

Synthesis of 9-cyanophenanthrene–furan and –benzene cyclodimers and their reversion



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In contrast to the previous report, the irradiation of 9-cyanophenanthrene (9-CP) and furan through a uranium filter yielded an *anti*-[2+2] adduct (**1**) as well as the *syn*-[2+2] cyclodimer (**2**) of 9-CP. A mechanistic study indicated that the photocycloaddition of furan occurred in the triplet state of 9-CP. The *anti*-[2+2] adduct (**1**) was prepared in the consumed yield of 69% by a photosensitized cycloaddition with Michler's ketone. The *anti*-[2+2] cyclodimer (**5**) of 9-CP and benzene was synthesized by the triplet-sensitized photocycloaddition of a substituted cyclohexa-1,3-diene to 9-CP followed by dehydroxylation. The thermoreversion and photoreversion of **1** and **5** prepared were studied. The photodissociation of **1** and **5** was found to be adiabatic with the efficiencies of 0.11 and 0.33.

Introduction

The cyclodimers of aromatic compounds have interesting physical and chemical properties due to their unique topology and high internal energy. In the studies on the chemistry of the cyclodimers, especially arenes–benzenes cyclodimers, adiabatic photodissociation,^{1–3} chemiluminescence,⁴ multi-photon IR absorption,^{3c} and through-bond interaction⁵ have been reported. These studies revealed some potential for photochemical energy storage. Several photochemical electrocyclic dissociations of dibenzenes, naphthalene–benzene cyclodimers, and anthracene–benzene cyclodimers generate their corresponding electronically excited products efficiently. Anthracene–furan cyclodimers⁶ and anthracene–naphthalene cyclodimers,⁷ which can be prepared by direct irradiation, were also found to undergo adiabatic photodissociation. However, the unit components of the cyclodimers studied thus far are limited to benzene, furan, naphthalene, and anthracene.

From this point of view, we were interested in the synthesis and chemical behavior of the cyclodimers with phenanthrene. Little is known about the photocycloaddition of 1,3-dienes to the phenanthrene ring. In contrast to many reports on the photoadditions of olefins to 9-cyanophenanthrene (9-CP),⁸ to the best of our knowledge only two attempts with 1,3-diene and furan have been reported in the literature.^{9,10} The irradiation of 9-CP and 2,5-dimethylhexa-2,4-diene quantitatively gave a single [2+2] cycloadduct, but the stereochemistry of the adduct was not studied. On the other hand, the irradiation of 9-CP and furan was reported to induce the photodimerization of 9-CP exclusively. In this paper, we report the synthesis of the *anti*-[2+2] cycloadducts of 9-CP and arenes, and their thermoreversion and photoreversion.

Results and discussion

Since the resonance energy (17.2 kcal mol⁻¹) of furan is much less than that (36 kcal mol⁻¹) of benzene,¹¹ the photocycloaddition of furan to phenanthrene might occur. A benzene solution of 9-CP and furan was irradiated through a uranium filter for 40 h under a nitrogen atmosphere. The reaction mixture was separated by chromatography to afford the unreacted 9-CP, the *anti*-[2+2] adduct (**1**) of 9-CP and furan, and the head-to-tail *syn*-[2+2] cyclodimer (**2**)¹² of 9-CP (Scheme 1). The isolated yields of **1** and **2** were 4% and 67% based on the consumed 9-CP. In contrast to the previous result with a glass filter (>300 nm),¹⁰ **1** was obtained with the uranium filter (>330 nm). How-

