Photochemistry of 9-Benzoylanthracene

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

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

Received June 24, 1993®

Photoexcitation of 9-benzoylanthracene (**1**) in toluene solution under argon results in head-to-tail dimerization by $4\pi + 4\pi$ cycloaddition to give dibenzoyl-substituted dianthracene in about 60% yield. The concomitant formation of both anthracene and 9,10-dibenzoylanthracene (~4% yield) suggests that intermolecular benzoyl group/hydrogen exchange may be an inefficient mode of deactivation of the intermediate excimer. Irradiation of crystalline **1** gave the head-to-tail dimer, without byproducts, in a maximal yield of 50%. It was established by X-ray diffraction that the asymmetric unit of **1** consists of two molecules, **1A** and **1B**, in which the carbonyl group is twisted out of the plane of the anthracene by 67.4° and 86.5°, respectively. Investigation of the packing pattern revealed that only parallel overlapping head-to-tail oriented molecules of **1A**, characterized by an interplanar spacing of 3.35 Å, can undergo photochemical dimerization by $4\pi + 4\pi$ cycloaddition. The spatial relation of adjacent molecules of **1B** is such as to preclude their involvement in the photochemical dimerization.

Introduction

There is nothing remarkable about anthracene derivatives which dimerize photochemically in solution to give dianthracenes, but remain unchanged upon irradiation in the crystalline state. This seemingly disparate behavior toward photoexcitation has been extensively investigated by X-ray diffraction, and contact distances of about 3.5 Å between parallel overlapping aromatic π-systems were found to be a prerequisite for intermolecular reaction in the crystalline state.[1,2] 9-Benzoylanthracene (**1**), however, appears to be unique in this context. It has been described to dimerize upon irradiation in the crystalline state,[3] but was found to be photochemically stable in solution.[4,5] Close proximity of adjacent molecules in the crystal on one hand and fast deactivation of the excited singlet state (S_1) of **1** in solution on the other are believed to account for the observed difference in photochemical behavior.[3] In spectroscopic investigations of photoexcited 9-benzoylanthracene, the absence of fluorescence over a wide temperature range has been rationalized by fast intersystem crossing to an n-π^* triplet state.[6] However, it was pointed out more recently that internal conversion to the electronic ground state (S_0), rather than intersystem crossing, may be the important (Φ ~0.5–~0.7) mode of deactivation of the S_1 state of anthracene **1**.[7]

Although the reported failure to bring about the dimerization in solution seemingly supports an efficient radiationless $S_1 \rightarrow S_0$ decay process for 9-benzoylanthracene, we deemed it appropriate to reinvestigate its photochemistry in view of the following considerations. If deactivation of the S_1 state by intersystem crossing proceeds with a quantum yield of ~0.3–~0.5, dimerization of **1** would have to involve the excited triplet state. Triplet-sensitized dimerizations of anthracene derivatives are known, they proceed typically with low quantum yields, and the formation of dianthracenes in that fashion has been rationalized in terms of triplet–triplet annihilation.[8] Therefore, the initial concentration of **1** would affect the dimerization efficiency, and the absence of oxygen could be essential. The photochemical properties of carbonyl-substituted bichromophoric anthracenes undergoing intramolecular cycloaddition reactions in the triplet-excited state are in line with these aspects.[9]

Results and Discussion

When a solution of 9-benzoylanthracene (~5×10^{-2} M) in benzene or toluene under argon is irradiated ($\lambda > 300$ nm), dianthracene **2** precipitates and can be isolated, simply by filtration, in 60% yield. Irradiation of **1** at the same concentration in air-saturated solution gives **2** in about 30% yield. The dimerization also proceeded when **1** was irradiated at a concentration of about 5×10^{-3} M, though the yield of dianthracene **2** then decreased to 20%. We have thus established that photoexcited 9-benzoylanthracene does dimerize in solution, and the findings suggest that the reaction probably involves the excited triplet state. Earlier statements[3-5] as to the photochemical stability of 9-benzoylanthracene in solution most likely apply to experimental conditions which preclude triplet–triplet annihilation.[10]

Dianthracene **2** forms colorless crystals which melt at 214–218 °C to regenerate 9-benzoylanthracene. Its 400-MHz ^{1}H NMR spectrum at room temperature is deceiving insofar as the protons of the dianthracene skeleton are readily recognized by the exhibition of one singlet, two doublets, and two triplets, but of the five protons of the benzoyl group, only the proton in the *para* position is discernible (see Experimental Section). Because of slow rotation about the phenyl–carbonyl single bond, signals due to the protons in the *ortho* and *meta* positions are so broadened as to coincide with the base line. Only at −50

® Abstract published in *Advance ACS Abstracts,* October 1, 1993.

