Use of linker for preparation of missing solid-state photoproducts: head-to-head photodimerization of anthracene-9-propionic acid in its crystalline double salt with cyclohexane-1,2-diamine

Yoshikatsu Ito *,[a] and Gunnar Olovsson [b]

[a] *Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan*
[b] *Department of Chemistry, University of British Columbia, Vancouver V6T 1Z1, Canada*

In order to realize the uncommon head-to-head photodimerization of 9-substituted anthracenes rather than the common head-to-tail photodimerization, a regiochemical control of the reaction through use of supramolecular linkers has been attempted in the solid state. Thus, crystalline double salts are prepared from anthracene-9-propionic acid (9-AP) and 1,2-diamines such as ethylenediamine (en), racemic or optically active (R,R)- or (S,S)-trans-cyclohexane-1,2-diamine (t-chxn), and cis-cyclohexane-1,2-diamine (c-chxn), and these salts are irradiated in the solid state. The 1,2-diamine is used as a linker molecule to connect two molecules of 9-AP by formation of a double salt. Like the previously published head-to-head photodimerization of (E)-cinnamic acids, the head-to-head photodimer of 9-AP is successfully produced from solid-state photolysis of the double salts of *gauche* 1,2-diamines, *i.e.* (R,R)- and (S,S)-t-chxn and c-chxn. The crystal structure for the low-photoreactivity double salt with (±)-t-chxn has been successfully solved.

Introduction

For the purpose of increasing the synthetic value of solid-state photodimerization, control of the reaction by using non-covalent-bonding (*i.e.*, supramolecular) linkers deserves intensive study. As a result of these studies, general methods to obtain missing or uncommon cycloaddition dimers may be achieved. In this connection, it has recently been shown that the solid-state photodimerization of (E)-cinnamic acids and their analogues can be controlled by formation of crystalline double salts with diamines.[1,2] Diamines are used as a linker molecule to connect two acid molecules. Thus, the double salts derived from 1,2-diamines in a *gauche* conformation tend to be highly photoreactive, leading generally to head-to-head dimers (β-truxinic dimers) upon irradiation, whereas the double salts with 1,2-diamines in an *anti* conformation are less photoreactive or, indeed, photoinert.

Photodimerizations of 9-substituted anthracenes in solution are efficient, usually giving rise to head-to-tail dimers rather than head-to-head dimers.[3,4] In an attempt to obtain missing or uncommon head-to-head photodimers of 9-substituted anthracenes, solid-state photolyses of the double salts prepared from anthracene-9-carboxylic acid (9-AC) and diamines were carried out. As was already reported,[5] however, the head-to-head dimer of 9-AC could not be obtained by this method. It appears that the near orthogonality of the carboxy group to the aromatic plane,[6,7] which is caused by steric hindrance at the *peri* positions, might have interfered with the head-to-head photodimerization. Therefore, as our next candidates for study, anthracene-9-propionic acid (9-AP) and anthracene-2-carboxylic acid (2-AC), which should possess less *peri* steric hindrance, were selected.

Irradiation of 9-AP in homogeneous solvents and in micellar solutions is reported to give the head-to-tail dimer **1** together with the head-to-head dimer **2** with the **1/2** ratio being approximately 9:1, although their spectral data were not given.[8] We have confirmed (Scheme 1) that 9-AP photodimerizes in methanol solution to give predominantly dimer **1**, but that dimer **2** is formed only in a very small amount, which is detectable only by HPLC. Furthermore, in contrast to the solution state, 9-AP is completely photostable in the solid state. We now
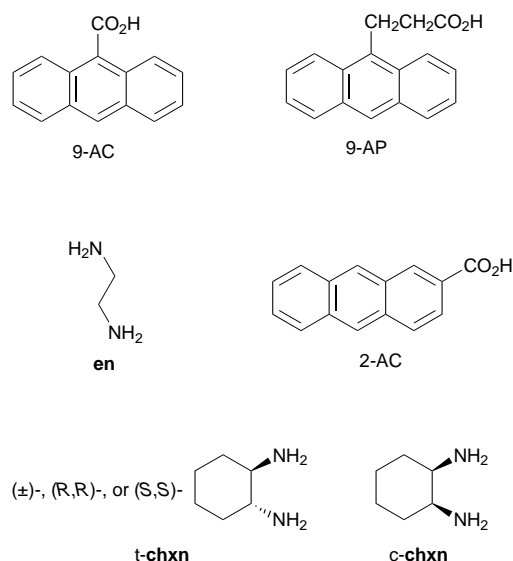
find that the head-to-head dimer of 9-AP, compound **2**, can be produced selectively from solid-state irradiation of its double salts with diamines such as (R,R)- or (S,S)-trans-cyclohexane-1,2-diamine (t-chxn) and cis-cyclohexane-1,2-diamine (c-chxn). The results are reported herein.

Results and discussion

The double salts were prepared by mixing 2 moles of 9-AP with 1 mole of diamine in a suitable solvent. The diamines used were ethylenediamine (en), racemic or optically active (R,R)- or (S,S)-trans-cyclohexane-1,2-diamine (t-chxn), and cis-cyclo-hexane-1,2-diamine (c-chxn). Since the 1,2-diamino groups of t-chxn and c-chxn are restricted to a *gauche* relationship,[9] predominant photodimerization of 9-AP into the head-to-head dimer **2** was expected.[1,2] Prior to photolysis, the double salt crystals were recrystallized and dried *in vacuo* at 35 °C for a few days. It was found from NMR and elemental analyses (see

Table 1 Solvents used for mixing and for recrystallization and analytical data for the double salts of 9-AP