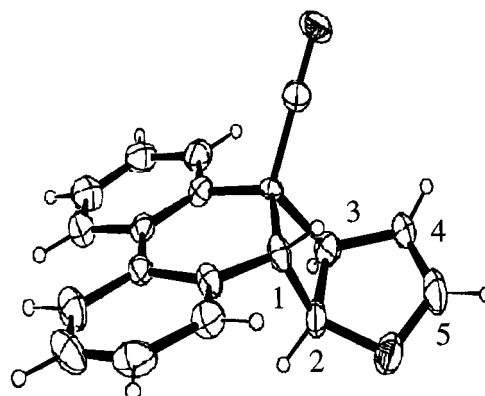
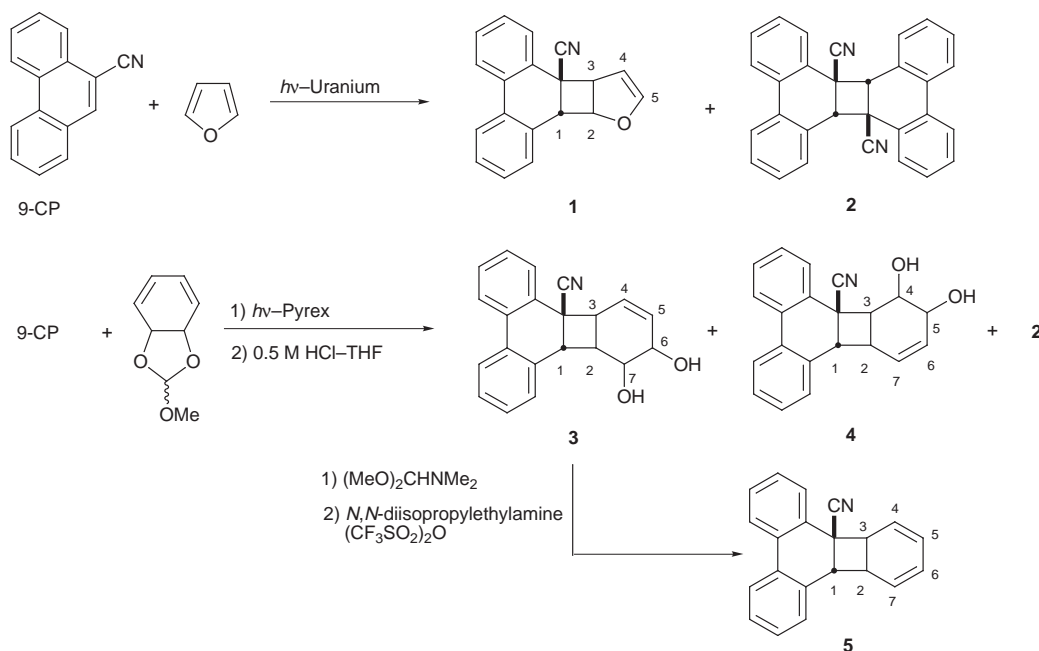


Fig. 1 X-Ray structure of **1**.

ever, inspection of the UV spectra of the reactants and the products indicated that the difference in the irradiation wavelength was not responsible for the results. The unreacted 9-CP among the compounds in the irradiated mixture mainly absorbs light above 300 nm. Irradiation through a Pyrex filter (>280 nm) was also found to produce **1**, and this was more practical than using the uranium filter.

The structure of **1** was established on the basis of spectroscopic data analyses. The mass (CI) spectrum of **1** exhibits a weak molecular ion peak (MH⁺) at *m/z* 272 and strong fragment peaks at *m/z* 204 and 69, indicating a 1 : 1 adduct of 9-CP and furan. The ¹H NMR peaks of 8 aromatic protons, 2 olefinic protons, and 3 cyclobutyl protons indicate that it is a [2+2] adduct. The regiochemistry was determined by the analysis of the COSY spectrum. Strong crosspeaks of H² (δ 4.89) ↔ H¹ (δ 4.34) and H² ↔ H³ (δ 3.93) suggest that the adduct has the head-to-tail structure. Crosspeaks of H¹ ↔ H⁴ (δ 5.61) and H¹ ↔ H⁵ (δ 6.61) and the absence of the proximity effect between H⁴ (or H⁵) and aromatic protons in its NOESY spectrum may indicate the *anti* orientation. This was confirmed by X-ray analysis (Fig. 1). A remarkable elongation (1.632 Å) of the bond C¹–C(CN) was found.

It is interesting to note that the major product was not **1** but **2**. In most singlet photocycloadditions of olefins to 9-CP, only a small amount of **2** was observed.⁸ In order to clarify the multiplicity of 9-CP, a relative rate study for the photocycloaddition to 9-CP under several conditions was conducted (Table 1). Addition of Michler's ketone (MK) in the irradiation of 9-CP and furan reduced the yield of **2** which has been established to be



Scheme 1 Synthesis of the cycloadducts **1** and **5**.