[1] Heller, E.; Schmidt, G. M. J. *Isr. J. Chem.* 1971, *9*, 449–462.

[2] Thomas, J. M.; Morsi, S. E.; Desvergne, J. P. *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: London, 1977; pp 63–151.

[3] Bouas-Laurent, H.; Lapouyade, R.; Faugère, J.-G. *C. R. Acad. Sc. Paris* 1967, *265*, 506–509.

[4] Lalande, R.; Calas, R. *Bull. Soc. Chim. Fr.* 1959, 766–770.

[5] Vember, T. M.; Kiyanskaya, L. A.; Cherkasov, A. S. *Zhur. Obshchei Khim.* 1963, *33*, 2342–2347. (*J. Gen. Chem. USSR* 1963, *33* 2281–2285.)

[6] (a) Hirayama, S.; Kobayashi, T. *Chem. Phys. Lett.* 1977, *52*, 55–58. (b) Hirayama, S. *J. Chem. Soc., Faraday Trans. 1* 1982, 2411–2421.

[7] Lai, T.-I.; Lim, E. C. *J. Am. Chem. Soc.* 1985, *107*, 1134–1137.

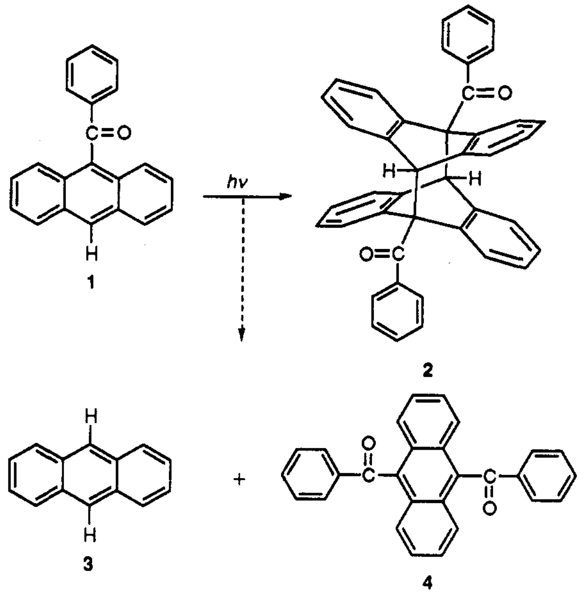
[8] (a) de B. Costa, S. M.; Melo, E. C. *J. Chem. Soc. Faraday Trans. 2* 1980, *76*, 1–13. (b) Charlton, J. L.; Dabestani, R.; Saltiel, J. *J. Am. Chem. Soc.* 1983, *105*, 3473–3476.

[9] Becker, H.-D. *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds.; Interscience Publishers: New York, 1990; Vol. 15, pp 139–227.

0022-3263/93/1958-6394$04.00/0

°C, when rotation of the phenyl group has come to a standstill, are the remaining protons of the benzoyl group clearly detectable in the ^{1}H NMR spectrum by the appearance of two doublets and two triplets. Also worth noting in the ^{1}H NMR spectrum of dianthracene 2 is the exceptional chemical shift (δ) of the singlet at 6.18 ppm due to the bridgehead proton, which is deshielded by the proximate carbonyl group. The bridgehead protons of dianthracene proper give rise to a singlet at 4.55 ppm, and the chemical shifts of the bridgehead protons of the head-to-tail photodimers of 9-acetylanthracene, 9-phenylanthracene, 9-methoxyanthracene, and 9-methylanthracene are 5.76, 5.60, 4.41, and 3.99 ppm, respectively.

Inspection of the irradiated solution of 1 by TLC showed, in addition to starting material and residual photodimer 2,the presence of three minor products. One of them, appearing sporadically, was identified as anthraquinone, whose formation probably is attributable to inadvertent autoxidation. The other two byproducts turned out to be anthracene (3) and 9,10-dibenzoylanthracene (4). Their formation formally represents an intermolecular exchange of a benzoyl group and a hydrogen at C-10 of 9-benzoylanthracene. It is conceivable that the formation of 3 and 4 involves the head-to-tail sandwich excimer of 1, whose deactivation by benzoyl group/hydrogen transfer competes, albeit inefficiently, with the $4\pi + 4\pi$ cycloaddition leading to dianthracene 2.



