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Bimolecular Solid-State Photoreactions in the Adduct Crystals of an Aromatic Nitro Compound with an Aromatic Amine

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Key words: solid-state photochemistry, adduct crystal, donor-acceptor complex

Abstract: Solid-state as well as solution-state photochemistry of the donor-acceptor complexes derived from an aromatic amine and an aromatic nitro compound was investigated. Of the twelve adduct crystals studied, only three involving m-DNB as the acceptor (9-MC/m-DNB, 9-EC/m-DNB and DMAP/m-DNB) were found to be photoreactive in the solid state, producing photoredox products probably through hydrogen abstraction by the excited nitro group. The FT-IR study has implicated that the NO_2 group of m-DNB may be interacting with the donor's amino group in the crystalline state.

We have been studying the photochemistry of organic multi-component crystals for a decade.[1] Recently the chemistry of multi-component crystals including hydrogen-bonded cocrystals, mixed crystals, host-guest complexes, salts, and donor-acceptor complexes has been attracting considerable attention from broad aspects of chemistry, biology, and materials science, e.g., solid-state molecular recognition, asymmetric synthesis in the solid state, and applications to organic conductors, superconductors, photoconductors, ferromagnets and nonlinear optical materials.[2-9] We noticed the fact, however, that little was known about the solid-state photoreactivities of charge-transfer complexes. Here, we report the photoreactions of the adduct crystals derived from an aromatic amine (donor) and an aromatic nitro compound (acceptor). The formation of donor-acceptor complexes between amines and nitro compounds have been long known.[10]

Cocrystallization of an aromatic amine (9-methylcarbazole (9-MC), 9-ethylcarbazole (9-EC), 9-isopropylcarbazole (9-IC), 9-benzylcarbazole (9-BC), 4-dimethylaminopyridine (DMAP), N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD)) and an aromatic nitro compound (o-, m-, p-dinitrobenzene (o-, m-, p-DNB)) from a suitable solvent afforded colored crystals (Table I). All these donor-acceptor systems exhibited the CT absorption bands in the visible region under high concentration conditions in acetonitrile (2.5×10^{-2} M), as exemplified by the system 9-MC/m-DNB (Figure 1a). In a dilute solution (2×10^{-5} - 2×10^{-4} M), however, the CT absorption bands were invisible in all cases (e.g., Figure 1b). The melting points of these adduct crystals are very broad except for those of 9-MC/m-DNB, 9-EC/m-DNB, 9-IC/m-DNB and TMPD/m-DNB (Table I). This may be ascribed to the inhomogeneities of the crystalline samples, probably due to the coexistence of molecular compounds and their individual components.

The adduct crystals were ground into a powder in a mortar and 30 mg of the powder was spread between two Pyrex plates and photolyzed at 4 °C for 5 h under a nitrogen atmosphere. Irradiation was carried out with a 400-W high-pressure mercury lamp. With the intention of comparison, photolyses in solution (30 mg of each adduct crystal in 10 mL of acetonitrile) were also carried out under similar conditions. The product mixtures were separated by using column or thin-layer chromatography and the results are summarized in eqs 1 - 3 and Table II.

The adducts derived from 9-MC or 9-EC as the donor and m-DNB as the acceptor underwent photochemical reactions in the solid state, but essentially did not in acetonitrile solution. In the cases of the crystals such as 9-MC(or 9-EC)/o-DNB(or p-DNB), 9-IC/m-DNB, 9-BC/m-DNB and TMPD/m-DNB, however, no photoreaction occurred in either the solid or solution phase.

The crystals involving DMAP as the donor contrast with the carbazole series in that the reaction was more efficient in solution than in the solid state. In solution, all three DMAP/DNB combinations were photoreactive. In the solid state, however, the photoreaction took place only for DMAP/m-DNB.

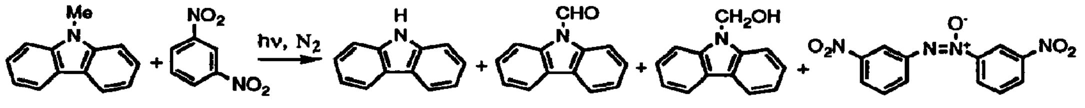
The products described in eqs 1 - 3 and Table II were probably formed through hydrogen abstraction by the excited nitro group. A possible reaction mechanism is illustrated in Scheme I.[11,12]