Double salt	Solvent		Calc. (%)			Found (%) [a]		
	mixing	recrystallization	C	H	N	C	H	N
9-AP·en	MeOH	MeOH	77.12	6.47	5.00 [b]	77.00	6.57	4.98
9-AP·(±)-t-chxn	MeOH	MeOH + Et$_2$O	76.13	7.17	4.33 [c]	76.43	7.33	4.32
9-AP·(R,R)-t-chxn	MeOH	MeOH	78.14	6.89	4.56 [d]	77.88	6.92	4.52
9-AP·(S,S)-t-chxn	MeOH	MeOH + Et$_2$O	77.69	6.91	4.53 [e]	77.59	6.90	4.46
9-AP·c-chxn	MeOH + Et$_2$O	Pr^{i}OH	76.53	7.47	4.15 [f]	76.55	7.33	4.11

[a] The crystals were dried *in vacuo* at 35 °C for a few days. [b] For (9-AP)$_2$en or C$_{36}$H$_{36}$N$_2$O$_4$. [c] For (9-AP)$_2$(±)-t-chxn(MeOH) or C$_{40}$H$_{42}$N$_2$O$_4$·1.0MeOH.
[d] For (9-AP)$_2$(R,R)-t-chxn or C$_{40}$H$_{42}$N$_2$O$_4$. [e] For (9-AP)$_2$(S,S)-t-chxn(H$_2$O)$_{0.2}$ or C$_{40}$H$_{42}$N$_2$O$_4$·0.2H$_2$O. [f] For (9-AP)$_2$c-chxn(Pr^{i}OH) or C$_{40}$H$_{42}$N$_2$O$_4$· 1.0 Pr^{i}OH.

Table 2 Mp, carbonyl stretching frequencies and solid-state emission maxima for the double salts of 9-AP

Double salt	Mp (T/°C)	C=O [a]		Emission [b]
		ν_{as}/cm^{-1}	ν_s/cm^{-1}	λ_{max}/nm
9-AP·en	175.5–179 [c]	1578, 1494	1403	448
9-AP·(±)-t-chxn	171–174	1558, 1543, 1525 (finely split)	1400	452
9-AP·(R,R)-t-chxn	152–169 [c]	1544	1407	474
9-AP·(S,S)-t-chxn	158–163 [c]	1544	1407	474
9-AP·c-chxn	169–170.5	1561	1403	448 [d]
9-AP	192–194	1700		442 [e]

[a] The asymmetric (ν_{as}) and symmetric (ν_s) stretching frequencies of the CO$_2^-$ group (CO$_2$H for 9-AP); in KBr. [b] The solid-state emission maxima; excited at 370 nm. [c] Resolidified above the mp. [d] Shoulders at 424 and 465 nm. [e] Weaker λ_{max} at 464 nm.
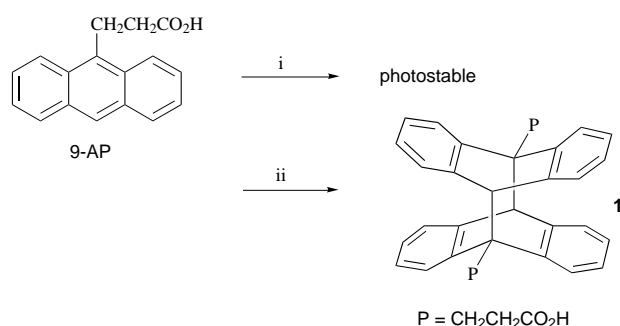

Scheme 1 *Reagents and conditions:* i, *hν*, 20 h, solid state; ii, *hν*, 8 h, MeOH (7.9 mM)

Table 1) that two double salts [9-AP·(±)-t-chxn and 9-AP·c-chxn] were solvated with one molecule of each recrystallization solvent, while others [9-AP·en, 9-AP·(R,R)-t-chxn and 9-AP·(S,S)-t-chxn] were not solvated.

The double salt crystals were ground into powders and about 20 mg of the powder was spread between two Pyrex plates. This was placed in a solid-state photolysis vessel [5] and irradiated for 2–20 h with a 400 W high-pressure mercury lamp, under argon. During the irradiation, the vessel was cooled by running water or by circulating water thermostatted at 4 °C. Immediately after the photolysis, the reaction mixture was dissolved in a suitable solvent and quickly analysed by HPLC and NMR spectroscopy to estimate the yields of products and recoveries. The results are summarized in Scheme 2. The amines were recovered unchanged, judging from NMR results.

As summarized in Scheme 2, double salt 9-AP·en [= (9-AP)$_2$en from Table 1] underwent no photoreaction. Double salt 9-AP·(±)-t-chxn [= (9-AP)$_2$(±)-t-chxn(MeOH)] gave a small yield of the head-to-tail dimer **1** but no head-to-head dimer **2**. In contrast, photoreaction of double salt 9-AP·(R,R)-t-chxn [= (9-AP)$_2$(R,R)-t-chxn] or 9-AP·(S,S)-t-chxn [= (9-AP)$_2$(S,S)-t-chxn(H$_2$O)$_{0.2}$] proceeded efficiently, producing the head-to-head dimer **2** as the sole product (>55% yield). Fig. 1 displays the NMR spectra of the reaction mixture obtained from irradiation of 9-AP·(R,R)-t-chxn. Similar spectra were ob-

tained for 9-AP·(S,S)-t-chxn. Large signals assignable to dimer **2**, which are indicated by arrows, were observed when the spectra were quickly measured in [²H$_6$]DMSO [Fig. 1(*a*)]. However, since the head-to-head dimer **2** was unstable, all peaks belonging to dimer **2** disappeared in two hours and only the signals for 9-AP remained [Fig. 1(*b*)]. The head-to-tail dimer **1** (δ 3.96 in [²H$_6$]DMSO for bridgehead methine proton) was undetectable in these NMR spectra. Double salt 9-AP·c-chxn [= (9-AP)$_2$-chxn(Pr^{i}OH)] gave a similar result, but the yield for the head-to-head dimer **2** was considerably lower (>35% yield) and a small amount of dimer **1** was detected as a by-product by HPLC.

