very well for the ^1H and ^{13}C NMR spectral features of **11c**. Also, protonolysis of **11c** gives **9a**, identified by comparison (^1H and ^{13}C NMR and GC) with an authentic sample prepared by protonolysis of **12a**. Rearrangement of **7c** in $CDCl_3$ gives **10c**, identified by its fast reaction with THF to give **11c**.

Studies of the decomposition of the other compounds **7** were carried out by allowing samples in $CDCl_3$ or $THF/CDCl_3$, in septum-covered NMR tubes to remain at room temperature for 1–2 days or at 50 °C for 3–6 h, respectively. Examination of the ^{13}C NMR spectra (Table I) indicated that the same rearrangement as observed with **7c** had occurred. The rearrangements were not always clean, especially in $CDCl_3$, and for **10g** a complex mixture was observed by ^{13}C NMR.

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged for this research (CHE-7918881) and for the purchase of the Varian XL-200 spectrometer (CHE-8004246).

Registry No. **2b**, 50586-18-0; **2c**, 13154-12-6; **2d**, 16538-47-9; **2f**, 64531-23-3; **2g**, 42843-49-2; **2h**, 52356-93-1; **3a**, 56962-83-5; **3e**, 62072-20-2; **4a**, 69322-45-8; **4e**, 73062-42-7; **5a**, 87393-77-9; **6a**, 79919-22-5; **6e**, 87393-78-0; **7b**, 87393-79-1; **7c**, 87393-80-4; **7d**, 87393-81-5; **7f**, 87393-82-6; **7g**, 87393-83-7; **7h**, 87393-84-8; **8b**, 87411-94-7; **8c**, 67826-84-0; **8d**, 87393-85-9; **8f**, 87393-86-0; **8g**, 87393-87-1; **8h**, 87393-88-2; **9a**, 16538-48-0; **9e**, 87393-89-3; **10b**, 87393-90-6; **10c**, 87393-91-7; **10d**, 87393-92-8; **10f**, 87393-93-9; **10g**, 87393-94-0; **10h**, 87393-95-1; **11b**, 87393-96-2; **11c**, 87393-97-3; **11d**, 87393-98-4; **11f**, 87393-99-5; **11g**, 87394-00-1; **11h**, 87394-01-2; **12a**, 87394-02-3; **12e**, 87394-03-4; Chx_2BH, 1568-65-6; 9-BBN, 280-64-8; *B*-(4-bromobutoxy)-9-BBN, 87394-04-5; *B*-bromo-9-BBN, 22086-45-9; 1-bromo-1-hexyne, 1119-64-8.

On the Relationship between Molecular Geometry and Excited-State Properties of 9-Anthrylalkenes†

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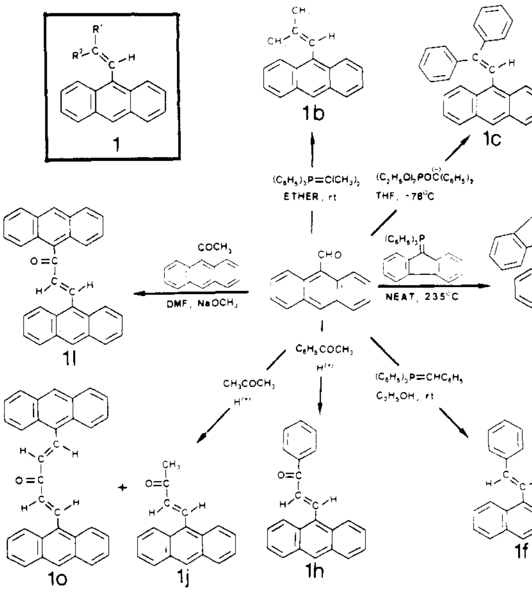
Received March 16, 1983

The excited-state properties of a series of 1-substituted and 1,1-disubstituted 2-(9-anthryl)alkenes have been investigated in terms of their fluorescence spectra and photochemical isomerizations. Large Stokes shifts of up to 10 000 cm^{-1} between absorption and emission maxima are attributed to geometrical differences between the ground state and the emitting excited state. The [cis]:[trans] ratio of the photostationary state was found to depend markedly on the nature of the 1-substituent. Photochemical isomerization of 1,3- and 1,5-bis(9-anthryl)-substituted trans olefins results in the formation of intramolecular [4π + 4π] or [4π + 2π] cycloaddition products. The cycloaddition reactions of carbonyl-substituted anthracenes are suggested to involve the triplet excited state.

The fluorescence spectrum of *trans*-1,2-bis(9-anthryl)ethylene in solution at room temperature is characterized by a Stokes shift of about 10 000 cm^{-1}, indicating the large difference between the molecular ground-state geometry and the geometry of the emitting singlet excited state.[1,2] By contrast, *cis*-1,2-bis(9-anthryl)ethylene in solution at room temperature is nonfluorescent, most likely because its molecular geometry, which is characterized by two overlapping anthracene π systems in close proximity, enhances radiationless decay.[3] Geometrical factors probably also contribute to the photochemical isomerization of the cis isomer by intramolecular Diels–Alder reaction, which involves one anthracene moiety as a diene and the other as a dienophile.[4]

We have now investigated the relationship between molecular geometry and excited-state properties of a series of 9-anthrylethylenes of general structure **1** (cf. Scheme I). In ethylenes **1a–e**, R^1 and R^2 are identical, and, consequently, no net chemical change will be achieved by way of photochemical cis–trans isomerization. However, the photophysical properties of **1a–e**, such as electronic absorption and emission spectra, may be affected as the steric demand of R^2 increases. Compounds **1f–k** are three pairs of geometrical isomers in which R^1/R^2, being phenyl, benzoyl, and acetyl, may govern the multiplicity of the reacting excited state. Finally, in ethylenes **1l–q**, R^1/R^2 incorporates an additional 9-anthryl moiety, such as 9-anthrylcarbonyl or 9-anthrylmethyl, so that these compounds represent bichromophoric systems. In addition to cis–trans isomerization, intramolecular photochemical reactions involving the anthracene moieties are conceivable for **1–q**.

Scheme I



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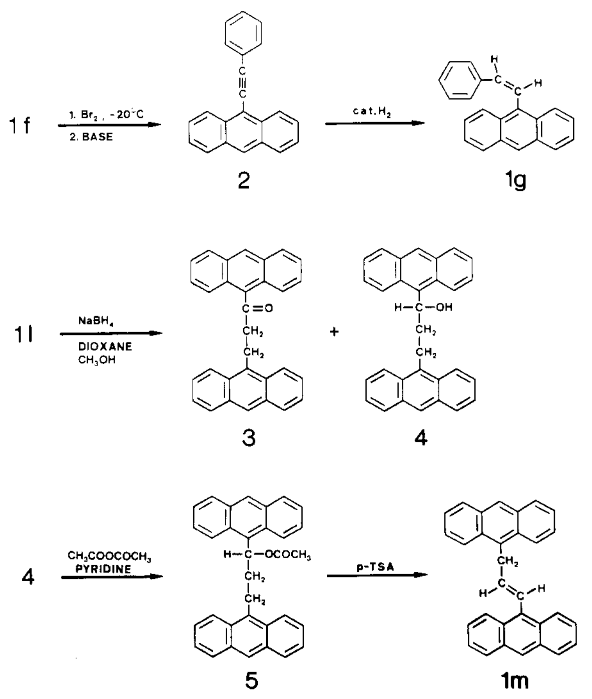
† Dedicated to Professor G. O. Schenck on the occasion of his 70th birthday.

