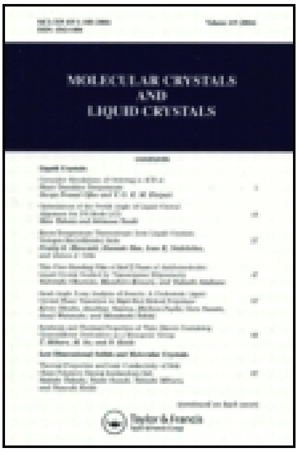

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Studies on Photodimerization of 9-Anthracenecarboxylic Acid in its Crystalline Double Salt with Diamine

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STUDIES ON PHOTODIMERIZATION OF 9-ANTHRACENECARBOXYLIC ACID IN ITS CRYSTALLINE DOUBLE SALT WITH DIAMINE

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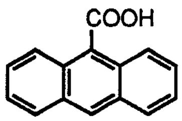
Abstract With the intention of obtaining uncommon head-to-head anthracene dimers, double salts of 9-anthracenecarboxylic acid (9-AC) with several diamines were photolyzed in the solid state. 9-AC underwent decarboxylation and reduction as well as dimerization. Although the head-to-tail dimer and an unsymmetrical dimer were obtained, the head-to-head one was not produced.

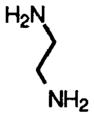
INTRODUCTION

Recently, the author has shown that the solid-state [2+2] photodimerization of trans-cinnamic acids and their analogs can be steered by double salt formation with diamines, leading predominantly to β-truxinic (syn head-to-head) dimers. It has been found that the conformation of the 1,2-diamine is gauche in the highly photoreactive double salts, whereas it is anti in the less photoreactive or photoinert double salts.[1,2] In view of our continued interests in the design of photoreactive multi-component crystals,[3] the author has been studying other double salts.

It is known that irradiation of 9-substituted anthracenes usually produces [4+4] dimers with the head-to-tail structure.[4] For example, 9-anthracenecarboxylic acid (9-AC) readily photodimerizes in solution to give the head-to-tail dimer, although, more recently, it was reported that 9-AC also yielded the head-to-head dimer as the minor photoproduct.[5,6] By contrast, 9-AC is almost photostable in the solid state.[7] In an attempt to obtain uncommon head-to-head anthracene dimers, the author has been studying solid-state photolyses of a series of double salts derived from anthracenecarboxylic acids and diamines. Here, the results of photolyses of the double salt crystals of 9-AC are described. The diamines used are ethylenediamine (**en**), trimethylenediamine (**tn**), racemic and optically active trans-cyclohexane-1,2-diamine ((±)- and (R,R)-t-**chxn**), and cis-cyclohexane-1,2-diamine (c-**chxn**). Since the 1,2-diamino groups of trans- and cis-cyclohexane-1,2-diamine are restricted to a gauche relationship,[8] predominant formation of the head-to-head dimer was expected.

