Photochemical Intramolecular $4_\pi + 4_\pi$ Cycloaddition of 1,2-Di(9-anthryl)ethanes

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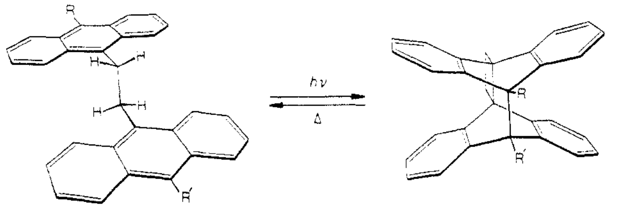
A series of 10-substituted and 10,10′-disubstituted 1,2-di(9-anthryl)ethanes has been prepared, and their photochemical properties have been studied by determining the quantum yields for intramolecular $4_\pi + 4_\pi$ cycloaddition and the quantum yields of fluorescence. In no case was the quantum yield for the cycloaddition reaction found to exceed 0.26, as had been established previously for the parent compound. In general, bulky substituents increase the fluorescence efficiencies and decrease the quantum yields for cycloaddition. In a competing photochemical reaction, dianthrylethanes can react with molecular oxygen to give bis(endoperoxides). The effect of substituents of the thermal stability of the intramolecular cycloaddition products is such as to decrease the activation barrier for the cycloreversion. The rate of the cycloreversion reaction also can be enhanced by trifluoroacetic acid, and the kinetics of the acid-catalyzed regeneration of dianthrylethane is indicative of a reaction intermediate.

Introduction

The photochemical conversion of 1,2-di(9-anthryl)ethane (**1a**) into its valence isomer **2a** has been the subject of numerous, mostly spectroscopic investigations.[1] The intramolecular $4_\pi + 4_\pi$ cycloaddition proceeds with a quantum yield of 0.26 and, because of its ground-state reversibility at elevated temperature, the photoisomerization of dianthrylethane **1a** and that of a variety of other linked anthracenes have been studied and evaluated for the chemical storage of photon energy.[2]

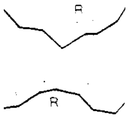


1a-k

2a-k

1,2:	a	b	c	d	e	f	g	h	i	j	k
R:	H	H	H	H	H	CH_3	OCH_3	OCH_3	OAc	n-C_4H_9	C_6H_5
R′:	H	CH_3	OCH_3	OAc	C_6H_5	CH_3	OCH_3	OAc	OAc	n-C_4H_9	C_6H_5

Very little is known about the effect of substituents on the photochemistry of dianthrylethanes **1**. Apparently, only the photochemical isomerization of 1,2-di(10-methyl-9-anthryl)ethane (**1f**) has been reported to give the cycloaddition product **2f**.[1f,h] Only since 1975 has it been recognized that a number of earlier reported "photoisomers" of dianthrylethanes **1** may not be photochemical $4_\pi + 4_\pi$ cycloaddition products **2** but may be lepidopterenes **3** formed nonphotochemically as byproducts in the then commonly applied synthesis of dianthrylethanes from 9-(halogenomethyl)anthracenes.[3]



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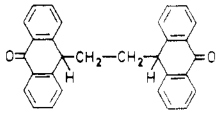

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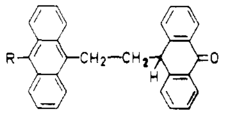

5a: R = H
5b: R = OCH_3

We have recently described a synthesis of dianthrylethanes from substituted anthrones **4** and **5** which circumvents the byproduct formation of lepidopterenes **3** and makes heretofore unknown unsymmetrically substituted dianthrylethanes conveniently accessible.[4] In the present paper, we report on the photochemical properties of dianthrylethanes **1a**–**1k** prepared by this method. Furthermore, the paper deals with the effect of substituents on the thermodynamic properties of the corresponding photoproducts **2**, and with their catalytic cycloreversion.

Results and Discussion

Dianthrylethanes **1a**–**1k** were prepared from the recently described[4] anthrones **4** and **5** by conventional reactions such as enolization, esterification, etherification, and nucleophilic addition. The syntheses of **1a** and that of symmetrically substituted dianthrylethanes **1f**, **1g**, **1i**, and **1k** have been described recently,[4] and the structures of the remaining dianthrylethanes (**1b**–**1e**, **1h**, and **1j**) are supported by analytical and spectral data (see Experimental Section). The electronic absorption spectra of dianthrylethanes **1** deserve comment inasmuch as they are of photochemical interest. Ground-state interactions in proximal anthracenes such as **1a** are considered to be negligible.[1h] We believe, however, that the UV absorption spectral data of dianthrylethanes **1** summarized in Table I actually are indicative of intramolecular electronic interaction. Thus, the electronic absorption spectra of unsymmetrically substituted dianthrylethanes are not merely superpositions of the respective component spectra but exhibit their maxima at different wavelengths, and, furthermore, the bathochromic shift of the longest wavelength absorption maximum in the spectra of symmetrically substituted dianthrylethanes is clearly noticeable. Direct evidence for intramolecular interaction is provided in the

