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CATION TO ANION TRIPLET-TRIPLET ENERGY TRANSFER IN CRYSTALLINE ORGANIC SALTS

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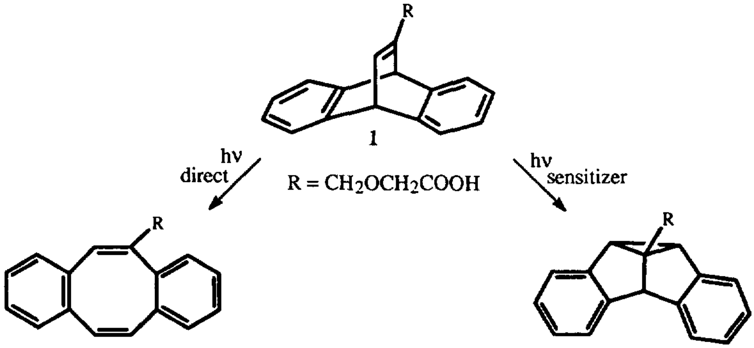
Abstract. Irradiation of crystalline salts formed between sensitizer-linked amines and photochemically reactive carboxylic acids at wavelengths where only the sensitizers absorb leads to characteristic triplet state reactivity of the carboxylate anions. Copyright © 1996 Elsevier Science Ltd

Recent work from our laboratories has been concerned with applying the "ionic auxiliary" concept to solid state organic photochemistry—an approach designed to overcome the difficulties associated with bringing together two dissimilar organic moieties in the crystalline state for the purpose of observing a chemical interaction between them.[1] Suppose, for example, that one wished to carry out a triplet-sensitized photoreaction in the crystalline state. One approach would be to look for a sensitizer that formed a continuous solid solution with the reactant—an unlikely prospect for most sensitizer-quencher combinations.[2] In the ionic auxiliary approach, however, a sensitizer-linked amine and a quencher-linked carboxylic acid (or *vice versa*) could be crystallized together in the form of a salt, a natural two component supramolecular assembly. In this communication we report the first successful use of such *ionic sensitizers* in the crystalline state.

Our first task was to select a probe molecule—a carboxylic acid (or amine) whose triplet excited state reactivity is unique, so that the appearance of the characteristic triplet product(s) serves as an indication of successful energy transfer. 9,10-Ethenoanthracene derivatives appeared to be promising candidates. Such compounds are well known to undergo triplet-sensitized di-π-methane photochemistry to form dibenzosemibullvalene derivatives, whereas direct (singlet state) irradiation typically produces dibenzocyclooctatetraenes;[3] both processes have been shown to occur in the crystalline state as well as in solution.[4] After some experimentation, we selected carboxylic acid derivative **1** (Scheme) as the probe molecule. This material was readily available from 11-hydroxymethyl-9,10-dihydro-9,10-ethenoanthracene, a known compound,[5] and its photochemistry fulfilled the requirements set out above in that acetone-sensitized photolysis utilizing a Pyrex filter afforded a 72:28 mixture of dibenzosemibullvalene derivatives **2** and **3**, whereas direct irradiation at 254 nm in acetonitrile gave mainly COT derivative **4** (77%) along with a lesser amount of **2** (23%).[6] Direct photolysis of compound **1** in the crystalline state (in the form of its methyl ester, mp 71-73 °C) likewise led mainly to COT **4**. After 2 hours of irradiation the conversion was 7%, and according to gas chromatography, the products consisted of 6% of **4** and 1% of **2**.

The next task was to select the sensitizer-linked amines. Among many possible candidates, 3-dimethylaminopropiophenone (**5**), 4-acetylpyridine (**6**) and 4'-piperazinoacetophenone (**7**) were chosen, primarily on the basis of their acetophenone-like chromophores and their commercial availability (Aldrich). Salts were formed between acid **1** and each of the sensitizer amines by adding an ethyl acetate solution of the acid to an ethanol solution of the amine and collecting the resulting precipitate. The salts were sharp melting, crystalline materials that were fully characterized by conventional methods; the melting points and anion:cation ratios are given in Table 1. In all three cases, X-ray crystal structures were successfully obtained.[7]



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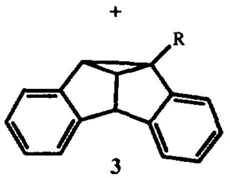

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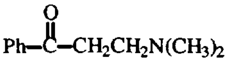

$Ph-\overset{O}{\overset{\|}{C}}-CH_2CH_2N(CH_3)_2$

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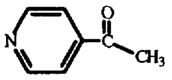

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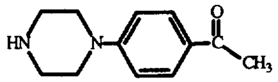

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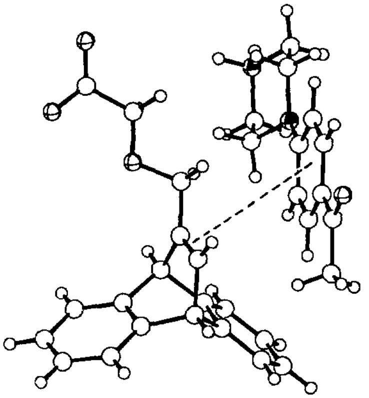
Table 1 also summarizes the results obtained when each of the salts was photolyzed in the solid state. The crystals were crushed between microscope slides, sealed under nitrogen in polyethylene bags and irradiated at λ > 330 nm where only the sensitizers absorb. Conversions were kept below 20% in order to minimize sample melting and other complications that might arise from photoproduct buildup. As can be seen from the table, characteristic triplet excited state behavior was observed for each salt, with **2**:**3** product ratios similar to those observed in the acetone-sensitized solution phase irradiations. We take these results as a clear indication that triplet-triplet energy transfer from cation to anion has occurred in the crystalline state.

