CH_2CHO), 1.86 (m, 2 H, OCH_2CH_2); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **73a/73b**) δ 179.17 (s, 1 C), 170.89 (s, 1 C), 140.57 (s, 1 C), 136.92 (s, 1 C), 127.9–128.4 (d, 3 C, overlapping peaks), 126.86 (d, 1 C), 76.89 (d, 1 C), 73.33 (d, 1 C), 66.08 (t, 1 C), 39.56 (t, 1 C), 38.62 (t, 1 C), 30.64 (t, 1 C), 24.82 (t, 1 C), 21.05 (q, 1 C). **73b**: ^1H NMR (400 MHz, peaks assigned from a mixture of **73a/73b**) δ 7.2–7.4 (m, 5 H, Ph), 6.55 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhCH=C), 5.14 (m, 1 H, CH(OAc)), 4.40 (m, 1 H, CHO), 3.37–3.43 (m, 2 H, OCH_2), 2.88 (ddd, part of AB, J = 17, 6.5, and 2 Hz, 1 H, $C{=}CH_2$), 2.81 (br d, part of AB, J = 17 Hz, 1 H, $C{=}CH_2$), 2.45–2.51 (m, 2 H, CH_2COOH), 2.1–2.2 (m, 2 H, CH(OAc)-CH_2CHO), 2.06 (s, 3 H, OAc), 1.92 (m, 2 H, OCH_2CH_2); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **73a/73b**) δ 179.17 (s, 1 C), 171.16 (s, 1 C), 140.74 (s, 1 C), 136.84 (s, 1 C), 127.9–128.4 (d, 3 C, overlapping peaks), 126.96 (d, 1 C), 76.95 (d, 1 C), 72.97 (d, 1 C), 65.93 (t, 1 C), 39.99 (t, 1 C), 37.62 (t, 1 C), 30.69 (t, 1 C), 24.82 (t, 1 C), 21.10 (q, 1 C).

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Supplementary Material Available: ^1H NMR spectra of compounds for which elemental analyses are lacking (74 pages). Ordering information is given on any current masthead page.

Photoreactions of *N*-Methylphenanthrene-9,10-dicarboximide with Alkenes and Dienes. Heavy-Atom Effect of Halides

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Photoreaction (>400 nm) of *N*-methylphenanthrene-9,10-dicarboximide (**1**) in benzene gave the dimer *syn*-**2**. Photoreaction (>400 nm) of **1** with alkenes and dienes **3** in benzene gave **2**, products **4** of insertion of the double bond of **3** into the C–N bond of **1**, and cyclobutanes **5** and **7**. Irradiation of **2**, **4a**, **4m,n**, and **5a** at a shorter wavelength (>320 nm) gave, respectively, **1**, decarbonylation product **6**, intramolecular cycloadducts **8m,n**, and **1** + **3a**. In the photoreaction of **1** with **3b**, addition of methyl iodide to benzene (1:1 v/v) suppressed the dimerization and insertion reactions, and only cyclobutanes **5b** and **7b** were formed. Methyl iodide and iodobenzene were equally effective in increasing the ratio (**5b** + **7b**)/**4b** with increasing halide concentration; butyl bromide and bromobenzene were less effective. The ratio **5**:**7** was independent of the concentration of methyl iodide. Dilution plots of insertion and cyclobutane formation in the photoreaction of **1** with **3b** showed that methyl iodide quenched the excited state of **1** which led to insertion. The results indicate that the syn dimerization and the insertion occurred from the singlet excited state of **1**, and the cyclobutane arose mainly from the triplet excited state. The activity of the halides in these photoreactions is attributed to the heavy-atom effect.

Introduction

Photochemistry of phthalimides in the presence of alkenes has been the subject of many investigations.[1] Several types of reactions have been observed, including alcohol addition (electron-transfer reaction),[2] insertion of the alkene into the imide moiety,[3] oxetane formation,[4] and photoreduction.[5] The effect of arene structure on the photochemistry of arenedicarboximides has been investigated.[6,7] We have studied the effect of an extended π-conjugation system and have reported photoreactions in which the arene structure plays a crucial role in determining the reaction pathway.[7] Thus the predominant reactions of *N*-methylnaphthalene-1,8-, -2,3-, and -1,2-dicarboximides with alkenes are cyclobutane formation,[7c] oxetane formation,[7d] and insertion of the alkene into the imide bond,[7b] respectively.

Here we report on the photoreactions of *N*-methylphenanthrene-9,10-dicarboximide (**1**) with alkenes dienes and on the heavy-atom effect on these reactions. Internal

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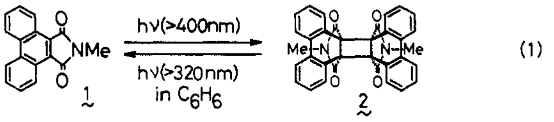
and external heavy atoms can enhance both radiative and nonradiative electronic relaxation probabilities because they enhance spin–orbit coupling. This phenomenon is well documented as the "heavy-atom effect" in photophysics.[8] In photochemical reactions, the heavy-atom effect can increase the yields of products derived from a triplet excited state over those from a singlet excited state because of the increase in the intersystem crossing rate. The few examples of heavy-atom effects that have been reported include the dimerization of acenaphthylene,[9] the cross cycloaddition of acenaphthylene with a variety of compounds,[10] and others.[11]

Results and Discussion

Photoreaction of 1 in Benzene. Irradiation (>400 nm) of 1 in benzene under N_2 gave *syn*-2 (95%, eq 1). No



(1)

anti-2 was detected by ^1H NMR. The cyclobutane structure was deduced from spectral data and was supported by the fact that 2 was almost quantitatively converted back to 1 by irradiation with light of shorter wavelength (>320 nm). The syn structure was confirmed by the shielding effect in ^1H NMR chemical shifts of the aromatic protons. Thus the signals of the four aromatic protons in 2 were shifted to higher field ($\Delta\delta$ = 0.19–0.24 ppm) compared with the corresponding signals of a model compound, *N*-methyl-9,10-dihydrophenanthrene-9,10-dicarboximide, whereas the NMe signal in 2 appeared at a slightly lower field (δ 3.09) compared with that of the model compound (δ 2.98).

This reaction seems to be the first example of photodimerization of arenedicarboximides. Although phenanthrene itself does not photodimerize under the usual conditions, substituted phenanthrenes have been reported to give dimers.[12] In these examples, syn dimers are derived from the singlet excited states of the substituted phenanthrenes and anti dimers exclusively from the triplet excited states.

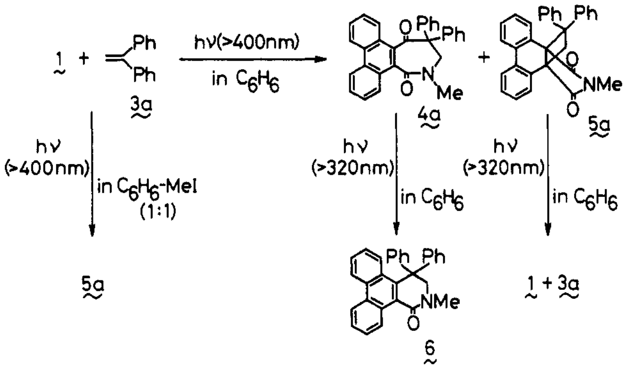
Photoreaction of 1 with Alkenes and Dienes. Photoreaction of 1 with alkenes and dienes in pure benzene gave two major products, and 2 became a minor product. One product resulted from insertion of the double bond of the alkenes and dienes into the imide ring of 1 (type i reaction).[3,7] The other product was produced by cycloaddition of the double bond of the alkenes and dienes to the phenanthrene-9,10 double bond of 1 (type ii reaction).

