

Photochemical Dimerization Modes of 9-Methoxyanthracenes and 9-(2-Hydroxy-2-propyl)anthracene

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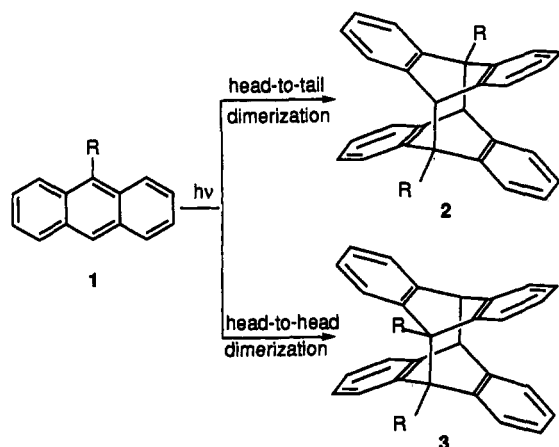
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Irradiation of 9-methoxyanthracene in ether solution at room temperature gives, in a ratio of about 55:45, head-to-tail and head-to-head substituted dianthracenes, which have been isolated by column chromatography on silica gel. Photochemical dimerization of 9-methoxy-10-methylanthracene afforded the known centrosymmetrical $4\pi + 4\pi$ cycloaddition product. By contrast, photoexcitation of 9-methoxy-10-methylanthracene in the presence of 9-methoxyanthracene results mainly in the formation of the two possible heterodimers by $4\pi + 4\pi$ cycloaddition. Photochemical head-to-tail dimerization of 9-(2-hydroxy-2-propyl)anthracene gives two diastereomeric dianthracenes which, due to their rotationally blocked 2-hydroxy-2-propyl substituents, are characterized by *i*- and C_2 -symmetry, respectively. Deviations from planarity of the aromatic π -system in crystalline 9-methoxy-, 9-methoxy-10-methyl-, and 9-(2-hydroxy-2-propyl)anthracene, and the effects of substituents on the molecular topology of various dianthracenes, have been evaluated by X-ray diffraction.

Introduction

Photoexcitation of *meso*-substituted anthracenes **1** in solution typically leads to head-to-tail dimers **2** by intermolecular $4\pi + 4\pi$ cycloaddition, though evidence for the concomitant formation of thermally more labile head-to-head dimers **3** has been obtained in some instances by ^1H NMR analysis of crude photoproducts.¹ Likewise, head-to-head substituted "heterodimers", deriving from two different 9-substituted anthracenes, have rarely been isolated because of their instability under ambient conditions.^{1,2}



Spatially demanding substitution of the anthracene skeleton, which causes the aromatic π -system to deviate from planarity, may impair or preclude the photochemical formation of dianthracenes in favor of unimolecular photochemistry.³ In particular, the thermally reversible

formation of 9,10-(Dewar anthracenes) by photochemical valence isomerization of geometrically distorted anthracenes such as 9-*tert*-butylanthracene has been studied extensively.⁴⁻⁶

Some years ago, irradiation of 9-methoxyanthracene (**4**) was suggested to give 9-methoxy-9,10-(Dewar anthracene) (**5**).⁷ Unfortunately, this isomerization was rationalized in the belief that 9-methoxyanthracene does not dimerize photochemically, though irradiation of **4** had earlier been described to give a dimethoxy-substituted dianthracene.⁸ The assumed photochemical formation of **5** also is surprising from a topological point of view, since an X-ray diffraction analysis of crystalline 9-methoxyanthracene had revealed that its aromatic π -system only slightly deviated from planarity.⁹

Our interest in the relationship between molecular topology and excited-state reactivity of anthracene derivatives¹⁰ has prompted us to reinvestigate the structure and photochemistry of 9-methoxyanthracene. Moreover, we have investigated the structures and photochemical

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(4) Hart, H.; Ruge, B. *Tetrahedron Lett.* 1977, 3143-3146.

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(6) (a) Güsten, H.; Mintas, M.; Klasinc, L. *J. Am. Chem. Soc.* 1980, 102, 7936-7937. (b) Dreeskamp, H.; Jahn, B.; Pabst, J. *Z. Naturforsch.* 1981, 36A, 665-668. (c) Jahn, B.; Dreeskamp, H. *Z. Naturforsch.* 1982, 37A, 376-379. (d) Jahn, B. Ph.D. Thesis, Technische Universität Braunschweig, Germany, 1983. (e) Kraljic, I.; Mintas, M.; Klasinc, L.; Ranogajec, F.; Güsten, H. *Nouv. J. Chim.* 1983, 7, 239-243. (f) Jahn, B.; Dreeskamp, H. *Ber. Bunsen-Ges. Phys. Chem.* 1984, 88, 42-47. (g) Dreeskamp, H.; Kapahnke, P.; Tochtermann, W. *Radiat. Phys. Chem.; Int. J. Radiat. Appl. Instrum. Part C* 1988, 32, 537-539.