The head-to-head dimer **2** photogenerated *in situ* as outlined above was much more stable as a solid than in solution. Furthermore, its solid-state stability depended on the amine component which was co-existent with it. Thus, a reaction mixture containing dimer **2** was stored as a solid in the dark at room temperature over days and the amount of compound **2** remaining was checked from time to time by quick NMR and HPLC measurements. It was found that dimer **2** formed from the solid-state irradiation of 9-AP·(R,R)-t-chxn or 9-AP·(S,S)-t-chxn decomposed with a half-life of *ca.* 6 days. On the other hand, dimer **2** formed from the solid-state irradiation of 9-AP·c-chxn underwent no degradation over a period of 25 days. However, when these solid-reaction mixtures were dissolved in [²H$_6$]-DMSO or MeOH, dimer **2** decomposed within two hours on storage in the dark at room temperature, regenerating 9-AP.

The absorption and fluorescence spectra of 9-AP in ethanol were vibrationally structured [λ_{max}/nm for absorption: 388 (ε/dm^3 mol^{-1} cm^{-1} 8200), 368 (8800), 349 (5700), 333 (2800) and 315^{shoulder}; λ_{max}/nm for emission: 391, 412 (strongest), 436 and 463] and were very similar to those of 9-methylanthracene. They were not affected by the addition of (R,R)-t-chxn (up to 4.4 x 10^{-3} mol dm^{-3}). The solid-state fluorescence spectrum of 9-AP exhibited maxima at 442 (stronger) and 464 nm.

Next, solid-state emission spectra of the double salts were measured. Unlike the above mentioned emission spectra of 9-AP, they were structureless [*e.g.*, see Fig. 3a for 9-AP·(S,S)-t-chxn] except that of 9-AP·c-chxn, where a slight structure could be seen. The emission maxima are summarized in Table 2. Both

Table 3 Solvents used for mixing and for recrystallization, analytical data and mps for the double salts of 2-AC

| Double salt | Solvent | | Calc. (%) | | | Found (%) [a] | | | Mps (T/°C) (decomp.) |
	mixing	recrystallization	C	H	N	C	H	N	
2-AC·en	EtOH + MeOH	EtOH	76.17	5.59	5.55 [b]	76.41	5.50	5.58	>239
2-AC·(±)-t-chxn	EtOH + MeOH	EtOH	77.39	6.13	5.01 [c]	77.43	5.97	4.82	>243
2-AC·(R,R)-t-chxn	EtOH	EtOH	77.39	6.13	5.01 [d]	77.25	6.06	4.79	>243
2-AC·c-chxn	EtOH	EtOH	77.39	6.13	5.01 [e]	77.52	6.06	5.00	>240
2-AC									281

[a] The crystals were dried *in vacuo* at 35 °C for a few days. [b] For (2-AC)$_2$en or C$_{32}$H$_{28}$N$_2$O$_4$. [c] For (2-AC)$_2$(±)-t-chxn or C$_{36}$H$_{34}$N$_2$O$_4$. [d] For (2-AC)$_2$(R,R)-t-chxn or C$_{36}$H$_{34}$N$_2$O$_4$. [e] For (2-AC)$_2$c-chxn or C$_{36}$H$_{34}$N$_2$O$_4$.
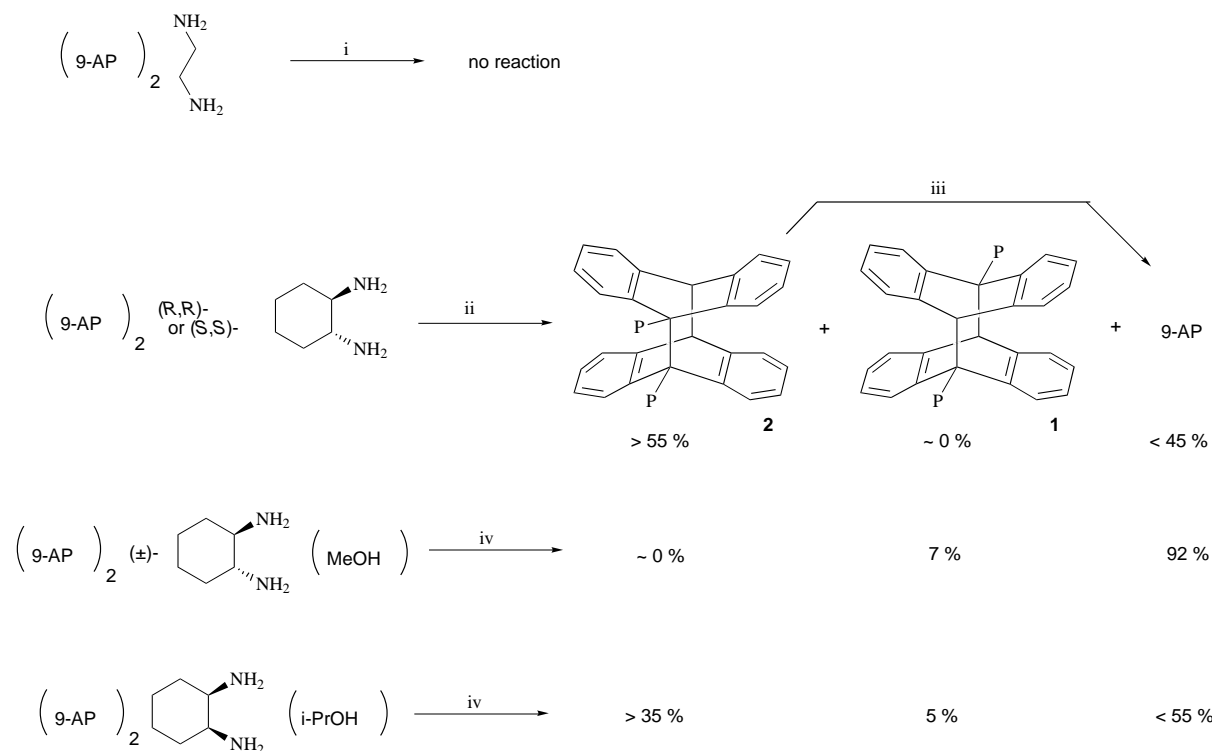
Scheme 2 *Reagents and conditions:* i, *hν*, 20 h, solid state; ii, *hν*, 2–10 h, solid state; iii, dark, room temp.; iv, *hν*, 10 h, solid state. (The yields were estimated by quick measurements of NMR spectra and HPLC.)