Table I. Photoreaction of 1 with Alkenes 3b–k and Dienes 3l–n[a]

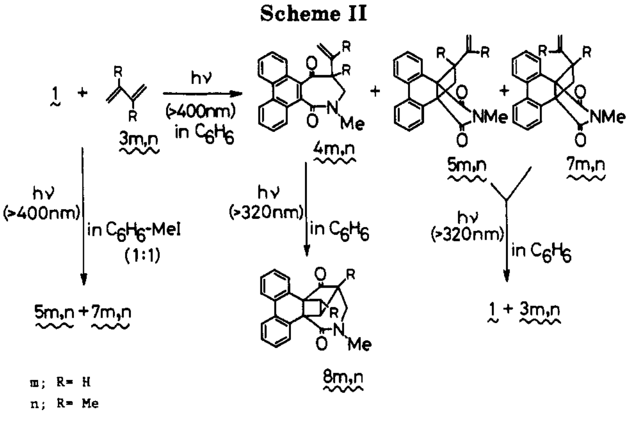
alkene or diene	solvent	yield,[b] %			
		2	4	5	7
3b	C_6H_6	0	48	15	9
	C_6H_6 + MeI[c]	0	0	50	32
3c	C_6H_6	0	44	7	15
	C_6H_6 + MeI[c]	0	0	25	51
3d	C_6H_6	86	0	0	
	C_6H_6 + MeI[c]	0	0	0	
3e	C_6H_6	20	31	36	
	C_6H_6 + MeI[c]	0	0	90	
3f	C_6H_6	45	0	40	0
	C_6H_6 + MeI[c]	0	0	trace[d]	0
3g	C_6H_6	43	0	42[e]	0
	C_6H_6 + MeI[c]	0	0	trace[d]	0
3h	C_6H_6	16	57	trace	trace
	C_6H_6 + MeI[c]	0	0	57	trace
3i	C_6H_6	18	34	24	trace
	C_6H_6 + MeI[c]	0	0	70	trace
3j	C_6H_6	40	17	30	
	C_6H_6 + MeI[c]	0	0	65	
3k	C_6H_6	36	31	24	
	C_6H_6 + MeI[c]	0	0	79	
3l	C_6H_6	14	45	26	
	C_6H_6 + MeI[c]	0	0	76	
3m	C_6H_6	7	43	trace	33
	C_6H_6 + MeI[c]	0	0	trace	83
3n	C_6H_6	trace	52	7	15
	C_6H_6 + MeI[c]	0	0	27	62

[a] Reaction conditions: [1] = 15 mM, [**3b–n**] = 200 mM, irradiation >400 nm, under N_2, at ambient temperature. [b] Yields were based on consumed 1. [c] Volume ratio = 1:1. [d] Conversion of 1 was slow. [e] Yield of **5f**.

Scheme I



Scheme II



For example, photoreaction (>400 nm) of 1 (15 mM) with 1,1-diphenylethylene (**3a**, 200 mM) in pure benzene under N_2 afforded **4a** (type i, 64%) and **5a** (type ii, 21%) (Scheme I). The structures of **4a** and **5a** were determined by spectroscopic properties and elemental analyses. These

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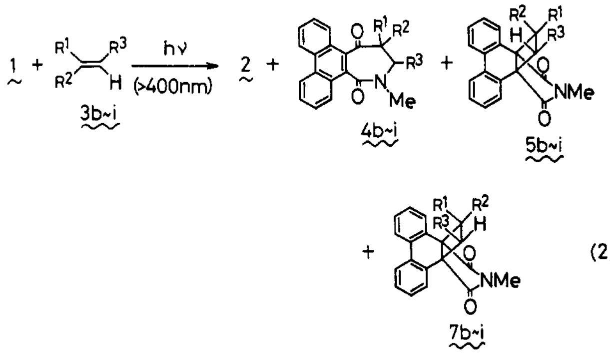
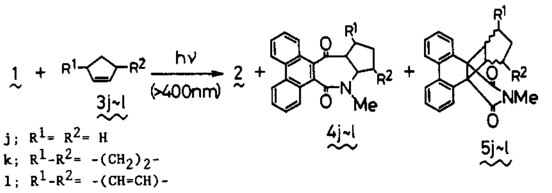
structures are supported by the fact that, on irradiation at >320 nm, **4a** was photodecarbonylated to **6**, possibly via α cleavage of the cyclic ketone moiety, whereas **5a** photodecomposed quantitatively to the starting materials **1** and **3a**. The structure of **6** was supported by ^{13}C NMR and IR spectra and elemental analysis. Photoreaction of **1** (15 mM) with **3a** (200 mM) at >320 nm in benzene gave **6** (85%) directly as a result of the secondary photoreactions mentioned above.

Other examples of photoreaction (>400 nm) of **1** with alkenes **3b–k** and dienes **3l–n** in benzene under N_2 are shown in eq 2 and 3, Scheme II, and Table I. In the reactions with α-methylstyrene (**3b**) and styrene (**3c**), type i (**4b,c**) and type ii (**5b,c** and **7b,c**) products were obtained, and the dimerization of **1** was suppressed. The structures of the cyclobutane isomers **5b** and **7b** were determined mainly on the basis of the anisotropic shielding of the aromatic ring in the ^{1}H NMR spectra. Thus the CMe (δ 1.21) and NMe (δ 2.70) signals of **5b** showed high-field shifts relative to the corresponding CMe (δ 1.67) and NMe (δ 3.04) signals of **7b**.



(2)

	R^1	R^2	R^3
b	Ph	Me	H
c	Ph	H	H
d	*n*-Bu	H	H
e	Me	Me	H
f	H	Me	Me
g	Me	H	Me
h	Me	Me	Me
i	OEt	H	H

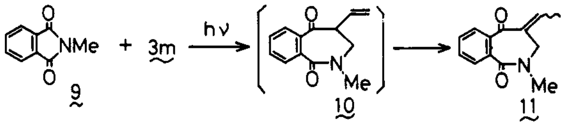


(3)

j; $R^1 = R^2 = H$
k; $R^1\text{-}R^2 = \text{-(CH}_2)_2\text{-}$
l; $R^1\text{-}R^2 = \text{-(CH=CH)-}$

Only dimerization to **2** was observed in the reaction with 1-hexene (**3d**). In the reactions with *trans*- and *cis*-2-butene (**3f** and **3g**) type i products were not observed, and only cyclobutane **5f** was obtained. Reactions with other aliphatic alkenes **3e,h–k** gave generally **2**, type i (**4e,h–k**), and type ii (**5e,h–k**) products.

The dienes, 2,5-norbornadiene (**3l**), 1,3-butadiene (**3m**), and 2,3-dimethyl-1,3-butadiene (**3n**), also reacted with **1** on irradiation (>400 nm) to give **2**, type i (**4l,m**), and type ii (**5l,n** and **7m,n**) products. When **4m,n** (15 mM) were irradiated at >320 nm in benzene, cyclobutanes **8m,n** were formed by intramolecular [2 + 2] cycloaddition in 76 and 83% yields, respectively (Scheme II). The structures of **8m,n** were assigned on the basis of spectroscopic properties. The IR spectra of **8m,n** show characteristic absorption bands for a five-membered cyclic ketone at 1752 and 1762 cm^{-1}, respectively. Photoreaction of **1** (15 mM) with **3m** (200 mM) at >320 nm in benzene gave **8m** (80%) directly. Mazzocchi et al. reported that the photoreaction of *N*-methylphthalimide (**9**) with **3m** gave **11** by insertion of a double bond of **3m** into the imide bond to give **10** followed by hydrogen migration (eq 4).[3a] However, **4m** underwent photochemical cycloaddition to **8m** in stead of hydrogen migration.