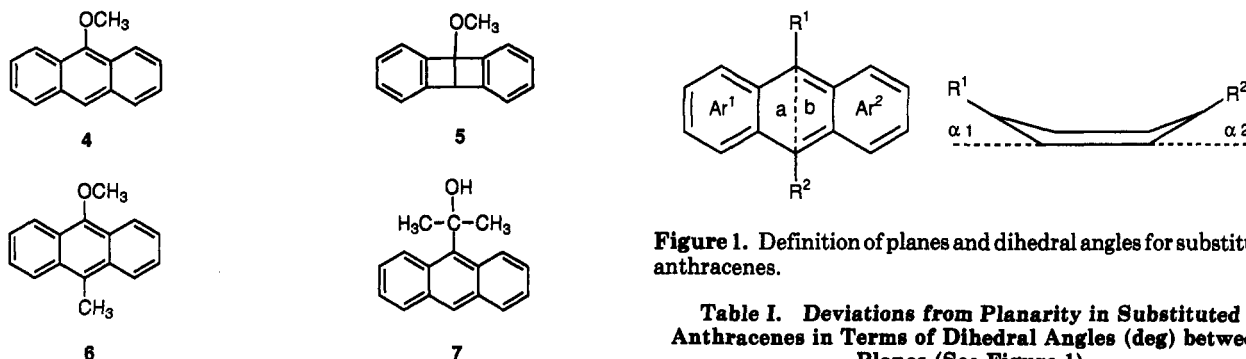
(7) Schoof, S.; Güsten, H. *Ber. Bunsen-Ges. Phys. Chem.* 1989, 93, 864-870. The formation of 9-methoxy-9,10-(Dewar anthracene) was deduced solely from the observation that the photochemical disappearance of 9-methoxyanthracene was thermally reversible. Any experimental details about the thermal regeneration of 9-methoxyanthracene were not reported. The statement that 9-methoxyanthracene is "a member of photostable anthracene derivatives" is incorrect insofar as it applies only to the crystalline state.

(8) (a) Lalande, R.; Calas, R. *Bull. Soc. Chim. Fr.* 1959, 766-770. (b) Lalande, R.; Calas, R. *Bull. Soc. Chim. Fr.* 1960, 144-147. (c) A quantum yield of 0.10 has been estimated for the photochemical dimerization of 9-methoxyanthracene (0.01 M) in benzene solution: Castellan, A. C. R. *Acad. Sci. Paris, Ser. C* 1975, 281, 221-224. See also: Vember, T. M.; Veselova, T. V.; Obyknovennaya, I. E.; Cherkasov, A. S.; Shirokov, V. I. *Bull. Acad. Sc. USSR, Phys. Ser. (Engl.)* 1973, 37, 133-136.

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dimerization of 9-methoxy-10-methylanthracene (6) and 9-(2-hydroxy-2-propyl)anthracene (7).

Results and Discussion

Substituent Effects on the Molecular Geometry of Anthracenes. The results of the X-ray diffraction analyses of 9-methoxyanthracene (4), 9-methoxy-10-methylanthracene (6), and 9-(2-hydroxy-2-propyl)anthracene (7) in terms of deviations from planarity of the anthracene skeleton (*cf.* Figure 1) are summarized in Table I. For comparison, the corresponding data for 9-*tert*-butylanthracene,¹¹ and for 1,2-bis(10-methoxy-9-anthryl)ethane (10), have been included. Also listed for 4, 6, and 10 are the angles by which the methoxy group is twisted out of the plane of the anthracene.

As for 9-methoxyanthracene, its earlier reported⁹ molecular geometry has been verified in the present study with an accuracy of present-day standard. The distortion of the anthracene π -system in terms of the folding angle $\alpha 1$ is negligible (1.4°) by comparison with the corresponding angle of 16.1° observed for 9-*tert*-butylanthracene. The deviations from planarity in 9,10-disubstituted anthracene 6 and of structurally related centrosymmetric 10 are similar to, or even smaller than, those found in 4. It is worth noting for both 4, 6, and 10 that their methoxy substituents are twisted out of the plane of the anthracene by about 85° (see Table I). The nearly orthogonal ground-state arrangement of the methoxy group with respect to the anthracene plane implies that one face of the anthracene π -system is unimpededly accessible in intermolecular $4\pi + 4\pi$ cycloaddition reactions involving the 9,10-positions.

