ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 97 (1996) 25–32

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photochemical dimerization modes of 1-acetylanthracene and methyl 1-anthracenecarboxylate

Hans-Dieter Becker *, Hans-Christian Becker, Vratislav Langer

Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden

Received 12 October 1995; accepted 9 January 1996

Abstract

Irradiation of 1-acetylanthracene in dichloromethane at light wavelengths above 400 nm gives five dimers in a ratio of about 2:1:1:1:1. In addition to the four typical modes of dimerization leading to symmetrical dianthracenes of *anti*-head-to-tail, *syn*-head-to-tail, *anti*-head-to-head and *syn*-head-to-head structures, 1-acetylanthracene undergoes dissymmetrical head-to-tail $4\pi+4\pi$ cyclodimerization involving the 1,4 and 9′,10′ positions. Selective photoexcitation of 1-acetylanthracene in the presence of anthracene gives the mixed 9,10–9′,10′ and 1,4–9′,10′ $4\pi+4\pi$ cycloadducts in a ratio of about 3:1. The photochemical dimerization of methyl 1-anthracenecarboxylate proceeds in the same fashion as that of 1-acetylanthracene.

Keywords: 1-Acetylanthracene; Dianthracenes; Dissymmetrical dimerization; Methyl 1-anthracenecarboxylate

1. Introduction

The photochemistry of laterally substituted anthracenes has received limited attention in comparison with the large number of investigations dealing with the photochemical dimerization of 9-anthryl compounds (for a comprehensive review on the dimerization of anthracene derivatives, see Ref. [1]). This disparity is presumably due to the experimental difficulties associated with the separation and structural characterization of the various regioisomeric dianthracenes which can be formed from anthracene derivatives lacking symmetry about the molecular 9,10 axis (examples of laterally substituted anthracenes undergoing dimerization in solution are given in Ref. [2] and examples of intramolecular dianthracene formation involving tethered 1- and 2-anthracenecarboxylates are given in Ref. [3]; see also Ref. [4]). Although the irradiation of *meso*-substituted anthracenes may lead to only two bridgehead-substituted dianthracenes by head-to-tail (HT) and head-to-head (HH) dimerization [1,5] (HH dimers of *meso*-substituted anthracenes are rarely isolated since they are thermally much more labile than the corresponding HT dimers; typically, HH dimers regenerate starting material during work-up at slightly elevated temperature), a laterally substituted anthracene, as shown in Scheme 1, can give one centrosymmetrical (i) *anti*-HT dimer (**1**), one *syn*-HT dimer (**2**) with a twofold axis (C_2) of symmetry, one C_2-symmetrical *anti*-HH dimer (**3**) and one *syn*-HH dimer (**4**) with mirror plane symmetry. Furthermore, the C_2-symmetrical dianthracenes **2** and **3** give rise to racemates with their respective mirror image stereoisomers.

In principle, the photochemical formation of isomeric dianthracenes of structures **1**–**4** can be established by ^{1}H NMR spectroscopy of product mixtures, as the bridgehead protons of the HT dimers should give rise to two doublets each, while the bridgehead protons of each HH dimer are recognizable by two singlets. Depending on the nature of the substituents, a distinction between *syn*- and *anti*-isomers may be based on appropriate NMR experiments involving shift reagents. The photochemical dimerization of 1-anthracenecarboxylic acid was analysed in this fashion, and found to give dianthracenes **1**–**4** (R=COOH) in a ratio of 12:7:5:1, corresponding to an HT:HH dimer ratio of about 3.2:1. [2e]. It is worth noting, however, that details concerning the isolation and spectroscopic characterization of laterally substituted dianthracenes have rarely been published, nor has X-ray diffraction been applied in establishing their structure.

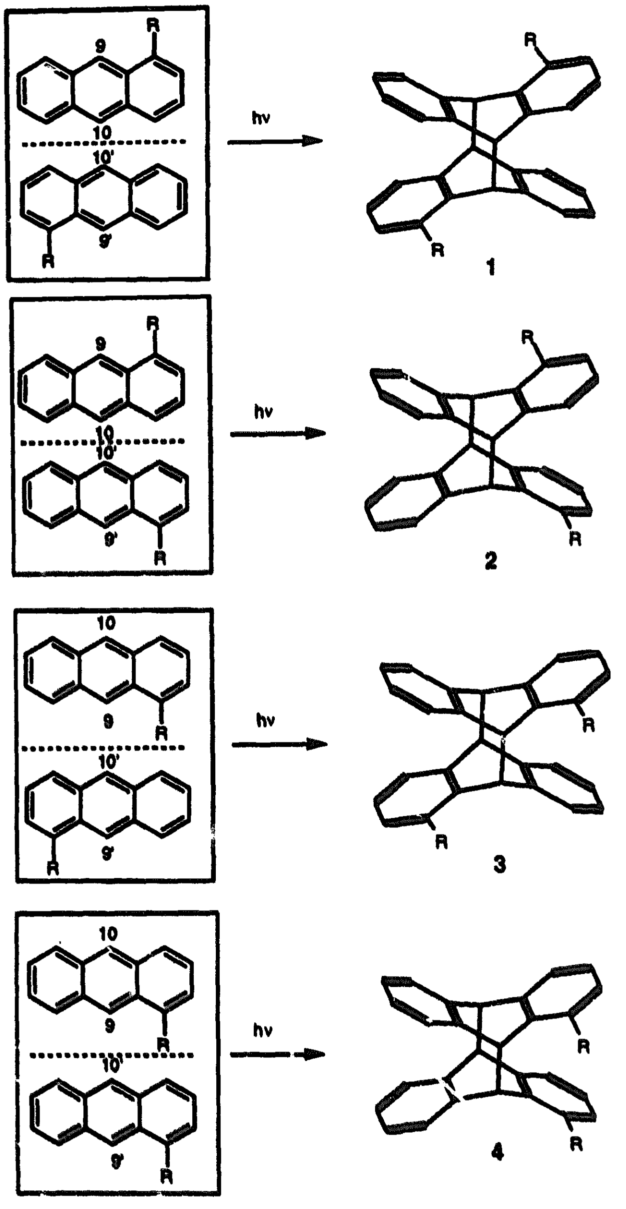
In this paper, we deal with the photochemical dimerization of 1-acetylanthracene (**5**) and methyl 1-anthracenecarboxylate (**6**) in dichloromethane.