9-AP·(R,R)-t-chxn and 9-AP·(S,S)-t-chxn, which were highly reactive in the solid state to give the head-to-head dimer **2** (Scheme 2), emitted with λ_{max} at 474 nm. Other double salts and 9-AP itself, which did not efficiently form dimer **2** in the solid state (Schemes 1 and 2), fluoresced with maxima between 442 and 452 nm. According to previous publications,[10] crystalline anthracene excimer fluoresces at 475 nm, which is very close to the fluorescence maximum of 9-AP·(R,R)-t-chxn and 9-AP·(S,S)-t-chxn. This fact indicates[7,11] that, in the double salt crystals of 9-AP·(R,R)-t-chxn or 9-AP·(S,S)-t-chxn, the anthracene rings are packed in a good overlap arrangement. Evidently, this good overlap is a reason for their high photodimerization reactivity. Unfortunately, the crystals of salts 9-AP·(R,R)-t-chxn and 9-AP·(S,S)-t-chxn were too small to allow us to carry out an X-ray study.

The X-ray crystal structure determination of 9-AP·(±)-t-chxn was, however, successful. There are 4 molecules of 9-AP (AP1, AP2, AP3, AP4), 2 molecules of t-chxn (X1, X2) and 2 molecules of MeOH (M1, M2) in the asymmetric unit (Fig. 2). The molecules form an infinite one-dimensional network of hydrogen bonds along the *c*-axis. The presence of four independent 9-AP molecules is reflected by the finely split ν_{as} (Table 2). AP1 and AP2 (C9---C9 = 4.34 Å, C10---C10 = 3.88 Å) as well as AP3 and AP4 (C9---C9 = 5.01 Å, C10---C10 = 4.76 Å) are arrayed in a semiparallel head-to-head fashion.

However, considering both the negligible yield of the head-to-head dimer **2** (Scheme 2) and the lack of the excimer emission (Table 2) from salt 9-AP·(±)-t-chxn, even the nearer pair AP1/AP2 do not seem to overlap ideally for dimerization. The most favourable head-to-tail arrangement is between AP3 and AP4′, but they overlap poorly, with long C9---C10 intermolecular distances (5.91 and >6 Å). At this stage, the observed production of a low yield (7%) of dimer **1** rather than dimer **2** (Scheme 2) is inexplicable from the crystal structure data.

As described above, the interconversion of 9-AP and dimer **2** is reversible. In order to examine the solid-state reversibility of this transformation, the reactions of salts 9-AP·(R,R)-t-chxn and 9-AP·(S,S)-t-chxn were followed by solid-state emission spectroscopy and diffuse reflectance spectroscopy. Fig. 3 shows the solid-state emission spectra for compound 9-AP·(S,S)-t-chxn measured before irradiation (a) and after irradiation (b–k). From the weak emission intensity observed immediately after irradiation (b), it appears that the photodimerization proceeded nearly to 100% conversion. With increasing time lapse after irradiation, the emission gradually recovered, but it did not return to the original intensity (a) even after complete disintegration of the head-to-head dimer **2** to 9-AP (k). The same results were obtained for salt 9-AP·(R,R)-t-chxn. We observed only ~40% recovery of the original emission intensity (a *vs.* k in Fig. 3) in spite of a nearly quantitative recovery of 9-AP
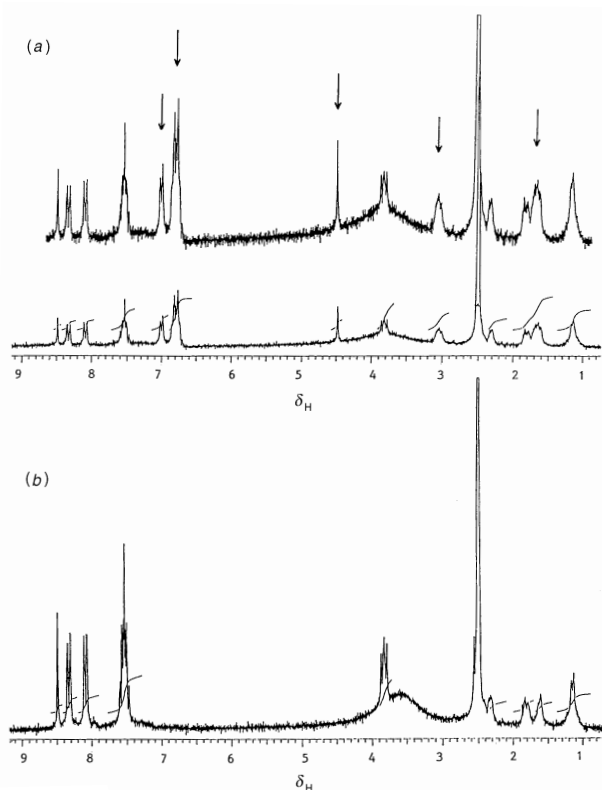
Fig. 1 ^{1}H NMR spectra (200 MHz; [^{2}H$_6$]DMSO) of the reaction mixture which resulted from solid-state irradiation of 9-AP·(R,R)-t-chxn: (*a*) measured immediately after irradiation for 10 h; (*b*) the same NMR sample as used in (*a*) but measured 2 h after the measurement (*a*)

(confirmed by NMR spectroscopy and HPLC). This is probably due to fluorescence quenching caused by formation of a small amount of by-product.