The asymmetric unit of crystalline 9-(2-hydroxy-2-propyl)anthracene (7) was found to consist of two independent molecules (7a/7b). The central ring of the anthracene moiety is bent about the 9,10-axis by 11.5° and 9.9°, the folding angles $\alpha 1$ being 13.6° and 11.5° in 7a and 7b, respectively. The deviations from planarity of the anthracene π -systems are most obvious from the dihedral angles of 17.5° and 15.3° between the lateral rings in 7a and 7b. The existence of two molecules in the asymmetric unit of 7, with noticeable differences in geometrical distortions, may be indicative of a higher degree of intramolecular flexibility than feasible for 9-*tert*-butylanthracene.

Figure 1. Definition of planes and dihedral angles for substituted anthracenes.

Table I. Deviations from Planarity in Substituted Anthracenes in Terms of Dihedral Angles (deg) between Planes (See Figure 1)

compd	R ¹	R ²	Ar ¹ /Ar ²	a/b	$\alpha 1$	$\alpha 2$	Anthr/OCH ₃
7a	C(CH ₃) ₃	H	18.8	13.8	16.1	7.0	
7b	C(CH ₃) ₂ OH	H	17.5	11.5	13.6	6.1	
4	OCH ₃	H	15.3	9.9	11.5	5.6	
6	OCH ₃	CH ₃	4.6	1.4	1.4	1.1	83.8
10	OCH ₃	CH ₂ ⁻	2.5	0.3	1.2	1.1	83.5
			0.3	0.7	0.8	0.4	85.6

Table II. Pertinent ¹H NMR Spectral Data (δ) of Dianthracenes in CDCl₃ (Chemical Shifts in ppm downfield from Me₄Si)^a

	8	9	12	13	14
OCH ₃	3.42	3.36	3.00	3.10; 3.31	3.26; 3.42
CH ₃			2.14	2.12	2.10
bridgehead H	4.41	4.49		4.40	3.86

^a Chemical shifts of aromatic H typically are in the range of δ 6.7–7.25 (*cf.* Figure 2).

Photochemical Reactions. When a solution of 9-methoxyanthracene in ether is irradiated through Pyrex, the consumption of starting material is associated with the formation of *two* photoproducts, which are distinguishable by TLC on silica gel/dichloromethane by their markedly different R_f values of 0.6 and 0.1 (see Experimental Section). Separation and isolation of both products is therefore easily accomplished by flash column chromatography. The photoproducts are formed in a ratio of about 55:45, they are colorless crystalline solids, and both are transparent in the UV spectrum at wavelengths >300 nm. As for their ¹H NMR spectra, the presence of one methoxy group and one aliphatic hydrogen per eight aromatic protons characterizes both photoproducts (*cf.* Table II), but obvious structural differences between the two photoproducts are most notably borne out in the aromatic region by the presence of a downfield doublet at δ 7.22 (see Figure 2) in the spectrum of the compound at low R_f value.

The photoproduct characterized by the R_f value of 0.6 melts with decomposition between 225 and 250 °C, in fair agreement with the thermal behavior of the previously reported dimethoxy-substituted dianthracene 8,^{8a,b} and we have no reason to doubt that the assigned structure is correct. As for the photoproduct with the R_f value of 0.1, it decomposes upon melting around 115 °C. It appears to be stable in the crystalline state under ambient conditions, but it is labile in solution. When a 5×10^{-5} M solution of the photoproduct in cyclohexane is kept at room temperature, clean and quantitative regeneration of 9-methoxyanthracene, established by UV spectroscopy, occurs within 5 h. We believe, therefore, that this photoproduct is identical with the spectroscopically detected elusive photoproduct suggested to be Dewar anthracene 5. However, neither can we accept the observed thermal lability as evidence for the existence of 5 nor does

(10) Becker, H.-D. Excited state reactivity and molecular topology relationships in chromophorically substituted anthracenes. In *Adv. Photochem.*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds.; Interscience Publishers: New York, 1990; Vol. 15, pp 139–227.