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[1] (a) Roitt, I. M.; Waters, W. A. *J. Chem. Soc.* **1952**, 2695. (b) Livingston, R.; Wei, K. S. *J. Am. Chem. Soc.* **1967**, *89*, 3098. (c) Hayashi, T.; Suzuki, T.; Mataga, N.; Sakata, Y.; Misumi, S. *Chem. Phys. Lett.* **1976**, *38*, 599. (d) Ferguson, J.; Morita, M.; Puza, M. *Chem. Phys. Lett.* **1976**, *42*, 288. (e) Hayashi, T.; Mataga, N.; Sakata, Y.; Misumi, S.; Morita, M.; Tanaka, J. *J. Am. Chem. Soc.* **1976**, *98*, 5910. (f) Bergmark, W. R.; Jones, G., II *Nouv. J. Chim.* **1977**, *1*, 271. (g) Hayashi, T.; Suzuki, T.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1977**, *81*, 420. (h) Bergmark, W. R.; Jones, G., II; Reinhardt, T. E.; Halpern, A. M. *J. Am. Chem. Soc.* **1978**, *100*, 6665. (i) Anderson, B. F.; Ferguson, J.; Morita, M.; Robertson, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 1832. (j) Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Chem. Phys. Lett.* **1980**, *76*, 390. (k) Ferguson, J. *Chem. Phys. Lett.* **1980**, *76*, 398.

[2] Jones, G., II; Reinhardt, T. E.; Bergmark, W. R. *Solar Energy* **1978**, *20*, 241.

[3] Felix, G.; Lapouyade, R.; Castellan, A.; Bouas-Laurent, H.; Gaultier, J.; Hauw, C. *Tetrahedron Lett.* **1975**, 409. Cf. also Becker, H.-D.; Andersson, K.; Sandros, K. *J. Org. Chem.* **1980**, *45*, 4549.

[4] Becker, H.-D.; Sanchez, D.; Arvidsson, A. *J. Org. Chem.* **1979**, *44*, 4247.

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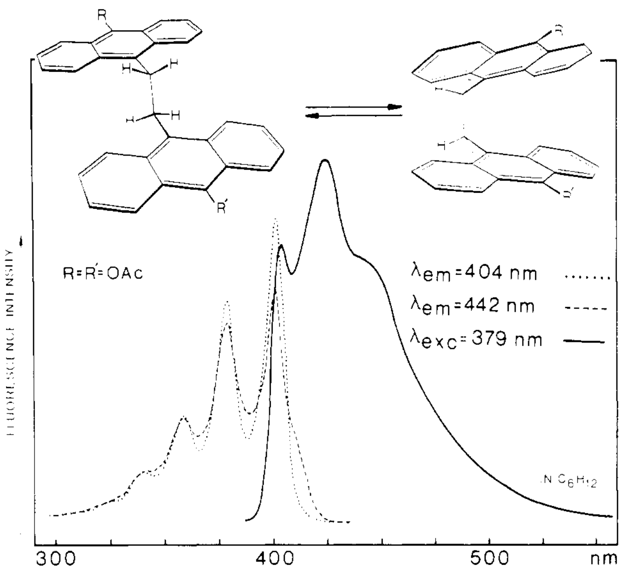

Figure 1. Emission spectrum (solid line) and wavelength-dependent excitation spectra (dotted and dashed lines) of **1i** in oxygen-saturated cyclohexane solution at room temperature.

case of acetoxy-substituted dianthrylethanes **1d**, **1h**, and **1i**. Their absorption spectra are characterized by a hump near the onset of the S_0–S_1 transition which we attribute to the presence of ground-state conformational isomers in which the two anthracene moieties are in more or less overlapping arrangement.[5,6] We see the presence of more than one conformational isomer confirmed spectroscopically by the emission wavelength dependence of the excitation spectrum of **1i** (see Figure 1). Emission spectroscopic evidence for the existence of various conformers of the parent compounds **1a** has previously been obtained in low-temperature experiments.[1d]

Irradiation of dianthrylethanes **1b**–**1i** under nitrogen in cyclohexane or methylene chloride solution smoothly affords valence isomers whose ^{1}H NMR spectra are in agreement with the structure of the corresponding $4_\pi + 4_\pi$ cycloaddition products **2** (see Table II). Characteristically, in the 270-MHz spectra of the monosubstituted photoproducts **2b**–**2e**, the cyclobutane protons give rise to an AA′BB′ spectrum as shown in Figure 2. For some reason, the ^{1}H NMR spectral data reported in the literature[3] for **2f** are at variance with those found in the present study.[7] By comparison with all other NMR data summarized in Table II, the ^{1}H NMR spectrum of **2f** of this report is in agreement with the assigned structure. Sterically hindered linked anthracenes have recently been found to undergo unsymmetrical $4_\pi + 4_\pi$ cycloaddition upon irradiation.[6,8] However, we have found no evidence for the formation of this type of photoproduct from dianthrylethanes **1**.