Table 1 Effect of sensitizer and quencher on the photocycloaddition of furan to 9-CP^{a,b}

entry	additive (M)	1 ^c	2 ^c	conversion ^d
1		1.0	25.4	31
2	MK (1×10^{-4})	1.0	8.4	11
3	MK (5×10^{-4})	1.1	2.2	5
4	isoprene (6.0)	0.0	43.6	88

^a Numbers reported are the average of at least two measurements. Error limit of the analysis is $\pm 5\%$. ^b Irradiated (>335 nm) in dichloromethane for 9 h, conc. of 9-CP = 0.025 M, conc. of furan = 0.75 M. ^c Relative yields compared to **1** in entry 1. ^d Based on the consumed (unrecovered) 9-CP.

formed through a singlet excimer.¹³ Addition of isoprene almost completely quenched the formation of **1**. These results indicated that the formation of **1** was attributed to the triplet state of 9-CP. Therefore, a sensitization experiment was carried out on a synthetic scale. Photoexcitation of MK through a uranium filter in the presence of 9-CP and furan afforded **1** in the consumed yield of 69%.

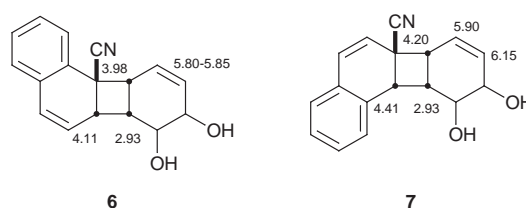
In the synthesis of the *anti*-[2+2] cycloadduct (**5**) of 9-CP and benzene, the "masked cyclohexa-1,3,5-triene" strategy¹⁻³ was used (Scheme 1). A benzene solution of 9-CP and the methyl orthoformate of *cis*-cyclohexa-3,5-diene-1,2-diol, which was prepared from cyclohexa-1,4-diene in 4 steps,^{3b} was irradiated through a Pyrex filter for 15 h. After hydrolysis, the resulting mixture was chromatographed to afford two [2+2] cycloadducts (**3** and **4**) in addition to **2** and 9-CP. The isolated yields of **3**, **4**, and **2** based on the consumed 9-CP were 8%, 2%, and 83%, respectively. Although some other cycloadducts formed were not separated completely by column chromatography and recrystallization, the ¹H NMR spectrum of the irradiated mixture revealed that **3** was the major cycloadduct.

The ¹H NMR and COSY spectra of the cycloadducts indicate that they are in the [2+2] structure with the regiochemistry as shown in Scheme 1. In the NOESY spectrum of **3**, the absence of the proximity effect between H⁴ (or H⁵) and aromatic protons may indicate the *anti* orientation. Compared with the ¹H NMR peaks of *syn*-[2+2] cycloadducts (**6** and **7**) of cyanonaphthalenes and *cis*-cyclohexa-3,5-diene-1,2-diol,¹⁴ the cyclobutyl protons (δ 3.65, 3.21, and 3.00) in **3** appear to be upfield shifted and the olefinic protons (δ 6.31 and 6.08) down-

Table 2 Activation parameters for the thermolysis of **1**, **5**, **8**, and **9** in DMF

	1 ^a	5 ^a	8 ^b	9 ^c
E_a /kcal mol ⁻¹	33.19 ± 1.18	25.72 ± 0.36	29.6	
ΔH^\ddagger /kcal mol ⁻¹	32.60 ± 1.18	25.13 ± 0.36	29.0	
ΔS^\ddagger /e.u.	12.55 ± 7.95	-0.15 ± 2.42	1.0	
ΔG^\ddagger /kcal mol ⁻¹	28.86 ± 3.55	25.17 ± 1.08	28.7	21.5

^a At 298.15 K. ^b Taken from ref. 6, at 298.15 K. ^c Taken from ref. 17, at 290.65 K.



field shifted, which strongly suggests the *anti* orientation.^{8,15} This was further confirmed by a triplet sensitization reaction. Photoexcitation of MK through a uranium filter in the presence of 9-CP and the methyl orthoformate of *cis*-cyclohexa-3,5-diene-1,2-diol followed by hydrolysis afforded **3** and **4** in the consumed yields of 51% and 8%.