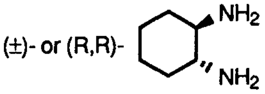


9-AC

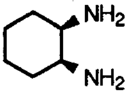


en

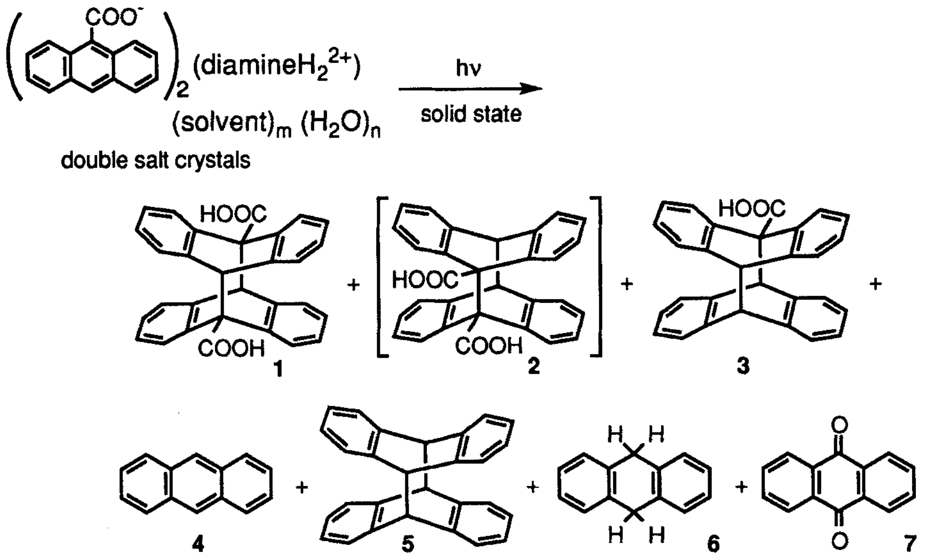
tn



(±)- or (R,R)-t-**chxn**



c-**chxn**



EXPERIMENTAL SECTION

General Procedures

^{1}H NMR, IR, UV/VIS, emission, and mass spectra were recorded on Varian Gemini-200, JASCO FT/IR-5M, JASCO UVIDEC-610, Shimadzu RF-500, and JEOL JMS-DX 300 spectrometers, respectively. HPLC analyses were performed with a Shimadzu LC-5A chromatograph equiped with a UV detector (fixed at 217 nm) by using a Cosmosil 5C$_{18}$-AR column (4.6 mm i.d. x 150 mm) and a mixture of M/50 acetate buffer (pH 3.6) and methanol as eluent.

Preparation of Double Salts

9-Anthracenecarboxylic acid (9-AC), ethylenediamine (**en**), trimethylenediamine (**tn**), racemic and optically active trans-cyclohexane-1,2-diamine ((±)- and (R,R)-t-**chxn**), and cis-cyclohexane-1,2-diamine (c-**chxn**) were purchased and were used as received. Typically, double salts 9-AC•c-**chxn**(I), 9-AC•c-**chxn**(II) and 9-AC•c-**chxn**(III) were prepared as follows.

A hot solution containing 1.478 g (6.65 mmol) of 9-anthracenecarboxylic acid (9-AC) in 30 mL of ethanol was mixed with a solution containing 0.380 g (3.32 mmol) of cis-cyclohexane-1,2-diamine (c-**chxn**) in 10 mL of ethanol. The mixture was heated in a water bath at 70 °C for 10 min and then filtered. The filtrate was allowed to stand in the dark at room temperature. After several hours, yellow prisms appeared. They were collected by filtration, weighing 1.83 g and were stored in a closed sample tube. (In another run, they were further recrystallized from EtOH.) This undried double salt is symbolized as 9-AC•c-**chxn**(I). From the NMR and elemental analyses, its composition was determined to be (9-AC)$_2$c-**chxn**(EtOH)$_{2.1}$. Next, the double salt 9-AC•c-**chxn**(I) was dried *in vacuo* at room temperature for two days. By this drying, the composition changed into (9-AC)$_2$c-**chxn**(EtOH). This double salt is symbolized as 9-AC•c-**chxn**(II). 9-AC•c-**chxn**(II) was further dried *in vacuo* at 65 °C for 15 h. It was found that some EtOH still remained, i.e., (9-AC)$_2$c-**chxn**(EtOH)$_{0.5}$ and this double salt is symbolized as 9-AC•c-**chxn**(III).

Other double salts were similarly prepared by mixing 9-AC with the corresponding diamine and were dried *in vacuo* at room temperature for a few days. The solvents employed for mixing 9-AC and diamine and the ones used for recrystallizing the resulting double salt are summarized in TABLE I, together with the analytical data. It was found that all the double salts studied included some solvent or/and water (see footnotes d - j in TABLE I). Melting points and IR and emission data for the double salt crystals are listed in TABLE II.