We have measured the FT IR spectra of the adducts and the DNBs both in the solid state (KBr) and in solution (5 x 10^{-2} M in chloroform) and examined the changes in the NO_2 group frequencies (Table III). Inspection of Table III readily shows that, in chloroform, no shifts are observable in ν_{as} and ν_s. In the KBr disc, however, ν_{as} and ν_s for the adduct crystals 9-MC/m-DNB, 9-EC/m-DNB, 9-IC/m-DNB and DMAP/m-DNB are red-shifted by 2 - 8 cm^{-1} as compared with those for m-DNB. This red shift may implicate that the acceptor's NO_2 group is interacting with the donor's amino group in these adduct crystals.[13] Therefore, it is interesting to note in Table II that only the three adducts involving m-DNB as the acceptor, i.e., 9-MC/m-DNB, 9-EC/m-DNB and DMAP/m-DNB, show the solid-state photoreactivity. Based on the fact that m-DNB crystallizes in a polar space group whereas there are no polar axes in the o- and p-DNB crystals,[14] we assume that polar donor molecules (9-MC, 9-EC, and DMAP) are relatively easily incorporated into the polar m-DNB crystals to form molecular compounds. It is likely that the adduct crystals prepared from o- or p-DNB are, at least in part, a simple mixture of the crystals of the components. Further studies by employing 3,5-dinitrobenzoic acid and 3,5-dinitrobenzonitrile as the acceptor and a variety of carbazoles as the donor are in progress.

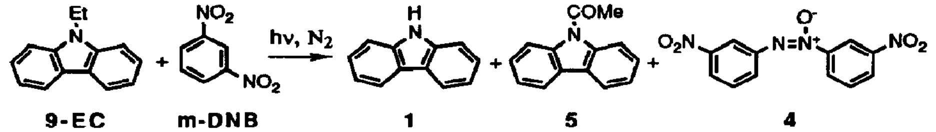
Table I. Adduct Crystals Studied Here.

donor (D)	acceptor (A)	ratio of dissolved D and A[a]	recrystallizn solvent	adduct crystals		
				color	D/A ratio[b]	mp,°C[c]
9-MC	m-DNB		chloroform	orange-yellow	1:1	49-49.5
9-MC	o-DNB		acetonitrile	pale yellow	1.1:1	66-106
9-MC	p-DNB	2.3:1	acetone	pale brown	1.3:1	69-172
9-EC	m-DNB		AcOEt	yellow	1:1	48.5-49
9-EC	o-DNB	1.5:1	acetone	pale yellow	0.9:1	54-103
9-EC	p-DNB	1.8:1	acetone	pale brown	1.2:1	62-167
DMAP	m-DNB		CH_2Cl_2	yellow	0.9:1	58-82
DMAP	o-DNB		AcOEt	yellow	1:1	74-103
DMAP	p-DNB	1.5:1	acetone	dark brown	1.3:1	98-168
9-IC	m-DNB		chloroform	orange-yellow	1:1	81-82
9-BC	m-DNB		chloroform	yellow	0.7:1	56-80
TMPD	m-DNB		AcOEt	black-violet	1:1	71-73

[a] 1 : 1, unless otherwise specified. [b] Estimated by NMR and elemental analyses. [c] Mp's (°C) of D and A: 9-MC 90-92; 9-EC 68-70; DMAP 112-114; 9-IC 123; 9-BC 118-120; TMPD 49-51; m-DNB 88-90; o-DNB 117-119; p-DNB 172-174.



(1)



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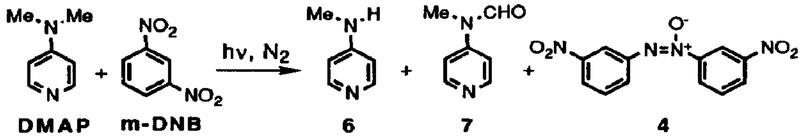


(3)

Table II. Photoreactivity of Adduct Crystals in the Solid State and in Solution (MeCN).

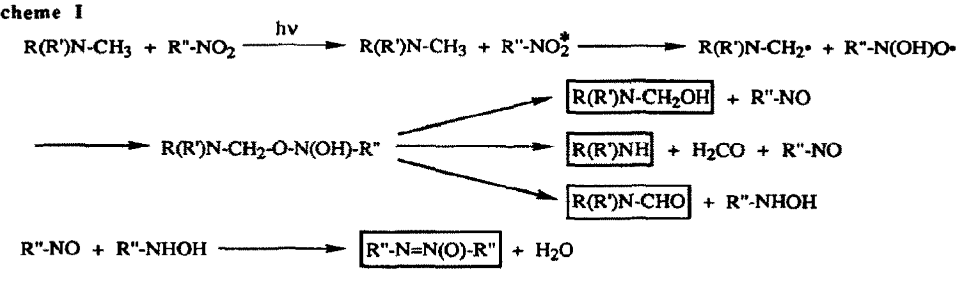
adduct crystals	solid	solution	adduct crystals	solid	solution
9-MC/m-DNB	yes[a]	trace	DMAP/m-DNB	yes[c]	yes[d]
9-MC/o-DNB	no	no	DMAP/o-DNB	no	yes[e]
9-MC/p-DNB	no	no	DMAP/p-DNB	no	yes[f]
9-EC/m-DNB	yes[b]	no	9-IC/m-DNB	no	no
9-EC/o-DNB	no	no	9-BC/m-DNB	no	no
9-EC/p-DNB	no	no	TMPD/m-DNB	no	no