(4)

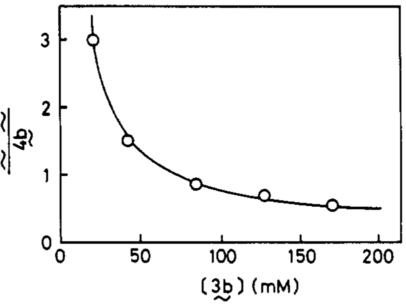


Figure 1. Effect of concentration of α-methylstyrene (**3b**) on the ratio (**5b** + **7b**)/**4b** in the photoreaction of **1** (3.8 mM) with **3b**.

A marked concentration dependency on the ratio of type ii to type i products was observed in the photoreaction of **1** with alkenes and dienes. For example, in the reaction of **1** with **3b**, the ratio (**5b** + **7b**)/**4b** decreased with increasing concentration of **3b** (Figure 1). On the other hand, the cyclobutane isomer ratio **5b**/**7b** remained almost constant over the concentration range 21–168 mM of **3b**. These results indicate that type i and type ii products arise mainly from different excited states of **1**.

Effect of Halides on the Photoreactions of 1 (External Heavy-Atom Effect). The relative amounts of products from the photoreactions of **1** were markedly affected by addition of methyl iodide to benzene (1:1 v/v). The photoreaction of **1** alone in the presence of methyl iodide gave no observable products even after prolonged irradiation (>400 nm). However, in the reaction of **1** with **3a**, addition of methyl iodide led to formation of only type ii product **5a** (84%) and no type i product **4a** (Scheme I). The formation of **2** and **4** was likewise completely suppressed by methyl iodide in the photoreactions (>400 nm) of **1** with alkenes **3b–k** and dienes **3l–n** (Table I).

Figure 2 shows the linear dependence of the ratio (**5b** + **7b**)/**4b** on the concentration of four halides in the photoreaction of **1** with **3b**. Iodobenzene had the same effect on this ratio as methyl iodide, whereas butyl bromide and bromobenzene did not affect the ratio as much as the iodides. However, the isomer ratio of the cyclobutanes **5b**/**7b** remained almost constant as a function of the concentration of both the iodides and bromides.

Character of the Excited States of 1 and Fluorescence Quenching. The absorption spectrum of **1** in benzene showed a broad band around 377 nm, which was shifted to a longer wavelength in ethanol. The fluorescence spectrum of **1** in air-saturated benzene (10^{-5} M) showed a broad band at λ_{max} 454 nm with a room-temperature lifetime τ of 15.1 ns. These data suggest that the lowest singlet excited state of **1** is π,π^*. The energy of the singlet excited state (E_S), estimated from the absorption and fluorescence spectra, was 69 kcal/mol. A strong phosphorescence band of **1** was observed at λ_{max} 568 nm in EPA at 77 K. The long lifetime (1.4 s) suggests that the lowest triplet excited state is also π,π^*. The energy of the triplet excited state (E_T), calculated from the 0–0 phoshorescene band, was 52 kcal/mol.

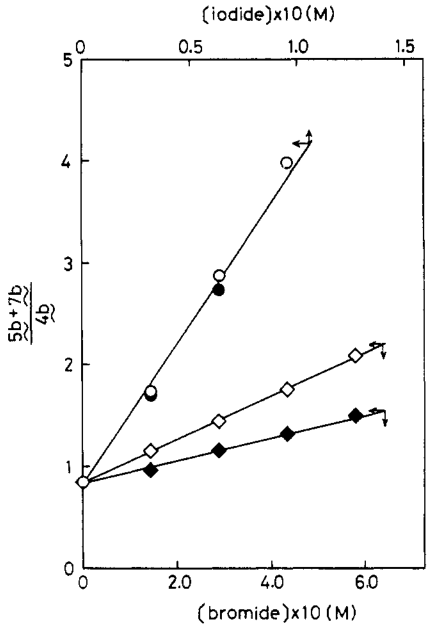


Figure 2. Effect of concentration of halide on the ratio (**5b** + **7b**)/**4b** in the photoreaction of **1** (3.8 mM) with **3b** (95 mM): ○, MeI; ●, PhI; ◇, BuBr; ◆, PhBr.

Table II. Fluorescence Quenching Stern–Volmer Slopes ($k_q\tau$) and Quenching Rate Constants (k_q) for 1-Alkene 3a–e,h,i Systems[a]

alkene	$k_q\tau$, mol^{-1} L	$10^{-7}k_q$,[b] mol^{-1} L s^{-1}
3a	7.35	48.7
3b	6.73	44.6
3c	1.21	8.01
3d	0	0
3e	*c*	*c*
3h	0.63	4.0
3i	1.40	9.27

[a] In air-saturated benzene at room temperature; [**1**] = 1×10^{-5} M. [b] Fluorescence lifetime of **1** (τ) in air-saturated benzene is 15.1 ns. [c] A very low value. The precise value could not be determined because of the low solubility of **3e**.

The fluorescence of **1** in benzene was quenched by alkenes to various extents without changing the shape and wavelength of the maximum emission. Stern–Volmer plots of the fluorescence quenching by alkenes **3a–e,h,i** in air-saturated benzene (eq 5) gave straight lines against alkene

$$\Phi_f^0/\Phi_f = 1 + k_q\tau[\text{alkene}] \qquad (5)$$

concentration. In eq 5 Φ_f^0 and Φ_f are the fluorescence quantum yields in the absence and presence of the alkene, respectively. Fluorescence quenching rate constants k_q were calculated from the Stern–Volmer slopes $k_q\tau$ (Table II).

Fluorescence of **1** in benzene is also quenched by halides without changing the shape and wavelength of the maximum emission. Stern–Volmer plots of the fluorescence quenching by halides in air-saturated benzene (eq 6) gave

$$\Phi_f^0/\Phi_f' = 1 + k_q'\tau[\text{halide}] \qquad (6)$$

straight lines against the halide concentration. In eq 6, Φ_f^0 and Φ_f are the fluorescence quantum yields in the absence and presence of the halide, respectively. The fluorescence quenching rate constants k_q' are shown in Table III. The rate constants of quenching by the iodides are comparable to the diffusion-controlled rate constant and are larger than those by the bromides by a factor of ~10. These results also support the suggestion of a heavy-atom effect in the reaction.

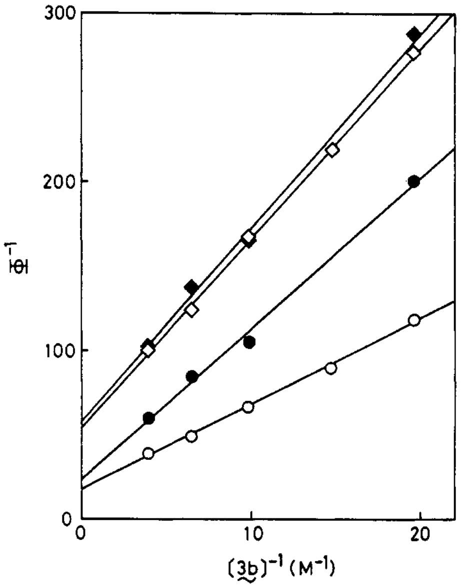


Figure 3. Dilution plots for the photoreaction of **1** (3.8 mM) with **3b**: ○, **4b** in C_6H_6; ●, **4b** in C_6H_6-MeI (32 mM); ◇, **5b** + **7b** in C_6H_6; ◆, **5b** + **7b** in C_6H_6-MeI (32 mM).