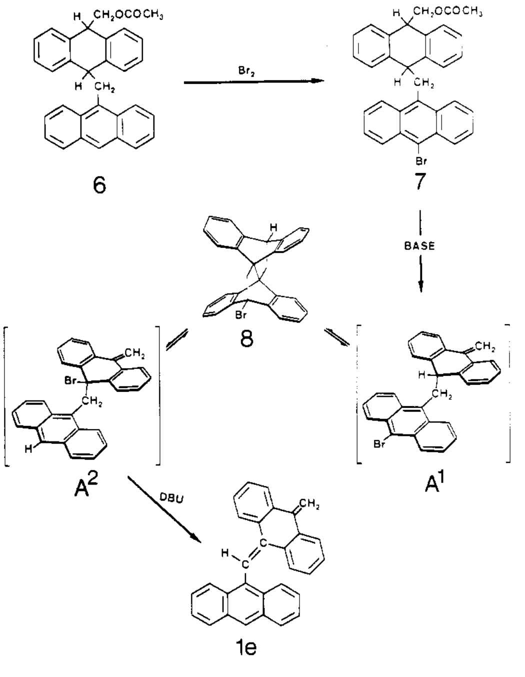
(1) Becker, H.-D.; Sandros, K.; Hansen, L. *J. Org. Chem.* **1981**, *46*, 821.
(2) Becker, H.-D. *Pure Appl. Chem.* **1982**, *54*, 1589.
(3) Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1981**, *46*, 5419.
(4) Becker, H.-D.; Sandros, K.; Andersson, K. *Angew. Chem.* **1983**, *95*, 507; *Angew. Chem. Suppl.* **1983**, 609–619.

0022-3263/83/1948-4542$01.50/0 © 1983 American Chemical Society

Scheme II



Scheme III



The preparation of 9-anthrylethylenes **1**, some of them previously known, involves the reactions outlined in Schemes I–III. Thus, symmetrically substituted 9-anthrylethylenes **1b–d** were prepared by way of Wittig–Horner reactions. Likewise, the reaction of 9-anthraldehyde with benzylidenetriphenylphosphorane gave *trans*-styrylanthracene **1f**. The corresponding cis isomer **1g** was prepared by catalytic hydrogenation of the heretofore unknown anthrylphenylacetylene **2**. Acid-catalyzed condensation of 9-anthraldehyde with acetophenone gave the benzoyl derivative **1h**. The corresponding reaction with acetone afforded both **1j** and the bis condensation product **1o**. Dianthrylpropenone **1l** was prepared by base-catalyzed condensation of 9-anthraldehyde with 9-acetylanthracene. Reduction of **1l** with sodium borohydride gave both dianthrylpropanone **3** and dianthrylpropanol **4**. The acetyl derivative of **4** (**5**) was converted into *trans*-dianthrylpropene **1m** by treatment with *p*-toluenesulfonic acid.

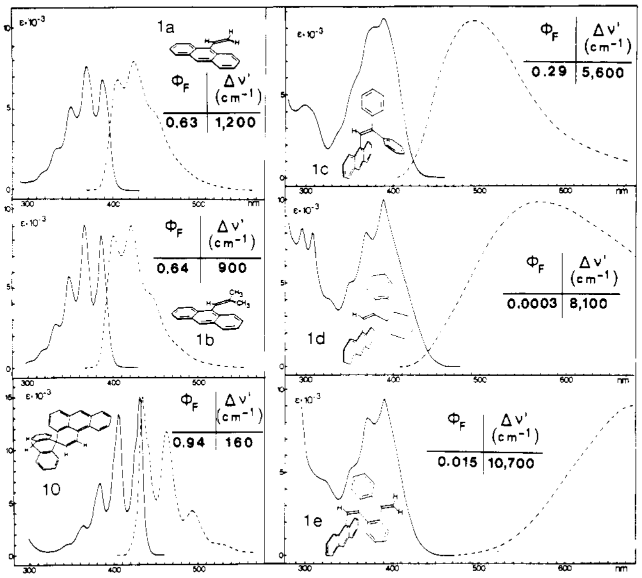
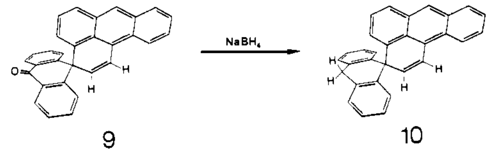


Figure 1. Electronic absorption spectra (solid curves) and emission spectra (dashed curves) of **1a–e** and **10** in cyclohexane.

The synthesis of **1e**, summarized in Scheme III, is rather unique. It is based on the preparation of bromolepidopterene **8** from anthracene **6** via its bromo derivative **7**. Because of the reversibility of the intramolecular Diels–Alder reaction involved in the formation of lepidopterenes,[5] bromolepidopterene **8** is in equilibrium with two different cycloreversion products, namely, A^1 and A^2, the latter of which affords **1e** by base-catalyzed elimination of HBr.

The cis-substituted ethylenes **1i,k,n,p,q** were prepared by photochemical reactions described in this paper. The model compound **10** was obtained by sodium borohydride reduction in the presence of hydrochloric acid of previously known spiro anthronyl derivative **9**.



Results and Discussion

The absorption and emission spectroscopic properties of symmetrically substituted 9-anthrylethylene **1a–e**, depicted in Figure 1, are found to be such as to reveal the varying geometrical differences between the electronic ground state and the fluorescent singlet excited state. Thus, the absorption spectra of 9-vinylanthracene (**1a**) and its dimethyl derivative **1b** in cyclohexane are typical of the anthracene chromophore, though the broadening of the absorption is clearly noticeable by comparison with the absorption spectrum of the rigid "vinylanthracene" **10**. Since the vinyl group and the anthracene system in **10** are coplanar, its fluorescence spectrum in cyclohexane (ϕ_F = 0.94) is characterized by a Stokes shift of only 160 cm^{-1}. By contrast, the angle[6] between the vinyl group and the aromatic π system in 9-vinylanthracene (**1a**) may be about 60°, and, because of the geometrical differences between the ground state and the emitting excited state, the Stokes

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(5) Becker, H.-D.; Andersson, K.; Sandros, K. *J. Org. Chem.* **1980**, *45*, 4549.

(6) LeFèvre, R. J. W.; Radom, L.; Ritchie, G. L. D. *J. Chem. Soc. B* **1968**, 775.

Table I. Deactivation of Photoexcited 9-Anthrylethylenes **1h–k** by Fluorescence (ϕ_F) and by Geometrical Isomerization (ϕ_i) in Methylene Chloride Solution

1	R^1	R^2	ϕ_F	ϕ_i	photostationary state [cis]:[trans] ratio
h	C_6H_5CO	H	0.0025	0.28	2.8
i	H	C_6H_5CO		0.1	
j	CH_3CO	H	0.0024	0.39	1.22
k	H	CH_3CO		0.32	

shift associated with the emission spectrum of **1a** is as large as 1200 cm^{-1}. Similar arguments apply to the fluorescence spectrum of the dimethyl derivative **1b**, whose Stokes shift is 900 cm^{-1}.

Aryl substitution in 9-anthrylethylenes **1c–e** visibly alters the shape of the long-wavelength absorption, though its energy remains largely unaffected (cf. Figure 1). Significantly, the energy gap between absorption and emission maxima markedly increases as the degree of conjugation is enhanced. For example, the Stokes shift in diphenyl-substituted **1c** is 5600 cm^{-1}, it is 8100 cm^{-1} in the fluorenylidene derivative **1d**, and it is 10700 cm^{-1} in **1e**, in which the conjugation is extended by a terminal ethylene moiety.