The quantum yields for the intramolecular cyclization of monosubstituted dianthrylethanes are higher than those

Table I. Electronic Absorption Maxima (nm) of Dianthrylethanes 1 in Cyclohexane ($\epsilon \times 10^{-3}$)

R = R′ = H	R = H, R′ = OAc	R = R′ = OAc	R = H, R′ = C_6H_5	R = R′ = C_6H_5	R = H, R′ = CH_3	R = R′ = CH_3	R = OAc, R′ = OCH_3	R = H, R′ = OCH_3	R = R′ = OCH_3	R = R′ = n-C_4H_9
392 (27.7)	399 (19.2)	401 (23.6)	399 (20.6)	402 (28.6)	402 (19.0)	405 (32.1)	405 (19.3)	405 (14.0)	407 (22.8)	406 (30.1)
371 (20.4)	394 (14.3)	379 (19.3)	393 (14.5) sh	380 (22.9)	397 (13.1)	382 (23.3)	401 (16.1) sh	399 (10.7) sh	384 (19.1)	383 (22.7)
352 (10.2)	378 (15.7)	359 (10.4)	378 (16.7)	360 (11.8)	391 (13.2)	362 (10.9)	383 (16.6) sh	391 (14.5)	364 (10.2)	363 (10.9)
335 (4.8)	372 (13.6) sh	342 (5.0)	372 (13.7) sh	342 (5.4)	380 (14.8)	344 (4.9)	361 (9.2)	385 (13.7)	347 (5.1) sh	345 (5.0)
320 (2.2)	358 (9.0)	326 (2.4) sh	358 (9.3)	326 (2.4) sh	371 (11.6) sh	330 (2.2) sh	345 (4.7)	370 (12.2)	330 (2.4) sh	330 (2.3) sh
	353 (8.4) sh		353 (8.3) sh		362 (8.7) sh		325 (2.0)	352 (7.4)		
	338 (4.5) sh		335 (4.0) sh		352 (7.3)			335 (3.7)		
	320 (2.1) sh		320 (1.9) sh		335 (3.7) sh			320 (1.7)		
					320 (1.7) sh					
256 (212)	257 (213)	258 (220)	257 (191)	260 (170)	259 (184)[a]	260 (229)	259 (202)	258 (171)[b]	260 (207)	261 (205)
249 (188)	250 (190)	251 (193)	250 (160)	254 (155)	252 (170)	252 (195)	252 (183)	251 (157)	253 (188)	253 (182)

[a] Shoulder at 263 nm (ϵ 89 000). [b] Shoulder at 263 nm (ϵ 82 000).

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(5) The head-to-head photodimerization of (9-anthryl)methylacetate has been attributed to possible intermolecular dipole–dipole interactions between the acetoxy groups: De Schryver, F. C.; Anand, L.; Smets, G.; Switten, J. *Polym. Lett.* **1971**, *9*, 777. See also: Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P. *Pure Appl. Chem.* **1980**, *52*, 2633.

(6) Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Nouv. J. Chim.* **1979**, *3*, 231.

(7) According to ref 3, in the ^{1}H NMR spectrum of **2f** in benzene at 30 °C, the CH_3 groups and the CH_2 groups give rise to singlets at δ 2.35 and 3.60, respectively. In the present study, the corresponding singlets of photoproduct **2f** in benzene at 35 °C (270-MHz spectrum) were found at δ 1.70 and 2.77, respectively. ^{1}H NMR data in $CDCl_3$ solution are summarized in Table II.

(8) Felix, G.; Lapouyade, R.; Bouas-Laurent, H.; Clin, B. *Tetrahedron Lett.* **1976**, 2277.

Table II. ^{1}H NMR Spectral Data of Photoproducts 2 in CDCl$_3$

substituents		chemical shift data				
R	R′	R	R′	CH$_2$CH$_2$	aromatic H	temp, °C
H	H	4.52 (s)	4.52 (s)	3.01 (s)	7.13-6.81	27
OAc	OAc	2.43 (s)	2.43 (s)	2.99 (s)	7.10-6.87	23
CH$_3$	CH$_3$	1.96 (s)	1.96 (s)	3.01 (s)	7.18-6.84	12
OCH$_3$	OCH$_3$	3.29 (s)	3.29 (s)	2.96 (s)	7.29-6.90	37
H	OAc	4.63 (s)	2.43 (s)	3.01^a (57 Hz)^b	7.18-6.79	37
H	C$_6$H$_5$	5.38 (s)	*c*	3.05^a (65 Hz)^b	8.50-6.32	0
H	CH$_3$	3.93 (s)	2.15 (s)	3.02^a (34 Hz)^b	7.20-6.79	27
H	OCH$_3$	4.36 (s)	3.39 (s)	2.98^a (65 Hz)^b	7.25-6.80	27
OAc	OCH$_3$	2.42 (s)	3.25 (s)	2.97 (s)	7.24-6.84	40

[a] Center of the AA′BB′ system. [b] Range of the AA′BB′ system. [c] Overlapping with aromatic protons of the dianthracene system.

