Formation of an Unstable Photodimer from 9-Anthracenecarboxylic Acid in the Solid State

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More than two decades ago,[1,2] Schmidt and Heller reported that 9-anthracenecarboxylic acid (9-AC) was photostable in the solid state (Scheme 1, eq 1). Then afterward, it was reported that 9-AC crystals exhibited excimer fluorescence.[3] The observation of the excimer fluorescence indicates a parallel packing arrangement of the anthracene rings, i.e., a situation favorable for photodimerization to occur.[1−3] In this connection, we have recently found that a crystalline double salt of 9-anthracenepropionic acid with a suitable diamine is highly photoreactive only when it emits anthracene excimer-like fluorescence, producing a head-to-head dimer **3** (Scheme 2).[4] The dimer **3** was thermally unstable, but could be characterized by NMR.

In contrast to the solid-state photostability of 9-AC claimed by Schmidt and Heller, the compound is photoreactive in solution, giving mainly a head-to-tail dimer **1** along with a small amount of a head-to-head dimer **2** (Scheme 1, eq 2, the ratio of **1**/**2** > 5).[5] Although **2** was not spectrally characterized because of its thermal instability, it is interesting to note the finding that the thermal stability of **2** (E_a = 28.0 kcal/mol in ether) is considerably higher than that of **3** (E_a = 21.5 kcal/mol in ether).[5] This result suggests that, if **2** is formed from 9-AC in the solid state, it should be observable by spectroscopic means. Therefore, we reinvestigated the solid-state photoreactivity of 9-AC. Now we report that in contrast to the previous publication,[1,2] 9-AC is indeed very photoreactive in the solid state, giving cleanly the head-to-head dimer **2** (Scheme 3).

Results and Discussion

Crystals of 9-AC, which were spread between two Pyrex plates, were placed in a solid-state photolysis vessel[6] and irradiated with a high-pressure mercury lamp for 4 h under an Ar atmosphere. During the irradiation, the photolysis vessel was cooled from the outside by circulation of cold water (2 °C). Figure 1A shows the 200-MHz ^{1}H NMR spectrum of a reaction mixture, which was quickly measured in DMSO-d_6 immediately after irradiation. New peaks other than those of 9-AC were observed around δ 4.60 (2 H, bridgehead H), 6.83 (12 H), and 7.35 (4 H), which are indicated by arrows. In the best case of experiments, their integration area amounted to 50% of the total integration. These peaks disappeared on allowing the sample solution to stand in the dark at room temperature for 2 days and changed into those of 9-AC (Figure 1B).

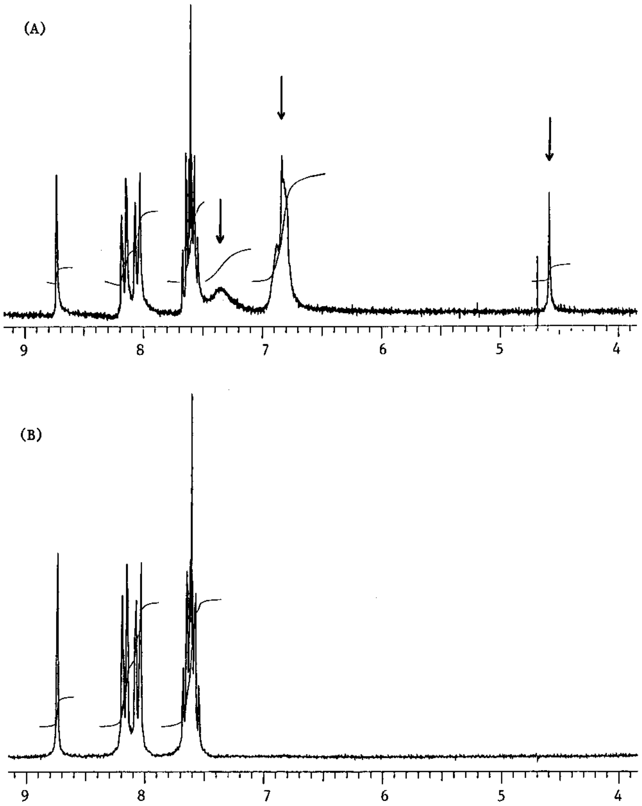

Figure 1. ^{1}H NMR spectra (200 MHz, in DMSO-d_6) of the reaction mixture which resulted from solid-state irradiation (for 4 h) of 9-AC: (A) measured immediately after irradiation and (B) the same sample as used in A but measured after standing for 2 days.