The fluorescence quantum yields of **1a–e** in cyclohexane drastically depend on the nature of the substituents R^1/R^2. Thus, both 9-vinylanthracene and its dimethyl derivative **1b** fluoresce with about equal quantum efficiencies, namely, 0.63 and 0.64, respectively. However, diphenyl-substituted **1c** has a decreased fluorescence quantum yield of 0.29. The quantum yield of emission of **1e** is 0.015, and it is as low as 0.0003 for the conformationally most restricted fluorenylidene derivative **1d**. In the electronic absorption spectra of **1c–e**, an absorption around 300 nm attributable to the diarylethylene moiety is clearly noticeable, suggesting that these diarylethylenes may have bichromophoric character. [The 270-MHz ^{1}H NMR spectra of **1c–e** indicate that the molecular geometry of these compounds is such as to have the ethylene moiety oriented more or less perpendicular to the plane of anthracene (cf. Table II). In the spectrum of the fluorenylidene derivative **1d**, the aromatic proton which is in closest proximity of the anthracene ring is strongly shielded and gives rise to a doublet at δ 6.1. A variety of nonradiative deactivation processes such as more efficient intersystem crossing or intramolecular electron transfer may contribute to lowering the fluorescence quantum yields of **1c–e** relative to those of **1a** and **1b**. It is worth noting in this context that the fluorescence of diaryl-substituted **1c–e** is quenched by polar solvents. Thus, the fluorescence quantum yield of the diphenyl derivative **1c** decreases from 0.29 in cyclohexane to 0.0003 in acetonitrile. Both **1d** and **1e** are nonfluorescent in solvents which are more polar than cyclohexane. By contrast, the fluorescence quantum yields of **1a** (R^1 = R^2 H) and **1b** (R^1 = R^2 = methyl) in acetonitrile are 0.72 and 0.50, respectively; i.e., they are about the same as they are in cyclohexane.

The absorption and emission spectroscopic properties of *trans*-9-(β-styryl)anthracene (**1f**; see Figure 2), in principle, are similar to those of diaryl-substituted 9-anthrylethylenes **1c–e**, suggesting that the loss of fine structure results from the conjugation of the phenyl substituent with the 9-vinylanthracene chromophore. In its electronic ground state, *trans*-styrylanthracene **1f** should deviate from molecular planarity as much as 9-vinylanthracene. As for the cis isomer **1g**, however, the geometrical restraints are such as to decrease the conjugation of the phenyl moiety with the vinylanthracene chromophore. Consequently, the absorption spectrum of **1g** is characterized by the exhibition of fine structure typical of the S$_0$–S$_1$ anthracene transition. In contrast to *cis*-stilbene and *cis*-1,2-bis(9-anthryl)ethylene, *cis*-9-(β-styryl)anthracene in solution at room temperature is fluorescent. The quantum yield of radiative S$_1$ → S$_0$ deactivation is 0.14, i.e., about one-third of that of that of the trans isomer **1f**. The deactivation of electronically excited cis isomer **1g** by geometrical isomerization to give the trans isomer **1f** proceeds with a quantum yield of 0.31 (in methylene chloride). However, all our attempts to bring about the photochemical conversion of the trans compound **1f** into its cis isomer **1g** were unsuccessful.

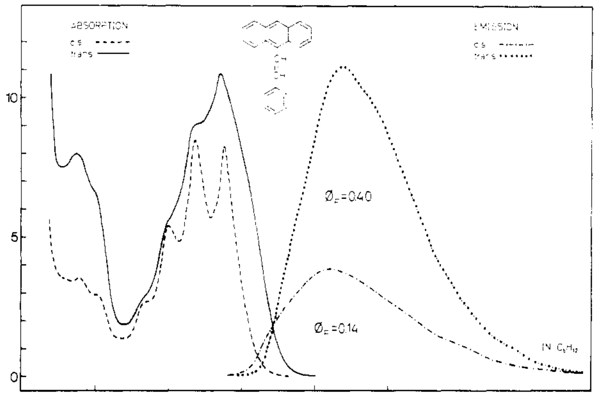

Figure 2. Electronic absorption and emission spectra of **1f** and **1g**.

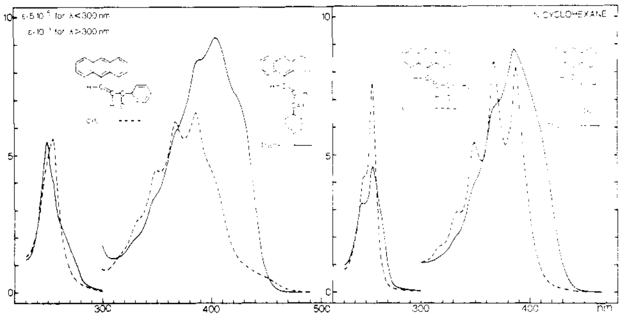

Figure 3. Electronic absorption spectra of **1h–k**.

In contrast to *trans*-styrylanthracene **1f**, *trans*-acyl-substituted 9-anthrylethylenes **1h** and **1j** are smoothly convertible into their cis isomers **1i** and **1k**, respectively, by photochemical excitation in solution.[7] In both cases, the quantum yields of isomerization and the photostationary [cis]:[trans] ratio (see Table I) are so favorable as to permit preparation and isolation of the cis isomers. Molecular oxygen was found to have virtually no effect on the photostationary state of 9-anthrylalkenes **1f–k**.[8]

The absorption spectral differences between cis and trans isomeric acyl-substituted 9-anthrylethylenes **1h–k** (see Figure 3) are in general agreement with the differences discussed for the absorption spectra of *cis*- and *trans*-styrylanthracenes **1g** and **1f**, but the bathochromic shift

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(7) Lutz, R. E.; Jordan, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4090.

(8) Styrylanthracene **1f** upon irradiation in the presence of oxygen forms an endoperoxide. The same endoperoxide is formed in the Rose Bengal sensitized autoxidation of both **1f** and its cis isomer **1g**.

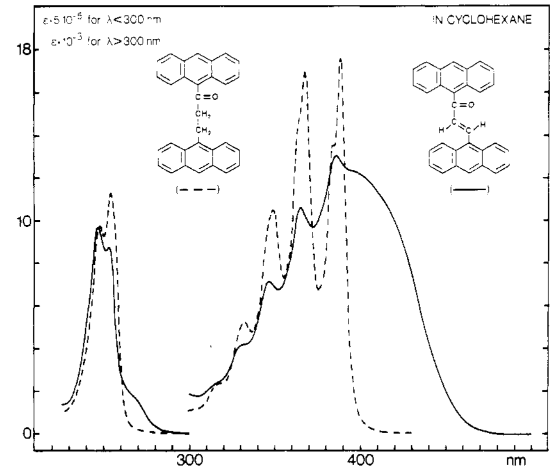
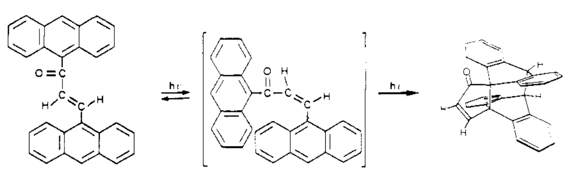


Figure 4. Electronic absorption spectra of bichromophoric anthracenes 1l and 3.

of the onset of absorption in the case of the cis-benzoyl derivative 1i is worth noting.[9]

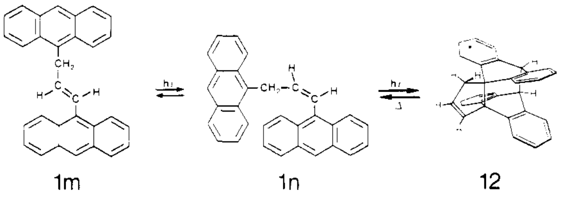
The absorption spectrum of *trans*-1,3-bis(9-anthryl)propenone (1l), we believe, reveals the bichromophoric nature of this compound: superimposed are a structureless absorption due to the 9-anthryl-substituted enone chromophore and a structured absorption, characteristic of a nonconjugated anthracene chromophore (see Figure 4). The comparison with the electronic absorption spectrum of dianthrylpropanone 3 is of interest, as it suggests that the carbonyl group and the anthracene moiety are perpendicular to each other.[10] We conclude, therefore, that the structured contribution to the absorption spectrum of 1l is attributable to the anthroyl chromophore.