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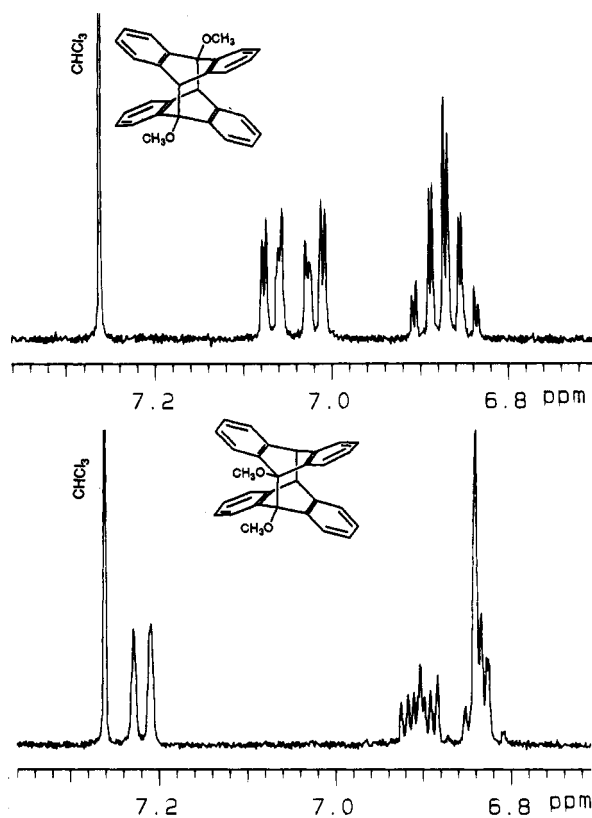
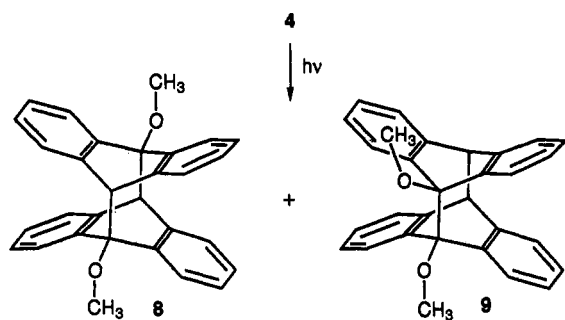


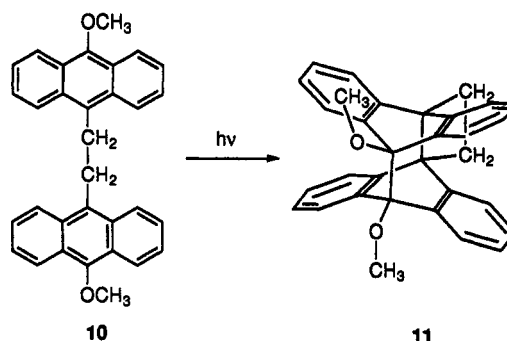
Figure 2. ^1H NMR (400 MHz) spectra of aromatic protons in dianthracenes 8 and 9.

the now-available ^1H NMR spectrum support a 9,10-(Dewar anthracene) structure. Rather, the following findings and considerations conclusively show that we are dealing with the head-to-head dimer 9 of 9-methoxyanthracene. Firstly, the mass spectrum obtained by positive FAB reveals the dimeric nature of the photoproduct by the molecular ion peak at m/e 417 (MH^+), as well as dimer-derived fragment peaks at 385 ($\text{M} - \text{OCH}_3$) and 354 ($\text{M} - 2\text{OCH}_3$). Second, we consider the low R_f value of the photoproduct in dichloromethane to be indicative of the 1,2-dimethoxyethane moiety in 9. The

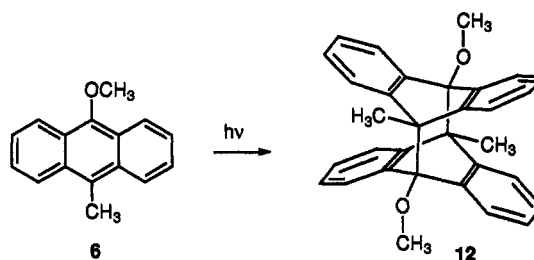


assumed planar *s-trans* conformations of the rotationally confined methoxy groups with respect to the photochemically formed $\text{sp}^3\text{-sp}^3$ bond derives from the ground-state geometry of parallel aligned pairs of head-to-head oriented 4, and the observed strong adsorption of 9 to silica is probably due to hydrogen bonding involving the exposed lone-pair electrons on oxygen. Significantly, the same chromatographic behavior ($R_f = 0.13$) is exhibited by the related dimethoxy-substituted dianthracene 11, which is formed by intramolecular $4\pi + 4\pi$ cycloaddition of 1,2-

bis(10-methoxy-9-anthryl)ethane (10). The half-life of 11 in cyclohexane solution at 25 °C is 142 min.¹²