TABLE I Solvents used for mixing and for recrystallization and analytical data for the double salts.

double salt	solvent		calcd			found		
	mixing	recrystzn	C	H	N	C	H	N
9-AC•**en**	EtOH + ether	EtOH[a]	71.09	5.97	5.18[d]	70.36	5.76	5.27
9-AC•**tn**	EtOH + ether	EtOH[a]	73.92	6.24	5.07[e]	73.80	6.19	5.00
9-AC•(±)-t-**chxn**	EtOH	EtOH[a]	76.40	6.41	4.81[f]	76.29	6.13	4.70
9-AC•(R,R)-t-**chxn**	MeOH	MeOH[a]	75.23	6.48	4.74[g]	75.49	6.26	4.63
9-AC•c-**chxn**(I)	EtOH	EtOH[b]	73.67	7.17	4.27[h]	73.54	7.08	4.04
9-AC•c-**chxn**(II)	EtOH	EtOH[a]	75.47	6.67	4.63[i]	75.60	6.49	4.69
9-AC•c-**chxn**(III)	EtOH	EtOH[c]	76.40	6.41	4.81[j]	76.35	6.24	4.82

[a] The crystals were dried *in vacuo* at room temperature for a few days. [b] The crystals were not dried. [c] The crystals of 9-AC•c-**chxn**(II) were further dried *in vacuo* at 65 °C for 15 h. [d] For (9-AC)$_2$**en**(H$_2$O)$_2$ or $C_{32}H_{28}O_4N_2$•2.0H$_2$O. The sample was contaminated with a trace amount of 7. [e] For (9-AC)$_2$**tn**(EtOH)$_{0.5}$(H$_2$O)$_{0.6}$ or $C_{33}H_{30}O_4N_2$•0.5EtOH•0.6H$_2$O. [f] For (9-AC)$_2$(±)-t-**chxn**(EtOH)$_{0.5}$ or $C_{36}H_{34}O_4N_2$•0.5EtOH. [g] For (9-AC)$_2$(R,R)-t-**chxn**(MeOH) or $C_{36}H_{34}O_4N_2$•1.0MeOH. [h] For (9-AC)$_2$c-**chxn**(EtOH)$_{2.1}$ or $C_{36}H_{34}O_4N_2$•2.1EtOH. [i] For (9-AC)$_2$c-**chxn**(EtOH) or $C_{36}H_{34}O_4N_2$•1.0EtOH. [j] For (9-AC)$_2$c-**chxn**(EtOH)$_{0.5}$ or $C_{36}H_{34}O_4N_2$•0.5EtOH.

Photolysis of Double Salts

Double salt crystals of 9-AC•**en** were ground into powders in a mortar and 17 mg of the powder was spread between two Pyrex plates. This was placed in our solid-state photolysis vessel (FIGURE 1), which is slightly different in design from the original one.[9] Irradiation was carried out with a 400-W high-pressure mercury lamp under an argon atmosphere for 20 h. During the irradiation, the vessel was cooled from outside by running water. After the photolysis, the reaction mixture was dissolved in MeOH or DMSO-d_6 for HPLC and NMR analyses, respectively, and the yields of products and the recoveries were estimated (TABLE III). Photolyses of other double salts were carried out in a similar manner and the results are summarized in TABLE III.

Among the photoproducts, the head-to-tail dimer of 9-AC (3,4:7,8:9,10:11,12-tetrabenzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene-1,5-dicarboxylic acid) (**1**), anthracene

TABLE II Melting points, carbonyl stretching frequencies, and solid-state emission maxima for the double salts.

double salt	mp, °C	C=O[a]		emission[b]
		ν_{as}, cm^{-1}	ν_s, cm^{-1}	λmax, nm
9-AC•**en**	164-187	1582,1523	1433	459
9-AC•**tn**	153-168.5	1562	1427	447
9-AC•(±)-t-**chxn**	218-227	1554	1428	446,421
9-AC•(R,R)-t-**chxn**	218-220	1555	1428	420
9-AC•c-**chxn**(I)	not measured	1558	1427	425
9-AC•c-**chxn**(II)	237.5-238.5	1558	1427	439
9-AC•c-**chxn**(III)	not measured	1558	1427	449
9-AC	220 (dec)	1681		483

[a]The asymmetric (ν_{as}) and symmetric (ν_{as}) stretching frequencies of the COO$^-$ group (or COOH for 9-AC); in KBr. [b]The solid-state emission maxima; excited at 370 nm.