Our attempt to prepare *cis*-1,3-bis(9-anthryl)propenone by irradiation of the trans compound 1l was unsuccessful insofar as the apparently inefficient geometrical isomerization was followed by a more efficient intramolecular [4π + 4π] cycloaddition. The quantum yield for the disappearance of 1l in benzene to give photoisomer 11 is less than 0.005.



1l 11

The photochemical isomerization of *trans*-1,3-bis(9-anthryl)propene (1m) to give the intramolecular [4π + 4π] cycloaddition product 12 was found to proceed smoothly but also with low quantum efficiency (<10^{-3}). Thermolytic cycloreversion of photoisomer 12 quantitatively gave *cis*-1,3-bis(9-anthryl)propene (1n). The electronic absorption spectra of both 1m and 1n are structured and are strikingly similar. The fluorescence quantum yield of *trans*-dianthrylpropene 1m is 0.13, while that of the *cis* isomer 1n is 0.06 (in cyclohexane).



1m 1n 12

An interesting question concerns the mechanism by which intramolecular cycloaddition products 11 and 12 are formed. Is the photochemical conversion of trans-substituted 1,3-bis(9-anthryl)alkenes into intramolecular cycloadducts a stepwise process which involves the intermediacy of the corresponding ground-state cis isomer, or does photoexcitation of the trans compounds result in the adiabatic formation of the electronically excited cis isomers undergoing cycloaddition? We have followed the photochemical reaction of *trans*-1,3-bis(9-anthryl)propenone (1l) in benzene solution by absorption spectroscopy and obtained a diagram of extinction differences[11] which, at the early stage of the reaction, clearly is nonlinear. Consequently, the formation of the cycloaddition product 11 involves an intermediate which we assume to be the cis isomer of 1l. By applying the same technique to the photochemical conversion of *trans*-1,3-bis(9-anthryl)propene (1m), we did obtain a *linear* diagram of extinction differences; i.e., no intermediate was detectable by absorption spectroscopy. However, we do not think that this result actually is at variance with the intermediacy of the ground-state cis isomer 1n. The similarity of the absorption spectra of the two isomers in question makes extinction differences difficult to measure. Moreover, the quantum yield for the intramolecular cycloaddition of the cis isomer appears to be quite high. We have estimated that the formation of the cycloadduct 12 from the cis isomer 1n proceeds about 15 times more efficiently than its geometrical isomerization to give the trans isomer 1m.

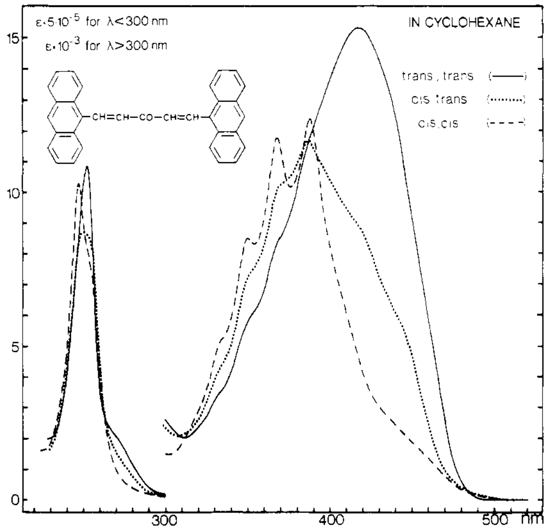


Figure 5. Electronic absorption spectra of 1o–q.

Mechanistically interesting results were obtained when the present investigation was extended to *trans,trans*-1,5-bis(9-anthryl)pentadienone 1o. Upon irradiation in methylene chloride solution, with light of λ > 360 nm, 1o is smoothly converted into the isomer 13 whose formation can be rationalized by an intramolecular Diels–Alder addition of the intermediate cis,trans isomer 1p. Inspection of Dreiding molecular models indicates that 1p may assume a conformation in which the plane of the *trans*-ethylene bond can be accommodated above the plane of the anthracene system so as to facilitate the intramolecular

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[9] The bathochromic shift of the onset of absorption also is noticeable in the electron spectrum of *cis*-benzalacetophenone relative to that of its trans isomer (cf. ref 7).

[10] In 9-acetylanthracene, the angle between the plane of the anthracene and that of the carbonyl group is 80°, as calculated from dipole measurements (see ref 6). In crystalline 9-acetylanthracene, the dihedral angle between the anthracene and the carbonyl group was found to be 88.8° (A. H. White, private communication).

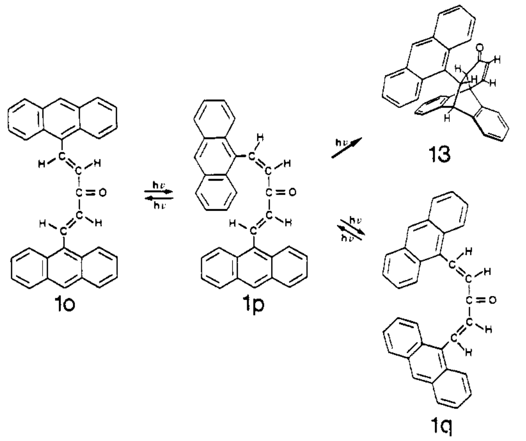
[11] Mauser, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1968**, *23B*, 1025 (cf.: Quinkert, G. *Angew. Chem.* **1972**, *84*, 1157).

Table II. 270-MHz ^1H NMR Data of 9-Anthrylalkenes 1a–q in $CDCl_3$

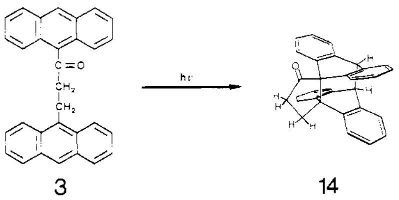
	chemical shift, ppm				
compd	aromatic H	H-10	$CH{=}CR^1R^2$	R^1	R^2
1a	8.31–7.34	8.31	hidden in arom region	5.92 (dd, $J = 11.3, 2.3$ Hz)	5.57 (dd, $J = 17.3, 2.3$ Hz)
b	8.17–7.42	8.38	6.80 (br s)	2.19 (d, $J = 1.3$ Hz)	1.52 (d, $J = 1.3$ Hz)
c	8.23–6.76	8.31	hidden in arom region		
d	8.17–6.09	8.52	8.21		
e	8.18–6.43	8.41	7.75	5.86 (s, $C{=}CH_2$)	5.83 (s)
f	8.38–7.32	8.38	7.91 (d, $J = 16.4$ Hz)		6.94 (d, $J = 16.4$ Hz)
g	8.22–6.80	8.41	7.20 or 7.13 (d, $J = 12.5$ Hz)	7.20 or 7.13 (d, $J = 12.5$ Hz)	
h	8.31–7.45	8.46	8.78 (d, $J = 16.3$ Hz)		7.52 (d, $J = 16.3$ Hz)
i	8.10–7.03	8.28	hidden in aromatic region		
j	8.20–7.44	8.43	8.46 (d, $J = 16.8$ Hz)	2.53 (s)	6.70 (d, $J = 16.8$ Hz)
k	8.08–7.46	8.46	7.77 (d, $J = 12.3$ Hz)	6.76 (d, $J = 12.3$ Hz)	1.44 (s)
l	8.60–7.23		hidden in arom region		hidden in arom region
m	8.52–7.24		6.94 (br d, $J = 16.1$ Hz)	4.78 (dd, $J = 5.5, 1.7$ Hz)	6.40 (dt, $J = 16.1, 5.5$ Hz)
n	8.51–7.07		7.16 (br d, $J = 11$ Hz)	6.43 (dt, $J = 11, 6.7$ Hz)	4.05 (dd, $J = 6.7, 1.8$ Hz, CH_2)
o	8.37–7.48	8.50	8.82 (d, $J = 15.9$ Hz)		7.21 (d, $J = 15.9$ Hz)
p	8.40–7.14		hidden in arom region	7.08 (d, cis, $J = 12.4$ Hz)	6.18 (d, trans, $J = 16.0$ Hz)
q	8.03–7.38	8.44	7.26 (d, $J = 12.2$ Hz)	6.29 (d, $J = 12.2$ Hz)	