Irradiation of 9-methoxy-10-methylantracene (6) in ether solution was found to give the previously known dianthracene 12,¹³ whose centrosymmetric structure we have established by X-ray diffraction (see below). TLC analysis of the crude reaction mixture did not indicate the presence of a head-to-head dimer. However, clear-cut evidence for a head-to-head dimethoxy-substituted dianthracene was obtained when we investigated the photochemical addition of 6 to 9-methoxyanthracene. Fortunately, the electronic adsorption spectrum of 6 (λ_{max} 401 nm; ϵ 8700 $\text{M}^{-1} \text{cm}^{-1}$; in cyclohexane) is bathochromically shifted by 13 nm relative to that of 4, so as to facilitate selective excitation of 6. By using an aqueous potassium nitrite filter solution, transmission of light absorbed by 9-methoxyanthracene (λ_{max} 388 nm; ϵ 8800 $\text{M}^{-1} \text{cm}^{-1}$; in cyclohexane) is negligible. Thus, irradiation of 6 in the presence of an equimolar amount of 4 in ether gave the symmetric dianthracene 12 only as minor product (about 10% of reacted 6). The two main products turned



out to be mixed dianthracenes 13 and 14 which, according to ^1H NMR analysis, were found in a ratio of about 1:1 and whose formation involves both orientationally possible $4\pi + 4\pi$ cycloadditions of photoexcited 9-methoxy-10-methylantracene to ground-state 9-methoxyanthracene.^{13a} Again, the detection and separation of head-to-tail and head-to-head dimethoxy-substituted dianthracenes 13 and 14 by flash-column chromatography on silica was facilitated by their characteristically different R_f value of 0.64 and 0.1, respectively. More important, it was possible to establish for both isomers their structures by X-ray diffraction and confirm for 14 the *s-trans-s-trans* conformation of the 1,2-dimethoxyethane moiety. Pertinent ^1H NMR spectral data for dianthracenes 12–14 are given in Table II. Essential topological features of dianthracenes

(12) Becker, H.-D.; Elebring, T.; Sandros, K. *J. Org. Chem.* 1982, 47, 1064–1068.

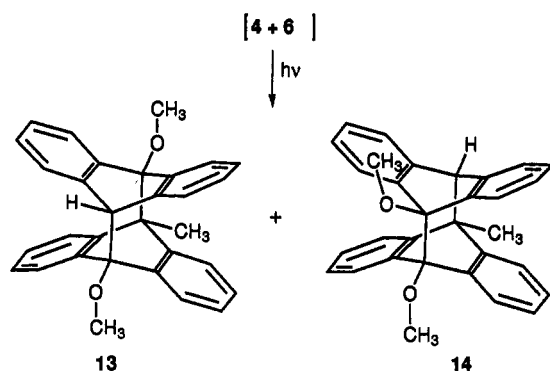
(13) Calas, R.; Lalande, R. *Bull. Soc. Chim. Fr.* 1959, 770–772. (a) Concerning the favored formation of dianthracenes 13 and 14 compared to 12, it is worth noting that the quantum yield for the dimerization of 9-methoxy-10-methylantracene (0.01 M) in benzene to give 12 is only 0.009. See ref 8c.

Table III. Structural Features of Dianthracenes: Length of Photochemically Formed Bonds and Dihedral Angles between Aromatic Rings (See Figure 3)

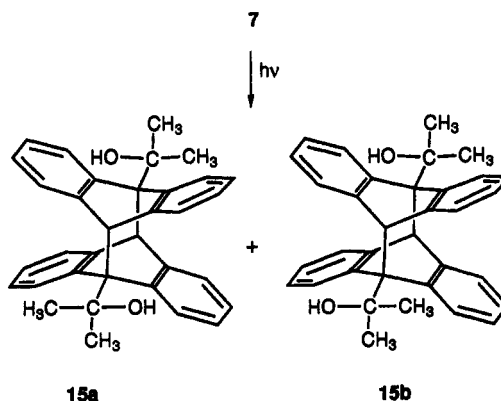
	R ¹	R ²	R ³	R ⁴	bond length ^a (Å)	dihedral angles (deg)			
						A/A'	B/B'	A/B	A'/B'
16a	H	H	H	H	1.624(3)	44.6	44.6	135.4	135.4 ^b
16b	OCHO	CH ₃	OCHO	CH ₃	1.646(4)	42.0	42.0	138.0	138.0 ^c
12	OCH ₃	CH ₃	OCH ₃	CH ₃	1.670(4)	40.6	40.6	139.4	139.4
13	OCH ₃	CH ₃	OCH ₃	H	1.639(2)	41.9	41.9	138.1	138.1
14	OCH ₃	OCH ₃	H	CH ₃	1.657(4)	43.2	43.4	130.7	143.0
					1.637(4)				
15a	R ¹ = R ³ = C(CH ₃) ₂ OH; R ² = R ⁴ = H				1.630(3)	50.4	50.4	129.6	129.6
15b	R ¹ = R ³ = C(CH ₃) ₂ OH; R ² = R ⁴ = H				1.615(7)	49.7	58.4	126.9	125.0
					1.618(7)				

^a Estimated standard deviations in parentheses. ^b From ref 16. ^c From ref 17.

in their crystalline state are summarized in Table III and discussed below.