---

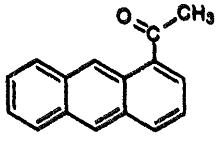
* Corresponding author.

1010-6030/96/$15.00 © 1996 Elsevier Science S.A. All rights reserved

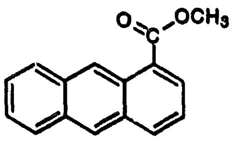
PII S1010-6030(96)04318-3



Scheme 1.



5



6

Both compounds have previously attracted attention because their photophysical properties, in terms of singlet lifetimes and intersystem crossing quantum yields, are strongly dependent on the solvent polarity [6,7]. The formation of regioisomeric dianthracenes from 5 and 6 has not been described before, but 1-acetylanthracene in ethanol solution has been reported to disappear on irradiation ($\lambda = 366$ nm) with about the same quantum yield as 9-bromoanthracene ($\Phi = 0.002$) [8]. Moreover, various anthracenecarboxylates tethered to or included in γ-cyclodextrin undergo photochemical $4\pi + 4\pi$ cyclodimerizations [2c,2e,3].

2. Results and discussion

Dichloromethane was chosen as reaction solvent because it avoided the undesirable precipitation of dimerization products during the course of irradiation. The UV absorption of 5 and 6 in dichloromethane solution extends into the visible region to near 450 nm (see Fig. 1 and Section 4), and irradiations were carried out with light wavelengths above 400 nm. We deemed it appropriate to use a corresponding cut-off filter in order to preclude inadvertent photoexcitation and consequential dissociation of the conceivable photodimers 1–4. The quantum yields of photolytic cycloreversion of laterally substituted dianthracenes to regenerate the starting material are close to unity [3a].

2.1. Dimerization of 1-acetylanthracene (5)

The irradiation of 5 in dichloromethane solution (0.02 M) was terminated at about 90% conversion of the starting material, and analysis of the reaction mixture by ^{1}H-NMR spectroscopy revealed the formation of dimerization products 7, 8, 9, 10 and 11 (see Scheme 2) in a ratio of 32:17:17:17:17.

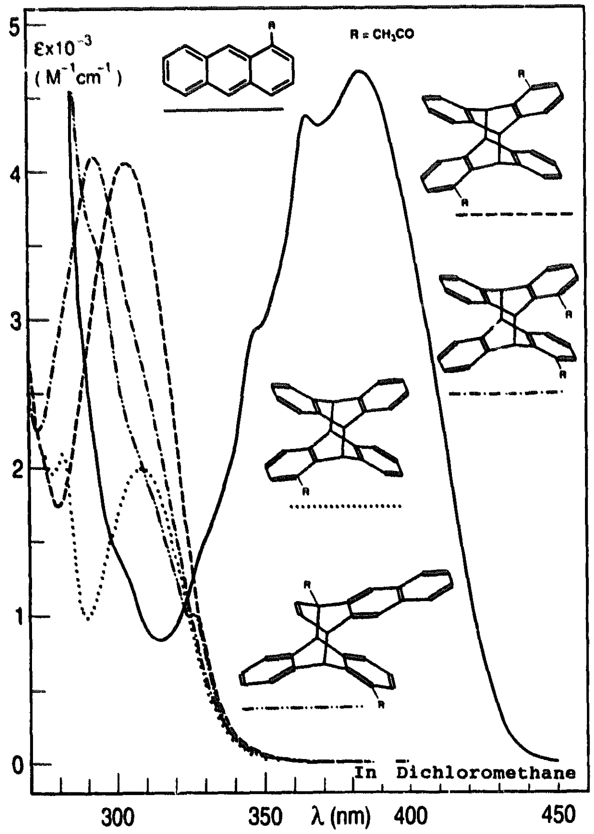
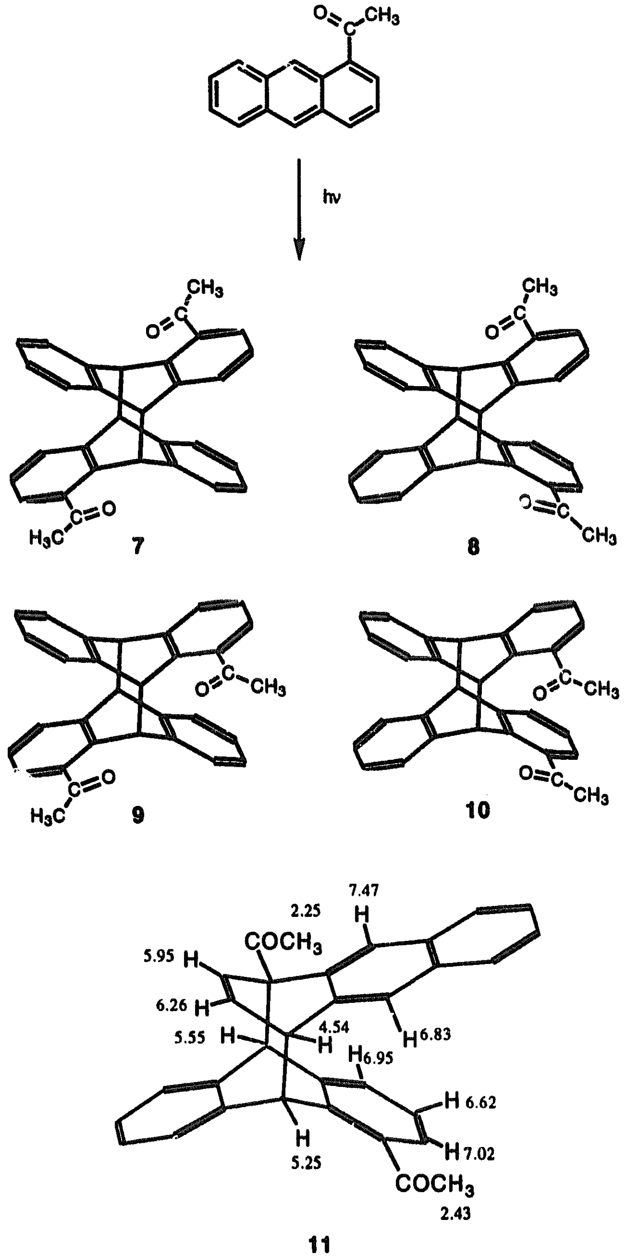
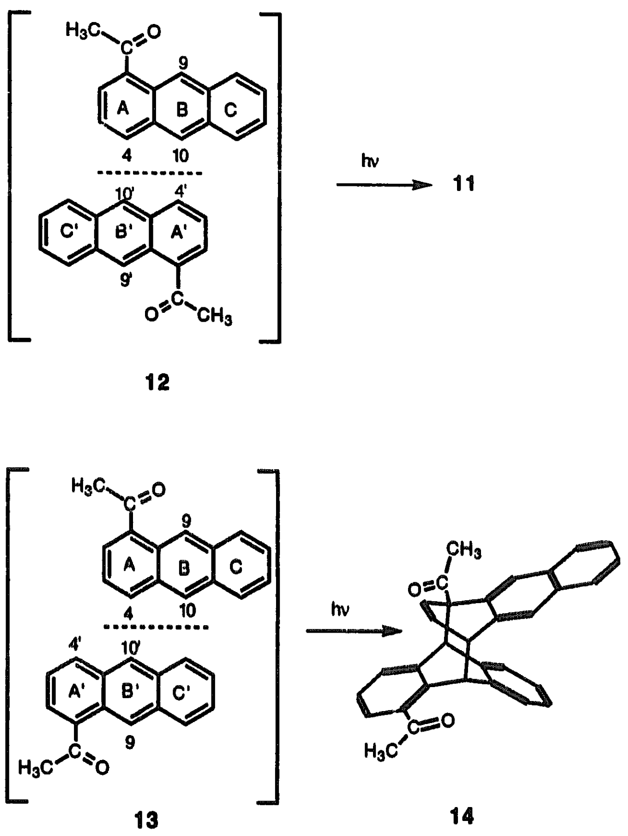