The diol **3** was treated with excess DMF dimethyl acetal to give the corresponding dimethylformamide acetal, which then underwent dehydroxylation in the presence of *N,N*-diisopropylethylamine and trifluoromethanesulfonic anhydride to give **5** in 45% yield. On the other hand, **4** failed to undergo dehydroxylation under the similar reaction conditions at several different temperatures. The resulting product was assigned to be the carbonate form¹⁶ of **4** on the basis of its IR (1798 and 1219 cm⁻¹) and ¹H NMR spectra (8 aromatic protons, 2 olefinic protons at δ 6.71 and 6.57, 2 protons at δ 4.27 and 4.17, and 3 cyclobutyl protons at δ 3.77–3.41).

Upon heating, **1** and **5** were quantitatively dissociated to their unit components. Kinetic analyses of the thermolysis of **1** and **5** in DMF were performed by UV spectroscopy, and the results are summarized in Table 2. The activation enthalpy for **1** is found to be 33.19 kcal mol⁻¹, which is about 7 kcal mol⁻¹ higher than that (25.72 kcal mol⁻¹) for **5**. Half-life times for the

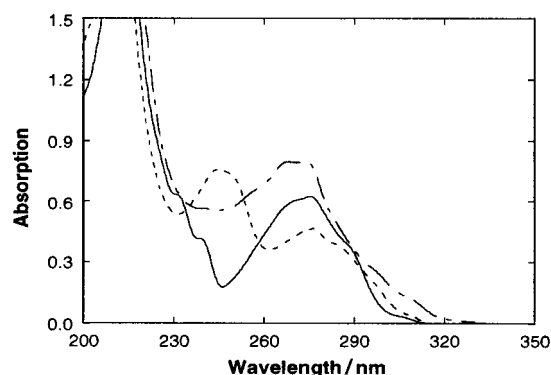


Fig. 2 UV spectra of **1** (---), **3** (—), and **5** (— · —) in ethanol (5.0×10^{-5} M).

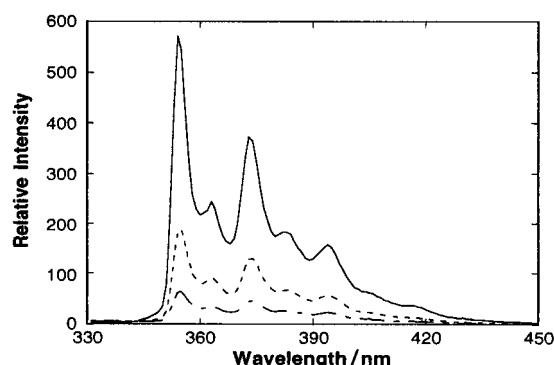
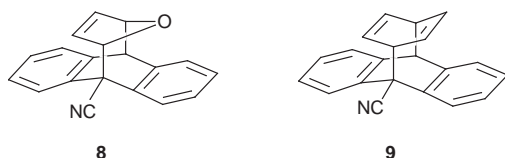


Fig. 3 Emission spectra of **1** (— · —), **5** (---), and 9-CP (—) in cyclohexane. These emission spectra are observed by the irradiation of UV light at 280 nm with the same absorbance at that wavelength.

thermal decomposition of **1** and **5** at 70 °C were estimated to be 28.4 h and 18 min, respectively. This can be explained by the lower exothermicity of the decomposition of **1** than that of **5**. High activation enthalpy and positive activation entropy indicate that the thermolysis of **1** proceeds *via* a biradical mechanism. A value of nearly zero for the activation entropy for **5** has sometimes been observed in a highly exoergic process.¹ Compared to the [4+4] cyclodimer (**8**) of 9-cyanoanthracene



and furan and the [4+4] cyclodimer (**9**) of 9-cyanoanthracene and benzene,^{6,17} **1** and **5** were found to be kinetically more stable. Since the resonance energy (92 kcal mol⁻¹) of phenanthrene is higher than that (84 kcal mol⁻¹) of anthracene,¹¹ the kinetic stability is related to the lower internal energy of the *anti*-[2+2] structure than the [4+4] structure.¹⁸