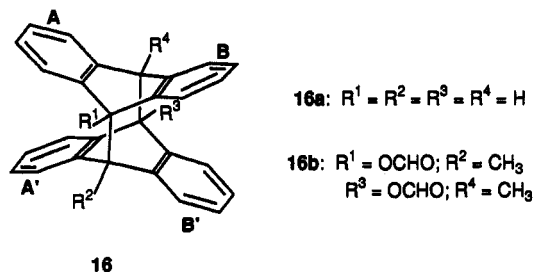


metrical distortion established for 7 obviously is insufficient to induce photochemical valence isomerization.



We deemed it worth extending the present investigation to 9-(2-hydroxy-2-propyl)anthracene (7), since we expected its more distorted molecular structure (*cf.* Table I) to be conducive to photochemical valence isomerization. Irradiation of 7 (about 0.001 M in dichloromethane) was found to result in virtually complete consumption of starting material and concomitant formation of *two* products. They were separated by column chromatography, and their rather high melting points indicated both photoproducts to be dianthracenes rather than Dewar anthracenes. Unexpectedly, both photoproducts were found to be interconvertible in boiling toluene, and their nearly identical ¹H NMR spectra (see Experimental Section) suggested them to be isomers of very similar structure. Model considerations then led to the conclusion that head-to-tail dimerization of 7 by 4π + 4π cycloaddition may give dianthracenes 15a and 15b in which the 2-hydroxy-2-propyl substituents are rotationally blocked,¹⁴ and the structures of both isomers were also established by X-ray diffraction. We are thus dealing with an example of stereoisomerism not previously encountered in dianthracenes, as centrosymmetric 15a differs from C₂-symmetric 15b merely with respect to the mutual orientation of the rotationally blocked bridgehead substituents.¹⁵ In view of the formation of dianthracenes 15, the geo-

Comments on Dianthracene Topology. The molecular geometry of dianthracenes 12–15 in terms of dihedral angles between planes of aromatic rings (see general structure 16) and lengths of photochemically formed bonds as revealed by X-ray diffraction are summarized in Table III. For comparison, the literature data for the parent dianthracene¹⁶ (16a) and the dianthracene 16b¹⁷ derived from 9-(formyloxy)-10-methylanthracene have been included. (The crystal structure of the mixed head-to-tail dimer 13 was found to be centrosymmetric because of statistical disorder, characterized by alternating positional occupation of bridgehead hydrogen and methyl groups.)



We deduce from the structural data that bridgehead substitution increases the dihedral angles between the benzene rings A/B and A'/B' from about 135° in the parent compound 16a to about 139° in dianthracene 12. The "head-to-head dimer" 14, however, in which the two methoxy groups occupy vicinal bridgehead positions,

(14) Rotational blocking about an *sp*³-*sp*³ bond has previously been observed in 1,6-bis(2-cyano-2-propyl)tritycene, which was found to exist in two stereoisomeric forms: Iwamura, H. *J. Chem. Soc., Chem. Commun.* 1973, 232. For a review, see: Oki, M. *Angew. Chem.* 1976, 88, 87–96.

(15) The possibility of rotational isomerism has recently been discussed for diphosphino-substituted dianthracenes, but the formation of diastereomers has not been observed: (a) Heuer, L.; Schomburg, D.; Schmutzler, R. *Chem. Ber.* 1989, 122, 143–146. (b) Wesemann, J.; Jones, P. G.; Schomburg, D.; Heuer, L.; Schmutzler, R. *Chem. Ber.* 1992, 125, 2187–2197.

(16) Choi, C. S.; Marinkas, P. L. *Acta Crystallogr., Sect. B* 1980, 36, 2491–2493.

(17) Becker, H.-D.; Skelton, B. W.; Turner, A. B.; White, A. H. *Aust. J. Chem.* 1988, 41, 1977–1982.

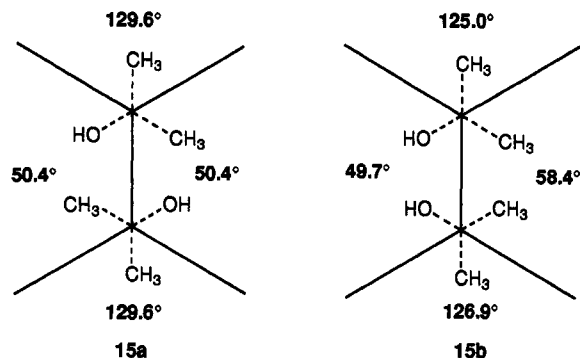


Figure 3. Schematic presentation of rotameric dianthracenes 15a and 15b. For racemic 15b, only one enantiomer is shown.

assumes a rather distorted molecular geometry, as is evidenced by the corresponding dihedral angles A/B and A'/B' of 130.7° and 143.0°, respectively. Also worth noting concerning the 1,2-dimethoxyethane segment in 14 is the length of 1.657(4) Å of the photochemically formed carbon-carbon single bond.