Fig. 1. Absorption spectra of 1-acetylanthracene (5), its dimerization products 7, 10 and 11 and its addition product 16 to anthracene in dichloromethane.



Scheme 2.

The separation of HT dimers (**7**, **8**, **11**) from HH dimers (**9**, **10**) by flash column chromatography on silica gel was possible because of their markedly different retention times [5]. Isolation of the individual *syn*- and *anti*-regioisomeric dianthracenes **7–10** and the dissymmetrical HT dimer **11** was then accomplished by column chromatography in conjunction with fractional crystallization. It was thus established that the photochemical dimerization of 1-acetylanthracene afforded an HT:HH dimer ratio of about 2:1. The proposed structures of the photoproducts were supported by ^{1}H-NMR spectral data (see Section 4), and were unambiguously established by X-ray diffraction analyses of the *anti*-HT dimer **7**, the racemic *anti*-HH dimer **9** and the racemic dissymmetrical dimer **11** (see Section 2.5).

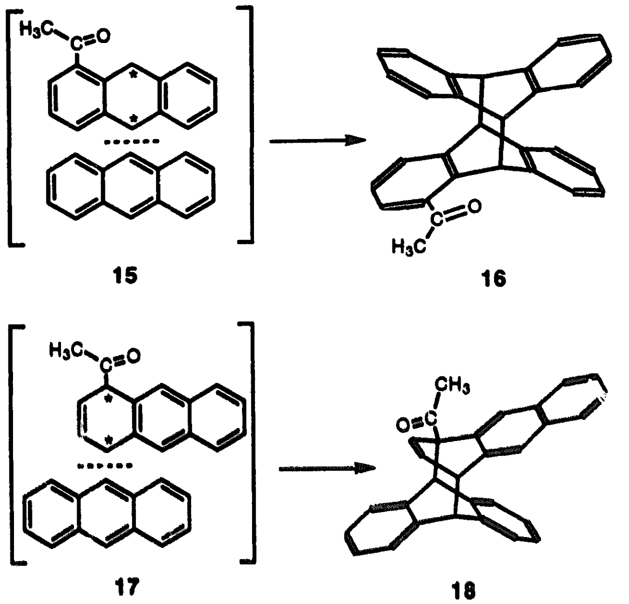


Scheme 3.

The photochemical dimerization of 1-acetylanthracene differs significantly from that of the structurally similar 1-anthracenecarboxylic acid [2e] by the formation of a dissymmetrical dimer. Only one other laterally substituted anthracene derivative, namely 2,6-didecyloxyanthracene, has previously been observed to undergo an analogous $4\pi+4\pi$ cyclodimerization involving the 1,4 and 9′,10′ positions, although ^{1}H-NMR analysis of the isolated product indicated, in that case, that the dissymmetrical dimer was actually a 1:1 mixture of *syn*- and *anti*-regioisomers [2d]. By contrast, we have found no evidence for the formation of the conceivable dissymmetrical HT dimer **14**, which may be considered to be the "*syn*"-counterpart of the "*anti*"-regioisomer **11**. We believe that the selective formation of **11** can be explained by the geometry of the precursor reaction complex **12**, which is characterized by a centre of symmetry (see Scheme 3). Thus both the $4\pi+4\pi$ cycloaddition involving rings A + B′ and the cycloaddition involving rings A′ + B will give the dissymmetrical dimer **11**. By contrast, formation of the "*syn*"-regioisomer **14** implies the involvement of reaction complex **13**, in which only one mode of cycloaddition, namely that of rings A + B′, would give the dissymmetrical product.