The thermally labile new peaks mentioned above should be assigned to the head-to-head dimer **2**, since the peaks for the head-to-tail dimer **1** were found at different fields, i.e., δ 5.63 (2 H, s, bridgehead H) and 6.7−6.94 (16 H, m). Although chemical shifts of bridgehead protons for head-to-head dimers of 9-substituted anthracenes generally appear at lower regions than those for the corresponding head-to-tail dimers,[4,7] the bridgehead methine proton of **2** resonanced at a higher field (δ 4.60) than that of **1** (δ 5.63).[8] This is because the bridgehead proton of **1** is deshielded by the adjacent carboxyl group.[9] The strong broadening of the peak around δ 7.35 for **2** (Figure 1A) was probably caused by hindered rotations of the carboxyl groups at the congested vicinal dicarboxyl moiety of the head-to-head dimeric structure.

^{13}C NMR (100 MHz) for **1** in 1:1 DMSO-d_6/CD_3OD showed signals at δ 175.47 (COOH), 143.40 (quaternary

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[1] Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647−678.

[2] Heller, E.; Schmidt, G. M. J. *Israel J. Chem.* **1971**, *9*, 449−462.

[3] Cohen, M. D.; Ludmer, Z.; Yakhot, V. *Phys. Status Solidi B* **1975**, *67*, 51−61.

[4] Ito, Y.; Olovsson, G. To be published.

[5] Wolff, T.; Müller, N. *J. Photochem.* **1983**, *23*, 131−140.

[6] Ito, Y. *Mol. Cryst. Liq. Cryst.* **1996**, *277*, 247−253. Ito, Y. *Mol. Cryst. Liq. Cryst.* **1992**, *219*, 29−36.

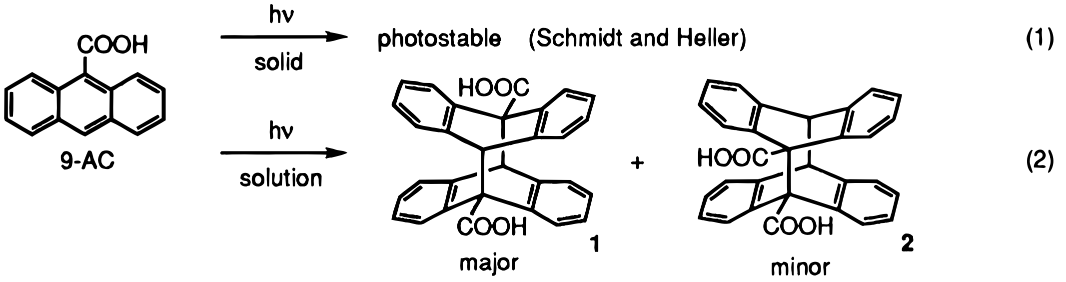
[7] Kaupp, G.; Teufel, E. *Chem. Ber.* **1980**, *113*, 3669−3674. Desvergne, J.-P.; Castellan, A.; Bouas-Laurent, H. *Tetrahedron Lett.* **1981**, *22*, 3529−3532. Wolff, T. *J. Photochem.* **1981**, *16*, 343−346. Becker, H.-D.; Langer, V. *J. Org. Chem.* **1993**, *58*, 4703−4708.

[8] One of the referees provided us with his own unpublished ^{1}H NMR data for **1** and **2** obtained in acetone-d_6: **1** δ 3.3 (2 H, s) and 6.7−7.1 (16 H, m); **2** δ 4.9 (2 H, s) and 6.7−7.1 (16 H, m). Note that the chemical shift of the bridgehead proton of **1** is higher than that of **2**. This is different from our data measured in DMSO-d_6 (see text) or in acetone-d_6 at 200 MHz: **1** δ 5.72 (2 H, s, bridgehead H) and 6.75−6.98 (16 H, m); **2** δ 4.65 (2 H, s, bridgehead H), 6.73−6.97 (12 H, m) and 7.45−7.6 (4 H, broad). Without experimental details, we are unable to judge the validity of the referee's data.