As for rotameric dianthracenes 15a and 15b, the results of the X-ray diffraction analysis can be summarized as follows. Dianthracene 15a, characterized by formal *i*-symmetry, also is crystallographically centrosymmetric; *i.e.*, the asymmetric unit consists of one molecular half. Dianthracene 15b is formally characterized by a 2-fold axis of symmetry, but this was not found to be the case in the crystalline state. The dihedral angles between aromatic rings in dianthracenes 15a and 15b depend on the mutual orientation of the bridgehead-positioned 2-hydroxy-2-propyl groups. In centrosymmetric 15a, in which methyl and hydroxyl groups are alternately phased "between the upper and lower wings" of the dianthracene skeleton, the dihedral angle A/A' (B/B') is 50.4° (see Figure 3). Thus, the steric demand of the hydroxy and methyl groups enlarges the dihedral angle between aromatic rings A/A' (B/B') by about 10°, compared to the substituted dianthracene 12. The increased steric crowding due to the "syn" orientation of two methyl groups in dianthracene 15b leads to structural dissymmetry, borne out by markedly different dihedral angles, *viz.* 49.7° and 58.4° between aromatic rings A/A' and B/B', respectively.

Experimental Section

Crystallographic data for structures 4, 6, 7, 10, and 12–15 have been accepted for publication in *Zeitschrift für Kristallographie*, and atomic coordinates are thus being deposited at Cambridge Crystallographic Data Centre.

Irradiations were carried out at 10–12 °C (unless indicated otherwise) with a 125-W high-pressure mercury lamp (Philips HPK 125 W) in a water-cooled immersion well apparatus (Pyrex), equipped with a liquid-filter sleeve of about 1-cm path length. During the irradiations, a stream of argon was passed through the solution. Flash-column chromatographic separations were performed with a column of 30-mm diameter and column lengths of about 20–30 cm. Melting points were determined on a hot-stage microscope and are uncorrected. ¹H NMR spectra were recorded in CDCl₃ on a Varian XL-400 instrument. Chemical shifts (δ) are given in ppm downfield from Me₄Si as internal standard. The FAB mass spectrum of dianthracene 9 was obtained on a Magnet Sector Instrument VG ZAB HF, data system VG 11-250, using 3-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by Analytische Laboratorien, Box 1315, D-51753 Engelskirchen, Germany.

Synthesis of 9-(2-Hydroxy-2-propyl)anthracene (7). Acetone (20 mL) was added by means of a syringe over a 5-min

period to an ice-cooled stirred suspension of 9-anthryllithium (20 mmol; prepared by addition of 8 mL of a 2.5 M solution *n*-butyllithium to a solution of 5.14 g of 9-bromoanthracene in 200 mL of ether). The reaction mixture was stirred for 2 h at 0 °C and subsequently for 2 h at room temperature. The reaction was then quenched by addition of aqueous ammonium chloride solution, and precipitated anthracene was removed by suction filtration. Flash column chromatography on silica gel/dichloromethane of the residue obtained on vacuum evaporation of solvent gave 1.9 g (40%) of 7 as pale greenish-yellow crystals, mp (after recrystallization from dichloromethane/hexane) 138–140 °C (lit.¹⁸ mp 136 °C). ¹H NMR: 2.08 (s, OH); 2.16 (s, 6); 7.3–7.45 (m, 4); 7.95 ("d", *J* = 8 Hz, 2); 8.32 (s, H-10); 8.77 (d, *J* = 8 Hz, 2).

Photochemical Dimerization of 9-Methoxyanthracene To Give 8 and 9. A solution of 4 (625 mg; 3 mmol) in ether (85 mL) was irradiated through Pyrex at about 5 °C for 1 h. The formation of a colorless precipitate became noticeable within the first 3 min of irradiation. Rotary vacuum evaporation of solvent from the suspension at room temperature gave a white microcrystalline residue. A sample checked by ¹H NMR in CDCl₃ revealed complete consumption of 4, and the formation of 8 and 9 in a ratio of 55:45. There were no other products detectable. The residue was triturated with dichloromethane (40 mL), and suction filtration gave 320 mg of dianthracene 8 as an insoluble residue, mp 225–250 °C dec, depending on the rate of heating (lit.^{8a} mp ~275 °C). Flash chromatography (column length 20 cm) of the filtrate with dichloromethane eluted an additional 25 mg of 8 (together with trace amounts of 4, detectable by its blue fluorescence). The total yield of 8 thus corresponds to 55%. Subsequent elution with ethyl acetate gave dianthracene 9, which migrates with the solvent front and frequently precipitates as needle-shaped crystals directly from the ethyl acetate solution. Vacuum evaporation of most of the solvent at room temperature leaves a suspension, which is diluted with little hexane. Suction filtration gives 9 as a white crystalline solid (240 mg; 38%). Its mp (dec) was found to range from 113 to 120 °C, depending on the rate of heating. In contrast to 8, dianthracene 9 is easily soluble in dichloromethane and can be recrystallized from saturated solutions by addition of either methanol or hexane. Typically, 9 forms needle-shaped colorless, solvated crystals which lose enclosed solvent upon exposure to air at room temperature. Anal. Calcd for C₃₀H₂₄O₂: C, 86.51; H, 5.81. Found: C, 86.35; H, 5.95.