2.2. Photochemical addition of 1-acetylanthracene to anthracene

Selective photoexcitation of 1-acetylanthracene in the presence of excess anthracene (molar ratio, 1:2) and subse-



Scheme 4.

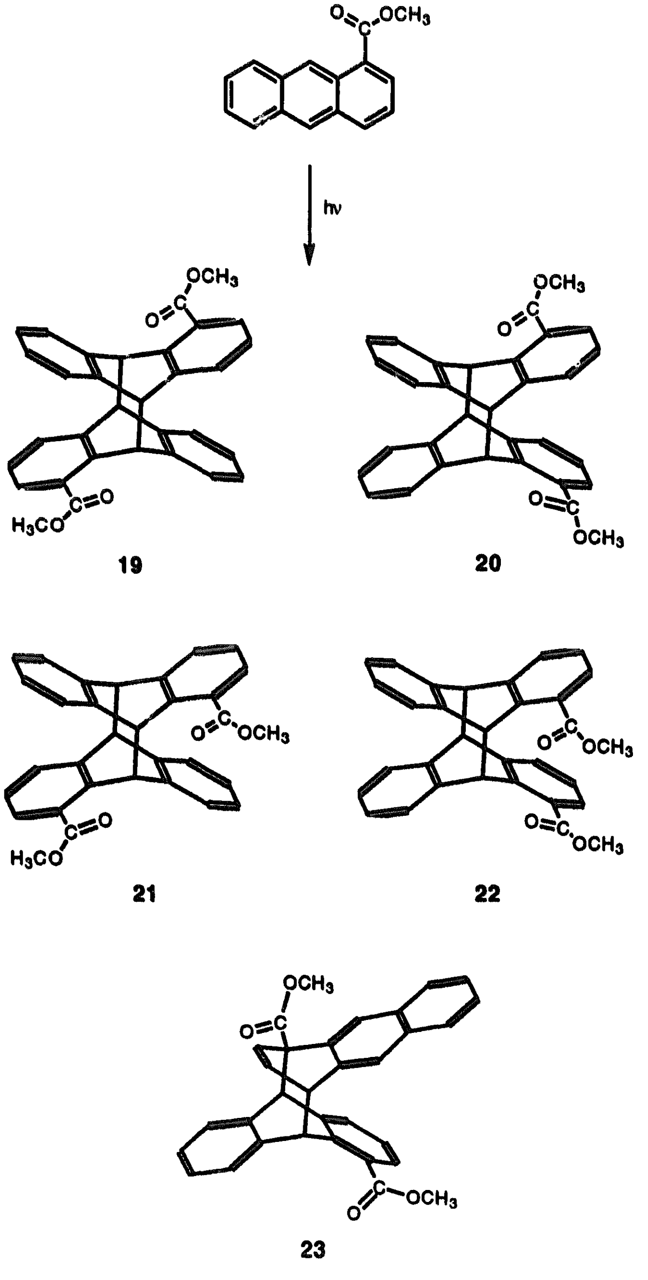
quent ^{1}H-NMR analysis of the product mixture revealed that 70% of the consumed 1-acetylanthracene had undergone addition to ground state anthracene. Two products, namely the acetyl-substituted dianthracene **16** and the 1,4–9′,10′ cyclodimer of structure **18** were found to be formed in a ratio of 3:1 by mixed addition. The formation of addition products **16** and **18** is of particular interest, because it suggests that both the resonance structure shown in reaction complex **15** and that shown in reaction complex **17** (see Scheme 4) contribute to the excited state reactivity of 1-acetylanthracene.

2.3. *UV spectra of acetyl-substituted dianthracenes*

The UV absorption spectra of dianthracenes **7–10** are characterized by the onset of absorption around 340 nm and by a maximum around 300 nm with an unexpectedly high ε value of about 4000 M^{-1} cm^{-1}. The absorption maximum is most probably attributable to the n–π* transition of the aryl carbonyl chromophore which, however, is strongly enhanced due to the β-aryl substitution inherent in the dianthracene structure. In agreement with this interpretation, the corresponding absorption maxima attributable to the acetophenone chromophores in the dissymmetrical dimer **11** (λ_{max} = 327 nm) and the 1-acetylanthracene–anthracene adduct **16** (λ_{max} = 309 nm) are characterized by decreased ε values of 1000 and 2000 M^{-1} cm^{-1} respectively (see Fig. 1).

2.4. *Dimerization of methyl 1-anthracenecarboxylate (6)*

Irradiation of **6** in dichloromethane (1.3 M) under the same conditions as described above for 1-acetylanthracene was found to give, in a ratio of 34:29:19:10:8, the centrosymmetrical HT dimer **19**, the C_2-symmetrical HT dimer **20**, the C_2-symmetrical HH dimer **21**, the mirror symmetrical HH dimer **22** and the dissymmetrical HT dimer **23** (see Scheme 5). Their separation was accomplished by column chromatography on silica gel, and structural assignments were based on ^{1}H-NMR spectral data in conjunction with X-ray diffraction analyses of HT dimer **19** and HH dimer **21**. The formation of **23** is of particular interest in view of the fact that dissymmetrical dimerizations of 1-anthracenecarboxylates have not been observed before. It should be noted, however, that the earlier reported photochemical dimerizations of laterally substituted anthracene derivatives typically involved light wavelengths above 300 nm [2e], i.e. conditions under which the photolytic cycloreversion of dimers occurs. Indeed, the UV spectra of dimers **19–23** (see Section 4) are characterized by the onset of absorption around 340 nm, and we have ascer-



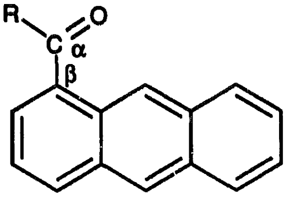
Scheme 5.

tained spectroscopically that photoexcitation at 313 nm results in the quantitative regeneration of the starting material. It is possible, therefore, that the formation of dissymmetrical dimers has previously escaped detection, and that the earlier observed composition of the product mixtures actually represented the composition of a photostationary state.