The UV spectra of **1**, **3**, and **5** in ethanol were compared (Fig. 2). The UV spectrum of **1** is characterized by the onset of absorption around 310 nm and a maximum at 277 nm. The absorption band of **5** was found to be shifted to a longer wavelength than that of **1** and to have a low-intensity tail up to about 330 nm. These may be explained by the through-bond interaction between the double bonds.⁵

The irradiation of **1** or **5** in cyclohexane through a Pyrex filter quantitatively yielded 9-CP. Quantum yields for the photodissociation of **1** and **5** irradiated at 280 nm were determined with the aid of ferrioxalate actinometry.¹⁹ When **1** or **5** was irradiated, very efficient emission of 9-CP was observed (Fig. 3). The efficiency for the formation of the excited 9-CP from **1** and **5** was determined by measuring the emission of 9-CP under

Table 3 Quantum yields for the photoreversion of **1**, **5**, **8**, and **10**

	1 ^a	5 ^a	8 ^b	10 ^c
Φ_{Ph}	0.46 ± 0.10	0.40 ± 0.08	0.45 ± 0.02	0.86 ± 0.06
Φ_{Ph^*}	0.11 ± 0.01	0.33 ± 0.02	0.15 ± 0.00	0.80 ± 0.08

^a In cyclohexane. ^b Taken from ref. 6, in cyclohexane. ^c Taken from ref. 3b, in methanol.

the same conditions. The results at room temperature are summarized in Table 3. Quantum yields (0.46 and 0.40) for the photodissociation of **1** and **5** were found to be moderate. It is noteworthy that the photodissociation of **1** is adiabatic although it is formed in direct irradiation. However, the quantum yield for the adiabaticity of **1** (0.11) is three times lower than that of **5** (0.33). Considering the resonance energy of furan and benzene, this observation seems to be reasonable. The higher exothermicity in the decomposition of **5** than **1** distorts the normal energy surfaces more, and thus allows greater production of the excited 9-CP. However, quantum yields were found to be lower than those for **8** and the [4+4] cyclodimer (**10**) of anthracene and benzene.^{3,6}

Experimental

9-CP was recrystallized from dichloromethane and *n*-hexane three times. Furan was distilled from CaCl₂.²⁰ Melting points were taken on a MEL-TEMP II melting point apparatus. 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. Mass spectra (MS) were obtained on a Hewlett-Packard 5890-JMS AX505WA. Peaks are reported as *m/z* (% intensity relative to a base peak). Some irradiated samples were analyzed on a Waters 600 HPLC. Fluorescence spectra were taken on an Aminco-Bowman series 2 luminescence spectrometer. All the irradiations were performed with a 450 W Hanovia medium-pressure mercury lamp through cylindrical glass filters or a filter solution. The filter solution was an aqueous solution of sodium bromide (0.54 g cm⁻³) and lead acetate (0.007 g cm⁻³) that blocked wavelengths below 335 nm.²¹