TABLE III Solid-state photolyses of double salts.

double salt	irrad time, h	product and recovery, %[a]						
		1	**3**	**4**	**5**	**6**	**7**	9-AC
9-AC•**en**	20	0	0	28	17	11	5	35
9-AC•**tn**	20	trace	trace	6	2	2	6	82
9-AC•(±)-t-**chxn**	10	7	8	5	3	3	3	70
9-AC•(R,R)-t-**chxn**	10	3	8	5	8	4	1	70
9-AC•c-**chxn**(I)	10	1	1	1	trace	trace	3	93
9-AC•c-**chxn**(II)	10	14	3	3	1	1	3	73
9-AC•c-**chxn**(III)	10	16	5	5	2	2	2	67
9-AC•**en**	3[b]	62	0	0	0	0	1	31

[a][(moles of product)/(moles of double salt employed)] x 100 % or [(moles of recovered 9-AC)/(moles of double salt employed)] x 0.5 x 100 %. [b]In EtOH.

(**4**), its photodimer (3,4:7,8:9,10:11,12-tetrabenzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene) (**5**), 9,10-dihydroanthracene (**6**), and anthraquinone (**7**) were commercially available (for **4**, **6**, and **7**) or were prepared by the published method (for **1** and **5**). Therefore, these photoproducts were not isolated. The head-to-head dimer of 9-AC (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**) is unstable.[6] It was here prepared[6] only to check its HPLC retention time. HPLC retention times (21 : 79 v/v acetate buffer/MeOH, 1.0 ml/min): **1**, 2.5; 9-AC, 2.9; **2**, 3.3; **3**, 4.7; **7**, 5.1; **6**, 8.6; **4**, 10.4; **5**, 11.3 min. Isolation of the unsymmetrical dimer