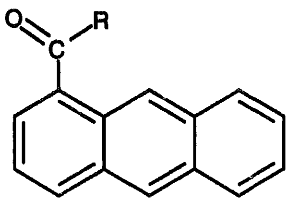
2.5. *Structural features of 1-acetylanthracene, methyl-1-anthracenecarboxylate and their photodimers*

Crystal structure analyses were carried out on the anthracene derivatives **5** [9] and **6**, and on the dimerization products **7**, **9**, **11**, **19** and **21**. Atomic coordinates and a detailed discussion of the structures will be given elsewhere in an appropriate crystallographic context. Some selected structural features are presented here, since the molecular geometry of 1-carbonylanthracenes is of photophysical interest, and the topology of laterally substituted dianthracenes has not been investigated previously by X-ray diffraction.

The molecular geometries of **5** and **6** in their crystal state can be summarized as follows. In both molecules, the carbonyl group is conformationally oriented with respect to the anthracene long axis as shown in structure **24**, rather than in structure **25**.



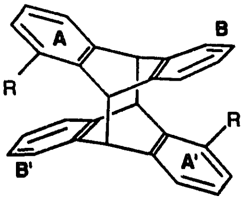
24



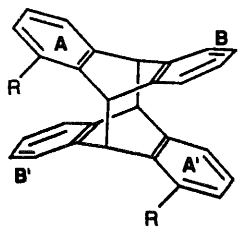
25

Both **5** and **6** are geometrically distorted, as is evident from the enlarged bond angles α and β (121° and 122° for 1-acetylanthracene, and 126° and 121° for methyl 1-anthracenecarboxylate). More importantly, however, **5** and **6** are characterized by non-coplanarity of the carbonyl group and the anthracene moiety, as borne out by the dihedral angles of 29° and 18° respectively. These findings support earlier suggestions, based on fluorescence measurements, that the molecular geometry of methyl 1-anthracenecarboxylate in its lowest excited singlet state differs from that of the electronic ground state by an enhanced coplanarity of the carbonyl and anthracene π systems [6].

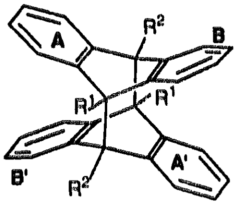
With regard to the laterally substituted dianthracenes, their molecular geometry in terms of the lengths of photochemically formed bonds and dihedral angles between aromatic rings, as shown in structures **26** and **27**, is summarized in Table 1. Thus, compared with the parent dianthracene **28a**, and dianthracenes such as **28b** and **28c** derived from *meso*-substituted anthracene derivatives, the photochemically formed bonds in dianthracenes of structures **26** and **27** are less elongated. The most pronounced topological difference between dianthracenes **28** and the laterally substituted dianthracenes is apparent in the increased dihedral angles between the aromatic rings A, B and A′, B′ [5,10–12].



26 (7; 19)



27 (9; 21)



28

28a: $R^1 = R^2 = H$

28b: $R^1 = H$; $R^2 =$ phenyl

28c: $R^1 =$ methyl; $R^2 =$ methoxy

The conformation of the carbonyl groups in dianthracenes investigated by X-ray diffraction was found to be as indicated in Schemes 2 and 5. In all cases, the carbonyl group deviates from coplanarity with the aromatic ring, the dihedral angles ranging from 22° to 36°.

3. Conclusions

It has been shown that the irradiation of both 1-acetylanthracene and methyl 1-anthracenecarboxylate leads to four regioisomeric dianthracenes and one dissymmetrical dimer. Head-to-tail dimerization is favoured over head-to-head dimerization by factors of 2 and 2.5 respectively. The observed regiochemistry of dissymmetrical dimerization may be rationalized by the involvement of a centrosymmetrical reaction complex.

4. Experimental section

Irradiations were carried out at about 10 °C 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. An aqueous solution of sodium nitrite (75 g per 100 ml) was used to block wavelengths below 400 nm. During irradiation, a stream of argon was passed through the solution. Flash column chromatographic separations were performed on silica gel/dichloromethane with a column of 3 cm in diameter and 30 cm in length. Conventional chromatography involved

Table 1
Molecular topology of dianthracenes. Lengths of photochemically formed bonds and dihedral angles between aromatic rings

Compound	Bond length (Å) [a]	Dihedral angles (°)			
		A/B′	B/A′	A/B	A′/B′
7	1.608(4)	55.4	55.4	124.6	124.6
9	1.601(6) 1.603(6)	57.6	57.2	122.8	122.5
19	1.603(5) 1.610(6)	52.2 51.1	52.2 51.1	127.8 128.9	127.8 128.9
21	1.58(2) 1.60(2)	46.8	48.7	136.0	128.0
28a	1.624(3)	44.6	44.6	135.4	135.4 [b]
28b	1.619(5)	45.9	45.9	134.1	134.1 [c]
28c	1.670(4)	40.6	40.6	139.4	139.4 [d]

[a] Estimated standard deviations in parentheses.
[b] From Ref. [10].
[c] From Ref. [11].
[d] From Refs. [5] and [12].

a column of 2.5 cm × 120 cm. Melting points were determined on a hot-stage microscope and are uncorrected. ^{1}H-NMR spectra were recorded in $CDCl_3$ on a Varian XL-400 instrument. Chemical shifts (δ) are given in parts per million downfield from Me_4Si as internal standard. Electronic absorption spectra were taken in dichloromethane solution on a Kontron UVICON 810 spectrometer. Elemental analyses were carried out by Analytische Laboratorien, D-51789 Lindlar, Germany.