Table III. Fluorescence Quenching Stern–Volmer Slopes ($k_q'\tau$) and Quenching Rate Constants (k_q') for 1-Halide Systems[a]

halide	$k_q'\tau$, mol^{-1} L	$10^{-8}k_q'$,[b] mol^{-1} L s^{-1}
MeI	31	21
PhI	47	31
BuBr	4.2	2.7
PhBr	5.0	2.3

[a] In air-saturated benzene at room temperature; [**1**] = 1×10^{-5} M. [b] Fluorescence lifetime of **1** (τ) in air-saturated benzene is 15.1 ns.

Table IV. Limiting Quantum Yields (Φ_{lim}) and Stern–Volmer Slopes (K_{SV}) for 1 and α-Methylstyrene (3b) from Dilution Plots (Figure 3)[a]

product	solvent	Φ_{lim}	K_{SV}, mol^{-1} L
4b	C_6H_6	0.055	3.6
	C_6H_6 + MeI (32 mM)	0.044	2.6
5b + **7b**	C_6H_6	0.019	4.8
	C_6H_6 + MeI (32 mM)	0.017	4.9

[a] In air-saturated benzene at room temperature; [**1**] = 3.8 mM.

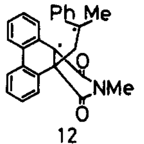
Quantum Yield Measurements. The effect of varying the concentration of **3b** on the quantum yields (Φ) of products in the photoreaction of **1** with **3b** was investigated. The relation between Φ and **3b** concentration is given by eq 7, if only one quenchable excited state is in-

$$\Phi^{-1} = \Phi_{\text{lim}}^{-1}(1 + K_{SV}^{-1}[\mathbf{3b}]^{-1}) \qquad (7)$$

volved in the formation of each type of product. In eq 7, Φ_{lim} is the quantum yield of the reaction at limiting **3b** concentration, and K_{SV} is the slope of the Stern–Volmer **3b** quenching of an excited state and is the product of the **3b** quenching rate constant and the lifetime of the corresponding excited state of **1**. The plots of Φ^{-1} vs $[\mathbf{3b}]^{-1}$ (dilution plots) for the type i and type ii reactions in benzene and benzene–methyl iodide are shown in Figure 3. The plots are linear, as expected from the eq 7, and indicate that **4b** and (**5b** + **7b**) are formed mainly from one excited state of **1**. The values of Φ_{lim} and K_{SV} obtained are shown in Table IV. The K_{SV} value from eq 7 for the type i reaction in benzene is 3.6, which is in fair agreement with the $k_q\tau$ value (6.73) obtained from fluorescence quenching (Table II). As shown in Table IV, methyl iodide was more effective in diminishing the K_{SV} value for the type i reaction than for the type ii reaction. This result is another manifestation of the heavy-atom effect in the reaction.

Excited-State Multiplicities and the Heavy-Atom Effect. Although the formation of **2** and the type i products were suppressed by the presence of the heavy atom, the formation of the type ii products was not. This result is rationalized by the hypothesis that the dimerization of **1** and the type i reaction occur from the π,π^* singlet excited state of **1** and the type ii reaction from the π,π^* triplet excited state. The type i reaction is known to proceed only from the singlet excited states of other arenedicarboximides.[3,7b] The hypothesis is supported by the fact that the ratio of type ii to type i product [(**5b** + **7b**)/**4b**] decreased with increasing concentration of **3b** in the absence of methyl iodide, since a marked decrease in products derived from the triplet state with increasing concentration of alkene has been reported when distinct products are generated from the singlet and triplet excited state in the photoreactions of other arenedicarboximides.[4c,5c]

The constant isomer ratio **5b**/**7b** at different concentrations of **3b** and halides may indicate that the type ii products are derived only from the triplet excited state of **1**, possibly via a triplet biradical such as **12**. The isomer ratio would be expected to change as a function of **3b** concentration if the type ii reaction proceeded from both the singlet and triplet excited states. Further information on the excited states leading to type ii products can be obtained from the following analysis. Assuming a mechanism



12

$$1 \xrightarrow{h\nu} {}^1\mathbf{1}^* \text{ (singlet excited state)} \qquad (8)$$

$${}^1\mathbf{1}^* \xrightarrow{k_{isc}} {}^3\mathbf{1}^* \text{ (triplet excited state)} \qquad (9)$$

$${}^1\mathbf{1}^* + \mathbf{3b} \xrightarrow{k_i} \mathbf{4b} \text{ (type i product)} \qquad (10)$$

$${}^3\mathbf{1}^* + \mathbf{3b} \xrightarrow{k_{ii}} \mathbf{5b} + \mathbf{7b} \text{ (type ii products)} \qquad (11)$$

then

$$(\Phi_{5b} + \Phi_{7b})/\Phi_{4b} = (\mathbf{5b} + \mathbf{7b})/\mathbf{4b} = k_{isc}/k_i[\mathbf{3b}] \qquad (12)$$

which should give a straight line with an intercept at 0 when (**5b** + **7b**)/**4b** is plotted against 1/[**3b**]. The plot (Figure 4) is linear, and the slope is close to 0 (0.18), indicating that **5b** + **7b** (type ii products) are derived mainly from the triplet excited state of **1**.

The syn dimerization must occur from the singlet excited state of **1**, since the reaction is quenched by the alkenes and completely suppressed by methyl iodide. The dimers obtained from the singlet excited state of substituted phenanthrenes are known to be syn.[12]

The addition of only 0.4% (v/v, 6.4×10^{-2} mol L^{-1}) of methyl iodide to the photoreaction of **1** with **3b** in benzene increased the ratio of type ii to type i products [(**5b** + **7b**)/**4b**] from 0.8 to 2.9 (Figure 2), indicating a potent external heavy-atom effect.

Internal Heavy-Atom Effect. The photoreaction of **1** with α-bromostyrene (**3o**) was investigated to determine the effect of an internal heavy atom. Irradiation (>400 nm) of **1** (15 mM) with **3o** (200 mM) in benzene under N_2 gave a mixture of the type ii products **5o** (68%) and **7o** (17%), with no detectable amounts of the type i product (eq 13).

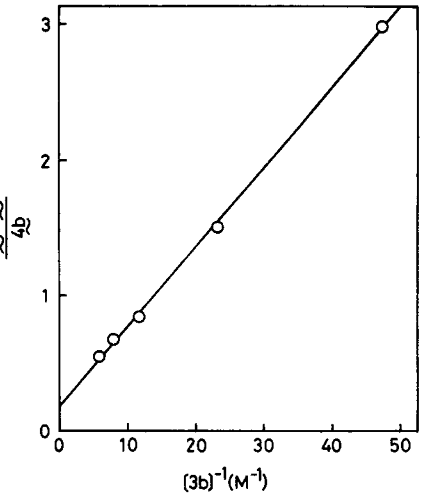
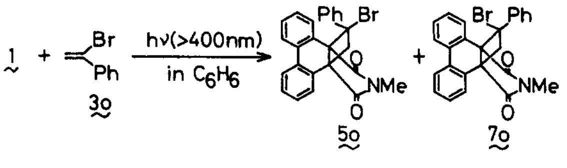


Figure 4. Inverse plots of concentration of α-methylstyrene (**3b**) on the ratio (**5b** + **7b**)/**4b** in the photoreaction of **1** (3.8 mM) with **3b**.