Photochemical Dimerization of 9-Methoxy-10-methylanthracene (6) To Give 12. A solution of 6 (200 mg) in ether (120 mL) was irradiated through Pyrex for 4 h. (After about 1 h, 12 began precipitating from the solution.) Filtration gave 100 mg of colorless crystals of 12, which were recrystallized from boiling dichloromethane, mp 160–163 °C dec (lit.¹³ mp ~185 °C).

Photochemical Addition of 9-Methoxyanthracene to 9-Methoxy-10-methylanthracene. A solution of 9-methoxyanthracene (520 mg; 2.5 mmol) and 9-methoxy-10-methylanthracene (555 mg; 2.5 mmol) in ether (175 mL) was irradiated at 12 °C for 4 h through an aqueous filter solution of sodium nitrite (75 g/100 mL; ~1-cm path length; λ cut-off <400 nm). After about 1 h of irradiation, colorless crystals started precipitating. Vacuum evaporation of solvent at room temperature left a colorless solid residue which was triturated with about 50 mL of dichloromethane. Filtration left a residue of 260 mg of colorless material undissolved, which by subsequent flash-chromatographic workup (SiO₂/CH₂Cl₂) of small portions of about 50 mg each was separated to give dianthracene 12 (about 40 mg; *R_f* = 0.72), mixed head-to-tail dimer 13, mp 140–145 °C dec (210 mg; *R_f* = 0.63), and small amounts (about 10 mg) of 8 (*R_f* = 0.6). (The chromatographic separation of 8, 12, and 13 is very tedious because of their very low solubility in dichloromethane.) Flash chromatography (silica gel/dichloromethane) of the original dichloromethane filtrate eluted a series of fractions (*R_f* 0.7–0.6) consisting of unreacted anthracenes 4 and 6 (190 mg; ether soluble) and dianthracene 13 (140 mg). Subsequent elution with ethyl acetate gave 400 mg of mixed head-to-head dimer 14, mp 130–135 °C dec. Pertinent ¹H NMR data for 12–14 are listed in Table

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II. Elemental analyses were as follows. Dianthracene 13. Anal. Calcd for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09. Found: C, 86.08; H, 6.23. Dianthracene 14. Anal. Calcd for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09. Found: C, 86.36; H, 6.26.

Photochemical Dimerization of 9-(2-Hydroxy-2-propyl)-anthracene To Give 15a and 15b. An argon-purged solution of **7** (50 mg) in dichloromethane (180 mL) was irradiated for 3 h. During the irradiation, a stream of argon was passed through the solution. The solid residue obtained after vacuum evaporation of solvent was washed with a little ether to give 35 mg of a colorless solid. TLC in conjunction with proton 1H NMR analysis revealed the solid to consist of a mixture of the two isomers **15a** ($R_f = 0.39$) and **15b** ($R_f = 0.31$) in a ratio of approximately 6:4. Separation was accomplished by flash chromatography on silica gel/dichloromethane. **15a**. 1H NMR: 1.95 (s, 3); 2.15 (s, OH); 2.36 (s, 3); 5.05 (s, 1 bridgehead H); 6.70–7.27 (m, 7), 8.02 (d, $J = 8$

Hz; 1). Anal. Calcd for $C_{34}H_{32}O_2$: C, 86.41; H, 6.82. Found: 86.39; H, 6.94. **15b**. 1H NMR: 1.95 (s, 3); 2.22 (1, OH); 2.38 (3, s); 5.05 (s, 1 bridgehead H); 6.70–7.32 (m, 7); 7.89 ("d", $J = 8$ Hz, 1). Anal. Calcd for $C_{34}H_{32}O_2$: C, 86.41; H, 6.82. Found: 86.28; H, 6.92. Upon heating, crystalline **15a** and **15b** turn opaque around 220 °C and begin melting around 265 °C. In both cases, a clear melt is formed around 300 °C. For X-ray crystallographic purposes, **15a** was recrystallized from dichloromethane/toluene and **15b** was recrystallized from dichloromethane/hexane.

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