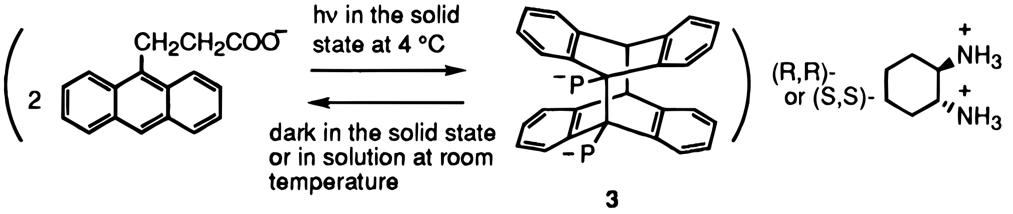
[9] Becker, H.-D.; Langer, V.; Becker, H.-C. *J. Org. Chem.* **1993**, *58*, 6394−6396.

S0022-3263(96)00486-0 CCC: $12.00

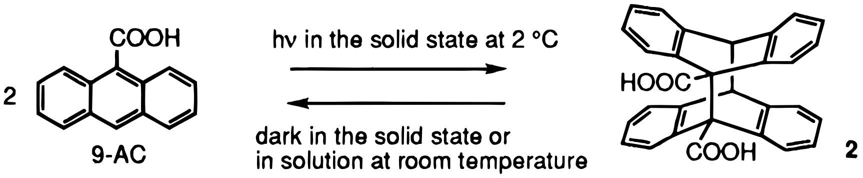
Scheme 1



Scheme 2



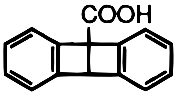
Scheme 3



C), 142.88 (quaternary C), 128.36, 127.41, 126.55, 126.09, 66.56 (*C*-COOH), and 55.45 (bridgehead CH). By means of gated decoupling and selective decoupling experiments, the carboxyl carbon was found to be coupled with the proximate bridgehead proton with $^{3}J_{\mathrm{CH}} = 6.8$ Hz.

^{13}C NMR of the reaction mixture containing 9-AC and **2** was similarly measured at −10 °C. Five signals which are clearly assignable to the head-to-head dimer **2** were observed at δ 174.57 (COOH, $\Delta\nu_{1/2} = 23$ Hz), 144.47 (quaternary C, $\Delta\nu_{1/2} = 20$ Hz), 142.19 (quaternary C, $\Delta\nu_{1/2} = 64$ Hz), 69.37 (*C*-COOH, $\Delta\nu_{1/2} = 39$ Hz), and 54.51 (bridgehead CH, $\Delta\nu_{1/2} = 12$ Hz). All these peaks, especially those at δ 142.19 and 69.37, were considerably broad, as seen from the values of their half-maximum intensity line width $\Delta\nu_{1/2}$: compare with $\Delta\nu_{1/2} = 3$ Hz for the carboxyl carbon of 9-AC. This broadening also indicates that the rotational motion of the carboxyl groups in **2** is hindered. Furthermore, in contrast to the case of **1** ($^{3}J_{\mathrm{CH}} = 6.8$ Hz), the coupling between the carboxyl carbon and the bridgehead proton was not observable. These results are consistent with the head-to-head dimer structure for **2**.

It is unlikely that the unstable **2** has the structure of the 9,10-Dewar anthracene **4**. The ^{1}H NMR signals for the aromatic protons of 9-*tert*-butyl-9,10-(Dewar anthracene) was observed at δ 7.[10] The observation of the aromatic protons at higher fields than δ 7 for both **1** and **2** strongly support their characteristic face-to-face dimer structure. Furthermore, the absence of $^{3}J_{\mathrm{CH}}$ as well as the hindered rotation observed for the carboxyl group of **2** argues against the Dewar anthracene structure for **2**.



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The head-to-head dimer **2** photogenerated as outlined above was found to be much more short-lived as a solid than in solution. Thus, a solid reaction mixture containing **2** was kept in the dark at room temperature, and the remaining **2** was checked at intervals by quick measurements of NMR and HPLC. It was found that **2** contained in the solid reaction mixture decomposed rapidly (within 1 h as compared with 2 days in a DMSO-d_6 or MeOH solution), regenerating 9-AC. Probably, this instability of **2** is the reason why Schmidt and Heller[1,2] failed to observe the photodimerization of 9-AC in the solid state. However, it is possible that the crystals which they dealt with possessed a different modification (and hence a different photoreactivity) than our crystals. This point remains to be clarified.