4.1. *1-Acetylanthracene (5) and methyl 1-anthracenecarboxylate (6)*

These compounds were prepared according to the literature [13,14]. Pertinent spectroscopic data are as follows. Compound **5**: UV (dichloromethane), onset of absorption at 450 nm; maxima (ϵ (M^{-1} cm^{-1})) at 384 nm (4700) and 365 nm (4400); minima at 370 nm (4300) and 315 nm (850); ^{1}H-NMR, 2.82 (s, 3), 7.4–8.2 (m, 7), 8.45 (s, 1), 9.48 (s, 1). Compound **6**: UV (dichloromethane), onset of absorption at 440 nm; maxima (ϵ (M^{-1} cm^{-1})) at 379 nm (5450) and 364 nm (5150); minima at 366 nm (5050) and 307 nm (450); ^{1}H-NMR, 4.06 (s, 3), 7.4–8.3 (m, 7), 8.47 (s, 1), 9.58 (s, 1).

4.2. *Photochemical dimerization of 1-acetylanthracene (5) to give 7–11*

In a typical experiment, a solution of **5** (330 mg; 1.5 mmol) in dichloromethane (75 ml) was irradiated for 8 h. ^{1}H-NMR analysis of the reaction mixture indicated about 90% consumption of the starting material, and the formation of dianthracenes **7**, **8**, **9**, **10** and **11** in an approximate percentage ratio of 32:17:17:17:17. Vacuum evaporation of the solvent from the reaction mixture gave a solid pale yellow residue which was suspended in dichloromethane (5 ml). The colourless undissolved substance (approximately 80 mg) was removed by suction filtration and found to be (^{1}H-NMR) virtually pure centrosymmetrical **7**. For the isolation of the photodimers **8–11**, the combined work-up of three identical irradiation experiments was found to be most convenient. The filtrate obtained after removal of the centrosymmetrical dimer **7** was subjected to flash chromatography on silica gel, with dichloromethane as eluent, removing first the dissymmetrical dimer **11** together with residual starting material (TLC $R_f = 0.49$), followed by a mixture of the HT dimers **7** and **8** (TLC $R_f = 0.41$) and both HH dimers **9** and **10** (TLC $R_f = 0.12$).

The two HT dimers **7** and **8** were found to be inseparable by column chromatography. However, suspending the mixture of **7** and **8** obtained by flash chromatography in a little acetone at room temperature preferentially dissolved dimer **8**. Filtration gave a solution containing the C_2- and *i*-symmetrical dimers in a ratio of 8:2. The mixture of HT dimers was then recrystallized from dichloromethane solution by the addition of methanol to give the C_2-isomer **8** contaminated by 15% of the *i*-isomer **7**. As for the mixture of HH dimers, the separation of C_2-symmetrical **9** (TLC $R_f = 0.60$) and mirror-symmetrical **10** (TLC $R_f = 0.53$) was accomplished by conventional column chromatography with dichloromethane on neutral alumina. Dimers **7–11** are characterized by the following analytical and spectroscopic data.

4.2.1. *Centrosymmetrical anti-HT dimer 7*

Colourless small needle-shaped crystals (melting point (m.p.), 293 °C) were obtained by recrystallization from boiling toluene. (The single crystal analysed by X-ray diffraction was obtained from chlorobenzene solution, and contained one solvent molecule as solvate.) ^{1}H-NMR: 2.54 (s, 3), 4.84 (d, $J = 11$ Hz, 1), 5.27 (d, $J = 11$ Hz, 1), 6.7–7.26 (m, 7). UV, nm (ϵ): λ_{max} 304 (4050), λ_{min} 280 (1750); absorption onset, 360 nm. Analysis: calculated for $C_{32}H_{24}O_2$ (440.55): C, 87.25; H, 5.49; found: C, 87.07; H, 5.48.

*4.2.2. C_2-symmetrical syn-HT dimer **8***

The sample contaminated by about 15% of **7** precipitated from dichoromethane–methanol solution as translucent square plate-shaped crystals, which decomposed at 260 °C. ^{1}H-NMR: 2.52 (s, 3), 4.85 (d, J = 11 Hz, 1), 5.21 (d, J = 11 Hz, 1), 6.78–7.26 (m, 7). UV, nm (ϵ): λ_{max} 299 (4000), λ_{min} 276 (3100); absorption onset, 360 nm. Analysis: calculated for $C_{32}H_{24}O_2$ (440.55): C, 87.25; H, 5.49; found: C, 87.21; H, 5.59.

*4.2.3. C_2-symmetrical anti-HH dimer **9***

Colourless crystals were obtained from dichloromethane solution by the addition of ethanol (m.p., approximately 263 °C (dec)). (For X-ray diffraction, good quality needle-shaped crystals of **9** containing solvent molecules in a 1:1 ratio were obtained by recrystallization from boiling chlorobenzene.) ^{1}H-NMR: 2.54 (s, 3), 4.59 (s, 1), 5.39 (s, 1), 6.70–7.22 (m, 7). UV, nm (ϵ): λ_{max} 305 (4000), λ_{min} 280 (1700); absorption onset, 360 nm. Analysis: calculated for $C_{32}H_{24}O_2$ (440.55): C, 87.25; H, 5.49; found: C, 87.08; H, 5.49.

*4.2.4. Mirror-symmetrical syn-HH dimer **10***

Colourless fluffy needle-shaped crystals were obtained from dichloromethane–ethanol (m.p., approximately 280 °C (dec)). ^{1}H-NMR: 2.48 (s, 3), 4.60 (s, 1), 5.53 (s, 1), 6.80–7.16 (m, 7). UV, nm (ϵ): λ_{max} 294 (4100), λ_{min} 274 (2250); absorption onset, 360 nm. Analysis: calculated for $C_{32}H_{24}O_2$ (440.55): C, 87.25; H, 5.49; found: C, 87.23; H, 5.39.