Direct irradiation of 9-CP and furan

A solution of 9-CP (4.05 g, 19.9 mmol) and furan (60 cm³, 825 mmol) in benzene (600 cm³) was irradiated through a uranium glass filter for 40 h under a nitrogen atmosphere. White powder was precipitated out during the irradiation. After the solvent was evaporated off, the reaction mixture was separated by silica gel column chromatography eluting with *n*-hexane–dichloromethane mixtures of increasing polarity to afford the unreacted 9-CP (2.49 g, 61%), **1** (88.0 mg, 4% based on consumed 9-CP), and **2** (1.05 g, 67% based on consumed 9-CP). **1**: Mp 127.5–128.5 °C (from dichloromethane and *n*-hexane); λ_{max} (cyclohexane)/nm 277 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 11 100); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3070, 2950, 2235, 1650, 1600, 1490, 1445, 1440 and 1140; δ_{H} (500 MHz; CDCl₃; Me₄Si) 7.93 (1H, dd, *J* 7.6, 1.7, ArH), 7.87 (1H, m, ArH), 7.46 (1H, m, ArH), 7.42–7.35 (3H, m, ArH), 7.29 (1H, ddd, *J* 7.5, 7.5, 1.2, ArH), 7.18 (1H, m, ArH), 6.61 (1H, dd, *J* 2.7, 1.6, H⁵), 5.61 (1H, dd, *J* 2.7, 2.7, H⁴), 4.89 (1H, dd, *J* 7.1, 5.1, H²), 4.34 (1H, dd, *J* 5.1, 0.7, H¹) and 3.93 (1H, m, *J* 7.1, 2.7, 1.6, H³); δ_{C} (125 MHz; CDCl₃; Me₄Si) 149.38, 131.89, 131.75, 130.51, 129.46, 129.23, 128.88, 128.74, 128.55, 123.80, 123.68, 120.74, 103.68, 83.62, 60.93, 50.12 and 38.86; *m/z* (CI) 272 (MH⁺, 11%), 244 (39), 233 (17), 232 (84), 205 (85), 204 (100), 203 (31) and 69 (28); HRMS calcd. for C₁₉H₁₄NO (MH⁺) *m/z* 272.1076, found 272.1072.

X-Ray structure of **1** †

Crystal data. C₁₉H₁₃NO, *M* = 271.31. Orthorhombic, *a* = 10.403(1), *b* = 14.172(2), *c* = 18.893(2) Å, *V* = 2785.5(6) Å³ (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, $\lambda = 0.71069$ Å), space group *Pca*2₁ (no. 29), *Z* = 8, *D_x* = 1.294 g cm⁻³. Colourless crystals. Crystal dimensions: 0.3 × 0.4 × 0.4 mm, *F*(000) = 1136, $\mu(\text{Mo-K}\alpha) = 0.080$ mm⁻¹.

Data collection, structure analysis and refinement. CAD4 diffractometer, graphite-monochromated Mo-K α radiation; 2583 reflections measured ($2.2 \leq \theta \leq 25.0^\circ$) at room temperature, 2535 independent reflections (*R*_{int} = 0.0091). Direct methods with SHELXS-86,²² full-matrix least-squares refinement with SHELXL-93,²³ all non-hydrogen atoms anisotropic, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0774P)^2]$ with $P = (F_o^2 + 2F_c^2)/3$. Final *R* indices [*I* > 2 σ (*I*)]: *R*1 = 0.0529, *wR*2 = 0.1161; *R* indices (all data): *R*1 = 0.1153, *wR*2 = 0.1757.

Mechanistic study

Several reaction solutions (Table 1, 4 cm³ each) in Pyrex test tubes were purged with nitrogen for 20 min. The samples in a merry-go-round apparatus were irradiated through the aqueous filter solution. The irradiation time was controlled to keep the conversion low and **1** detectable by HPLC. The reaction mixtures were analyzed with a Nova-Pak silica column (3.9 × 150 mm; flow rate, 1.1 cm³ min⁻¹) using *n*-hexane and ethyl acetate. The chromatogram was integrated relative to an internal standard of 5,7-dimethoxycoumarin. Retention times (min) were 18 for 9-CP, 27 for **1**, and 40 for **2** (from 0.5% ethyl acetate to 2% over 26 min and to 5% over the next 2 min).

Synthesis of **1** by sensitized irradiation

A solution of 9-CP (1.26 g, 6.20 mmol), excess furan (50 cm³, 688 mmol), and MK (0.175 g, 0.65 mmol) in benzene (110 cm³) was irradiated through a uranium glass filter for 50 h under a nitrogen atmosphere. Silica gel column chromatography provided the unreacted 9-CP (1.16 g, 92%) and **1** (92 mg, 69% based on consumed 9-CP).