The absorption and emission spectra of 9-AC in ethanol were vibrationally structured [λ_{max} for absorption 385 (ϵ 7500), 366 (8300), 348 (5500), 331 (2700), 315$^{\mathrm{sh}}$ (1100) nm; λ_{max} for emission 388, 410 (strongest), 434, 460 nm]. In the solid state, however, the emission spectrum became structureless and red-shifted, showing the maximum at 484 nm (Figure 2a). According to the previous publication,[3] this emission should be ascribed to fluorescence from the 9-AC excimer. The X-ray structure analysis demonstrated that the 9-AC crystals are packed with a β-type structure with considerable parallel overlap of the anthracene rings in a head-to-head arrangement.[2,3]

As described above, the interconversion between 9-AC and **2** is reversible. In order to examine the solid-state reversibility of this interconversion, the reaction was followed by solid-state emission spectroscopy and diffuse reflectance spectroscopy. Figure 2 shows the solid-state emission spectra for 9-AC, which were measured before irradiation (a) and after irradiation (b−g). From the

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(10) Güsten, H.; Mintas, M. *J. Am. Chem. Soc.* **1980**, *102*, 7936−7937.

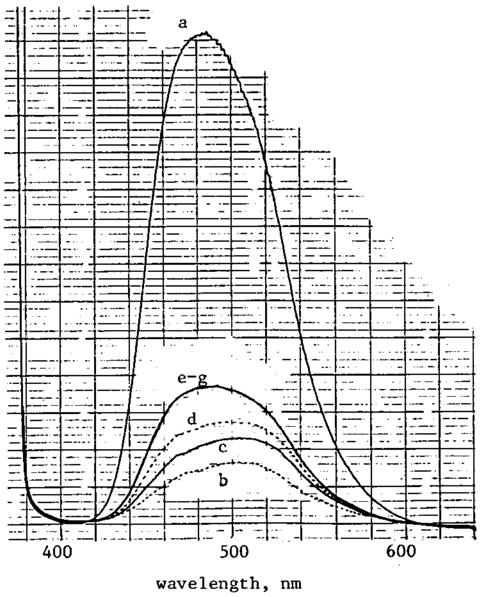

Figure 2. Solid-state emission spectra (λ_{exc} = 370 nm) recorded before and after irradiation (for 4 h) of 9-AC in the solid state: (a) before irradiation, (b−g) t (min) after irradiation; t = 10, 15, 20, 45, 100, and 200 min, respectively.

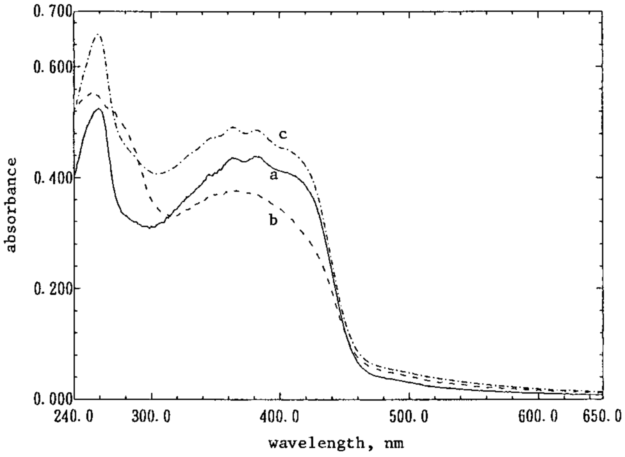

Figure 3. Diffuse reflectance spectra recorded before and after irradiation (for 2 h) of 9-AC in $BaSO_4$: (a) before irradiation, (b) 5 min after irradiation, and (c) 20 h after irradiation.

weak emission intensity observed immediately after the irradiation (b), it appears that the photodimerization went on to high conversion. On standing at room temperature in the dark, the emission rapidly recovered within 45 min (b−e), but it did not return to the original intensity (a) even after 200 min (g), where a complete cleavage of the head-to-head dimer **2** to 9-AC was confirmed by NMR and HPLC. Only about 30% recovery of the original emission intensity (a vs e−g in Figure 2) in spite of nearly quantitative recovery of 9-AC is probably due to fluorescence quenching caused by formation of a small amount of byproducts.

Reversibility in the diffuse reflectance spectra was also not good. The spectra were measured in $BaSO_4$ by using a $BaSO_4$ powder as the standard of reflectivity. As seen from Figure 3, a slight vibrational structure can be seen before irradiation (a). After irradiation, the spectrum became structureless and the baseline appears to have been considerably raised at shorter wavelength regions (b). The baseline was not lowered to the original level even after a complete disintegration of **2** into 9-AC (c). This change in the level of baseline also suggests the formation of some byproducts upon photolysis.