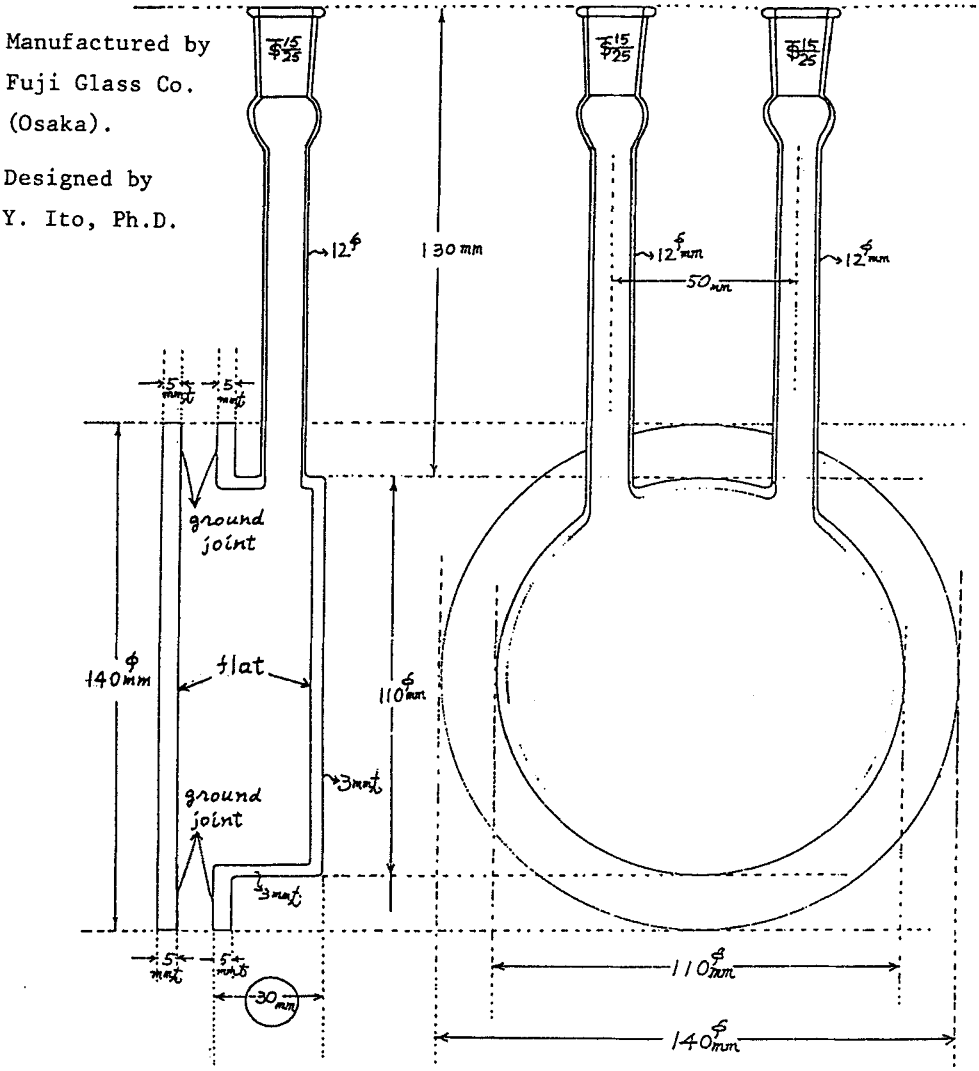


FIGURE 1 Apparatus for solid-state photolysis (Pyrex or quartz).

(3,4:7,8:9,10:11,12-tetrabenzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene-1-carboxylic acid) (**3**) was carried out as follows.

Isolation of **3**

The reaction mixture obtained from photolysis of double salt 9-AC•(±)-t-**chxn** (176 mg) was extracted with 30 mL of a 0.05 M aqueous solution of NaOH. The extract was acidified with 0.1 M HCl solution to pH 4. The resulting browish yellow precipitate was collected by filtration and was dissolved in 10 mL of MeOH/benzene (2 : 1 v/v). Into this solution was added 2 mL of trimethylsilyldiazomethane (10 % in hexane). After being allowed to stand at room temperature for 2 h, the mixture was evaporated and was separated with preparative TLC on silica gel (Merck Kieselgel 60 F_{254}, benzene). The methyl ester of **3** (4.5 mg, 3.5 % yield) was obtained and was recrystallized from hexane/benzene to afford colorless crystals: mp 221-222.5 °C, ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.94 (3 H, s, Me), 4.48 (1 H, d, *J* = 10.5 Hz), 4.63 (1 H, d, *J* = 10.5 Hz), 5.64 (1 H, s), 6.63-6.71 (2 H, m, aromatic), 6.71-7.03 (14 H, m, aromatic); MS m/e (rel intensity) 414 (1, M^+), 236 (100, [9-AC Me ester]$^{\bullet+}$), 178 (100, [anthracene]$^{\bullet+}$), 78 (50); IR (KBr) 1725 (COOMe), 1476, 1454, 1238, 1027, 773, 685, 631 cm^{-1}.

In a separate experiment, the browish yellow precipitate was fractionally crystallized with MeOH, and then with ether to give a mixture of **3** and 9-AC (ca. 1 : 2 w/w). **3**: ^{1}H NMR ($(CD_3)_2SO$, 200 MHz) δ 4.57 (1 H, d, *J* = 10.5 Hz), 4.73 (1 H, d, *J* = 10.5 Hz), 5.52 (1 H, s), 6.71-7.01 (16 H, m, aromatic).

RESULTS AND DISCUSSION

The double salts were prepared by mixing 2 moles of 9-AC with 1 mole of diamine in a suitable solvent. They were usually formed as a precipitate upon mixing the component acids and bases and were recrystallized from alcohol and dried *in vacuo* at room temperature for a few days. From NMR and elemental analyses, the obtained double salt crystals were found to include some solvent or/and water as summarized in TABLE I.

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 the solid-state photolysis vessel and irradiated for 10 - 20 h with a 400-W high-pressure mercury lamp under an argon atmosphere. During the irradiation, the vessel was cooled by running water. After the photolysis, the reaction mixture was dissolved in MeOH or DMSO-d_6 for HPLC and NMR analyses, respectively, and the yields of products and recoveries were estimated. The results are summarized in TABLE III. Most of the amine must have been recovered unchanged, since no significant uncharacterized peaks were present in the NMR and HPLC charts of the reaction mixture.