(13)

Experimental Section

NMR spectra were obtained on JEOL JNM-MH-100 (100 MHz) and JEOL JNM-GX-270 (270 MHz) instruments. Chemical shifts are reported in ppm (δ) relative to internal $SiMe_4$. IR spectra were recorded by use of a Hitachi 650 spectrometer. Fluorescence (phosphorescence) spectra and lifetimes were measured by a Hitachi 850 spectrophotometer and a Horiba NAES-1100 time-resolved spectrofluorimeter, respectively. Melting points were recorded by using a Yanagimoto micro-melting-point apparatus and are uncorrected.

Materials. *N*-Methylphenanthrene-9,10-dicarboximide (**1**) was prepared by the reaction of phenanthrene-9,10-dicarbyoxylic anhydride and methylamine followed by dehydration.[13] Alkenes **3a–k** and dienes **3l–n** were commercially available and purified by distillation if liquid or by recrystallization if solid. α-Bromostyrene (**3o**) was prepared as described by McConaghy and Lwowski.[14]

General Procedure for Irradiation and Product Isolation. UV irradiation was carried out with an Eikosha EHB-W-300 high-pressure Hg lamp through Pyrex and about a 1-cm-path-length saturated $CuSO_4$ aqueous solution filter [341 (50% transmittance), 330 (25%), 320 (5%), 310 nm (0%)] (>320 nm) or through an approximately 1-cm-path-length aqueous filter prepared from 27 g of $CuSO_4 \cdot 5H_2O$, 30 g of $NaNO_2$, and 50 mL of concentrated NH_4OH diluted with water to 1000 mL [410 (30% transmittance), 400 (7%), 390 nm (0%)] (>400 nm)[15] at ambient temperature. The reaction was monitored by TLC (Merck, Kieselgel 60 F_{254}) and by ^{1}H NMR measurements. After evaporation of the solvent, the resuidue was subjected to column chromatography [Wakogel C-200 (silica gel, 74–149 μm)] with dichloromethane–ether as the eluant.

Irradiation of 1. Irradiation (>400 nm) of **1** in benzene under N_2 gave **2**.

***syn*-8b,8c,16b,16c-Tetrahydrophenanthro[9′,10′:3,4]cyclobuta[1,2-*l*]phenanthrene-8b,8c,16b,16c-tetracarboxdiimide (2):** mp 180 °C (decomposed probably to **1** at this temperature

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[13] Kubo, Y.; Asai, N.; Araki, T. *J. Org. Chem.* **1985**, *50*, 5484.

[14] McConaghy, J. S.; Lwowski, W. *J. Am. Chem. Soc.* **1967**, *89*, 2357.

[15] Schaap, A. P.; Prasad, G.; Gagnon, S. D. *Tetrahedron Lett.* **1983**, 3047.

and remelted at 228–229 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.09 (s, 6 H, NMe), 7.11 (dt, *J* = 1.9, 7.3 Hz, 4 H), 7.15 (dt, *J* = 1.9, 7.3 Hz, 4 H), 7.49 (dd, *J* = 1.9, 7.3 Hz, 4 H), 7.72 (dd, *J* = 1.9, 7.3 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 23.7 (q, NMe), 56.7 (s, cyclobutane C), 122.8 (d), 127.7 (d), 128.3 (s), 129.1 (d), 130.5 (d), 132.0 (s), 174.2 (C=O); IR (KBr) 1780 and 1722 (imide), 1422, 1368, 754 cm^{-1}; mass spectrum (20 eV), *m/e* 523 (M$^+$). Anal. Calcd for $C_{34}H_{22}N_2O_4$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.41; H, 4.36; N, 5.30.

N-Methyl-9,10-dihydrophenanthrene-9,10-dicarboximide: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.98 (s, 3 H, NMe), 4.33 (s, 2 H, CHCH), 7.35 (dt, 2 H), 7.38 (dt, 2 H), 7.72 (dd, 2 H), 7.91 (dd, 2 H).

Irradiation of 1 and 1,1-Diphenylethylene (3a). Irradiation (>400 nm) of **1** and **3a** in benzene under N_2 gave **4a** and **5a**.

12,12-Diphenyl-10-methyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,13(10*H*)-dione (4a): mp 256–259 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.62 (s, 3 H, NMe), 3.59 and 5.20 (ABq, *J* = 14.2 Hz, 2 H, CH_2, the corresponding ABq signals in CD_3SOCD_3, 3.83 and 5.23, *J* = 15.1 Hz, coalesced to singlet at 117 °C), 7.03 (d, 1 H), 7.1–7.4 (m, 12 H), 7.53 (t, 1 H), 7.55 (t, 1 H), 8.51 (d, 1 H), 8.60 (d, 1 H), 8.67 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.0 (q, NMe), 58.2 (t, CH_2), 71.1 (s, CPh_2), 122.3 (d), 122.6 (d), 126.6 (d), 126.6 (d), 127.4 (d), 127.4 (d), 127.5 (d), 128.1 (d), 128.2 (d), 128.5 (d), 128.5 (d), 128.8 (d), 129.0 (d), 129.1 (s), 130.1 (d), 131.0 (s), 131.6 (s), 131.7 (s), 133.6 (s), 137.4 (s), 137.4 (s), 142.7 (s), 166.9 (lactam), 202.1 (ketone); IR (KBr) 1685 (ketone), 1642 (lactam), 1440, 715, 700 cm^{-1}. Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.60; H, 5.44; N, 3.21.

1,1-Diphenyl-*N*-methyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5a): mp 228–230 °C; ^{1}H NMR ($CDCl_3$) δ 2.77 (s, 3 H, NMe), 3.63 and 3.73 (ABq, *J* = 13.2 Hz, 2 H, CH_2), 6.7–6.9 (m, 5 H), 7.1–7.6 (m, 9 H), 7.69 (d, 1 H), 7.77 (d, 1 H), 7.80 (d, 1 H), 7.94 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.6 (q, NMe), 44.5 (s), 47.6 (t, CH_2), 59.5 (s), 60.5 (s), 122.9 (d), 122.9 (d), 126.3 (d), 127.0 (d), 127.1 (d), 127.9 (d), 128.0 (d), 128.3 (d), 128.4 (d), 128.4 (d), 128.5 (d), 128.6 (d), 128.9 (d), 129.1 (s), 130.8 (d), 130.8 (s), 131.1 (s), 132.3 (s), 140.2 (s), 142.6 (s), 177.2 and 179.0 (imide); IR (KBr) 1765 and 1703 (imide), 1448, 1422, 738, 700 cm^{-1}. Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.51; H, 5.29; N, 3.16.

Irradiation of 4a. Irradiation (>320 nm) of **4a** (15 mM) in benzene under N_2 gave **6** (86%).