Table III. Deactivation of Electronically Excited Dianthrylethanes by Intramolecular $4_\pi + 4_\pi$ Cycloaddition and by Fluorescence[a]

1, 2	a	b	c	d	e	f	g	h	i	j	k
R	H	H	H	H	H	CH$_3$	OCH$_3$	OCH$_3$	OAc	*n*-C$_4$H$_9$	C$_6$H$_5$
R′	H	CH$_3$	OCH$_3$	OAc	C$_6$H$_5$	CH$_3$	OCH$_3$	OAc	OAc	*n*-C$_4$H$_9$	C$_6$H$_5$
$\phi_{4\pi+4\pi}$	0.26	0.26	0.24	0.14	0.034	0.14	0.11	0.068	0.015	<<0.015	<<0.015
ϕ_F	0.20	0.15	0.14	0.40	0.61	0.16	0.30	0.45	0.74	0.70	0.79

[a] In cyclohexane.

found for disubstituted analogues. Most likely, steric hindrance due to substitution at the 10,10′ position of **1** impairs the photochemical cycloaddition. We have not been able to isolate intramolecular cycloaddition products from photoexcited di-*n*-butyldianthrylethane (**1j**) and diphenyldianthrylethane (**1k**) which deactivate to ground state with high fluorescence efficiency ($\phi_F \simeq 0.7$). In general, the lower the fluorescence quantum yields of dianthrylethanes, the more efficiently proceeds the intramolecular $4_\pi + 4_\pi$ cycloaddition. However, the quantum yield data summarized in Table III clearly reveal that photoexcited dianthrylethanes **1** may deactivate by some additional process, as has been discussed in detail by other authors.[1h] As to whether or not this mode of deactivation involves intramolecularly formed biradicals is a matter of current debate.[1k,9]

In order to assess the effect of substitution on the thermal stability of the photoproducts **2**, we have investigated their cycloreversion in solution. Regarding the thermal stability of the parent compound **2a**, the earlier found[1h] activation energy of 32.8 kcal/mol associated with the cycloreversion to **1a** in *o*-dichlorobenzene was recently challenged to be incorrect, as a lower activation barrier of 25.85 kcal/mol (in *n*-hexane) was reported.[1i] In the present study, we find the thermally induced conversion of **2a** into **1a** in *o*-dichlorobenzene to be associated with an activation energy of 34.2 kcal/mol, the Arrhenius preexponential factor being 6 × 10^{14}.[10] Thus, unsubstituted photoproduct **2a** at 25 °C has a half-life of about 400 years. Increasing the crowdedness around the bridgehead decreases the thermal stability of photoproducts **2** in rather drastic steps (see Table IV). For example, the half-life of monomethyl-substituted **2b** at 25 °C is about 40 years, but that of the dimethyl-substituted **2f** is less than 40 min.

During the reinvestigation of **2a** we have found that the rate for the formation of **1a** is drastically affected by the presence of solvent impurities and, significantly, can be increased by proton catalysis. For example, in the presence of trifluoroacetic acid (TFA) in *o*-dichlorobenzene solution, **2a** smoothly reverts to **1a** at room temperature. The kinetics of the acid-catalyzed formation of **1a** from **2a** indicate that the reaction involves an intermediate (**I**; Figure 3) which, conceivably, may be formed from **2a** by addition of TFA to the cyclobutane moiety.