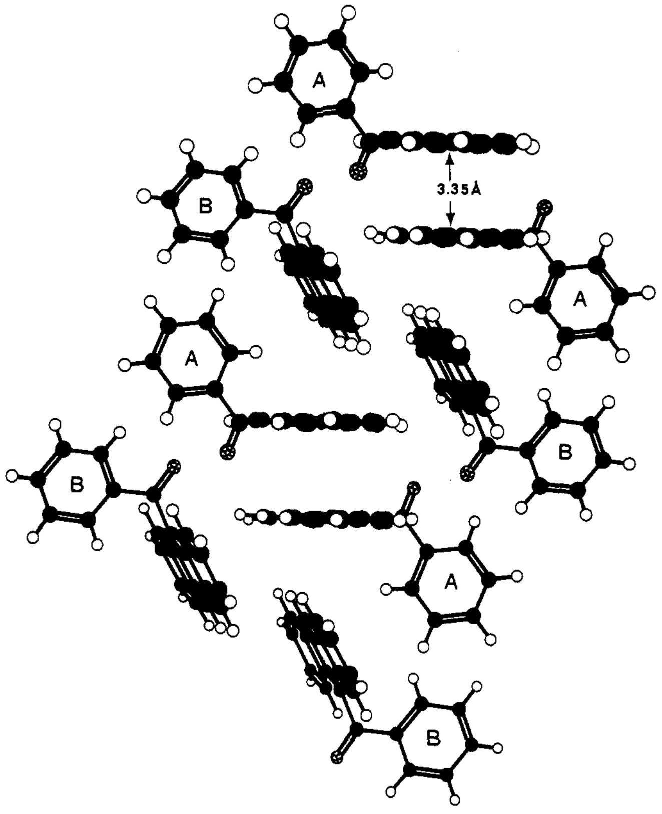


Figure 1. Perspective view of alternating 9-benzoylanthracene molecules 1A and 1B along the crystallographic a-axis.

Since no analytical data of the photodimer obtained previously by irradiation of crystalline 1 have been published, we deemed it essential to ascertain that the dianthracene 2 formed in solution indeed was identical with the product of solid state photochemistry. Moreover, it appeared desirable to establish the crystal structure of 1 in order to gain insight into the topochemical aspects of the cycloaddition reaction. We realized in connection with the preparation of 1, that its dimerization in the crystalline state did not require the application of an ultraviolet lamp but proceeded upon exposure to ordinary artificial laboratory light in the presence of air (see Experimental Section). It had previously been stated that solid 9-benzoylanthracene is autoxidized in the presence of light giving anthraquinone,[11] but we have not been able to confirm this finding. ^{1}H NMR spectroscopic analysis of the irradiated crystals indicated 1 and 2 to be present in a near-perfect molar ratio of 2:1, no other products being detectable. We found it remarkable, however, that we were never able to achieve more than 50% conversion of 1 in the crystalline state. By contrast, irradiation of crystalline 9-acetylanthracene under the same conditions led to complete consumption of starting material, and autoxidation to give anthraquinone was found to compete with the formation of the head-to-tail substituted diacetyldianthracene.

Analysis of crystalline 9-benzoylanthracene by X-ray diffraction revealed the asymmetric unit to consist of two independent molecules, 1A and 1B, whose carbonyl groups are twisted out of the planes of the anthracene moieties by 67.4° and 86.5°, respectively. The dihedral angle between the carbonyl group and the phenyl ring is 21.2° in 1A and 14.9° in 1B. However, the most intriguing and photochemically relevant result of the X-ray diffraction analysis of 9-benzoylanthracene turned out to be the unique crystal-packing pattern, in which parallel adjacent pairs of 1A alternate along the crystallographic a-axis with parallel adjacent pairs of 1B (see Figure 1). In both types of pairs, the 9-benzoylanthracene molecules are head-to-tail oriented, as they are related by a center of symmetry,

---

(10) Experimental details of earlier unsuccessful attempts to dimerize 9-benzoylanthracene (1) by irradiation in solution (see refs 3 and 4) have not been published. In a spectroscopic investigation (ref 5), there was no reaction detectable when 1 was irradiated at a concentration of 10^{-3} M in ethanol; also 9-acetylanthracene, previously (refs 3 and 4) described to dimerize photochemically, was found to be stable under these conditions. The formation of a photodimer of 9-benzoylanthracene was noted, however (Tamaki, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1145–1152), in the photoinduced Friedel–Crafts acylation of anthracene with benzoyl chloride, where the concentration of 1 may have been10 times as high. It is also conceivable that the "white isomer" of 9-benzoylanthracene melting at 203 °C, which is mentioned in a brief polemic note on the Friedel–Crafts reaction of benzoyl chloride with anthracene, actually was a photodimer of 1 (see Perrier, G. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 816). Again, relevant experimental details were not reported.