Diels–Alder reaction. Interestingly, the formation of the Diels–Alder product **13** was found to be efficiently suppressed when the irradiation of the trans,trans compound **1o** was carried out in the presence of molecular oxygen, but geometrical isomerization of **1o** proceeded smoothly. Thus, on illumination of oxygen-saturated solutions of **1o** in methylene chloride with conventional fluorescent "warm white" light tubes, the preparation of the cis,trans isomer **1p** and its subsequent conversion into the cis,cis isomer **1q** were easily accomplished (cf. Figure 5). By spectroscopically following the photochemical reaction of the cis,trans isomer **1p** in the absence of oxygen, its disappearance by both intramolecular Diels–Alder reaction and by geometrical isomerization to give the cis,cis compound **1q** was established (see Scheme IV).

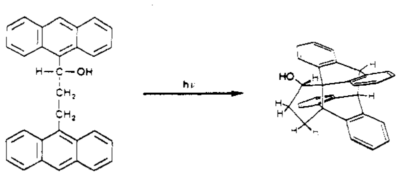
Scheme IV



The suppression of the formation of **13** by molecular oxygen is of particular interest because this finding suggests the triplet state to be involved in the photochemical Diels–Alder reaction of **1p**. Conceivably, triplet-state reactions are of importance for the photochemistry of ketone-substituted bichromophoric anthracenes in general. For example, we find that the formation of the intramolecular [$4\pi + 4\pi$] cycloaddition product **14** by irradiation of dianthrylpropanone **3** also is efficiently suppressed by molecular oxygen. In the absence of oxygen, however, **14** is formed with a quantum yield of 0.65. This value is atypically large for the intramolecular cyclomerization of a linked anthracene.[2,12] The photochemical cycloaddition of dianthrylpropanol **4**, for which intersystem crossing to the triplet state should be less efficient than for its generically related ketone **3**, leads to **15** with a quantum yield of 0.14. By the same token, the fluorescence quantum yield of dianthrylpropanol **4** is 0.27, but that of dianthrylpropanone **3** is as low as 2.6×10^{-4}.



3 14



4 15

Experimental Section

Electronic absorption and emission spectra were obtained on a Varian Cary 210 spectrophotometer and an Aminco SPF 500 (corrected spectra) spectrofluorometer, respectively. ^1H NMR spectra (in $CDCl_3$), summarized in Tables II and III, were recorded on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Melting points were determined on a hot-stage microscope and are uncorrected. Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark.

Photochemical Experiments. Preparative photoisomerizations were carried out in water-cooled immersion well reactors made of Pyrex by using high-pressure mercury lamps and filter sleeves as indicated in the experimental descriptions. Quantum yields of isomerization were determined in an optical bench arrangement by using a Corning narrow-band-pass filter for the 366-nm mercury line (Type 7-83). The photocyclization of 1,2-bis(9-anthryl)ethane ($\Phi = 0.26$)[13] was used as the actinometer. Quantum yields of geometrical isomerization were determined at low conversion (<10%). Quantum yields of cycloadditions apply to conversions of about 50%. Quantum yields of fluorescence are based on the fluorescence quantum yield of 9,10-di-

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Table III. 270-MHz ^{1}H NMR Data of Compounds 2–15 in $CDCl_3$

	chemical shift, ppm (*J*, Hz)	
compd	aromatic H	olefinic and aliphatic H
2	8.67–7.40	
3	8.44–7.40	4.25 (m, 2 H), 3.50 (m, 2 H)
4	8.60–7.34	6.40 (m, 1 H), 4.0 (m, 1 H), 3.63 (m, 1 H), 2.96 (m, 1 H), 2.58 (m, 1 H), 2.35 (br s, OH)
5	8.65–7.30	3.82 (m, 1 H), 3.32 (m, 1 H), 2.94 (m, 1 H), 2.74 (m, 1 H), 2.12 (s, 3 H)
6	8.41–6.63	4.75 (d, 2 H), 4.52 (t, 1 H), 4.47 (t, 1 H), 4.05 (2 H, d, *J* = 7 in all cases)
7	8.60–6.61	4.72 (d, 2 H, *J* = 7.0), 4.44 (t, 1 H, *J* = 7.6), 4.43 (t, 1 H, *J* = 7.0), 4.01 (d, 2 H, *J* = 7.6)
8	7.87–6.70	4.61 (t, 1 H), 3.45 (s, 2 H), 2.90 (d, *J* = 3, 2 H)
9	8.47–6.72	7.84 (d, 1 H), 6.15 (d, *J* = 10, 1 H)
10	8.52–6.85	7.61 (d, 1 H), 6.27 (d, 1 H), 4.37 ("s", (*J* = 10) 2 H)
11	6.99–6.65	8.08 (d, 1 H), 7.01 (d, 1 H), 4.64 (s, (*J* = 6), 2 H)
12	7.13–6.74	6.48 (dt, 1 H, *J* = 6.3, 2.4), 5.75 (dt, 1 H, *J* = 6.3, 2.4), 4.56 (d, 1 H, *J* = 11.1), 4.47 (d, 1 H, *J* = 11.1), 3.59 (t, 2 H, *J* = 2.4)
13	7.95–7.14	8.58 (d, 1 H, *J* = 6.2), 8.33 (s, 1 H), 6.52 (d, 1 H, *J* = 6.2), 4.67 (d, 1 H, *J* = 10), 4.60 (s, 1 H), 4.06 (d, 1 H, *J* = 10)
14	7.13–6.74	4.57 (s, 2 H), 3.16 (t, 2 H), 2.94 (t, *J* = 7.6, 2 H)
15	7.65–6.74	5.29 (m, 1 H), 4.50 (s, 2 H), 3.0–2.44 (m, 4 H), 1.85 (d, *J* = 3.6, OH)

phenylanthracene ($\Phi = 0.83$).[14]

9-Vinylanthracene (1a) was prepared according to the literature[15] and purified by column chromatography (SiO_2/CH_2Cl_2).

1-(9-Anthryl)-2-methylpropene (1b). A 1.6 M solution of *n*-butyllithium in hexane (5 mL) was added under nitrogen blanketing to a suspension of isopropyl triphenylphosphonium bromide (2.3 g, 6 mmol) in ether (40 mL) to give a deep red suspension. After 30 min, a solution of 9-anthraldehyde (1.03 g, 5 mmol) in ether was added whereupon the color of the reaction mixture changed to pale yellow as triphenylphosphine oxide precipitated. It was removed by filtration, and the residue obtained from the filtrate after vacuum evaporation of the solvents was purified by column chromatography on silica gel/methylene chloride. Final recrystallization from methylene chloride by precipitation with methanol gave pale yellow crystals: 940 mg (81% yield); mp 58–59 °C. Anal. Calcd for $C_{18}H_{16}$ (mol wt 232.33): C, 93.06; H, 6.94. Found: C, 93.32; H, 6.99.