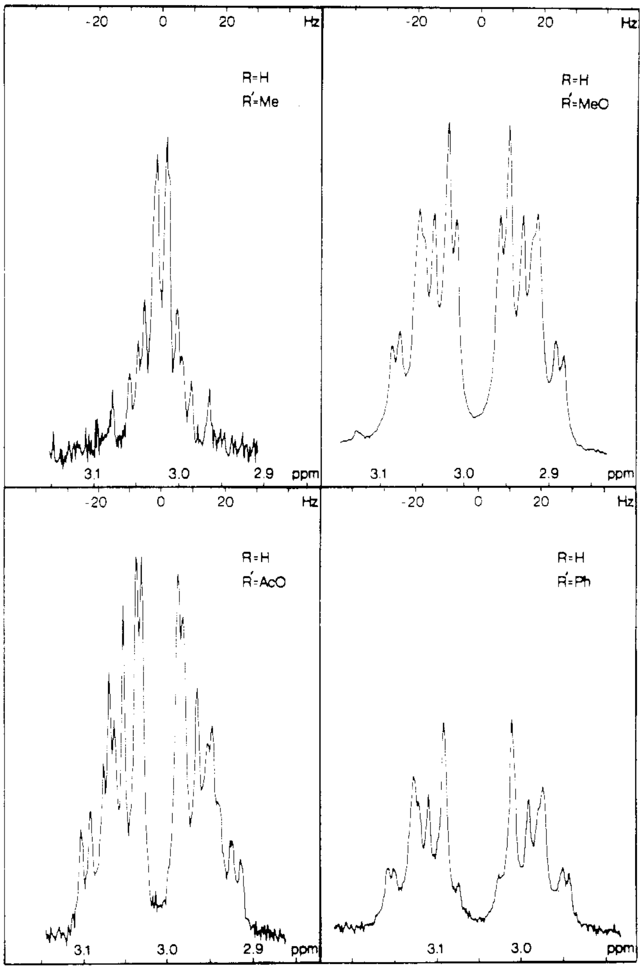

Figure 2. 270-MHz ^{1}H NMR spectra of the cyclobutane moieties of **2b**–**2e** in CDCl$_3$.

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(9) Jones, G., II; Bergmark, W. R.; Halpern, A. M. *Chem. Phys. Lett.* **1980**, *76*, 403.

(10) The thermodynamic data of ref 1i imply a negative ΔS^* term. By contrast, a positive ΔS^* term is associated with the thermodynamic data of ref 1h, and those of this study.

Table IV. Kinetic Parameters for the Cycloreversion of Photoproducts **2**[a]

R	H	H	H	H	H	OCH_3	OAc	OCH_3	CH_3
R′	H	OAc	OCH_3	CH_3	C_6H_5	OAc	OAc	OCH_3	CH_3
E_a, kcal/mol	34.2	34.3	32.3	31.0	29.3	28.5	25.5	25.9	24.3
log A[b]	14.8	15.4	14.4	13.5	14.1	16.5	14.4	14.9	14.4
half-life at 25 °C	385 years	130 years	39 years	38 years	187 days	260 min	234 min	142 min	33 min

[a] **2a–e** in *o*-dichlorobenzene and **2f–2i** in cyclohexane. [b] For the preexponential factor, A, the unit s^{-1} is used.

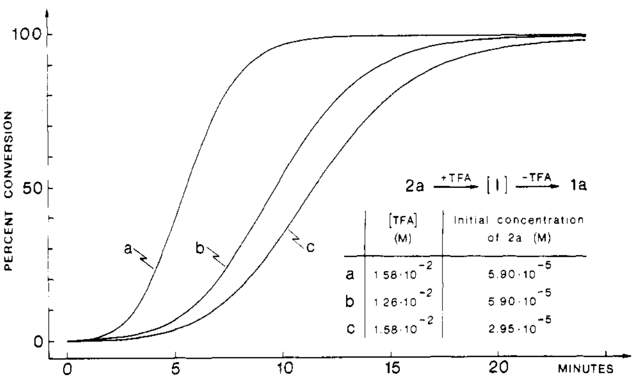
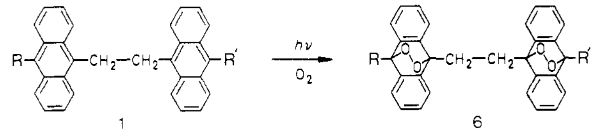


Figure 3. Kinetic behavior of the acid-catalyzed cycloreversion of **2a** in *o*-dichlorobenzene solution.

In view of the remarkable instability of the dimethyl-substituted photoisomer **2f** at room temperature, we were intrigued about a report[11] claiming dimethyldianthrylethane **1f** to undergo intramolecular photocyclization "caused by ordinary light in the laboratory". The yellow starting material had been found to turn white when allowed to stand in the laboratory.[11] Indeed, we also found that a white crystalline substance precipitated when solutions of **1f** (in methylene chloride or carbon disulfide) were exposed to sunlight. However, this photoproduct of **1f** is not the valence isomer **2f** but the heretofore unknown bis(endoperoxide) **6f**. Likewise, we find dimethoxydianthrylethane **1g**, di-*n*-butyldianthrylethane **1j**,[12] and diphenyldianthrylethane **1k** to form bis(endoperoxides) (**6g**, **6j**, and **6k**, respectively) upon exposure to sunlight in the presence of air. Evidently, it has previously been overlooked that the bimolecular reaction of photoexcited dianthrylethanes **1** with molecular oxygen can compete with the intramolecular $4_\pi + 4_\pi$ cycloaddition reaction.



