×10^{-4} M solution in DMF was used, and the temperature was in the range of 101.0–140.0 °C. The data were fitted to eqn. (2).

$$\ln k = 32.86 - 16073 (\pm 354)/T \quad R^2 = 0.999 \quad (2)$$

Determination of quantum yields for photodissociation

Quantum yields for the photodecomposition of **1** and **2** were determined by potassium ferrioxalate actinometry.¹⁴ The procedure was tested until consistent results could be obtained. To avoid uneven stirring effects, a narrow quartz cell was used. Before irradiation, the absorbances of sample solutions in cyclohexane were adjusted to 0.068–0.114 at 280 nm. The degassed solution was irradiated at 280 nm through a 2 nm slit.

Determination of quantum yield for the formation of the excited 9-MP

The quantum yield for the formation of excited 9-MP was determined by comparing the emission spectra with a similar absorbance of 9-MP. Excitation and emission slits were set at 2 nm. The absorbances of degassed solutions of **1**, **2** and 9-MP in cyclohexane were in the range of 0.050–0.079 at 280 nm.

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