*4.2.5. Dissymmetrical HT dimer **11***

Colourless rod-shaped crystals (m.p. (dec), 165 °C) were obtained from dichloromethane solution by the addition of methanol or ethanol. (The sample should be held briefly at about 70 °C in order to remove dichloromethane as solvate.) ^{1}H- NMR: 2.25 (s, 3), 2.43 (s, 3), 4.54 (ddd, J = 11, 7, 1 Hz, 1), 5.25 (d, J = 11 Hz, 1), 5.95 (dd, J = 8, 1 Hz, 1), 6.26 (dd, J = 8, 7 Hz, 1); aromatic protons (J typically about 8 Hz): 6.62 (t, 1), 6.83 (s, 1), 6.95 ("d", 1), 7.02 ("d", 1), 7.1–7.32 (m, 6), 7.47 (s, 1), 7.52 (m, 2); the ^{1}H-NMR chemical shift assignments of structure **11** are based on the results of decoupling experiments. UV, nm (ϵ): λ_{max} 327 (1000), λ_{min} 325 (980), sh 295 (3500); absorption onset, 365 nm. Analysis: calculated for $C_{32}H_{24}O_2$ (440.55): C, 87.25; H, 5.49; found: C, 87.30; H, 5.55.

*4.3. Irradiation of 1-acetylanthracene in the presence of anthracene to give 4π+4π cycloadducts **16** and **18***

A solution of 1-acetylanthracene (330 mg; 1.5 mmol) and anthracene (535 mg; 3 mmol) in dichloromethane (80 ml) was irradiated for 4.5 h. Vacuum evaporation of the solvent gave a virtually colourless solid residue. Combined work-up of two identical experiments involved flash chromatographic removal of excess anthracene (TLC R_f = 0.78), followed by column chromatographic separation of the mixed dissymmetrical adduct **18** (212 mg; TLC R_f = 0.65), mixed 4+4 adduct **16** (629 mg; TLC R_f = 0.56) and dissymmetrical dimer **11** (15 mg; TLC R_f = 0.49). The spectroscopic and analytical data of the mixed adducts are as follows.

*4.3.1. 9,9′,10,10′-Adduct **16***

Colourless crystals were obtained from dichloromethane by the addition of ethanol (m.p. (dec), around 235–240 °C). ^{1}H-NMR: 2.54 (s, 3), 4.54, 4.61 (A–B pattern, J = 11 Hz, 2), 4.79 (d, J = 11 Hz, 1), 5.29 (d, J = 11 Hz, 1); the 15 aromatic protons give rise to signals between 6.7 and 7.25 ppm. UV, nm (ϵ): λ_{max} 309 (2000), λ_{min} 290 (1000), λ_{max} 282 (2100), λ_{min} 278 (2000); absorption onset, 360 nm. Analysis: calculated for $C_{30}H_{22}O$ (398.51): C, 90.42; H, 5.56; found: C, 90.20; H, 5.66.

*4.3.2. 1,4,9′,10′-Adduct **18***

Colourless to pale yellow crystals were obtained from dichloromethane–methanol. Partial decomposition occurred during column chromatographic isolation. On heating, **18** dissociates into its precursors around 135 °C, forming a clear yellow melt around 175 °C. ^{1}H-NMR: 2.56 (s, 3), 4.32 (dd, J = 11, 7 Hz, 1), 4.47 (d, J = 11 Hz, 1), 5.49 (s, 1), 5.97 (d, J = 8 Hz, 1), 6.24 ("t", J = 8 Hz, 1), 6.87 (s, 1), 7.28 (s, 1); the remaining 10 aromatic protons give rise to multiplets between 6.5 and 7.6 ppm. Analysis: calculated for $C_{30}H_{22}O$ (398.51): C, 90.42; H, 5.56; found: C, 90.31; H, 5.66.

*4.4. Photochemical dimerization of methyl 1-anthracenecarboxylate (**6**) to give **19–23***

A solution of **6** (236 mg; 1 mmol) in dichloromethane (75 ml) was irradiated for 7.5 h. ^{1}H-NMR analysis of the reaction mixture indicated 95% consumption of the starting material, and the formation of dimers **19**, **20**, **21**, **22** and **23** in a ratio of 34:29:19:10:8. Work-up of three identical irradiation experiments gave a nearly colourless solid residue. It was suspended in dichloromethane (10 ml), followed by suction filtration, to give 265 mg (37%) virtually pure centrosymmetrical HT dimer **19** as a colourless crystalline residue. From the filtrate, residual starting material **6** (TLC R_f = 0.58), dissymmetrical dimer **23** (TLC R_f = 0.46), C_2-symmetrical HT dimer **20** (TLC R_f = 0.43), mirror-symmetrical HH dimer **22** (TLC R_f = 0.25) and C_2-symmetrical HH dimer **21** (TLC R_f = 0.21) were isolated by flash chromatography. The overlapping fractions of HT and HH dimers were then separated by conventional column chromatography on silica gel/dichloromethane. (It is essential to separate the centrosymmetrical dimer **19** as described above since its R_f value is the same as that of the dissymmetrical dimer **23**.) The dimerization products of methyl 1-anthracenecarboxylate are characterized by the following analytical and spectroscopic data.

4.4.1. Centrosymmetrical anti-HT dimer 19

Colourless crystals (m.p., 298 °C (dec)) were recrystallized from boiling dichloromethane. (The single crystal of **19** analysed by X-ray diffraction was obtained from boiling chlorobenzene and was found to be a 1:1 solvate.) ^{1}H-NMR: 3.95 (s, 6), 4.82 (d, J = 11.2 Hz, 1), 5.52 (d, J = 11.2 Hz, 1), 6.76–7.40 (14 arom H). UV, nm (ϵ): λ_{max} 295 (4700), λ_{min} 271; absorption onset, around 340 nm. Analysis: calculated for $C_{32}H_{24}O_4$ (472.55): C, 81.34; H, 5.12; found: C, 81.18; H, 5.02.

4.4.2. C_2-symmetrical syn-HT dimer 20

Colourless needle-shaped crystals (m.p., 235–240 °C) were obtained from dichloromethane–ethanol solution. ^{1}H-NMR: 3.94 (s, 6), 4.83 (d, J = 11.2 Hz, 1), 4.48 (d, J = 11.2 Hz, 1), 6.78–7.38 (14 arom H). UV, nm (ϵ): λ_{max} 288 (4800), sh 310 (2500), λ_{min} 269; absorption onset, around 340 nm. Analysis: calculated for $C_{32}H_{24}O_4$ (472.55): C, 81.34; H, 5.12; found: C, 81.15; H, 5.19.