1,6:	f	g	j	k
R :	CH_3	OCH_3	$n\text{-}C_4H_9$	C_6H_5
R′ :	CH_3	OCH_3	$n\text{-}C_4H_9$	C_6H_5

Experimental Section

Electronic absorption and emission spectra were recorded on a Beckman Acta III spectrophotometer and an Aminco SPF 500 (corrected spectra) spectrofluorometer, respectively. ^1H NMR spectra were obtained on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. High-resolution mass spectra were obtained on an AEI MS 902 instrument. Melting points were determined on a hot-stage microscope and are uncorrected. Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark.

1-(9-Anthryl)-2-(10-methyl-9-anthryl)ethane (1b). Methyllithium (3 mL, 1.6 M in ether) was added to a stirred solution of anthronylanthrylethane **5a** (202 mg) in benzene (50 mL) under nitrogen. After 40 min of refluxing, the reaction mixture was acidified with aqueous hydrochloric acid. The crude product isolated from the organic layer by usual workup was purified by column chromatography on SiO_2 (CH_2Cl_2): yield, 170 mg (85%) of yellow crystals; mp 234–235 °C (lit.[13] mp 236 °C); ^1H NMR ($CDCl_3$) δ 8.52–7.46 (m, 17 aromatic H), 4.04 (s, 4), 3.13 (s, CH_3); high-resolution mass spectrum calcd for $C_{31}H_{24}$ 396.1878, found 396.189 (M^+).

1-(9-Anthryl)-2-(10-methoxy-9-anthryl)ethane (1c). Sodium borohydride (50 mg) was added under nitrogen to a stirred suspension of **5b** (140 mg) in dioxane (15 mL). The reaction mixture was refluxed for 1 h and subsequently acidified with aqueous hydrochloric acid. The crude product which precipitated after part of the solvent was removed by vacuum evaporation was purified by column chromatography (SiO_2/CH_2Cl_2) to give 90 mg (67%) of yellow crystals; mp 197–199 °C (after recrystallization from CH_2Cl_2 by addition of methanol); ^1H NMR ($CDCl_3$) δ 8.40–7.42 (m, 17 aromatic H), 4.13 (s, OCH_3), 4.02 (s, 4); high-resolution mass spectrum calcd for $C_{31}H_{24}O$ 412.1828, found 412.1932 (M^+).

1-(10-Acetoxy-9-anthryl)-2-(9-anthryl)ethane (1d). A suspension of **5a** (100 mg) in acetic anhydride (2 mL) containing pyridine (3 drops) was refluxed for 30 min to give a clear solution. Workup by addition of ethanol (10 mL) followed by vacuum evaporation of solvent gave a solid residue which was purified by column chromatography (SiO_2/CH_2Cl_2). Two identical experiments afforded 205 mg (88%) of yellow crystals: mp 216–218 °C (after recrystallization from CH_2Cl_2/CH_3OH); ^1H NMR ($CDCl_3$) δ 8.43–7.44 (m, 17 aromatic H), 4.06 (s, 4), 2.65 (s, OAc). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49. Found: C, 87.64; H, 5.62.

1-(9-Anthryl)-2-(10-phenyl-9-anthryl)ethane (1e). Phenyllithium (3 mL; 16.8% in benzene/ether, 70:30) was added to a stirred solution of **5a** (95 mg) in benzene (5 mL). Addition of aqueous HCl after 25 min followed by usual workup of the organic layer gave a crude product which was purified by column chromatography (SiO_2/CH_2Cl_2). Recrystallization of chromatographed product gave 95 mg (87%) of yellow crystals: mp 200–203 °C; ^1H NMR ($CDCl_3$) δ 8.47–7.31 (m, 22 aromatic H), 4.13 (s, 4); high-resolution mass spectrum calcd for $C_{36}H_{26}$ 458.2034, found 458.2020 (M^+).

1-(10-Acetoxy-9-anthryl)-2-(10-methoxy-9-anthryl)ethane (1h). The previously described[4] compound **5b** (100 mg) was acetylated by refluxing in acetic anhydride (2.5 mL) in the presence of pyridine (4 drops) for 30 min. Workup by dilution with ethanol followed by vacuum evaporation of solvent gave crude **1h** which was purified by column chromatography and subsequent recrystallization from CH_2Cl_2/CH_3OH. Two identical experiments afforded 200 mg (91%) of yellow crystals: mp 220–225 °C; ^1H NMR ($CDCl_3$) δ 8.38–7.47 (m, 16 aromatic H), 4.13 (s, OCH_3), 4.04 (s, 4), 2.64 (s, OAc); high-resolution mass spectrum calcd for $C_{33}H_{26}O_3$ 470.1882, found 470.1755 (M^+).

