JOC Notes

Unsymmetrical Photodimerization of a 9-Aminomethylanthracene in the Crystalline Salt

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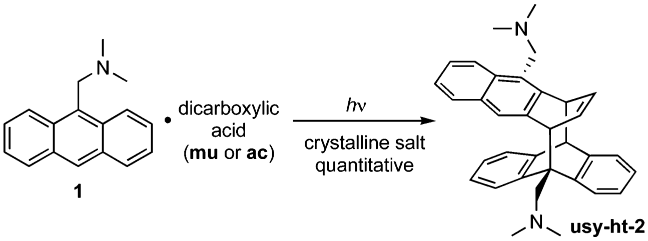
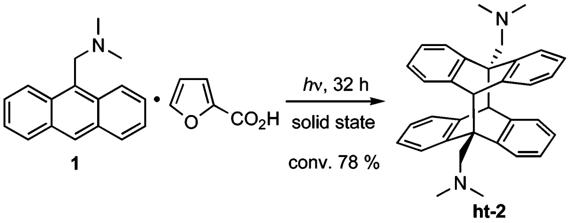


By the salt formation with particular nonaromatic dicarboxylic acids, rapid and selective photodimerization of 9-(*N*,*N*-dimethylaminomethyl)anthracene (**1**) was accomplished in the solid state. For instance, the salt with *trans*,*trans*-muconic acid or acetylenedicarboxylic acid was led quantitatively to the 9,10:4′,1′ photodimer **usy-ht-2**, the first example of the unsymmetrical [4+4] photodimerization of anthracene in the solid state. The reactions were rationalized by the relevant C···C distances between the reacting carbons.

Recently, the study on supramolecular photochemistry has been attracting broad attention.[1] We are exploiting supramolecular two-component crystals with the intention of increasing the variety and diversity of solid-state photochemical reactions,[2] which is still lacking as compared with that in solution.[3] Photodimerization of anthracenes has been studied both in solution[4] and in the solid state.[5] For example, Ihmels et al. have reported that the solid-state irradiation of 9-(*N*,*N*-dimethylaminomethyl)anthracene (**1**) does not result in a photoreaction, while its crystalline salt, with a certain aromatic carboxylic acid (i.e., 2-furancarboxylic acid) is photoreactive to give the head-to-tail dimer **ht-2** (Scheme 1).[5b] It seems to us, however, that the aromatic carboxylic acid is generally not a good candidate to induce the photodimerization of **1** in crystal, because a potential herringbone or stacking interaction[2b] of the aromatic ring of the acid with the anthracene ring of **1** will disturb its photodimerization. Here we will report our recent study on controlling the solid-state photodimerization of **1** by using nonaromatic dicarboxylic acids. The α,ω-dicarboxylic acids of symmetric structures afforded good salt crystals with **1** relatively easily.

SCHEME 1. Previous Reaction Reported by Ihmels et al.[5b]



We employed six dicarboxylic acids, oxalic acid (**ox**), succinic acid (**su**), adipic acid (**ad**), fumaric acid (**fu**), *trans*,*trans*-muconic acid (**mu**), and acetylenedicarboxylic acid (**ac**). Each crystalline salt was obtained by the recrystallization of a 1:0.5 (molar ratio) mixture of **1** and dicarboxylic acid from MeOH or *i*-PrOH. As summarized in Table 1, crystalline salts with the 1:0.5 or 1:1 stoichiometry of amine/dicarboxylic acid were obtained. Salt **1ac** crystallized out with or without inclusion of methanol (**1ac**·MeOH or **1ac**, respectively), depending on the solvent used. The composition of the **1**/acid in the salt was determined on the basis of the ^{1}H NMR and elemental analysis. Salt formation was ascertained with the IR spectroscopy from which the carbonyl absorption of the carboxylate anion was observed at 1560−1624 (asymmetric stretch) and 1326−1405 cm^{-1} (symmetric stretch).