4.4.3. C_2-symmetrical anti-HH dimer 21

Colourless needle-shaped crystals (m.p., 240–245 °C) were obtained from dichloromethane–ethanol solution. ^{1}H-NMR: 3.98 (s, 6), 4.60 (s, 2), 5.67 (s, 2), 6.74–7.40 (14 arom H). UV, nm (ϵ): λ_{max} 296 (4400), λ_{min} 270; absorption onset, around 340 nm. Analysis: calculated for $C_{32}H_{24}O_4$ (472.55): C, 81.34; H, 5.12; found: C, 81.55; H, 5.28.

4.4.4. Mirror-symmetrical syn-HH dimer 22

Colourless square plate-shaped crystals (m.p., 240–245 °C) were obtained from dichloromethane–ethanol solution. ^{1}H-NMR: 3.93 (s, 6), 4.60 (s, 2), 5.87 (s, 2), 6.82–7.36 (14 arom H). UV, nm (ϵ): λ_{max} 286 (4800), λ_{min} 268; absorption onset, around 340 nm. Analysis: calculated for $C_{32}H_{24}O_4$ (472.55): C, 81.34; H, 5.12; found: C, 81.37; H, 5.11.

4.4.5. Dissymmetrical HT dimer 23

Colourless square crystals (m.p., about 170 °C (dec)) were obtained from dichloromethane–ethanol solution. ^{1}H-NMR ($CDCl_3$): 3.91 (s, 3), 3.96 (s, 3), 4.47 ("dt", J = 10.8, 4 Hz, 1), 5.39 (s, 1), 5.48 (d, J = 10.8 Hz, 1), 6.14 ("s", 1), 6.15 ("s", 1), 6.64 (t, J = 8 Hz, 1), 7.00 (s, 1), 7.15 (m, 4), 7.26 (m, 4), 7.41 (s, 1), 7.54 (br m, 2). ^{1}H-NMR (CD_3COCD_3): 3.93 (s, 3), 3.98 (s, 3), 5.41 (s, 1), 4.49 (ddd, J = 10.8, 6.4, 1.6 Hz, 1), 5.53 (d, J = 10.8 Hz, 1), 6.09–6.17 (m, from which coupling constants of 8.8, 6.8 and 1.6 Hz were deduced, 2), 6.68 (t, J = 8 Hz, 1), 7.1–7.35 (m, 10), 7.44 (s, 1), 7.55–7.65 (m, 2). Essential ^{13}C-NMR signals: 175.6, 167.9, 61.96, 56.37, 53.29, 52.09, 49.41, 47.62; aromatic and olefinic C, 146.1–122.7. UV, nm (ϵ): λ_{max} 328 (500), λ_{min} 324 (400), sh 312 (1480), sh 294 (4200); absorption onset, around 340 nm. Analysis: calculated for $C_{32}H_{24}O_4$ (472.55): C, 81.34; H, 5.12; found: C, 81.20; H, 5.04.

References

[1] H. Bouas-Laurent and J.-P. Desvergne, Cycloaddition reactions involving 4n electrons: (4+4) cycloaddition reactions between unsaturated conjugated systems, in H. Dürr and H. Bouas-Laurent (eds.), *Photochromism; Molecules and Systems*, Elsevier, Amsterdam, 1990, Chapter 14, pp. 561–630.

[2] (a) J.-P. Desvergne, F. Chekpo and H. Bouas-Laurent, *J. Chem. Soc., Perkin Trans. II*, (1978) 84–87; (b) Y.-C. Lin and R.G. Weiss, *Macromolecules, 20* (1987) 414–417; (c) T. Tamaki, T. Kokubu and K. Ichimura, *Tetrahedron, 43* (1987) 1485–1494; (d) F. Fages, J.-P. Desvergne, I. Frisch and H. Bouas-Laurent, *J. Chem. Soc., Chem. Commun.*, (1988) 1414–1415; (e) A. Ueno, F. Moriwaki, Y. Iwama, I. Suzuki, T. Osa, T. Ohta and S. Nozoe, *J. Am. Chem. Soc., 113* (1991) 7034–7036; (f) R. Calas and R. Lalande, *Bull. Soc. Chim. Fr.*, (1959) 763–765.

[3] (a) F.C. DeSchryver, M. De Brackeleire, S. Toppet and M. Van Schoor, *Tetrahedron Lett.*, (1973) 1253–1256; (b) H. Sasaki, S. Kobayashi, K. Iwasaki, S. Ohara and T. Osa, *Bull. Chem. Soc. Jpn., 65* (1992) 3103–3107. See also Ref. [2c].

[4] F. Weigert and O. Krüger, *Z. Phys. Chem., 85* (1913) 579–622.

[5] H.-D. Becker and V. Langer, *J. Org. Chem., 58* (1993) 4703–4708.

[6] T.C. Werner, T. Mathews and B. Soller, *J. Phys. Chem., 80* (1976) 533–541.

[7] T. Tamaki, *Bull. Chem. Soc. Jpn., 53* (1980) 577–582; *55* (1982) 1756–1760; *55* (1982) 1761–1767.

[8] T.M. Vember, L.A. Kiyanskaya and A.S. Cherkasov, *J. Gen. Chem. USSR, 33* (1963) 2281–2285.

[9] V. Langer and H.-D. Becker, *Z. Kristallogr., 206* (1993) 155–157.

[10] C.S. Choi and P.L. Marinkas, *Acta Crystallogr., Sect. B, 36* (1980) 2491–2493.

[11] S. Sundell and H.-D. Becker, *Z. Kristallogr., 209* (1994) 995–996.

[12] V. Langer and H.-D. Becker, *Z. Kristallogr., 206* (1993) 265–267.

[13] P.H. Gore and C.K. Thadani, *J. Chem. Soc. C*, (1966) 1729–1733.

[14] S. Akiyama, S. Misumi and M. Nakagawa, *Bull. Chem. Soc. Jpn., 35* (1962) 1826–1829.