1,2-Bis(10-*n*-butyl-9-anthryl)ethane (1j). *n*-Butyllithium (2 mL, 20% in hexane) was added to a solution of dianthronylethane (**4**; 210 mg) in benzene (50 mL) under nitrogen. After 45 min of refluxing, the reaction mixture was acidified with aqueous hydrochloric acid. The crude product isolated from the organic layer by usual workup was purified by column chromatography (SiO_2/CH_2Cl_2) and subsequent recrystallization from CH_2Cl_2/CH_3OH. Two identical experiments afforded 175 mg (21%) of yellow crystals: mp 201–202 °C (lit.[14] mp 202–203 °C); ^1H NMR

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[11] Cristol, S. J.; Perry, J. S., Jr. *Tetrahedron Lett.* **1974**, 1921.

[12] Most likely, the disappearance of fluorescence upon irradiation of **1j** in dilute solution, previously attributed to photodimerization (see ref 14), also is due to endoperoxide formation.

[13] Beckwith, A. L. J.; Waters, W. A. *J. Chem. Soc.* **1956**, 1108.

($CDCl_3$) δ 8.45–7.40 (m, 16 aromatic H), 4.05 (s, 4), 3.65–3.59 (t, 4 butyl H), 1.86–1.77 (m, 4 butyl H), 1.74–1.53 (m, 4 butyl H), 1.09–1.04 (t, 6 butyl H); high-resolution mass spectrum calcd for $C_{38}H_{38}$ 494.2974, found 494.3062 (M^+).

Photochemical Experiments. Preparative intramolecular cycloadditions were carried out by irradiating solutions of dianthrylethanes **1** (50 mg) in methylene chloride (125 mL) under nitrogen in a Pyrex immersion well apparatus at 5 °C for 30 min, using a Philips high-pressure mercury lamp HPK (125 W). Vacuum evaporation of most of the solvent at about 10 °C followed by addition of cyclohexane gave photoproducts **2** as colorless crystalline precipitates. The conversions usually were quantitative. Upon heating to 150–170 °C, monosubstituted photoproducts **2b–2e** turned yellow, melting finally at the melting point of the corresponding dianthrylethanes. In view of their thermal lability, photoproducts **2f–2i**, isolated by workup at ~5 °C, were analyzed by ^1H NMR only (see Table II).

Photoproduct 2a: UV (cyclohexane) λ_{max} 282 nm (ϵ 1380), 273 (1830).

Photoproduct 2b: UV (cyclohexane) λ_{max} 282 nm (ϵ 1360), 273 (1870, sh). Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 94.38; H, 5.67.

Photoproduct 2c: UV (cyclohexane) λ_{max} 282 nm (ϵ 1360), 273 (1870, sh); high-resolution mass spectrum calcd for $C_{31}H_{24}O$ 412.1828, found 412.1858 (M^+).

Photoproduct 2d: UV (cyclohexane) λ_{max} 282 nm (ϵ 1000). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49. Found: C, 87.08; H, 5.39.

Photoproduct 2e: UV (cyclohexane) λ_{max} 283 nm (ϵ 1090, sh), 271 (1910, sh); high-resolution mass spectrum calcd for $C_{36}H_{26}$ 458.2034, found 458.2041 (M^+).

Photochemical Autoxidation of 1,2-Bis(10-methyl-9-anthryl)ethane. Bis(endoperoxide) 6f. A solution of **1f** (102 mg) in carbon disulfide (75 mL), placed in a Pyrex round-bottom flask, was exposed to oxygen and irradiation for 24 h with a 60-W tungsten lamp. Colorless crystals precipitated during the irradiation. The solvent was removed by vacuum evaporation, and the colorless residue was dissolved in CH_2Cl_2. Traces of insoluble material were removed by filtration through Celite. Addition of ether to the filtrate gave 103 mg (87%) of colorless crystals: mp ~275 °C dec; ^1H NMR ($CDCl_3$) δ 7.48–7.24 (m, 16 aromatic H), 3.25 (s, 4), 2.19 (s, 2 CH_3); high-resolution mass spectrum calcd for $C_{32}H_{26}O_4$ 474.1831, found 474.1822 (M^+); UV (chloroform) λ_{max} 280 nm (ϵ 1220), 271 (1330). Anal. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 80.52; H, 5.50.

Bis(endoperoxide) 6g. A solution of **1g** (221 mg) in carbon disulfide (100 mL) was treated in the same fashion as **1f**. Recrystallization from methylene chloride/cyclohexane gave 46 mg (18%) of colorless crystals: mp ~325 °C dec; ^1H NMR ($CDCl_3$) δ 7.60–7.24 (m, 16 aromatic H), 4.06 (s, 2 CH_3O), 3.22 (s, 4); high-resolution mass spectrum calcd for $C_{32}H_{26}O_6$ 506.1730, found 506.1743 (M^+).