First, as a control experiment, solution photolysis of **1** was conducted with 0.018 M of **1** in MeOH under an Ar atmosphere at 5 °C. Irradiation was performed with a 400-W high-pressure mercury lamp through a Pyrex filter. As shown in Scheme 2, free amine **1** yielded **ht-2** together with lepidopterene (**3**)[6] and **4**. The formation of **3** and **4** was explained previously by considering, respectively, head-to-tail and head-to-head coupling

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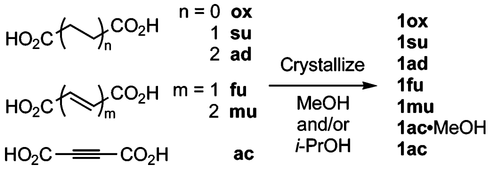
10.1021/jo060315i CCC: $33.50

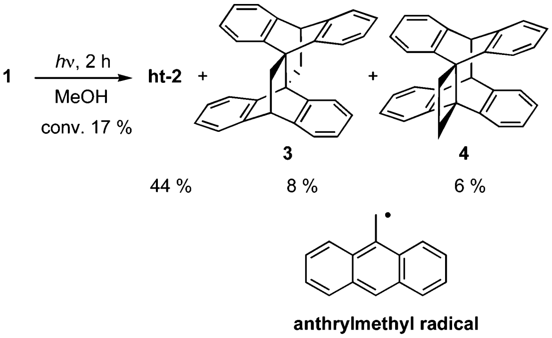
TABLE 1. Preparation of the Crystalline Salts



salt	solvent	composition **1**/acid
1ox	MeOH	1:1
1su	MeOH	1:0.5
1ad	*i*-PrOH	1:1
1fu	MeOH	1:0.5
1mu	MeOH	1:0.5
1ac•MeOH	MeOH	1:0.5:0.5 MeOH[a]
1ac	MeOH/*i*-PrOH (1:2)	1:0.5

[a] MeOH is included in the crystal lattice.

SCHEME 2. Solution Photolysis of 1[a]

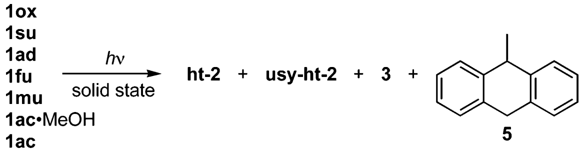


[a] Product yields are based on the consumed reactant.

of the anthrylmethyl radical intermediate photogenerated from **1**.[7] The conversion of **1** was low (17%), probably because intramolecular electron transfer from the basic nitrogen to the anthracene moiety quenched the responsible excited state. In fact, in the presence of the added acid, **ac** (molar ratio **ac**/**1** = 0.5), the conversion remarkably increased up to ~100% (yield: **ht-2**, 41%; **3**, 7%; **4**, 9%).

Results for the solid-state photolysis are summarized in Table 2. Free amine **1** recrystallized from *i*-PrOH was almost photoinert, as reported by Ihmels et al.[5b] Only a trace of anthraquinone was produced by the photolysis (5 h).[8] By contrast, the salt **1ox** underwent complete conversion to yield the dimer **ht-2** quantitatively. Thus, compared with the solution photoreaction of **1** (Scheme 2), much more selective dimerization was accomplished. In the case of **1su**, **1ad**, and **1fu**, the reactions were not as effective as **1ox**. Lepidopterene (**3**) and a reduced product **5** were produced in low yields from the salt **1su**, whereas **1ad** and **1fu** showed no reactivity. Interestingly, **1mu** and **1ac**·MeOH underwent unsymmetrical dimerization in the 9,10:4′,1′ cycloaddition manner. In both cases, the dimer **usy-ht-2** was selectively formed with high conversions. As will be discussed later in more detail, this unsymmetrical photodimerization of anthracene derivatives in the solid state is unprecedented, while the analogous reactions are known to occur in solution.[9,10] On the contrary to the salt **1ac**·MeOH, the corresponding salt without included MeOH (**1ac**) gave **ht-2** and **3**, but no **usy-ht-2**.

TABLE 2. Solid-State Photolysis of the Crystalline Salts[a]



salt	irrad. time (h)	conv. (%)	yield[b] (%)			
			ht-2	**usy-ht-2**	**3**	**5**
1ox	2	100	100	0	0	0
1su	5	37	0	0	35	5
1ad	5	9	0	0	0	0
1fu	5	0	0	0	0	0
1mu	5	85	0	100	0	0
1ac•MeOH	5	73	0	100	0	0
1ac	5	100	51	0	18	0

[a] Pulverized salts were irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter under an Ar atmosphere at 3−7 °C. [b] Yields are based on the consumed reactant.