Synthesis of **3** and **4** by direct irradiation

A solution of 9-CP (3.0 g, 14.7 mmol) and methyl orthoformate of *cis*-cyclohexa-3,5-diene-1,2-diol (8.0 g, 51.9 mmol) in benzene (120 cm³) was irradiated through a Pyrex glass filter for 15 h. After the solvent was evaporated off, the resulting oily residue was dissolved in THF (100 cm³), and treated with aqueous 0.5 M HCl solution (100 cm³). After stirring overnight, the reaction mixture was neutralized with aqueous 1 M NaOH solution, and extracted with dichloromethane (4 × 100 cm³). Combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated. Separation by silica gel column chromatography eluting with *n*-hexane–dichloromethane–ethyl acetate mixtures afforded the unreacted 9-CP (1.06 g, 35%), **3** (232 mg, 8% based on consumed 9-CP), **4** (47 mg, 2% based on consumed 9-CP), and **2** (1.60 g, 83% based on consumed 9-CP). **3**: Mp 127–128 °C (from dichloromethane and *n*-hexane); λ_{max} (ethanol)/nm 275 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 10 500); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3560, 3450, 3020, 2950, 2225, 1600, 1450, 1220 and 1060; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.95 (1H, dd, *J* 9.1, 1.8, ArH), 7.91 (1H, d, *J* 7.9, ArH), 7.52 (1H, dd, *J* 7.0, 2.0, ArH), 7.43 (2H, m, ArH), 7.38 (1H, m, ArH), 7.29 (1H, d, *J* 7.4, ArH), 7.04 (1H, d, *J* 7.4, ArH), 6.31 (1H, m, *J* 10.4, H⁴), 6.08 (1H, dd, *J* 10.4, 1.4, H⁵), 4.61 (1H, broad s, H⁶), 4.11 (1H, broad s, H⁷), 3.65 (1H, d, *J* 9.6, H¹), 3.21 (1H, broad s, H³), 3.00

(1H, m, H²), 2.49 (1H, broad s, OH) and 2.07 (1H, broad s, OH); δ_{C} (75 MHz; CDCl₃; Me₄Si) 132.01, 131.86, 131.57, 131.34, 130.51, 129.31, 129.23, 128.59, 128.35, 126.94, 124.05, 123.69, 120.28, 65.62, 65.57, 45.46, 42.48, 42.39 and 39.87; *m/z* (FAB) 316 (MH⁺, 6%), 298 (7), 204 (100) and 95 (30); HRMS calcd. for C₂₁H₁₈NO₂ (MH⁺) *m/z* 316.1338, found 316.1331. **4**: Mp 191–192 °C (from ethyl acetate); λ_{max} (ethanol)/nm 274 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1 380); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3457, 3352, 2915, 2232, 1645, 1442 and 1371; δ_{H} (500 MHz; DMSO-d₆; Me₄Si) 8.15 (1H, m, ArH), 8.07 (1H, m, ArH), 7.81 (1H, m, ArH), 7.55–7.31 (5H, m, ArH), 6.66 (1H, dd, *J* 7.5, 7.1, H⁷), 6.43 (1H, dd, *J* 7.2, 7.1, H⁶), 4.47–4.32 (2H, broad s, OH), 3.54 (1H, m, H⁵), 3.42 (1H, d, *J* 3.0, H¹), 3.27 (1H, dd, *J* 7.6, 2.0, H³), 3.19 (1H, dd, *J* 7.5, 2.6, H⁴) and 3.05 (1H, m, H²); *m/z* (EI) 315 (M⁺, 8%), 240 (13), 204 (89), 203 (100) and 112 (55); HRMS calcd. for C₂₁H₁₇NO₂ (M⁺) *m/z* 315.1260, found 315.1260.

Synthesis of **3** and **4** by sensitized irradiation

A solution of 9-CP (1.0 g, 4.9 mmol), methyl orthoformate of *cis*-cyclohexa-3,5-diene-1,2-diol (2.6 g, 16.9 mmol), and MK (132 mg, 0.49 mmol) in dichloromethane (110 cm³) was irradiated through a uranium glass filter for 30 h. The reaction mixture was subjected to the same hydrolysis and work-up procedures to give the unreacted 9-CP (862 mg, 86%), **3** (109 mg, 51% based on consumed 9-CP), and **4** (17 mg, 8% based on consumed 9-CP).