Bis(endoperoxide) 6j. A solution of **1j** (50 mg) in methylene chloride (10 mL) was exposed to air and sunlight for 1 day. Colorless crystals precipitated during the exposure. Vacuum evaporation of most of the solvent followed by addition of ether (2 mL) gave 29 mg (51%) of colorless crystals: mp 243–246 °C dec; ^1H NMR ($CDCl_3$) δ 7.47–7.17 (m, 16 aromatic H), 3.24 (s, 4), 2.74–2.68 (t, 4 butyl H), 1.93–1.82 (m, 4 butyl H), 1.68–1.54 (m, 4 butyl H), 1.09–1.04 (t, 6 butyl H); high-resolution mass spectrum calcd for $C_{38}H_{38}O_4$ 558.2770, found 558.2788 (M^+).

Bis(endoperoxide) 6k. A solution of **1k** (50 mg) in methylene chloride (10 mL) was treated in same fashion as **1j** and gave, after recrystallization, 15 mg (27%) of colorless crystals: mp 246–248 °C dec; ^1H NMR ($CDCl_3$) δ 7.68–6.98 (m, 26 aromatic H), 3.39 (s, 4); high-resolution mass spectrum calcd for $C_{42}H_{30}O_4$ 598.2144, found 598.2122 (M^+).

Trifluoroacetic Acid Catalyzed Cycloreversions. In a typical experiment, a solution of photoproduct **2a** (6.1×10^{-5} M) and TFA (1.3×10^{-2} M) in *o*-dichlorobenzene was kept at room temperature, and the cycloreversion was followed absorption spectroscopically over a period of about 1 h by the appearance of the typical absorption of **1a** around 390 nm. Likewise, TFA-catalyzed cycloreversions of **2a** in $CDCl_3$ were monitored by ^1H NMR spectroscopy.

Quantum Yield Determinations. Quantum yields (ϕ) of photocyclization were determined by irradiating highly diluted solutions of dianthrylethanes **1** (absorbance <0.05) with 366-nm light, i.e., the fraction of absorbed light is proportional to the absorbance. This implies that the fluorescence intensity I_F is proportional to the concentration C of the dianthrylethane. It follows:

$$\mathrm{d}C/\mathrm{d}t = -\phi I_{abs} = -\phi I_0 \epsilon C$$

$$\ln C_0/C = \phi I_0 \epsilon t$$

since $C_0/C = I_{0,F}/I_F$,

$$\phi_{ref}/\phi = \frac{\epsilon t}{\epsilon_{ref} t_{ref}} \frac{\ln (I_{0,F}/I_F)_{ref}}{\ln (I_{0,F}/I_F)}$$

or

$$\phi = \frac{\phi_{ref} \epsilon_{ref} t_{ref} \ln (I_{0,F}/I_F)}{\epsilon t \ln (I_{0,F}/I_F)_{ref}}$$

As actinometer reference, the cyclization quantum yield for **1a** → **2a** (0.26)[1b] was used.

Fluorescence quantum yields of dianthrylethanes **1a–1k** were measured in cyclohexane solution and are based on the fluorescence quantum yield of 9,10-diphenylanthracene (ϕ = 0.83).[15]

Thermodynamic Measurements. The cycloreversions of **2** → **1** were carried out at three or more temperatures (temperature interval ~15 °C; accuracy ±0.1 °C) and were followed spectroscopically by the appearance of the absorption of **1** around 400 nm. Thermodynamic measurements with **2a–2e** were performed on 10^{-4} M solutions of isolated photoproducts in *o*-dichlorobenzene, and the temperature ranged from ~90 to ~130 °C. Cycloreversions of **2f–2i** were performed between 25 and 50 °C with in situ generated photoproducts in cyclohexane solution in a 10-cm water-jacketed UV cell. The Guggenheim method[16] for analysis of first-order kinetics gave straight lines (correlation coefficients ≤ –0.999). Conversions involved at least 3 half-lives, and activation energies (E_a) and preexponential factors (A) were derived from the Arrhenius equation $\ln k = \ln A - E_a/RT$ (correlation coefficient ≤ –0.999).

Registry No. 1a, 4709-79-9; **1b**, 80515-03-3; **1c**, 80515-04-4; **1d**, 80515-05-5; **1e**, 80515-06-6; **1f**, 53545-70-3; **1g**, 71582-25-7; **1h**, 80515-07-7; **1i**, 58382-04-0; **1j**, 80515-08-8; **1k**, 71582-26-8; **2a**, 17277-99-5; **2b**, 80515-09-9; **2c**, 80515-10-2; **2d**, 80515-11-3; **2e**, 80515-12-4; **2f**, 53545-71-4; **2g**, 80515-13-5; **2h**, 80515-14-6; **2i**, 80515-15-7; **2j**, 18713-04-7; **2k**, 80515-16-8; **4**, 58382-11-9; **5a**, 71582-28-0; **5b**, 21859-40-5; **6f**, 80515-17-9; **6g**, 80515-18-0; **6j**, 80515-19-1; **6k**, 80515-20-4.

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(16) Cf. Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism"; Wiley: New York, 1961; p 49.