Upon irradiation, anthracenes generally yield symmetric head-to-tail or head-to-head dimers, that is, 9,10:10′,9′ or 9,10:9′,10′ [4+4] cycloadducts, respectively.[4,5] In addition, they sometimes undergo unsymmerical photodimerization to give 9,10:4′,1′ or 9,10:1′,4′ [4+4] cycloadducts[9,10] and 9,10:1′,2′ [4+2] cycloadducts.[4a,b] Very recently, formation of a novel 1,2:2′,1′ [2+2] cycloadduct has been reported.[11] In the solid state, however, only the symmetric [4+4] dimerization reactions have been reported to date.[5] Therefore, to the best of our knowledge, formation of **usy-ht-2** is the first example of the solid-state unsymmetrical photodimerization of anthracenes.

To rationalize the observed solid-state photoreactivity of the salts, the X-ray diffraction studies were carried out. Suitable single crystals could be obtained with **1ox**, **1su**, **1ad**, **1mu**, **1ac**·MeOH, and **1ac**. Their crystal structures (see Figure 1 and Supporting Information) except that of **1ad** consist of two layers: one is formed from the anthracene moiety and another from the dicarboxylic acid and the amino moiety. For **1ac**·MeOH, the methanol molecule is included in the latter layer.

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(8) We successfully solved the crystal structure of **1**, but this was published recently by Howie, R. A.; Wardell, S. M. S. V. *Acta Crystallogr.* **2005**, *E61*, o1686-o1688. The neighboring anthracene rings are not arranged face-to-face, which is in agreement with its low photodimerization reactivity in the solid state.

(9) The unsymmetrical intramolecular dimerizations of covalently linked bisanthracenes, some of which proceed quantitatively, have been known. (a) Felix, G.; Lapouyade, R.; Bouas-Laurent, H.; Clin, B. *Tetrahedron Lett.* **1976**, *26*, 2277−2278. (b) Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Nouv. J. Chim.* **1979**, *3*, 231−237. (c) Bouas-Laurent, H.; Castellan, A.; Daney, M.; Desvergne, J.-P.; Guinand, G.; Marsau, P.; Riffaud, M.-H. *J. Am. Chem. Soc.* **1986**, *108*, 315−317. (d) Desvergne, J.-P.; Bitit, N.; Castellan, A.; Webb, M.; Bouas-Laurent, H. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1885−1894. (e) Marquis, M.; Desvergne, J.-P.; Bouas-Laurent, H. *J. Org. Chem.* **1995**, *60*, 7984−7996.