Reversibility in the diffuse reflectance spectra is also not good for both salts 9-AP·(R,R)-t-chxn and 9-AP·(S,S)-t-chxn. Fig. 4 shows the result for 9-AP·(S,S)-t-chxn. The same result was obtained for 9-AP·(R,R)-t-chxn. Before irradiation (a), slight vibrational structure can be seen. After the photolysis, the baseline was considerably raised at the shorter-wavelength region (b) and it was not lowered to the original level even after the complete cleavage of dimer **2** into 9-AP (c). This change in baseline may also indicate the formation of some by-products upon photolysis.

The double salts of 2-AC with en, (±)-t-chxn, (R,R)-t-chxn and c-chxn were likewise studied. Solvents used for their preparation, analytical data and melting points are summarized in Table 3. Unlike the double salts of 9-AP (Table 1), none of these double salts was solvated. Their solid-state photolyses were briefly studied (Scheme 3). As was reported previously,[12] irradiation of 2-AC in ethanol solution produced four isomeric dimers **3**–**6**, with compounds **3** and **4** as major products. 2-AC was photostable in the solid state. The double salt crystal 2-AC·en was nearly photostable and only a trace of anthraquinone-2-carboxylic acid (2-AQC) was formed. The double salt crystals 2-AC·(±)-t-chxn, 2-AC·(R,R)-t-chxn and 2-AC·c-chxn underwent slight photoreaction to yield small amounts of compounds **3**–**6** and 2-AQC. Although assignments of these four dimers are not confirmed, major dimers produced were estimated to be compounds **5** and **6**. It is noticeable that the two carboxy groups in structures **5** or **6** are *syn* to each other.

In conclusion, like the directed head-to-head photodimerization of (*E*)-cinnamic acids,[1,2] the uncommon head-to-head photodimerization of 9-AP was successfully realized by the method of crystalline double salt formation with *gauche* 1,2-diamines.
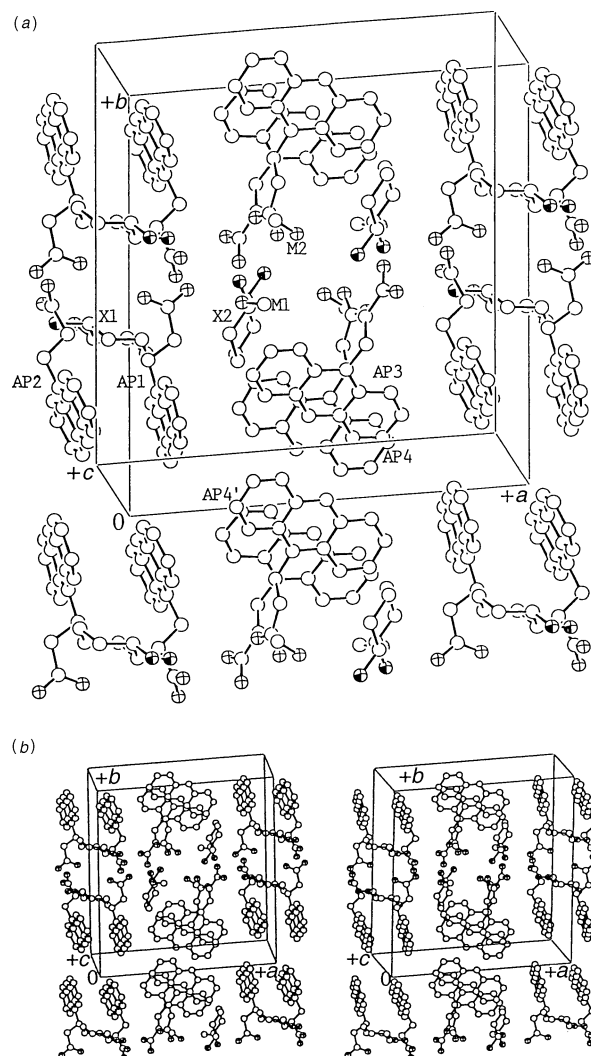
Fig. 2 X-Ray crystal structure for 9-AP·(±)-t-chxn: (*a*) a view of the unit cell; (*b*) a stereoview. Hydrogens are removed for clarity.

Experimental

General procedures

^{1}H NMR spectra (200 MHz) were recorded for samples in [^{2}H$_6$]DMSO on a Varian Gemini-200 spectrometer. *J* Values are given in Hz. IR, UV/VIS, emission and mass spectra were taken with JASCO FT/IR-5M, Shimadzu UV-2400PC, Shimadzu RF-500 and JEOL JMS-SX 102A spectrometers, respectively. Diffuse reflectance spectra were measured with a Shimadzu UV-2400PC spectrometer equipped with a diffuse-reflectance attachment, and BaSO$_4$ powder was used as a standard of reflectivity. HPLC analyses were performed with a Shimadzu LC-5A chromatograph equipped with a UV detector (fixed at 217 nm) by using a Cosmosil 5C$_{18}$-AR column (4.6 nm i.d. x 150 mm) and a mixture of M/50 acetate buffer (pH 3.6) and methanol (24 : 76 v/v, 1.0 cm^3 min^{-1}) as eluent.

Materials

9-AP was prepared according to the published procedure.[13] 2-AC was available from Tokyo Kasei and en, (±)-, (R,R)- and (S,S)-t-chxn and c-chxn were purchased from Nakarai or Aldrich. These were used as received.