A characteristic feature of the solid-state photochemistry of anthracenes is that their photodimerization reactions often violate the topochemical rule, i.e., their photodimerization products cannot be predicted from their crystal structures.[1,11] 9-AC having a potentially photoreactive β-type crystal structure was considered to be one of such examples.[1] However, we have now disclosed that a topochemically expected reaction 9-AC → **2** in fact occurs. This fact cautions that careful reinvestigations in search of unstable dimers may be required for other nontopochemical cases such as 9-chloroanthracene, 9-cyanoanthracene, and 9-anthraldehyde.

In conclusion, in contrast to Schmidt's report,[1,2] 9-AC is very photoreactive in the solid state, giving the head-to-head dimer **2** as a nearly sole product. This dimer is thermally unstable especially in the solid state and readily cleaves back to 9-AC at room temperature.

Experimental Section

General. ^1H NMR spectra were recorded at 200 or 400 MHz and ^{13}C NMR spectra at 100 MHz. HPLC analyses were performed on a C-18 reverse-phase column (4.6 mm i.d. × 150 mm) by using a mixture of M/50 acetate buffer (pH 3.6) and methanol (25:75 v/v, 1.0 mL/min) as eluent and a UV detector (fixed at 217 nm).

9-Anthracenecarboxylic acid (9-AC) was purchased from Aldrich and recrystallized from EtOH.

Irradiation. (a) NMR Spectra Measurements. Crystals of 9-AC (10 mg) were uniformly spread between two Pyrex plates and this was placed in our solid-state photolysis vessel.[6] Irradiation was then carried out with a 400-W high-pressure mercury lamp for 4 h under a slow stream of argon. During the irradiation, the vessel was cooled from the outside by circulation of cold water (2 °C). Immediately after irradiation, the reaction mixture was dissolved in DMSO, DMSO-d_6, or 1:1 v/v DMSO-d_6/CD_3OD without heating and analyzed by HPLC, 200-MHz ^1H NMR, and 100-MHz ^{13}C NMR, respectively. The HPLC and ^1H NMR analyses were performed as quickly as possible. The ^1H NMR spectrum (Figure 1A) demonstrated a clean production of the head-to-head dimer (3,4:7,8:9,10:11,12-tetrabenzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene-1,2-dicarboxylic acid) (**2**) (50% yield in the best case). The head-to-tail dimer **1** was virtually undetectable by NMR (a singlet around δ 5.63 for the bridgehead methine proton for **1** was absent) as well as by HPLC (retention times, **1** 4.1 min; 9-AC 4.6 min; **2** 5.4 min). The ^{13}C NMR spectrum was measured at −10 °C, where **2** was found to be essentially stable.

The head-to-head dimer **2** was not stable at room temperature. As readily seen from Figure 1B, all the peaks corresponding to **2** disappeared in 2 days on allowing the NMR sample solution to stand at room temperature, changing into those peaks for 9-AC.

The head-to-head dimer **2** was much more unstable in the solid state than in solution. Thus, when the reaction mixture was stored as a solid in the dark at room temperature and analyzed at intervals by quick measurements of NMR and HPLC, it was found that almost all of **2** decomposed in 1 h with concomitant regeneration of 9-AC.

(b) Solid-State Emission Spectra Measurements. Crystals of 9-AC (3 mg) were uniformly spread between two quartz plates. After the emission spectrum of this sample was measured, it was irradiated for 4 h under similar conditions as described above. Immediately after irradiation, the reaction mixture was directly subjected to a quick measurement of the emission spectrum at room temperature and subsequently the spectral changes were followed at intervals (Figure 2).

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(11) Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 595−598. Ramamurthy, V.; Weiss, R. G.; Hammond, G. S. *Adv. Photochem.* **1993**, *18*, 67−234.

(c) Diffuse Reflectance Spectra Measurements. Crystals of 9-AC (20 mg) were mixed with 200 mg of $BaSO_4$, and the mixture was pressed into a shallow hollow for the diffuse reflectance spectrum measurement. A $BaSO_4$ powder was used as a standard of reflectivity. After the spectrum of the mixture was measured, it was irradiated for 2 h under similar conditions as described above. Immediately after irradiation, the reaction mixture was directly subjected to a quick measurement of the diffuse reflectance spectrum at room temperature, and then the spectral changes were monitored at intervals (Figure 3).

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