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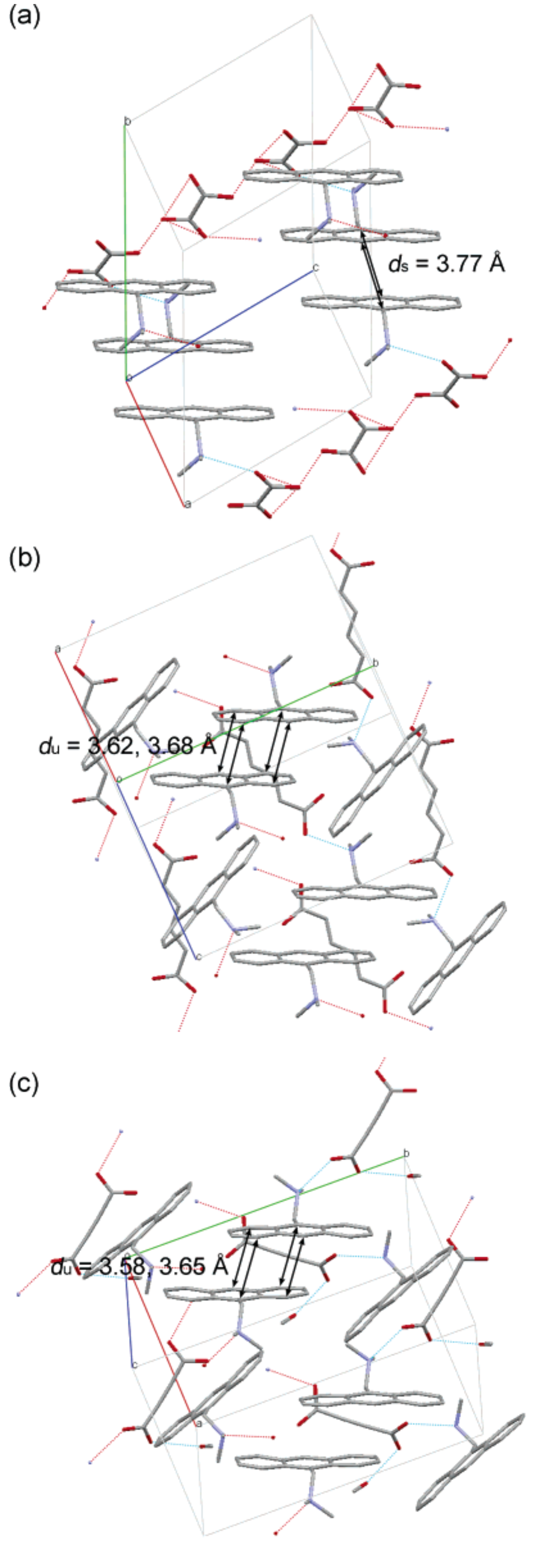
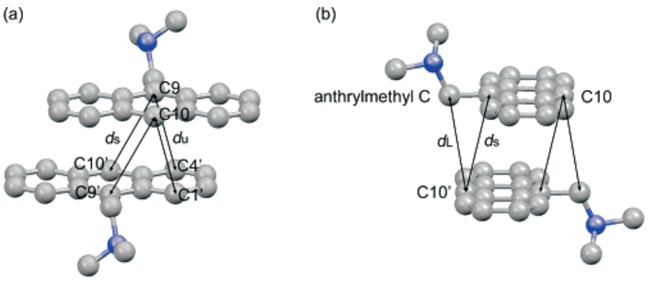


FIGURE 1. Crystal packing in the salts (a) **1ox**, (b) **1mu**, and (c) **1ac•**MeOH. Hydrogen atoms are omitted.

The packing behavior of the molecule **1** in the crystals of **1mu** and **1ac**·MeOH is very similar. In all the cases, there is a pair of anthracene rings, which are arranged parallel and face each other in a head-to-tail fashion. These situations are different from the Ihmels' salts ((a) **1**·4-nitrobenzoic acid, (b) **1**·2-furancarboxylic acid, and (c) **1**·9-anthracenecarboxylic acid), where the nearest anthracene rings are twisted to each other for (b) and (c), and only (b) is packed so as to yield **ht-2** slowly, while (a) and (c) are photoinert.[5b] From our own inspection of their crystal packing, the aromatic acids in (a)−(c) are interacting with **1** in a herringbone (C−H···π) or stacking mode.

TABLE 3. Distances d_s, d_u, and d_L for the Nearest Faced Anthracene Moieties



	d_s (Å)		d_u (Å)		d_L (Å)	
salt	A	B	A	B	A	B
1ox	3.77		3.86, 3.90		3.62	
1su	3.93		3.64, 3.64		3.85	
1ad	4.84		3.90, 3.93		4.51	
1mu	4.78		3.62, 3.68		4.89	
1ac•MeOH[a]	4.85	5.26	3.58, 3.65	3.79, 3.88	4.86	5.35
1ac	3.94		3.64, 3.67		3.92	

[a] Salt **1ac•**MeOH contains two independent molecules of **1** in the asymmetric unit.

The distances between reacting points for symmetric (d_s) and unsymmetrical (d_u) dimerization and for the formation of **3** (d_L) are listed in Table 3. The value d_s refers to the C9···C10′ or C10···C9′ separation, d_u to the C9···C4′ or C10···C1′ separation, and d_L to the anthrylmethyl carbon···C10′ separation. In the salt **1ox**, which yielded **ht-2** quantitatively, the distance d_s is quite short (3.77 Å), and, hence, the normal symmetric photodimerization may well occur efficiently. In other salts, because d_s is longer (>3.93 Å), the efficiency for the formation of **ht-2** should drop, thereby leading to the occurrence of other reactions. Thus, for **1su** and **1ac**, where the distance d_L is relatively short (3.85 Å and 3.92 Å), lepidopterene (**3**) may be formed through the competitive C−N bond homolysis followed by the coupling of two anthrylmethyl radicals.[7] For **1mu** or **1ac•**MeOH, although both d_s and d_L are large, the distance d_u is short (3.58−3.68 Å), resulting in the selective formation of **usy-ht-2**. In **1ad**, because the two anthracene moieties are considerably separated from each other in the oblique direction, all the distances, d_s, d_u, and d_L, are long. Hence, **1ad** should be photoinert.