1-(9-Anthryl)-2,2-diphenylethylene (1c). A solution of *n*-butyllithium in hexane (3 mL, 1.6 M) was added to a stirred solution of diethyl (diphenylmethyl)phosphonate[16] (912 mg, 3 mmol) in THF (25 mL) at −78 °C under nitrogen blanketing to give an orange solution. After 30 min, a solution of 9-anthraldehyde (618 mg, 3 mmol) in THF (50 mL) was added, and the reaction mixture was allowed to warm to room temperature over a period of about 12 h. A work up by addition of water (50 mL) followed by extraction with ether and column chromatography (SiO_2/CH_2Cl_2) gave 567 mg (53%) of yellow crystals, mp 170–172 °C (after recrystallization from CH_2Cl_2/C_6H_{12}). Anal. Calcd for $C_{28}H_{20}$ (mol wt 356.47): C, 94.34; H, 5.66. Found: C, 94.28; H, 5.58.

Fluorenylidene(9-anthryl)methane (1d). A mixture of 9-anthraldehyde (1.6 g, 7.8 mmol) and fluorenylidenetriphenylphosphorane[17] (2.13 g, 5 mmol) was kept under nitrogen for 1 h at 235 °C. The reaction mixture was dissolved in methylene chloride, and ethylene **1d** was separated by column chromatography on silica gel/methylene chloride. Final recrystallization from methylene chloride solution by addition of methanol gave 1.77 g (90%) of yellow crystals, mp 238–239 °C (lit.[18] mp 230 °C).

Conversion of Bromolepidopterene 8 into 1e. A solution of **8** (50 mg) and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU, 100 mg) in toluene (10 mL) was refluxed for 3 h. Suction filtration through a sintered-glass filter gave a yellow filtrate which was subjected to flash chromatography on silica gel/toluene to give yellow crystals. Recrystallization from methylene chloride/methanol gave **1e**: 33 mg (88%); mp 261–263 °C. (Around 190 °C, a change in crystal modification is noticeable.) Anal. Calcd for $C_{30}H_{20}$ (mol wt 380.49): C, 94.70; H, 5.30. Found: C, 94.25; H, 5.26.

***trans*-1-(9-Anthryl)-2-phenylethylene (1f).** A solution of lithium ethoxide, prepared from lithium (105 mg) in absolute ethanol (80 mL), was added to a stirred solution of 9-anthraldehyde (3.09 g, 15 mmol) and benzyltriphenylphosphonium bromide (6.55 g, 15.1 mmol) in absolute ethanol (320 mL) under nitrogen blanketing. A green-yellow precipitate formed after 15 min. Vacuum evaporation of solvent after 4 h left a residue from which pure **1f** [3.77 g (90% yield); mp 130–132 °C (lit.[19] mp 132 °C)] was isolated by column chromatography on silica gel/CH_2Cl_2.

***cis*-1-(9-Anthryl)-2-phenylethylene (1g).** A solution of acetylene **2** (50 mg) in ethyl acetate (25 mL) was hydrogenated under ambient conditions over Lindlar catalyst (200 mg; Fluka-Switzerland). After the uptake of 1 molar equiv of hydrogen (20 min), the catalyst was removed by filtration. Vacuum evaporation of the solvent from the filtrate gave a yellow crystalline residue which was recrystallized from methylene chloride/methanol: yield 23 mg (46%); yellow, needle-shaped crystals; mp 107–108 °C (lit.[19] mp 111 °C). Anal. Calcd for $C_{22}H_{16}$ (mol wt 280.37): C, 94.25; H, 5.75. Found: C, 94.05; H, 5.74.

***trans*-1-(9-Anthryl)-3-phenyl-1-propen-3-one (1h).** This compound was prepared from 9-anthraldehyde (4 g) and acetophenone (3 g) in ethyl acetate in the presence of hydrogen chloride as described in the literature: yield 5.15 g (86%); mp 120–122 °C (lit.[20] mp 120 °C).

***cis*-1-(9-Anthryl)-3-phenyl-1-propen-3-one (1i) by Photochemical Isomerization of 1h.** A solution of **1h** (100 mg) in benzene (175 mL) was irradiated for 1 h (nitrogen atmosphere, 6 °C, 150-W tungsten lamp). Vacuum evaporation of the solvent left a residue which was dissolved in methylene chloride. Addition of *n*-pentane gave crude **1i** (60 mg) as yellow needles. It was purified by column chromatography on SiO_2/CH_2Cl_2 to give **1i**: 45 mg; mp 147–148 °C. Anal. Calcd for $C_{23}H_{16}O$ (mol wt 308.38): C, 89.58; H, 5.23. Found: C, 89.90; H, 5.21.

***trans*-1-(9-Anthryl)-1-buten-3-one (1j) and *trans,trans*-1,5-Bis(9-anthryl)penta-1,4-dien-3-one (1o).** A solution of 9-anthraldehyde (4.12 g, 20 mmol) and acetone (11.6 g, 200 mmol) in ethyl acetate (50 mL) was saturated with hydrogen chloride gas. After 24 h at room temperature, the orange crystalline precipitate was removed by filtration and recrystallized by Soxhlet extraction with methylene chloride to give **1o**: 2.2 g (51%); mp 292–294 °C (lit.[18] mp >250 °C). Vacuum evaporation of solvent from the original ethyl acetate filtrate left an oily residue from which **1j** [yellow crystals, mp 109–110 °C (lit.[18] mp 115 °C)] was isolated by column chromatography on silica gel/methylene chloride.

***cis*-4-(9-Anthryl)-3-buten-2-one (1k) by Photochemical Isomerization of 1j.** A solution of **1j** (100 mg) in benzene (175 mL) was irradiated for 1 h (nitrogen atmosphere, 6 °C, 150-W

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tungsten lamp). The residue obtained after vacuum evaporation of solvent was subjected to column chromatography (SiO_2/CH_2Cl_2) to give yellow crystalline **1k**: yield 59 mg; mp 91–93 °C (after recrystallization from CH_2Cl_2/pentane). Anal. Calcd for $C_{18}H_{14}O$ (mol wt 246.31): C, 87.78; H, 5.73. Found: C, 87.63; H, 5.65.

***trans*-1,3-Bis(9-anthryl)propenone (1l).** Sodium methoxide (1.5 g) was added under nitrogen to a stirred solution of 9-anthraldehyde (2.06 g) and 9-acetylanthracene (2.2 g) in DMF (30 mL) to give a deep red-brown reaction mixture from which yellow crystals precipitated within seconds. After 16 h, the reaction mixture was diluted with methanol (30 mL), and the precipitate (3.3 g) was removed by filtration. Recrystallization by Soxhlet extraction with methylene chloride gave, yellow crystals: 2.8 g (69%); mp around 300 °C. Anal. Calcd for $C_{31}H_{20}O$ (mol wt 408.50): C, 91.15; H, 4.93. Found: C, 91.50; H, 4.92.

***trans*-1,3-Bis(9-anthryl)propene (1m).** A solution of 1-acetoxy-1,3-bis(9-anthryl)propane (**5**, 1 g) and *p*-toluenesulfonic acid hydrate (30 mg) in benzene (500 mL) was refluxed for 4.5 h. The benzene solution was washed with water, and the benzene was removed by vacuum evaporation to give a crystalline yellow residue. It was washed with ether to give pale yellow crystals: 800 mg (92%); mp 236–239 °C. Anal. Calcd for $C_{31}H_{22}$ (mol wt 394.52): C, 94.38; H, 5.62. Found: C, 94.07; H, 5.57.

***cis*-1,3-Bis(9-anthryl)propene (1n).** Crystalline photoproduct **12** (30 mg) was placed in an NMR tube and kept for 30 s at 280 °C (metal bath). ^{1}H NMR analysis showed complete conversion into *cis*-dianthrylpropene **1n**. Crystallization from methylene chloride solution by precipitation with methanol gave pale green-yellow needles, mp 270 °C. Anal. Calcd for $C_{31}H_{22}$ (mol wt 394.52): C, 94.38; H, 5.62. Found: C, 93.96; H, 5.52.