4,4-Diphenyl-2-methyl-3,4-dihydrodibenz[*f*,*h*]isoquinolin-1(2*H*)-one (6): mp 255–258 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.17 (s, 3 H, NMe), 4.20 and 4.63 (ABq, *J* = 18.3 Hz, 2 H, CH_2), 6.58 (d, 1 H), 6.72 (t, 1 H), 6.9–7.5 (m, 14 H), 7.79 (d, 1 H), 8.20 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 34.7 (q, NMe), 54.4 (s, CPh_2), 55.6 (t, CH_2), 123.3 (d), 125.1 (d), 126.5 (d), 126.6 (d), 127.5 (d), 127.6 (d), 127.7 (d), 127.7 (d), 127.8 (d), 128.0 (d), 128.2 (d), 128.3 (s), 128.5 (d), 129.5 (d), 129.8 (d), 133.4 (s), 133.8 (s), 134.5 (s), 134.6 (s), 137.8 (s), 138.0 (s), 142.8 (s), 167.8 (lactam); IR (KBr) 1646 (lactam), 1494, 1448, 754, 701 cm^{-1}. Anal. Calcd for $C_{30}H_{23}NO$: C, 87.14; H, 5.61; N, 3.39. Found: C, 87.26; H, 5.76; N, 3.35.

Irradiation of 1 and α-Methylstyrene (3b). Irradiation (>400 nm) of **1** and **3b** in benzene under N_2 gave **4b**, **5b**, and **7b**.

10,12-Dimethyl-12-phenyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,13(10*H*)-dione (4b): mp 229–232 °C; ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 3 H, CMe), 3.25 (s, 3 H, NMe), 2.98 and 4.62 (ABq, *J* = 15 Hz, 2 H, CH_2), 7.8–8.0 (m, 10 H), 8.3–8.7 (m, 3 H); IR (KBr) 1696 (ketone), 1644 (lactam), 1442, 1392, 772, 722 cm^{-1}. Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.29; H, 5.58; N, 3.69. Found: C, 82.07; H, 5.42; N, 3.58.

***cis*-*N*,1-Dimethyl-1-phenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5b)**: mp 183–186 °C; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3 H, CMe), 2.70 (s, 3 H, NMe), 2.48 and 3.25 (ABq, *J* = 12 Hz, 2 H, CH_2), 7.2–8.1 (m, 13 H); IR (KBr) 1764 and 1706 (imide), 1451, 1432, 1380, 738 cm^{-1}. Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.29; H, 5.58; N, 3.69. Found: C, 82.51; H, 5.63; N, 3.71.

***trans*-*N*,1-Dimethyl-1-phenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (7b)** as a mixture of **5b** and **7b** (4:1): mp 125–132 °C; ^{1}H NMR ($CDCl_3$) δ 1.67 (s, 3 H, CMe), 3.04 (s, 3 H, NMe), 2.72 and 3.48 (ABq, *J* = 13 Hz, 2 H, CH_2), 7.1–8.1 (m, 13 H); IR (KBr) 1762 and 1702 (imide), 1453, 1432, 1380, 740 cm^{-1}. Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.29; H, 5.58; N, 3.69. Found: C, 82.48; H, 5.75; N, 3.75.

Irradiation of 1 and Styrene (3c). Irradiation (>400 nm) of **1** and **3c** in benzene under N_2 gave **4c** and a mixture of **5c** and **7c**.

10-Methyl-12-phenyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,10(10*H*)-dione (4c): mp 212–215 °C; ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 3 H, NMe), 3.3–3.6 (m, 1 H, CH), 4.3–4.7 (m, 2 H, NCH_2), 6.9–8.0 (m, 10 H), 8.3–8.6 (m, 3 H); IR (KBr) 1700 (ketone), 1640 (lactam), 1448, 1366, 758, 722 cm^{-1}. Anal. Calcd for $C_{25}H_{19}NO_2$: C, 82.17; H, 5.24; N, 3.83. Found: C, 81.85; H, 5.05; N, 3.72.

Mixture of *cis*- and *trans*-*N*-methyl-1-phenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (**5c** and **7c**, 1:2): mp 195–205 °C; ^{1}H NMR of **5c** ($CDCl_3$) δ 2.91 (s, 3 H, NMe), 2.8–3.1 (m, 2 H, CH_2), 4.14 (t, *J* = 8 Hz, 1 H, CH), 7.0–8.2 (m, 13 H, Ar H); ^{1}H NMR of **7c** ($CDCl_3$) δ 3.12 (s, 3 H, NMe), 2.9–3.2 (m, 2 H, CH_2), 4.06 (t, *J* = 8 Hz, 1 H, CH), 6.8–8.2 (m, 13 H); IR (KBr) 1768 and 1700 (imide), 1424, 1376, 754 cm^{-1}. Anal. Calcd for $C_{25}H_{19}NO_2$: C, 82.17; H, 5.24; N, 3.83. Found: C, 82.43; H, 5.52; N, 3.68.

Irradiation of 1 and Isobutene (3e). Irradiation (>400 nm) of **1** and **3e** in benzene under N_2 gave **4e** and **5e**.

10,12,12-Trimethyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,13(10*H*)-dione (4e): mp 257–259 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3 H, CMe), 1.48 (s, 3 H, CMe), 2.91 and 3.94 (ABq, *J* = 15 Hz, 2 H, CH_2), 3.28 (s, 3 H, NMe), 7.4–7.9 (m, 5 H), 8.2–8.8 (m, 3 H); IR (KBr) 1702 (ketone), 1638 (lactam), 1092, 778, 728 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.72; H, 6.17; N, 4.48.

***N*,1,1-Trimethyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5e)**: mp 103–107 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 3 H, CMe), 1.22 (s, 3 H, CMe), 2.36 and 2.58 (ABq, *J* = 12 Hz, 2 H, CH_2), 3.03 (s, 3 H, NMe), 7.2–7.5 (m, 4 H), 7.7–8.1 (m, 4 H); IR (KBr) 1763 and 1705 (imide), 1422, 1376, 782, 758 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.57; H, 6.30; N, 4.42.

Irradiation of 1 with *trans*- or *cis*-2-Butene (3f or 3g). Irradiation (>400 nm) of **1** with **3f** or **3g** in benzene under N_2 gave **5f**.

***N*,1,2-Trimethyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5f)**: mp 114–117 °C; ^{1}H NMR ($CDCl_3$) δ 0.84 (d, *J* = 7 Hz, 3 H, CMe), 1.14 (d, *J* = 7 Hz, 3 H, CMe), 2.1–2.5 (m, 2 H, CHCH), 2.92 (s, 3 H, NMe), 7.0–7.3 (m, 4 H, Ar H), 7.5–8.0 (m, 4 H); IR (KBr) 1762 and 1700 (imide), 1444, 1423, 1376, 752 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.76; H, 6.28; N, 4.31.

Irradiation of 1 and 2-Methyl-2-butene (3h). Irradiation (>400 nm) of **1** and **3h** in benzene under N_2 gave **4h** and **5h**.

10,11,12,12-Tetramethyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,13(10*H*)-dione (4h): mp 216–218 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3 H, CMe), 1.24 (d, *J* = 7 Hz, 3 H, CH*Me*), 1.32 (s, 3 H, CMe), 3.12 (s, 3 H, NMe), 4.27 (q, 1 H, C*H*Me), 7.5–7.8 (m, 5 H), 8.3–8.8 (m, 3 H); IR (KBr) 1694 (ketone), 1640 (lactam), 1446, 1392, 1078, 770, 722 cm^{-1}. Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.90; H, 6.26; N, 4.12.

***N*,1,1,2-Tetramethyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5h)**: mp 85–88 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 3 H, CMe), 1.08 (s, 3 H, CMe), 1.13 (d, *J* = 7 Hz, 3 H, CH*Me*), 2.50 (q, *J* = 7 Hz, 1 H, C*H*Me), 2.99 (s, 3 H, NMe), 7.1–8.1 (m, 8 H); IR (KBr) 1762 and 1700 (imide), 1422, 1374, 784, 750 cm^{-1}. Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.49; H, 6.27; N, 4.18.