The reason for **1mu** and **1ac•**MeOH to take the similar packing pattern to yield **usy-ht-2** is a profound issue. Both of the molecules, **mu** and **ac**, are packed with an approximately planar geometry. Although **ac** is spatially less-demanding than **mu** (the intramolecular distances between the carboxylic carbons for **mu** and **ac** are 6.32 and 4.13 Å, respectively), the methanol molecule in the **ac** layer is making up for the room. Phenomenologically, we point out that the carbon chains of **mu** (diene) and **ac** (alkyne) have higher unsaturation than that of other acids (**ox**, **su**, **ad**, and **fu**; none, alkane, alkane, and alkene) and has lower unsaturation than the Ihmels' case (aromatics). Therefore, it appears that the intermediate unsaturation of the acid component brought about a higher chance of the unsymmetrical photodimerization of **1**, that is, a small lateral deviation from the normal stacking, leading to the **usy-ht-2** rather than **ht-2** formation.

Finally, we examined the thermal stability of **usy-ht-2**, because the chemistry of intermolecular unsymmetrical anthracene dimers has rarely been reported. This compound dissociated quantitatively to monomer **1** within 0.5 h at 100 °C in DMSO-d_6. From the kinetic plot, the first-order rate constant at 40 °C was calculated as $k = 4.8 \times 10^{-6}\ \mathrm{s}^{-1}$. Therefore, **usy-ht-2** seems more labile than the corresponding unsymmetrical photodimer of methyl 9-anthracenecarboxylate ($t_{1/2} \sim 3$ h at 100 °C in DMF).[10c]

In conclusion, we achieved the rapid and selective photodimerization of **1** in the solid state by utilizing salt formation with particular dicarboxylic acids. The crystalline salt **1ox** yielded **ht-2**, and **1mu** and **1ac**·MeOH yielded **usy-ht-2** quantitatively. From the crystal structures of these salts, we rationalized their solid-state reactivities.

Experimental Section

Materials. The detailed synthetic procedure for 9-(*N*,*N*-dimethylaminomethyl)anthracene (**1**) is described in Supporting Information. All dicarboxylic acids and all solvents for crystallization are available from commercial sources.

Preparation of Crystalline Salts. A warm solution containing **1** and acid (molar ratio 1:0.5) in suitable solvent (Table 1) was allowed to stand at room temperature. After a few days, the corresponding salt crystals appeared. They were collected by filtration and dried in vacuo. The composition of the **1**/acid of the salt was determined on the basis of the ^{1}H NMR and elemental analysis. Further details are described in Supporting Information.

Photoirradiation. Irradiation was carried out with a 400-W high-pressure mercury lamp. A solution sample was placed in a Pyrex test tube. After bubbling Ar gas for 0.5 h, the tube was sealed with a rubber septum and was irradiated. A powdered solid sample was sandwiched between two Pyrex plates and was set in our solid-state photolysis vessel[2a,b] or in a polyethylene bag.[3b,d] In either case, the irradiation was carried out under an Ar atmosphere. During the irradiation, the samples were cooled by refrigerated circulating water (3−7 °C).

The yields of the photoproducts were estimated by measuring the ^{1}H NMR spectra of the reaction mixture immediately after the photolysis. The products were separated by thin-layer or column chromatography on silica gel. The data for the compound characterization are summarized in Supporting Information.

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Supporting Information Available: Synthetic procedures for **1** and the crystalline salts. Spectral data of the products **ht-2**, **usy-ht-2**, **3**, **4**, and **5**. Dissociation kinetics of **usy-ht-2**. The X-ray crystal data and the CIF format for the salts **1ox**, **1su**, **1ad**, **1mu**, **1ac**•MeOH, and **1ac** and the dimer **usy-ht-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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