Synthesis of **5**

Diol **3** (116.0 mg, 0.37 mmol) and excess DMF dimethyl acetal (25 cm³) were stirred at 50 °C for 1 h, and the reaction mixture was concentrated under reduced pressure. To the resulting yellow oil was added *N,N*-diisopropylethylamine (93 mg, 0.72 mmol) in dichloromethane (25 cm³). A solution of trifluoromethanesulfonic anhydride (102 mg, 0.36 mmol) in dichloromethane (10 cm³) was then added over a period of 3 min. After 30 min, the reaction mixture was washed with saturated sodium bicarbonate solution and brine, and dried over sodium sulfate. Removal of the solvent under reduced pressure afforded a yellow solid residue, which was separated by a silica gel column chromatography to afford **5** (47 mg, 45%). Mp 90–91 °C (from methanol); λ_{max} (ethanol)/nm 275 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 18 200); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 3060, 3005, 2920, 2210, 1480, 1450 and 1230; δ_{H} (300 MHz; CDCl₃; Me₄Si) 7.92 (1H, m, ArH), 7.88 (1H, dd, *J* 7.9, 0.5, ArH), 7.47–7.32 (4H, m, ArH), 7.25 (1H, m, ArH), 7.08 (1H, ddd, *J* 7.4, 1.4, 0.8, ArH), 6.19–6.10 (2H, m, H⁵, H⁶), 5.90 (1H, ddd, *J* 9.4, 5.8, 1.2, H⁴), 5.64 (1H, dd, *J* 9.5, 5.8, H⁷), 4.47 (1H, d, *J* 9.3, H¹), 3.52 (1H, dd, *J* 10.1, 1.3, H³) and 3.19 (1H, m, *J* 9.3, 5.8, H²); δ_{C} (75 MHz; CDCl₃; Me₄Si) 132.24, 131.87, 129.36, 129.10, 129.04, 128.52, 128.41, 128.23, 125.79, 124.83, 124.45, 123.84, 123.73, 123.41, 120.16, 109.58, 50.11, 49.22, 44.75 and 38.34; *m/z* (FAB) 282 (MH⁺, 3%), 280 (9), 204 (100), 203 (93) and 77 (8); HRMS calcd. for C₂₁H₁₆N (MH⁺) *m/z* 282.1284, found 282.1286.

Kinetic study on the thermolysis of **1** and **5**

A 6.20 × 10⁻⁵ M solution of **1** in DMF (3 cm³) was deaerated by six freeze–pump–thaw cycles at 0.02 mmHg. Kinetic experiments were conducted in the temperature range of 71.8–97.7 °C (±0.3 °C). The amounts of **1** and 9-CP were estimated by the UV spectrophotometer. The data were analyzed by the first order reaction rate law. After five kinetic measurements were conducted, the activation energy of the reaction was obtained using the Arrhenius equation. By the least squares method, the data for the thermolysis of **1** were fitted to eqn. (1).

$$\ln k = 36.76 - 16700/T \quad R^2 = 0.996 \quad (1)$$

In the thermolysis of **5**, a 1.08 × 10⁻³ M solution in DMF

† CCDC reference number 188/167. See <http://www.rsc.org/suppdata/p2/1999/1299> for crystallographic files in .cif format.

was used, and the temperature was in the range of 52.4–71.7 °C. The data were fitted to eqn. (2).

$$\ln k = 30.39 - 12950/T \quad R^2 = 0.999 \quad (2)$$

Determination of quantum yield for the photodissociation

Quantum yields for the photodecomposition of **1** and **5** were determined with the aid of a potassium ferrioxalate actinometer.¹⁹ To avoid uneven stirring effects, a narrow quartz cell with 1 cm³ volume capacity and 1 cm path length was used. Before irradiation, the optical density was adjusted to 0.078–0.105 at 280 nm. The degassed solution was irradiated at 280 nm through a 2 nm slit with a 150 watt xenon lamp.

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

Quantum yield for the formation of the excited 9-CP was determined by comparing the emission spectra with similar optical density of 9-CP at 280 nm. Both the excitation monochromator slit and emission slit were set at 5 nm. The optical density of degassed solutions of **1**, **5**, and 9-CP in cyclohexane was in the range of 0.043–0.048. The observed monomer fluorescence was subtracted from the emission irradiated at 355 nm, where **1** and **5** do not absorb.^{7b} Each sample was used once to avoid the interference from 9-CP formed during the measurement.

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