Preparation of double salts

Typically, double salt 9-AP·en was prepared as follows. A hot solution containing 158.8 mg (0.635 mmol) of 9-AP in 3 cm^3 of methanol was mixed with a solution containing 19.1 mg (0.318 mmol) of en in 1 cm^3 of methanol. A solid soon appeared and it
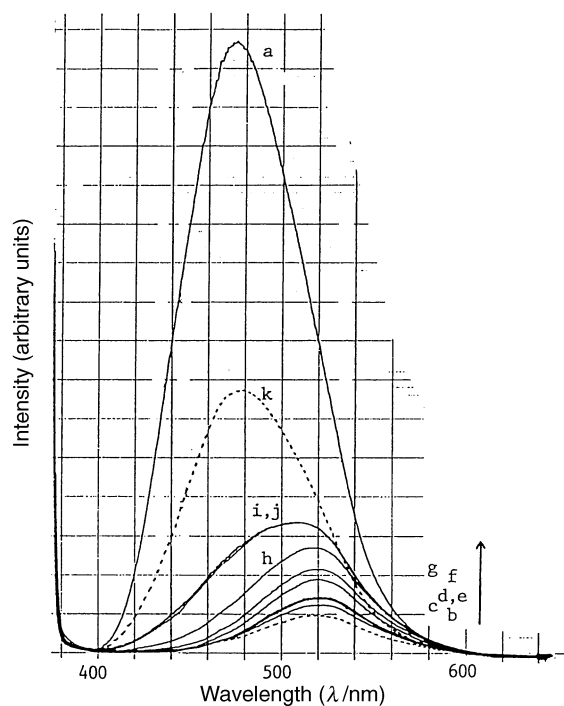
Fig. 3 Solid-state emission spectra recorded before and after irradiation of 9-AP·(*S,S*)-t-chxn in the solid state. a, Before irradiation. b–k, *t* h (or days) after irradiation for 6 h: b–j, *t* = 0.25 h, 0.5 h, 1.5 h, 3 h, 2 days, 4 days, 8 days, 15 days, 22 days at room temperature; k, *t* = 22 days at room temperature + *t* = 2 h at 60 °C.
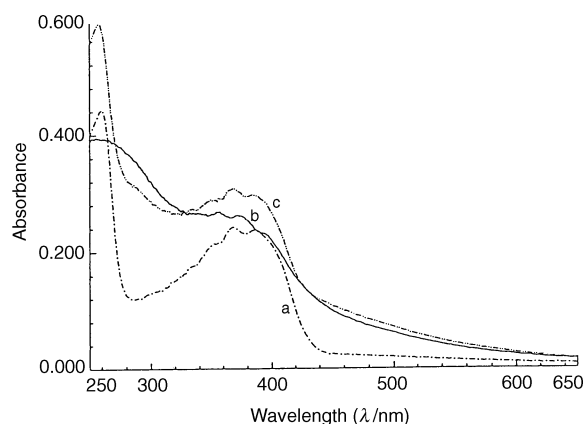

Fig. 4 Diffuse reflectance spectra recorded before and after irradiation of 9-AP·(*S,S*)-t-chxn in BaSO₄. a, Before irradiation. b–c, *t* min (or h) after irradiation for 2 h: b, *t* = 8 min at room temperature; c, *t* = 3 h at room temperature + *t* = 4 h at 60 °C.

was collected by filtration and was recrystallized with methanol (10 cm³) to give 127 mg (71% yield) of the double salt as yellow flakes. This was dried *in vacuo* at 35 °C for two days. The data for microanalysis, spectroscopy (IR and solid-state emission) and mp are listed in Tables 1 and 2.

Other double salts were similarly prepared by mixing 9-AP or 2-AC with the corresponding diamine and were dried *in vacuo* at 35 °C for a few days. The solvents employed for mixing 9-AP or 2-AC with the diamine and those used for recrystallizing the resulted double salts are summarized in Tables 1 and 3, together with the analytical data. It was found that double salts 9-AP·(±)-t-chxn and 9-AP·c-chxn included recrystallization solvent in the crystal (see footnotes *c* and *f* in Table 1). Mps as well as IR and emission spectral data for all the double salts of 9-AP are summarized in Table 2. All the double salts of 2-AC decomposed above 239 °C without melting (Table 3).

Irradiation of double salts

(a) 9-AP·en. Double salt crystals of 9-AP·en (10.6 mg) were crushed and spread between two Pyrex plates. This set-up was placed in our solid-state photolysis vessel.[5,14] Irradiation was carried out with a 400 W high-pressure mercury lamp, under argon for 20 h. During the irradiation, the vessel was cooled from outside by circulation of cold water (4 °C). After the irradiation, the reaction mixture was dissolved in MeOH or [²H₆]DMSO for HPLC and NMR analyses, respectively. No reaction products were detectable.

(b) 9-AP·(*R,R*)-t-chxn. Double salt crystals of 9-AP·(*R,R*)-t-chxn (5.0 mg) were similarly irradiated for 10 h. Immediately after the irradiation, the reaction mixture was dissolved in DMSO or [²H₆]DMSO without heating and was analysed by HPLC and NMR spectroscopy. These procedures of dissolution and analysis were performed as quickly as possible. The NMR spectrum [Fig. 1(*a*)] demonstrated a clean production of the head-to-head dimer (heptacyclo[8.6.6.6²,⁹.0³,⁸.0¹¹,¹⁶.0¹⁷,²². 0²³,²⁸]octadocosa-3,5,7,11,13,15,17,19,21,23,25,27-dodecaene-1,2-dipropionic acid) **2** (55% yield). In Fig. 1(*a*), the signals for dimer **2** were observed at δ 1.65 (4 H, br), 3.04 (4 H, br), 4.48 (2 H, s), 6.7–6.88 (12 H, m, ArH) and 7.00 (4 H, d, *J* 7.5, ArH). The peaks for 9-AP appeared at δ 2.5 (2 H, overlap with residual protons of [²H₆]DMSO), 3.83 (2 H, t, *J* 8), 7.47–7.63 (4 H, m, ArH), 8.08 (2 H, d, *J* 8.5, ArH), 8.34 (2 H, d, *J* 8.5, ArH) and 8.48 (1 H, s, ArH), and those for (*R,R*)-t-chxn at δ 1.14 (4 H, br), 1.61 (2 H, br), 1.81 (2 H, br) and 2.31 (2 H, br). The head-to-tail dimer **1** was virtually undetectable by NMR spectroscopy (a singlet around δ 3.96 for the bridgehead methine proton for dimer **1** was absent) as well as by HPLC (retention times: **1**, 5.0; 9-AP, 7.9; **2**, 9.5 min).