[a] **1**, 8; **2**, 10; **3**, 25; **4**, 23 %. [b] **1**, 21; **5**, 7; **4**, 10 %. [c] **6**, 23; **7**, 8; **4**, 2 %. [d] **6**, 36; **7**, 6; **4**, 16 %. [e] **6**, 11; **7**, 7 %. [f] **6**, 20; **7**, 8; 4,4'-dinitroazoxybenzene, 5 %. (Yields are based on the initial amount of the starting materials. A significant amount of the starting materials remained unreacted.)

Table III. The Asymmetric (ν_{as}) and Symmetric (ν_s) Stretching Frequencies for the NO_2 Group.

	KBr, cm^{-1}		$CHCl_3$, cm^{-1}	
	ν_{as}	ν_s	ν_{as}	ν_s
m-DNB	1541	1349	1542	1347
9-MC/m-DNB	1536	1341	1542	1347
9-EC/m-DNB	1537	1344	1542	1347
9-IC/m-DNB	1537	1344	1542	1347
DMAP/m-DNB	1538	1347	1542	1347
o-DNB	1528	1354	1545	1351
9-MC/o-DNB	1528	1354	1545	1351
9-EC/o-DNB	1528	1354	1545	1350
DMAP/o-DNB	1527	1354	1545	1351
p-DNB	1559	1345	1554	1341
9-MC/p-DNB	1559	1347	1554	1340
9-EC/p-DNB	1559	1340	1554	1341
DMAP/p-DNB	1560	1345	1554	1341

Scheme I



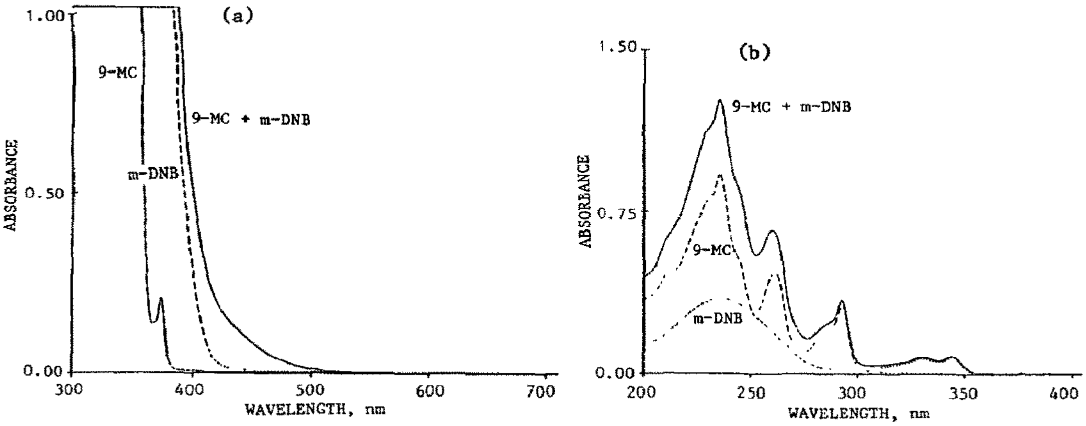


Figure 1. Absorption spectra of the system 9-MC/m-DNB in acetonitrile (path length, 1 cm). (a) 9-MC, 2.5 x 10^{-2} M; m-DNB, 2.5 x 10^{-2} M. (b) 9-MC, 2.0 x 10^{-5} M; m-DNB, 2.0 x 10^{-5} M.

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13. In fact, the X-ray analysis of the adduct crystal of 9-MC with 3,5-dinitrobenzoic acid demonstrated a heterosoric stacking of the donor and acceptor molecules with the orientation that allows the interaction between the amino and the NO_2 groups. The details will be published later. The adduct crystals listed in Table I were too small to carry out the X-ray study. For the hydrogen-bond interaction between nitro and amino groups, see T. W. Panunto, Z. Urbánczyk-Lipkowska, R. Johnson, and M. C. Etter, *J. Am. Chem. Soc.* **1987**, *109*, 7786-7797.
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