***trans,trans*-1,5-Bis(9-anthryl)penta-1,4-dien-3-one (1o).** See under **1j**.

***cis,trans*-1,5-Bis(9-anthryl)penta-1,4-dien-3-one (1p).** Four stoppered 250-mL Erlenmeyer flasks, each containing an oxygen-saturated solution of trans,trans compound **1o** (50 mg) in methylene chloride (150 mL), were placed under two 18-W "warm white" fluorescent light tubes (55-cm length) and irradiated for 1.5 h. Vacuum evaporation of solvent left a yellow residue which upon trituration with toluene left 35 mg of unreacted starting material undissolved. Pressure chromatography (SiO_2/toluene) of the filtrate gave as the first fraction 42 mg (21%) of the cis,trans isomer **1p** as yellow crystals, mp 164–166 °C (from ether/pentane). Anal. Calcd for $C_{33}H_{22}O$ (mol wt 434.54): C, 91.22; H, 5.10. Found: C, 90.89; H, 5.08. The second chromatographic fraction gave 25 mg (13%) of the cis,cis isomer **1q** (cf. the following experiment).

***cis,cis*-1,5-Bis(9-anthryl)penta-1,4-dien-3-one (1q).** In an experimental setup as described for the preparation of **1p**, an oxygen-saturated solution of **1o** (200 mg) in methylene chloride (600 mL) was irradiated for 6 h. Vacuum evaporation of the solvent left an oily residue which was dissolved in toluene and subjected to pressure chromatography (SiO_2/toluene) to give cis,trans isomer **1p** (14 mg, 7%) and cis,cis isomer **1q** (86 mg, 43%) as yellow crystals, mp 198–202 °C (from ether/pentane). Anal. Calcd for $C_{33}H_{22}O$ (mol wt 434.54): C, 91.22; H, 5.10. Found: C, 90.91; H, 5.08.

1-(9-Anthryl)-2-phenylacetylene (2).[21] A solution of bromine (1.6 g, 10 mmol) in carbon tetrachloride (10 mL) was added over a period of 25 min to a stirred solution of *trans*-styrylanthracene **1f** (2.8 g, 10 mmol) in carbon tetrachloride (100 mL) at −20 °C. Stirring was continued for additional 10 min. Partial evaporation in vacuo of the solvent to a volume of about 15 mL, followed by addition of hexane gave 3.82 g (87%) of the crude dibromoethane which was removed by filtration and used without further purification. Thus, a freshly prepared solution of this product (1.76 g, 4 mmol) in dry THF (25 mL) was added under nitrogen to a stirred solution of potassium *tert*-butoxide, prepared from potassium (313 mg, 8 mmol) and *tert*-butyl alcohol (8 mL). After 3 h, the reaction mixture was diluted with methylene chloride (20 mL) to give a suspension from which inorganic material was removed by filtration. Vacuum evaporation of solvents from the filtrate gave a residue which was subjected to column chromatography on silica gel/methylene chloride to give, after recrystallization from methylene chloride/hexane, yellow crystalline **2**: 840 mg (76%); mp 108–109 °C. Anal. Calcd for $C_{22}H_{14}$ (mol wt 278.36): C, 94.93; H, 5.07. Found: C, 94.86; H, 5.04.

1,3-Bis(9-anthryl)propan-1-one (3). Sodium borohydride (100 mg) was added to a suspension of **1l** (500 mg) in a mixture of dioxane (30 mL) and methanol (10 mL). The stirred suspension was kept at 75 °C for 5 min to give a clear pale yellow solution. Addition of water (20 mL) gave a pale yellow precipitate (400 mg) which was removed by filtration and purified by column chromatography (SiO_2/CH_2Cl_2): yield 300 mg (60%); pale yellow crystals; mp 213–215 °C. Anal. Calcd for $C_{31}H_{22}O$ (mol wt 410.52): C, 90.70%; H, 5.40. Found: C, 90.73; H, 5.42.

1,3-Bis(9-anthryl)propan-1-ol (4). The aqueous filtrate obtained in the preparation of dianthrylpropane **3** described in the preceding experiment was diluted with additional water (50 mL) and extracted with methylene chloride. The residue obtained on vacuum evaporation of the solvents was purified by column chromatography on silica gel (CH_2Cl_2) to give **4**: 100 mg (20%); pale yellow crystals (from CH_2Cl_2/*n*-hexane); mp 207–210 °C. Anal. Calcd for $C_{31}H_{24}O$ (mol wt 412.54): C, 90.26; H, 5.86. Found: C, 89.84; H, 5.77.

1-Acetoxy-1,3-bis(9-anthryl)propane (5). Sodium borohydride (3 g) was added over a period of 15 min to a boiling solution of dianthrylpropenone **1l** (1 g) in a mixture of dioxane (40 mL) and methanol (10 mL). Refluxing was continued for 15 min, and the reaction mixture was then diluted with water (400 mL) to give a pale yellow solid precipitate which was removed by filtration. It was dissolved in a mixture of acetic anhydride (50 mL) and pyridine (10 mL), and the solution was kept at refluxing temperature for 15 min. A workup by addition of ethanol followed by vacuum evaporation of the solvents gave a yellow solid crystalline residue which was recrystallized from methylene chloride by addition of ethanol or hexane: yield 1g (90%); mp 230–232 °C. Anal. Calcd for $C_{33}H_{26}O_2$ (mol wt 454.57): C, 87.19; H, 5.77. Found: C, 87.18, H, 5.73.

9-(Acetoxymethyl)-10-[(10-bromo-9-anthryl)methyl]-9,10-dihydroanthracene (7). A solution of bromine (0.72 g, 4.5 mmol) in carbon disulfide (4 mL) was added dropwise over a 15-min period to a stirred solution of 9-(acetoxymethyl)-10-(9-anthrylmethyl)-9,10-dihydroanthracene (**6**;[22] 2.0 g, 4.5 mmol) in carbon disulfide (30 mL). After additional 5 min, the reaction mixture was diluted with hexane (20 mL), and part of the hydrogen bromide was removed by passing a stream of nitrogen through the solution. Vacuum evaporation of the solvent gave a yellow oily residue which was chromatographed on SiO_2/CH_2Cl_2 to give yellow needle-shaped crystals (from CH_2Cl_2/CH_3OH): 2.08 g (89%); mp 166–168 °C. Anal. Calcd for $C_{32}H_{25}BrO_2$ (mol wt 521.46): C, 73.71; H, 4.83. Found: C, 73.28; H, 4.83.

Bromolepidopterene (8). Potassium *tert*-butoxide (3.5 g) was added to a suspension of **7** (900 mg) in mixture of benzene (5 mL) and ethanol (5 mL) under nitrogen blanketing. After the mixture was refluxed for 5 min, a light brown solution formed from which colorless crystals precipitated. After an additional 15 min of refluxing, the reaction mixture was diluted with methanol (15 mL), and the precipitate was removed by filtration. ^{1}H NMR analysis revealed the precipitate to consist of bromolepidopterene **8** and lepidopterene (ratio 3:1). A brown impurity was easily removed by treating the crude product in methylene chloride with activated charcoal. Separation of bromolepidopterene and lepidopterene was accomplished by flash chromatography with silica gel/toluene. Recrystallization from CH_2Cl_2/CH_3OH gave colorless crystals: 350 mg (44%); mp >174 °C dec. Anal. Calcd for $C_{30}H_{21}Br$ (mol wt 461.40): C, 78.09; H, 4.59. Found: C, 77.99; H, 4.54.

Spiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracene] (10). The preparation of **10**, in principle, is analogous to that of the corresponding dihydro derivative described previously.[23] A solution of **9**[23] (100 mg) and sodium borohydride (800 mg) in a mixture of dioxane (10 mL) and methanol (5 mL) was refluxed for 30 min. After further addition of sodium borohydride (800 mg) and dioxane (10 mL), the reaction mixture was acidified with concentrated HCl (5 mL), and refluxing was continued for 30 min. The workup involved addition of water (50 mL), extraction with ether, and chromatography on silica gel/methylene chloride. The

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fast-moving hydrocarbon fraction thus obtained was rechromatographed on silica gel with hexane/ethyl acetate (30:1) as the eluant: yield 15 mg; bright yellow, needle-shaped crystals; mp 226–229 °C. Anal. Calcd for $C_{30}H_{20}$ (mol wt 380.49): C, 94.70; H, 5.30. Found: C, 94.50; H, 5.30.

Photochemical Isomerization of Dianthrylpropenone 1l To Give 11. A solution of **1l** (300 mg) in benzene (175 mL) was irradiated under argon for 90 min (450-W Hanovia medium-pressure mercury lamp, 30 °C). Vacuum evaporation of the solvent gave a solid residue which was washed with ether and then recrystallized from a mixture of methylene chloride and ether to give colorless crystals: 210 mg (70%); mp 275–277 °C dec. Anal. Calcd for $C_{31}H_{20}O$ (mol wt 408.50): C, 91.15; H, 4.93. Found: C, 91.13; H, 4.96.

Photochemical Isomerization of Dianthrylpropene 1m To Give 12. A solution of **1m** (100 mg) in methylene chloride (150 mL) was irradiated at 20 °C under nitrogen for 1.5 h (125-W high-pressure mercury lamp, Philips HPK 125W; cutoff filter; $\lambda > 340$ nm). Vacuum evaporation of the solvent from the pale yellow solution gave a crystalline residue which was washed with benzene and recrystallized from methylene chloride by precipitation with methanol: yield 40 mg (40%); colorless crystals; mp 252 °C. After resolidification, the substance melts at 270 °C. Anal. Calcd for $C_{31}H_{22}$ (mol wt 394.52): C, 94.38; H, 5.62. Found: C, 94.00; H, 5.55.

Photochemical Isomerization of *trans,trans*-1,5-Bis(9-anthryl)penta-1,4-dien-3-one (1o) To Give 13. A solution of **1o** (50 mg) in methylene chloride (550 mL) was irradiated under nitrogen (125-W Philips high-pressure mercury lamp HPK 125W; cutoff filter, $\lambda > 360$ nm).[24] At 10-min intervals, 50 mg samples of **1o** were added. After 105 min, when a total of 500 mg of **1o** had been irradiated, the solvent was removed by vacuum evaporation. The residue thus obtained was purified by column chromatography on silica gel/CH_2Cl_2 to give 375 mg (75%) of pale yellow crystals, which were recrystallized from methylene chloride solution by addition of diethyl ether; mp 220–223 °C dec. Anal. Calcd for $C_{33}H_{22}O$ (mol wt 434.54): C, 91.22; H, 5.10. Found: C, 90.89, H, 5.07.

Photochemical Isomerization of 1,3-Bis(9-anthryl)-propan-1-one To Give 14. A solution of **3** (150 mg) in benzene (175 mL) was irradiated under nitrogen for 30 min (Philips high-pressure mercury lamp, HPK 125W; cutoff filter; $\lambda > 360$ nm; 20 °C). Vacuum evaporation of the solvent gave a solid residue which was washed with ether to remove a yellow byproduct. The remaining colorless solid was recrystallized from a warm benzene solution by precipitation with *n*-hexane: yield 140 mg (93%); colorless crystals; mp 265–270 °C dec. Anal. Calcd for $C_{31}H_{22}O$ (mol wt 410.52): C, 90.70; H, 5.40. Found: C, 90.87; H, 5.42.

Photochemical Isomerization of 4 To Give 15. A solution of **4** (50 mg) in methylene chloride (65 mL) was irradiated for 30 min at 10 °C under argon (Philips HPK 125W mercury lamp). The workup by vacuum evaporation of solvent left a colorless crystalline residue which was recrystallized from methylene chloride/cyclohexane: yield 38 mg (76%); mp ~245 °C dec. Anal. Calcd for $C_{31}H_{24}O$ (mol wt 412.54): C, 90.26; H, 5.86. Found: C, 90.00; H, 5.86.

Acknowledgment. We are gratefully indebted to Dr. Kjell Sandros for recording the emission spectra of **1d** and **1e** and to Gunnar Svensson for skillful technical assistance.

Registry No. **1a**, 2444-68-0; **1b**, 38080-19-2; **1c**, 84599-88-2; **1d**, 84599-89-3; **1e**, 84599-90-6; **1f**, 42196-97-4; **1g**, 87337-00-6; **1h**, 53744-36-8; **1i**, 87337-01-7; **1j**, 87337-02-8; **1k**, 87337-03-9; **1l**, 84599-77-9; **1m**, 84599-76-8; **1n**, 87337-04-0; **1o**, 84599-83-7; **1p**, 87337-05-1; **1q**, 87337-06-2; **2**, 87337-07-3; **3**, 84599-75-7; **4**, 84599-73-5; **5**, 84599-74-6; **6**, 68975-25-7; **7**, 87337-08-4; **8**, 87337-09-5; **9**, 69469-61-0; **10**, 28641-52-3; **11**, 84599-81-5; **12**, 84599-80-4; **13**, 87337-10-8; **14**, 84599-79-1; **15**, 84599-78-0.

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[24] The use of a cutoff filter is essential. Product **13** upon photoexcitation undergoes an isomerization which we have not yet investigated.

Optical Rotatory Dispersion Studies. 136.[1] Enzymatic Reduction of 2-Methyl-2-(trideuteriomethyl)cyclohexane-1,3-dione. Unusual Conformation of 2,2-Dimethyl-3-hydroxycyclohexanone

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Received May 9, 1983

The enzymatic reduction of 2-methyl-2-(trideuteriomethyl)cyclohexane-1,3-dione with Kloeckera magna is not stereospecific with respect to the α center. The reaction product, 2-methyl-2-(trideuteriomethyl)-3-hydroxycyclohexanone, was shown to possess the 3*S* configuration. The circular dichroism and X-ray crystallographic data lead to the unexpected conclusion that the reduction product assumes the conformation with an axially oriented hydroxyl group.

The enzymatic reduction of 2,2-dialkyl-substituted cyclopentane-1,3-diones has been investigated in considerable detail by Kosmol et al.[3] and has found application as the chirality-introducing step in the industrial total synthesis of estradiol. With the appropriate choice of the microbiological system, the reduction can be carried out with nearly complete stereoselectivity; i.e., only one of the four possible stereoisomers **2–5** (Scheme I) is obtained. In a more recent study, Brooks et al.[4] carried out a similar investigation designed to establish a relationship between stereoselectivity and size differences of both alkyl substituents. As anticipated, the stereoselectivity of the reaction was found to be strongly dependent on this pa-

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[1] For the preceding paper in this series, see: Harris, R. N.; Sundararaman, P.; Djerassi, C. *J. Chem. Am. Soc.* **1983**, *105*, 2408.

[2] (a) Stanford University. (b) Gesellschaft Für biotechnologische Forschung. (c) Medical Foundation of Buffalo.

[3] Kosmol, H.; Kieslich, K.; Vossing, R.; Koch, H.-J.; Petzold, K.; Gibian, H. *Liebigs Ann. Chem.* **1967**, *701*, 199.

[4] Brooks, D. W.; Grothaus, P. G.; Irwin, W. L. *J. Org. Chem.* **1982**, *47*, 2820.