The head-to-head dimer **2** was quite unstable in solution (DMSO or methanol). As readily seen from Fig. 1(*b*), all the peaks corresponding to compound **2** disappeared in 2 h on storage at room temperature and changed into those for 9-AP. In contrast, dimer **2** was fairly stable in the solid state. When the reaction mixture was stored as a solid in the dark at room temperature and was analysed from time to time over a period of 15 days by NMR spectroscopy and HPLC, a significant amount of compound **2** still remained at the end. From this result, the half-life of dimer **2** was estimated as about 6 days.
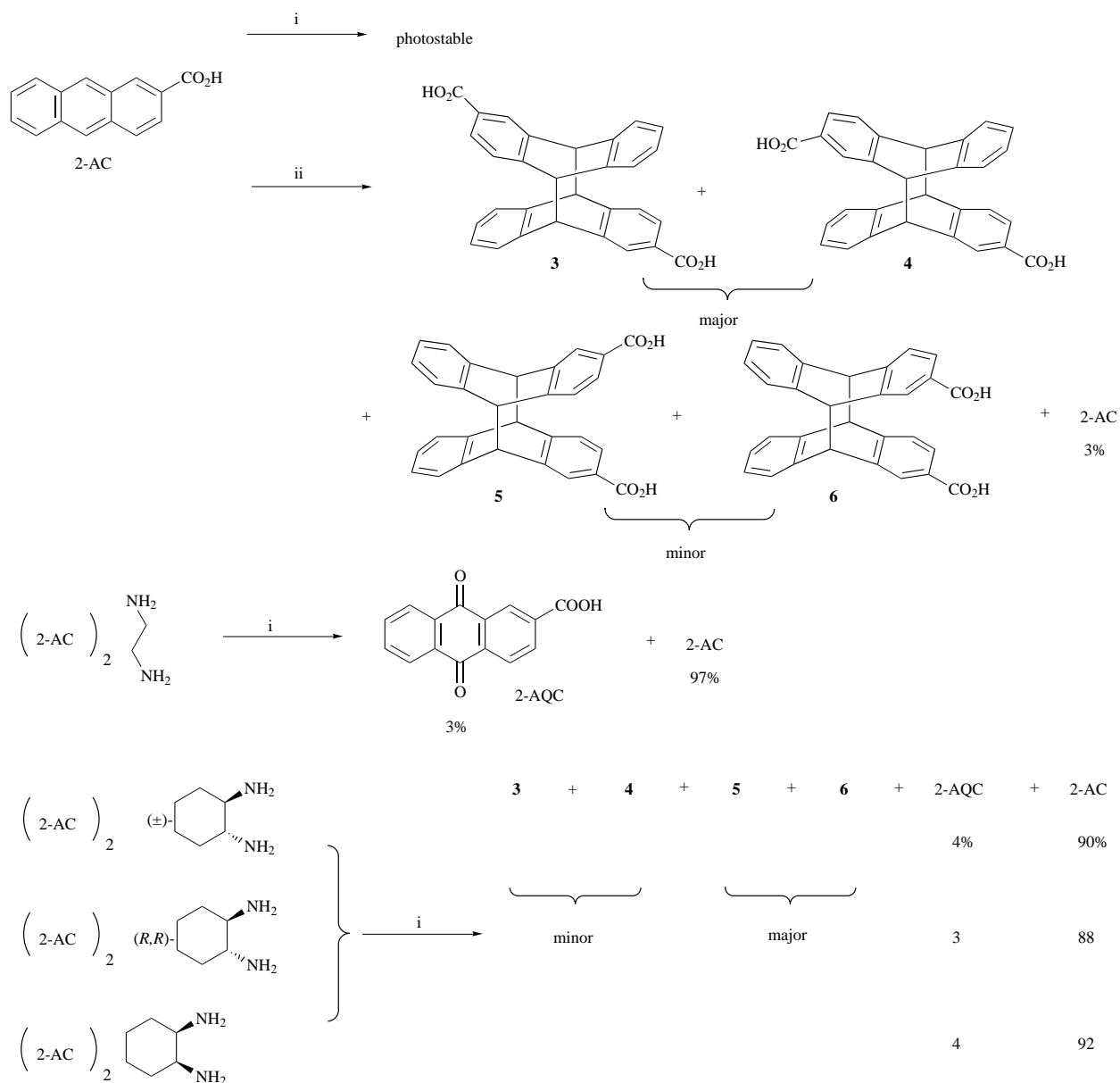
(c) 9-AP·(*S,S*)-t-chxn. Double salt crystals of 9-AP·(*S,S*)-t-chxn (5.7 mg) were similarly irradiated for 6 h and the reaction mixture was quickly analysed by HPLC and NMR spectroscopy. Essentially the same results as those from 9-AP·(*R,R*)-t-chxn were obtained.