As TABLE III shows, double salt 9-AC•**en** [= $(9\text{-AC})_2$**en**$(H_2O)_2$ from TABLE I] underwent mainly photodecarboxylation and photoreduction. Main products are anthracene (**4**), its photodimer (**5**), 9,10-dihydroanthracene (**6**), and anthraquinone (**7**), but no photodimers of 9-AC were formed. In ethanol solution, however, 9-AC•**en** was effectively converted to yield the photodimer **1** like the photodimerization of 9-AC in solution.[5,6]

The solid-state photolysis of double salt 9-AC•**tn** [= $(9\text{-AC})_2$**tn**$(EtOH)_{0.5}(H_2O)_{0.6}$] gave a similar result. It produced **4** - **7**, although the yields for **4** - **6** were considerably lower. Formation of the 9-AC photodimers were also negligible.

By contrast, in the case of double salts 9-AC•(±)-t-**chxn** [= $(9\text{-AC})_2$(±)-t-**chxn** $(EtOH)_{0.5}$], 9-AC•(R,R)-t-**chxn** [= $(9\text{-AC})_2$(R,R)-t-**chxn**(MeOH)], and 9-AC•c-**chxn** (II) [= $(9\text{-AC})_2$c-**chxn**(EtOH)], photodimerization of 9-AC did occur, leading to production of the head-to-tail dimer **1** and the unsymmetrical dimer **3** in addition to **4** - **7**. However, formation of the expected head-to-head dimer **2** was undetectable (by HPLC). The dimer **3** was identified as its methyl ester after treatment of the acid with trimethylsilyldiazomethane.[10]

The effect of an enclosed solvent on the solid-state photoreactivity was studied for double salt 9-AC•c-**chxn**. The amount of included EtOH was adjusted by changing the degree of drying. An undried sample 9-AC•c-**chxn**(I) included about two ethanol molecules, i.e., 9-AC•c-**chxn**(I) = $(9\text{-AC})_2$c-**chxn**$(EtOH)_{2.1}$, and its irradiation led to formation of only minor products. On the other hand, the aforementioned dried sample 9-AC•c-**chxn**(II) [= (9-AC)$_2$c-**chxn**(EtOH)] as well as highly dried (at 65 °C *in vacuo*) 9-AC•c-**chxn**(III) [= (9-AC)$_2$c-**chxn**(EtOH)$_{0.5}$] afforded products in much higher yields (TABLE III). This observation suggests that intermolecular distances between 9-AC molecules decreased as the quantity of included EtOH decreased and, as a result, the double salt crystals became more prone to dimerization upon drying.

IR and emission spectra of the double salt crystals were measured. The asymmetric (ν_{as}) and symmetric (ν_s) stretching frequencies of the COO$^-$ group and the wavelengths of the solid-state emission maxima (λmax) are listed in TABLE II. The ν_{as} value for 9-AC •**en** is quite different from that for the other double salts. This difference may be correlated with the unique photoreactivity of 9-AC•**en**, where the extensive photodecarboxylation but no photodimerization of 9-AC occurred (TABLE III).

The emission data likewise seem to be difficult to understand. The author simply notes that the emission maxima for 9-AC•c-**chxn** shifted to longer wavelength with decreasing quantity of included EtOH (TABLE II). This red shift of the emission maxima may be reflecting an increased intermolecular interactions between 9-AC molecules and, hence, may have something to do with the above-mentioned effect of included solvent on the photoreactivity for 9-AC•c-**chxn**. However, because of the lack of crystal structures for the present double salt crystals, the detailed discussion on their solid-state photoreactivities must be awaited at this stage. All attempts to prepare suitable crystals for X-ray crystallography were unsuccessful.

The unsymmetrical dimer **3** may have be formed through photocycloaddition between 9-AC and anthracene (**4**) or through decarboxylation of the elusive head-to-head dimer **2**. This problem also remains to be elucidated.

In conclusion, the head-to-head dimer of 9-AC **2** could not be obtained by the method of double salt formation with diamine. Recently, however, the head-to-head dimer of 9-anthracenepropionic acid has been successfully obtained by the method of double salt formation with (R,R)-t-**chxn** or (S,S)-t-**chxn**. The results will be reported elsewhere.

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