Table 1. Salts studied and solid state photolysis results[a]

Salt	Anion to Cation Ratio	mp (° C)	hυ time (h)	Anion to Cation Distance[b] (Å)	Photoproduct Composition (%) 1	2	3	4
1•5	1:1	65-66	9	4.03	93	6	1	0
1•6[c]	2:1	112-114	9	5.39	94	5	1	0
1•7	1:1	143-145	8	4.11	81	15	4	0

[a]Photolyzed at $\lambda > 330$ nm, where only the sensitizers absorb; photolysate composition determined by capillary gas chromatography following diazomethane workup of reaction mixtures; the **2**:**3** ratios in each case are probably not significantly different within experimental error. [b]Closest approach between the center of the aromatic ring of the sensitizer and the mid-point of the ethenoanthracene double bond as determined by X-ray crystallography. [c]the X-ray crystal structure shows that this material is best described as a non-ionic hydrogen-bonded complex rather than a salt.

Amine **7** was clearly the best sensitizer of those tested. Its solid state reaction was not only more efficient than the others but was cleaner as well (fewer minor peaks on GC). The efficiency of this amine may stem in part from its very high molar extinction coefficient at the wavelengths employed; salt **1•7** exhibited an ε of 20,700 at a λ_{max} (methanol) of 325 nm.[8] Another factor that undoubtedly contributes to the efficiency of energy transfer in the case of salt **1•7** is the excellent donor-acceptor arrangement in the crystal. As shown in the X-ray crystal structure-derived figure at the right, the aromatic ring of the sensitizer is close (4.11 Å, dotted line) to the ethenoanthracene double bond.[9]



Each of the salts was also photolyzed at $\lambda >$ 330 nm in methanol at a concentration of 10^{-2} to 10^{-3} M. Under these conditions, conversions were 1-2% after 6 h, with mixtures of photoproducts **2** and **3** being formed. We assume that the dissociated salts are too dilute to allow much energy transfer to take place during the excited state lifetimes of the sensitizers.

In conclusion, the success of the ionic sensitizer concept demonstrated above significantly widens the scope of solid state organic photochemistry. Photochemists can now investigate both the triplet as well as the singlet excited state properties of molecules embedded in crystal lattice matrices and carry out crystal structure-reactivity correlation studies for reactions that were previously inaccessible. Given the success of the sensitization experiments, there is every reason to think that competitive quenching of reactive excited states will also be possible in the crystalline state.

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References and Footnotes

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2. See, however, Garcia-Garibay, M.; Scheffer, J.R.; Trotter, J.; Wireko, F. *Tetrahedron Lett.* **1987**, *28*, 1741.
3. (a) Such singlet-triplet reactivity differences are characteristic of ethenoanthracenes that do not possess carbonyl-containing substituents attached to the bridging double bond. See Scheffer, J.R.; Yang, J. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W.M.; Song, P-S., Eds.; CRC Press: Boca Raton, FL, 1995, Chapter 16; (b) For a recent, general review of the di-π-methane photorearrangement, see Zimmerman, H.E. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991, vol. 11, Chapter 1.
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6. Photoproducts **2**, **3** and **4** were isolated and characterized as the corresponding methyl esters following diazomethane treatment of the photolysis mixtures. All new compounds reported in this communication gave satisfactory elemental analyses and exhibited spectroscopic data fully in accord with their assigned structures. The **2**:**3** photoproduct ratio is normal.[3a]
7. Salt **1•5**: C2/c; $a = 37.712(3)$, $b = 8.977(1)$, $c = 15.922(1)$ Å; $\beta = 92.055(6)^\circ$; $Z = 8$; $R = 4.5\%$. Complex **1•6**: P1; $a = 12.344(1)$, $b = 18.439(3)$, $c = 8.2721(7)$ Å; $\alpha = 101.789(9)$, $\beta = 94.525(8)$, $\gamma = 95.05(1)^\circ$; $Z = 2$; $R = 5.1\%$. Salt **1•7**: P1; $a = 9.760(1)$, $b = 16.254(2)$, $c = 9.114(1)$ Å; $\alpha = 99.47(1)$, $\beta = 109.17(1)$, $\gamma = 88.10(1)^\circ$; $Z = 2$; $R = 4.4\%$. Full crystallographic details will be published separately.
8. A negative feature of the high molar extinction coefficient of salt **1•7** is a very shallow photon penetration depth within the crystal. For this reason, it is important that finely crushed samples be used.
9. Whether the double bond is more relevant for energy transfer than one of the benzo rings of substrate **1** is a moot point. For adducts in which the bridging double bond bears conjugating substituents, this site is certainly implicated as the locus of initial excitation.

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