(d) 9-AP·(±)-t-chxn and 9-AP·c-chxn. Photolyses of 9-AP·(±)-t-chxn (4.8 mg) and 9-AP·c-chxn (5.1 mg) were similarly carried out for 10 h and the reaction mixtures were quickly analysed by HPLC and NMR spectroscopy. The head-to-head dimer **2** involved in the reaction mixture of 9-AP·c-chxn was unstable in solution (DMSO or methanol) and cleaved into 9-AP on storage at room temperature for 2 h. However, when the reaction mixture was left as a solid in the dark at room temperature, no decomposition of dimer **2** was observed over a period of 25 days by NMR spectroscopy or HPLC.

(e) 2-AC·en, 2-AC·(±)-t-chxn, 2-AC·(*R,R*)-t-chxn and 2-AC·c-chxn. These double salt crystals (6–8 mg) were irradiated for 20 h under similar conditions as described above. The reaction mixtures were analysed by NMR spectroscopy and HPLC and small amounts of four dimers **3**–**6** and anthraquinone-2-carboxylic acid (2-AQC) were detected. The four dimers were not isolated. Their structures were tentatively assigned on the basis of HPLC retention times by reference to previous results.[12]

The results from the experiments (**a**)–(**e**) are schematically summarized in Schemes 2 and 3.

Monitoring of the solid-state photoreactions by solid-state emission spectroscopy and diffuse reflectance spectroscopy was carried out as described previously.[15]

Scheme 3 (chemical structures)

2-AC

i → photostable

ii →

HO₂C ... 3 ... CO₂H + HO₂C ... 4 ... CO₂H

major

+ 5 (CO₂H, CO₂H) + 6 (CO₂H, CO₂H) + 2-AC 3%

minor

$(2\text{-AC})_2$ with NH₂CH₂CH₂NH₂ → i → 2-AQC (with COOH) + 2-AC

3% 97%

$(2\text{-AC})_2$ (±)-t-chxn →
$(2\text{-AC})_2$ (R,R)- → i → 3 + 4 + 5 + 6 + 2-AQC + 2-AC
$(2\text{-AC})_2$ (cis) →

	3 +	4 +	5 +	6 +	2-AQC +	2-AC
		minor		major	4%	90%
					3	88
					4	92

Scheme 3 *Reagents and conditions:* i, *hv*, 20 h, solid state; ii, *hv*, 7 h, EtOH (6.3 mM). (The yields were estimated by HPLC.)

Irradiation of 9-AP or 2-AC

Solid-state irradiation of 9-AP or 2-AC (6 mg) was performed for 20 h as described above for the double salts. No products were detectable by NMR spectroscopy and HPLC. Irradiation of 9-AP in solution was done as follows.

A solution containing 9-AP (29.5 mg) in methanol (15 cm³) was irradiated for 8 h under argon bubbling. NMR and HPLC analyses showed that the head-to-tail dimer of 9-AP (heptacyclo-[8.6.6.6^{2,9}.0^{3,8}.0^{11,16}.0^{17,22}.0^{23,28}]octadocosa-3,5,7,11,13,15,17,19, 21,23,25,27-dodecaene-1,9-dipropionic acid) **1** was formed in 74% yield as the almost exclusive product (Scheme 1). The yield of the head-to-head dimer **2** was estimated at 1% by HPLC. Evaporation of the reaction mixture, followed by recrystallization with methanol (5 ml), afforded 15.1 mg (15%) of dimer **1** as crystals; mp 219.5–230 °C; *m/z* 250 (M⁺/2, 45%) and 191 (100; ν_{max}(KBr)/cm⁻¹ 1705 (CO₂H), 1474, 1453, 780 and 693; δ_H(200 MHz; CD₃OD) 2.32 (4 H, t, *J* 7.6, CH₂CO), 3.13 (4 H, t, *J* 7.6, C*H₂*CH₂CO), 3.98 (2 H, s, bridgehead CH), 6.78–6.94 (8 H, m, ArH) and 6.94–7.23 (8 H, m, ArH). Photodimerization of 9-AP to yield dimers **1** and **2** in solution has been reported[8] but their physical and spectroscopic data were not given.

Irradiation of 2-AC[12] in ethanol was similarly carried out, but isolation of the photoproducts was not attempted.

X-Ray crystal structure determination

A yellow plate-shaped crystal (0.10 x 0.30 x 0.35 mm) of 9-AP·(±)-t-chxn C₈₂H₉₂N₄O₁₀ (Mr 1293.65) was analysed on a Rigaku AFC-6S diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å). Crystal data: triclinic $P\bar{1}$, a = 17.670(2), b = 19.594(2), c = 10.4751(9) Å, α = 93.031(8), β = 102.576(8), γ = 84.280(9)°, V = 3520.2(6) Å³, Z = 2, D_x = 1.220 g cm³, $F(000)$ = 1384. A total of 14 839 reflections were collected (2θ < 155.2°) at 21 ± 1 °C. The number of unique reflections was 14 349 (R_{int} = 0.019). Corrections: Lorentz-polarization; absorption (μ = 6.35 cm⁻¹; transmission factors 0.84–1.00); decay (14% decline); secondary extinction [coefficient: 6.9(3)e − 07].

The structure was solved by direct methods using SIR92.[16] The non-hydrogen atoms were refined anisotropically. All 12 hydrogen atoms attached to the four amine nitrogen atoms and the OH hydrogen atoms of the two methanol molecules were refined isotropically, the rest were included in fixed positions (the isotropic temperature factors of the methanol CH₃ hydrogen atoms were refined as a group, but their positions were fixed). The final cycle of full-matrix least-squares refinement was based on 7284 reflections [I > 3.00σ(I)] and 924 variable parameters and converged with $R(F)$ = 0.045 and $R_W(F)$ =

0.043. The standard deviation of an observation of unit weight was 2.33. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.18 and -0.17 e$^-$ Å^{-3}, respectively. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.†,[17]

Acknowledgements

‡ Tables of atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre under the accession number 207/60. See *Instructions for Authors*, in the January issue.

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