(11) Gore, P. H.; Hoskins, J. A. *J. Chem. Soc.* **1964**, 5666–5674.

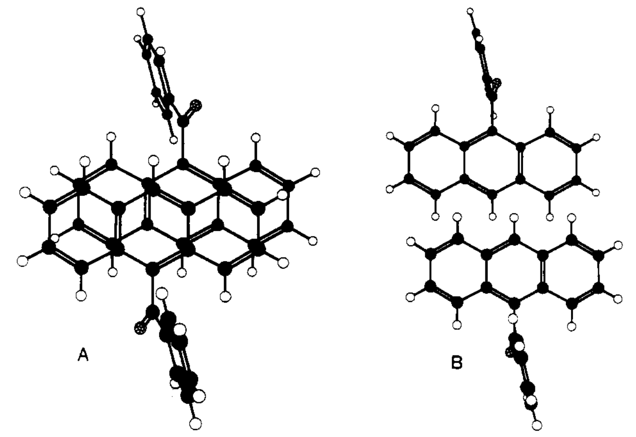


Figure 2. Projection perpendicular to the plane of the anthracene moiety of centrosymmetically related parallel adjacent molecules of 9-benzoylanthracene **1A** and **1B**.

Table I. Deviations (Å) from Total Overlap of Anthracene π-Systems in Parallel Adjacent Molecules in Crystalline 1 and 9-Acetylanthracene

	long-axis shift	short-axis shift	interplanar spacing
1A	1.10	0.89	3.35
1B	0.72	5.03	2.91
9-acetylanthracene	1.35	0.88	3.42

but only **1A**/**1A** pairs are characterized by a topology conducive to photochemical formation of dianthracene **2**. Thus, in pairwise arranged **1A** molecules, the anthracene moieties deviate from total overlap by only small shifts of 0.89 and 1.10 Å along the short and long anthracene axes, respectively (see Figure 2), and the interplanar separation of the interacting π-systems is 3.35 Å. These data are quite similar to those established previously for the intermolecular geometry of crystalline 9-acetylanthracene (see Table I).[12] By contrast, parallel adjacent molecules of **1B** do not overlap at all (see Figure 2 and Table I) and, therefore, cannot dimerize by $4\pi + 4\pi$ cycloaddition. Consequently, it is not an accidental result that **1** and **2** are found to be present in a molar ratio of 2:1 in irradiated crystals of **1**. Rather, we conclude from the X-ray diffraction analysis that, in the absence of any crystallographic dislocations or imperfections,[2] 50% conversion of 9-benzoylanthracene into dianthracene **2** represents the maximum which can be achieved for the photochemical dimerization in the crystalline state.

Experimental Section

Irradiations of solutions were carried out under argon at 10–12 °C with a 125-W high-pressure mercury lamp (Philips HPK 125 W) in a water-cooled immersion well apparatus (Pyrex). 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 ppm downfield from Me_4Si as internal standard. Elemental analyses were carried out by Analytische Laboratorien, Engelskirchen, Germany. Crystallographic data for 9-benzoylanthracene have been accepted for publication in *Zeitschrift für Kristallographie.*

9-Benzoylanthracene was prepared according to the literature by benzoylation of anthracene in carbon disulfide in the presence of aluminum chloride.[11] The crude product was treated with activated charcoal in dichloromethane to remove dark-colored impurities, subsequently purified by column chromatography on silica gel/dichloromethane, and finally recrystallized from boiling ethanol. The product thus obtained formed yellow needle-shaped crystals which melted at 148 °C (lit.[11] mp 148 °C).