Irradiation of 1 and Ethyl Vinyl Ether (3i). Irradiation (>400 nm) of **1** and **3i** in benzene under N_2 gave **4i** and **5i**.

12-Ethoxy-10-methyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,13(10*H*)-dione (4i): mp 194–196 °C; ^{1}H NMR ($CDCl_3$) δ 1.14 (t, 3 H, OCH_2*Me*), 3.04 (s, 3 H, NMe), 3.1–4.4 (m, 5 H), 7.4–8.0 (m, 4 H), 8.2–8.8 (m, 4 H); IR (KBr) 1708 (ketone), 1634 (lactam), 1442, 1396, 1088, 764, 720 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.79; H, 5.88; N, 4.23.

1-Ethoxy-*N*-methyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5i): mp 93–97 °C; ^{1}H NMR ($CDCl_3$) δ 1.16 (t, 3 H, OCH_2*Me*), 2.67 (dd, *J* = 5, 12 Hz, 1 H, one of cyclobutane CH_2), 2.89 (dd, *J* = 8, 12 Hz, 1 H, one of cyclobutane CH$_2$), 3.03 (s, 3 H, NMe), 3.41 (dq, *J* = 7, 10 Hz, 1 H, one of OC*H*$_2$Me), 3.95 (dq, *J* = 7, 10 Hz, 1 H, one of OC*H*$_2$Me), 4.19 (dd, *J* = 5, 8 Hz, 1 H, CH), 7.2–7.5 (m, 4 H), 7.7–8.1 (m, 4 H); IR (KBr) 1770 and 1704 (imide), 1422, 1372, 1118, 734 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.93; H, 6.04; N, 4.16.

Irradiation of 1 and Cyclopentene (3j). Irradiation (>400 nm) of **1** and **3j** in benzene under N_2 gave **4j** and **5j**.

13-Methyl-11,12,12a,13-tetrahydrocyclopenta[*b*]phenanthr[9,10-*c*]azepine-9(9a*H*),14(10*H*)-dione (4j): mp 202–204 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.1–2.3 (m, 6 H), 3.24 (s, 3 H, NMe), 3.2–3.4 (m, 1 H), 3.9–4.1 (m, 1 H, NCH), 7.6–8.0 (m, 5 H), 8.30–8.5 (m, 1 H), 8.7–8.9 (m, 2 H); IR (KBr) 1702 (ketone), 1640 (lactam), 1090, 778 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.49; H, 6.01; N, 4.38.

***N*-Methyl-8c,9,10,11,11a,11b-hexahydro-8b*H*-cyclopenta[1′,2′:3,4]cyclobuta[1,2-*l*]phenanthrene-8b,11b-dicarboximide (5j):** mp 162–165 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.7–1.0 (m, 1 H), 1.2–1.9 (m, 5 H), 3.09 (s, 3 H, NMe), 3.27 (d, *J* = 6 Hz, 2 H), 7.2–7.5 (m, 4 H), 7.6–7.8 (m, 2 H), 7.8–8.0 (m, 2 H); IR (KBr) 1772 and 1704 (imide), 1434, 1378, 740 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.36; H, 6.08; N, 4.25.

Irradiation of 1 and 2-Norbornene (3k). Irradiation (>400 nm) of **1** and **3k** in benzene under N_2 gave **4k** and **5k**.

14-Methyl-10,11,12,13,13a,14-hexahydro-10,13-methano-9*H*-benzo[*b*]phenanthr[9,10-*c*]azepine-9,15(9a*H*)-dione (4k): mp 154–157 °C; ^{1}H NMR (CDCl$_3$) δ 0.8–2.0 (m, 6 H), 2.7–3.4 (m, 3 H), 3.17 (s, 3 H, NMe), 4.00 (br d, *J* = 8 Hz, 1 H, NCH), 7.4–8.0 (m, 5 H), 8.3–9.0 (m, 3 H); IR (KBr) 1715 (ketone), 1638 (lactam), 1451, 1370, 768, 722 cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.36; H, 6.15; N, 4.03.

***N*-Methyl-8b,8c,9,10,11,12,12a,12b-octahydro-9,12-methanobenzo[1′,2′:3,4]cyclobuta[1,2-*l*]phenanthrene-8b,12b-dicarboximide (5k):** mp 202–205 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.76 (d, *J* = 11.2 Hz, 1 H), 1.03 (dd, *J* = 2.5, 7.6 Hz, 2 H), 1.28 (d, *J* = 11.2 Hz, 1 H), 1.43 (d, *J* = 7.6 Hz, 2 H), 2.16 (br s, 2 H), 2.79 (s, 2 H), 3.04 (s, 3 H, NMe), 7.2–7.5 (m, 4 H), 7.6–7.8 (m, 2 H), 7.8–8.0 (m, 2 H); IR (KBr) 1772 and 1704 (imide), 1430, 1380, 738 cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.26; H, 5.95, N, 4.01.

Irradiation of 1 and 2,5-Norbornadiene (3l). Irradiation (>400 nm) of **1** and **3l** in benzene under N_2 gave **4l** and **5l**.

14-Methyl-10,13,13a,14-tetrahydro-10,13-methano-9*H*-benzo[*b*]phenanthr[9,10-*c*]azepine-9,15(9a*H*)-dione (4l): mp 170–173 °C; ^{1}H NMR (CDCl$_3$) δ 1.6–2.0 (m, 2 H), 2.8–3.5 (m, 3 H), 3.19 (s, 3 H, NMe), 3.97 (br d, *J* = 8 Hz, 1 H, NCH), 5.9–6.1 (m, 1 H, =CH), 6.2–6.5 (m, 1 H, =CH), 7.5–8.1 (m, 4 H), 8.3–8.9 (m, 4 H); IR (KBr) 1718 (ketone), 1638 (lactam), 1452, 1364, 1094, 754, 722 cm^{-1}. Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.76; H, 5.69; N, 4.05.

***N*-Methyl-8b,8c,10,11,12a,12b-hexahydro-9,12-methanobenzo[1′,2′:3,4]cyclobuta[1,2-*l*]phenanthrene-8b,12b-dicarboximide (5l):** mp 253–256 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.82 (d, *J* = 10.1 Hz, 1 H), 1.08 (d, *J* = 10.1 Hz, 1 H), 2.58 (s, 2 H), 2.79 (s, 2 H), 3.03 (s, 3 H, NMe), 6.70 (s, 2 H, =CH), 7.2–7.5 (m, 4 H), 7.6–7.8 (m, 2 H), 7.8–8.0 (m, 2 H); IR (KBr) 1770 and 1700 (imide), 1425, 1378, 1282, 738 cm^{-1}. Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.82; H, 5.64; N, 3.79.

Irradiation of 1 and 1,3-Butadiene (3m). Irradiation (>400 nm) of **1** and **3m** in benzene under N_2 gave **4m** and **7m**.

10-Methyl-12-vinyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,13(10*H*)-dione (4m): mp 250–253 °C; ^{1}H NMR (CDCl$_3$) δ 3.1–3.4 (m, 1 H, CH), 3.26 (s, 3 H, NMe), 3.8–4.2 (m, 2 H, NCH$_2$), 5.0–5.5 (m, 3 H, CH=CH$_2$), 7.5–8.0 (m, 5 H), 8.3–8.5 (m, 1 H), 8.5–8.7 (m, 2 H); IR (KBr) 1700 (ketone), 1645 (lactam), 1448, 778, 723 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.16; H, 5.62; N, 4.47.