Irradiation of 9-Benzoylanthracene in Solution under Argon. A solution of **1** (1 g) in toluene (70 mL) was irradiated for 24 h. The colorless crystalline precipitate (510 mg) formed during the irradiation was removed by filtration. Further workup by vacuum evaporation of solvent from the filtrate gave a pale yellow solid residue which was treated with a mixture of dichloromethane (20 mL) and ether (10 mL) to leave additional colorless crystalline dianthracene **2** (110 mg) undissolved. The yields of **2** in a series of identical experiments in benzene solution ranged from 580 to 630 mg. Dianthracene **2** is only slightly soluble in boiling dichloromethane. It may be recrystallized from boiling toluene, or by Soxhlet extraction with dichloromethane. It decomposes upon melting between 214–218 °C to regenerate 9-benzoylanthracene. ^{1}H NMR (20 °C) 6.18 (s, 1), 6.29 (d, 2), 6.54 (t, 2), 6.78 (t, 2), 7.05, (d, 2), 7.28 (t, 1); ^{1}H NMR (–50 °C) 6.18 (s, 1), 6.29 (d, 2), 6.42 (d, 1), 6.54 (t, 2), 6.70 (t, 1), 6.78 (t, 2), 7.05, (d, 2), 7.31 (t, 1), 7.48 (t, 1), 8.40 (d, 1). Coupling constants are about 8 Hz. Anal. Calcd for $C_{42}H_{28}O_2$: C, 89,34; H, 5.00. Found: 89.48; H, 5.12. Flash chromatographic workup (silica gel/dichloromethane) of the residue obtained from the filtrate after removing **2** gave anthracene (about 5 mg; $R_f = 0.73$), dimer **2** (about 5 mg; $R_f = 0.69$), unreacted **1** (350 mg; $R_f = 0.57$), and a mixture of anthraquinone ($R_f = 0.41$) and 9,10-dibenzoylanthracene ($R_f = 0.39$). Anthraquinone (10 mg) was removed from the mixture by vacuum sublimation (12 mm/150 °C). The remaining 9,10-dibenzoylanthracene (25 mg) was purified by flash column chromatography (silica gel/dichloromethane) and finally recrystallized from boiling dichloromethane/acetone to give pale yellow crystals: mp 337–339 °C (lit.[11] mp 331–333 °C); ^{1}H NMR 7.40 (m, 4) 7.45 (t, 4), 7.62 (t, 2), 7.78 (m, 4), 7.87 (d, 4).

Irradiation of 9-Benzoylanthracene in Air-Saturated Solution. An air-saturated solution of **1** (1 g) in toluene (70 mL) was irradiated for 24 h. After about 20 h of irradiation, the formation of a crystalline precipitate became noticeable. Filtration gave 170 mg of dimer **2**. Additional 110 mg of dimer **2** were isolated after workup of the filtrate in the same manner as described above. The residual reaction mixture was found (TLC) to consist of starting material, dimer **2**, 9,10-dibenzoylanthracene, anthracene, and anthraquinone.

Irradiation of 9-Benzoylanthracene in the Crystalline State. A ^{1}H NMR tube containing crystalline **1** (3 mg) was attached to a "white light" tube, and the sample was irradiated for 24 h. (The amount of sample is dictated by the low solubility of the product **2**,in conjunction with its subsequent analysis in solution.) During the irradiation, the originally yellow transparent crystals assumed an opaque "white" color and disintegrated. Analysis of the sample, dissolved in deuteriochloroform, by ^{1}H NMR indicated clean conversion of 50% of **1** into dimer **2**. We have ascertained that the result is reproducible. Also, when a crystalline sample (3 mg) of **1** was irradiated for 48 h, analysis by ^{1}H NMR again indicated the presence of **1** and **2** in a molar ratio of 2:1, and no other products were detectable.

Photochemical Dimerization of 9-Acetylanthracene in Solution. A solution of 9-acetylanthracene (500 mg) in benzene (70 mL) was irradiated for 7 h. The formation of a colorless crystalline deposit on the immersion well, impairing the transmission of light, became noticeable after about 3 h of irradiation. Vacuum evaporation of solvent from the reaction mixture left a yellowish solid residue which was first washed with ether and then recrystallized from boiling dichloromethane to give 100 mg of colorless crystalline diacetyl-substituted dianthracene: mp 245–250 °C, depending on the rate of heating (lit.[4] mp about 285 °C); ^{1}H NMR 2.20 (s, 3), 5.76 (s, 1), 6.49 (d, 2), 6.77 (t, 2), 6.84 (t, 2), 6.96 (d, 2). Coupling constants are about 8 Hz.

Irradiation of 9-Acetylanthracene in the Crystalline State. Crystalline 9-acetylanthracene (3 mg), placed in an NMR tube attached to a "white light" tube, was irradiated for 24 h. The crystal sample had turned yellowish brown during the irradiation. Analysis by ^{1}H NMR in deuteriochloroform showed virtually complete consumption of starting material and the formation of diacetyl-substituted dianthracene, together with anthraquinone (~10%).

Acknowledgment. We are gratefully indebted to Mr. Gunnar Svensson for skillful technical assistance.

---

(12) Andersson, K.; Becker, H.-D.; Engelhardt, L. M.; Hansen, L.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 1337–1340.