***trans*-*N*-Methyl-1-vinyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (7m):** mp 83–89 °C; ^{1}H NMR (CDCl$_3$) δ 2.46 (dd, *J* = 7, 13 Hz, 1 H, one of CH$_2$), 2.83 (dd, *J* = 8, 13 Hz, 1 H, one of CH$_2$), 3.04 (s, 3 H, NMe), 3.43 (br t, 1 H, CHC=C), 4.8–5.6 (m, 3 H, CH=CH$_2$), 7.2–8.1 (m, 8 H); IR (KBr) 1778 and 1710 (imide), 1428, 1378, 792 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.25; H, 5.59; N, 4.31.

16-Methyl-16-azahexacyclo[16.2.1.0^{1,14}.0^{2,7}.0^{8,13}.0^{14,19}]heneicosa-2,4,6,8,10,12-hexaene-15,21-dione (8m): mp 260–262 °C; ^{1}H NMR (CDCl$_3$) δ 1.75 (d, *J* = 8.3 Hz, 1 H, one of cyclobutane CH$_2$), 2.82 (s, 3 H, NMe), 2.90 (dd, *J* = 3.7, 8.3 Hz, 1 H, one of cyclobutane CH$_2$), 3.10–3.13 (m, 1 H, CH), 3.23–3.28 (m, 1 H, CH), 3.64 (dd, *J* = 2.9, 12.5 Hz, 1 H, one of NCH$_2$), 3.73 (dd, *J* = 2.5, 12.5 Hz, 1 H, one of NCH$_2$), 7.2–7.5 (m, 5 H), 7.86 (d, 1 H), 7.88 (d, 1 H), 8.06 (d, 1 H); ^{13}C NMR (CDCl$_3$) δ 34.3 (q, NMe), 39.9 (dd, cyclobutane CH$_2$), 41.6 (d, CH), 48.7 (d, CH), 49.2 (t, NCH$_2$), 56.9 (s), 67.8 (s), 124.4 (d), 124.5 (d), 125.7 (d), 127.7 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.6 (s), 128.7 (d), 133.5 (s), 134.1 (s), 135.4 (s), 167.8 (s, lactam), 206.4 (ketone); IR (KBr) 1752 (ketone), 1645 (lactam), 1442, 1318, 762 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 79.73; H, 5.38; N, 4.41.

Irradiation of 1 and 2,3-Dimethyl-1,3-butadiene (3n). Irradiation (>400 nm) of **1** and **3n** in benzene under N_2 gave **4n** and a mixture of **5n** and **7n**.

10,12-Dimethyl-12-isopropenyl-11,12-dihydro-9*H*-phenanthr[9,10-*c*]azepine-9,13(10*H*)-dione (4n): mp 211–213 °C; ^{1}H NMR (CDCl$_3$) δ 1.61 (s, 3 H, CMe), 1.77 (s, 3 H, CMe), 3.09 and 4.54 (ABq, *J* = 13 Hz, 2 H, CH$_2$), 3.38 (s, 3 H, NMe), 4.65 and 4.89 (br s, 2 H, =CH$_2$), 7.4–7.9 (m, 5 H), 8.3–8.5 (m, 1 H), 8.5–8.8 (m, 2 H); IR (KBr) 1688 (ketone), 1648 (lactam), 1444, 764, 720 cm^{-1}. Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.32; H, 6.30; N, 4.14.

Mixture of *cis*- and *trans*-*N*,1-Dimethyl-1-isopropenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5n and 7n, 1:3): mp 95–99 °C; ^{1}H NMR of **5n** (CDCl$_3$) δ 1.01 (s, 3 H, CMe), 1.96 (s, 3 H, CMe), 2.30 and 3.22 (ABq, *J* = 12 Hz, 2 H, CH$_2$), 2.96 (s, 3 H, NMe), 4.75 and 4.94 (two s, 2 H, =CH$_2$), 7.1–7.4 (m, 4 H), 7.7–8.1 (m, 4 H); ^{1}H NMR of **7n** (CDCl$_3$) δ 1.31 (s, 3 H, CMe), 1.42 (s, 3 H, CMe), 2.48 and 3.01 (ABq, *J* = 12 Hz, 2 H, CH$_2$), 3.03 (s, 3 H, NMe), 4.58 and 4.64 (two s, 2 H, =CH$_2$), 7.1–7.4 (m, 4 H), 7.7–8.1 (m, 4 H); IR (KBr) 1768 and 1702 (imide), 1428, 1376, 784, 758 cm^{-1}. Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.73; H, 6.41; N, 3.88.

16,18,19-Trimethyl-16-azahexacyclo[16.2.1.0^{1,14}.0^{2,7}.0^{8,13}.0^{14,19}]heneicosa-2,4,6,8,10,12-hexaene-15,21-dione (8n): mp 253–255 °C; ^{1}H NMR (CDCl$_3$) δ 1.23 (s, 3 H, CMe), 1.34 (s, 3 H, CMe), 1.78 and 2.51 (ABq, *J* = 8 Hz, 2 H, cyclobutane CH2), 2.81 (s, 3 H, NMe), 3.30 an 3.45 (ABq, *J* = 12 Hz, 2 H, NCH$_2$), 7.1–8.2 (m, 8 H); IR (KBr) 1762 (ketone), 1655 (lactam), 1496, 1338, 762 cm^{-1}. Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.51; H, 6.30; N, 4.17.

Irradiation of 1 with α-Bromostyrene (3o). Irradiation (>400 nm) of **1** with **3o** in benzene under N_2 gave a mixture of **5o** and **7o**.

Mixture of *cis*- and *trans*-1-Bromo-*N*-methyl-1-phenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene-2a,10b-dicarboximide (5o and 7o, 4:1): mp 155–158 °C; ^{1}H NMR of **5o** (CDCl$_3$) δ 3.09 (s, 3 H, NMe), 3.62 and 3.91 (ABq, *J* = 14 Hz, 2 H, CH$_2$), 6.8–8.2 (m, 13 H); ^{1}H NMR of **7o** (CDCl$_3$) δ 2.68 (s, 3 H, NMe), 3.42 and 4.06 (ABq, *J* = 13 Hz, 2 H, CH$_2$), 7.2–8.2 (m, 13 H); IR (KBr) 1778 and 1708 (imide), 1442, 1378, 738 cm^{-1}. Anal. Calcd for $C_{25}H_{18}NO_2Br$: C, 67.58; H, 4.08; , 3.15. Found: C, 67.29; H, 3.83; N, 3.05.

Fluorescence Quenching of 1 by Alkene and Halide. For each quenching experiment five samples were prepared in 10-mL volumetric flasks, each containing 5×10^{-5} M of **1** and appropriate concentrations of alkene or halide in spectrophotometric grade benzene. Fluorescence intenstities at 454 nm were measured for each sample at an excitation wavelength of 400 nm. Stern–Volmer plots were linear, and slopes are shown in Tables II and III.

Quantum Yield Measurements. Light intensities were measured by using ferrioxalate actinometry.[16] Quantitative experiments were carried out in solutions in sealed test tubes in a merry-go-round apparatus using a Hg lamp and the solution filter (>400 nm). Irradiations were carried out to conversions of <15%.

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[16] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. B* **1953**, *140*, 470.