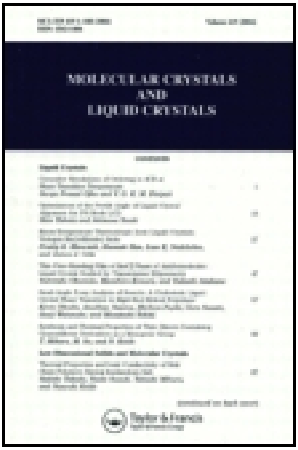

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Photoreactivities of Donor-Acceptor Crystals between 3,5-Dinitrobenzoic Acid and N-Alkylcarbazoles

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PHOTOREACTIVITIES OF DONOR-ACCEPTOR CRYSTALS BETWEEN 3,5-DINITROBENZOIC ACID AND N-ALKYLCARBAZOLES

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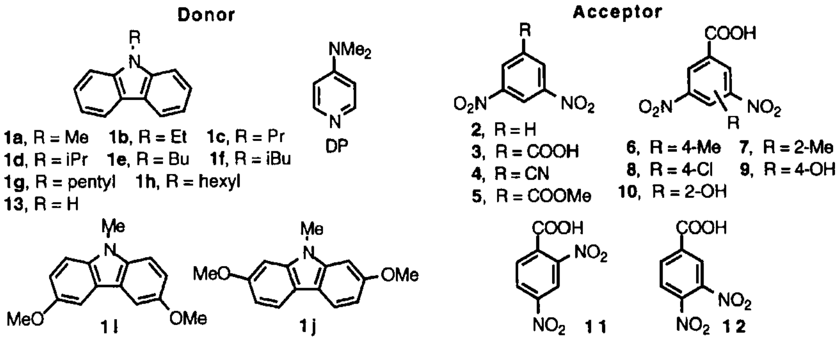
Abstract A variety of 1 : 1 charge-transfer (CT) crystals were prepared by using mainly dinitrobenzoic acids (as the acceptor) and carbazoles (as the donor). Most of the CT crystals prepared from 3,5-dinitrobenzoic acid (**3**) and a series of N-alkylcarbazoles (**1a-1h**) underwent photoredox reactions initiated by the excited nitro group, leading to α-oxidation of N-alkyl groups (**13 - 15**). The reactions were much more efficient in the solid state than in solution. These solid-state photoreactivities could be, on the whole, correlated with the C•••O distances between the carbazole N-α-carbon atom and the nitro oxygen atoms nearby.

Keywords solid-state photoreactivity; charge-transfer crystals; donor-acceptor crystals; 3,5-dinitrobenzoic acid; N-alkylcarbazoles

INTRODUCTION

Although studies on the chemical and physical properties associated with charge-transfer (CT) crystals are basis for materials science,[1] their solid-state photoreactions have been little studied so far.[2] We have already communicated the solid-state photoreactions of the adduct crystals that were prepared from ortho-, meta-, or para-dinitrobenzene (acceptor) and an aromatic amine (donor).[3] These adducts failed to grow into suitable crystals in size and quality for X-ray structure analysis. Further studies, however, have shown that the acceptors such as 3,5-dinitrobenzoic acid (**3**) and its derivatives (**4-10**) can form usually good CT adduct crystals with a series of N-alkylcarbazoles **1a-1j** and 4-(dimethylamino)-pyridine (DP). We will now describe the photoreactivities of the CT crystals prepared from **3** or **4** and N-alkylcarbazoles **1a-1j**.

Another aim of this research was the preparation of a new class of materials for second order nonlinear optics. The intermolecular charge-transfer complexes are potentially as capable of generation of efficient second-order nonlinearities as are the intramolecular ones.[4] In this connection, the efficiency of frequency doubling by four non-centric CT crystals which we presently prepared are also reported.



RESULTS AND DISCUSSION

TABLE I. Melting Points and IR Absorption Frequencies for the 1 : 1 Charge-Transfer Crystals.

CT crystals	mp (°C) of the CT crystals (recryst solvent)	IR[a] ν_{as}	IR[a] ν_s	IR[a] $\nu_{C=O}$
1a•3	197-200 (AcOEt)	1554(10),1538(-6)	1338(-10)	1704(1)
1b•3	164-166 (MeCN)	1543(-1)	1341(-7)	1705(2)
1c•3	154-157 (MeCN)	1545(1)	1345(-3)	1705(2)
1d•3	164-167 (MeCN)	1545(1)	1346(-2)	1707(4)
1e•3	137-142 (MeCN)	1544(0)	1344(-4)	1709(6)
1f•3	130-132 (acetone)	1545(1)	1344(-4)	1709(6)
1g•3	114-118 (MeCN)	1545(1)	1345(-3)	1707(4)
1h•3	121-124 (MeCN)	1545(1)	1342(-6)	1711(8)
1i•3	188-192 (THF)	1545(1)	1342(-6)	1707(4)
1j•3	180-181 (ether)	1545(1)	1342(-6)	1708(5)
13•3	210-215 (MeCN)	1536(-8)	1342(-6)	1708(5)
1a•4	116-118 (CH_2Cl_2)	1542(-1)	1346(-6)	2214(-34)[b]
1b•4	77-78 (AcOEt)	1546(3)	1344(-8)	2236(-12)[b]
1d•4	131-133 (AcOEt)	1546(3)	1343(-9)	2245(-3)[b]
1a•2[c]	49-49.5 ($CHCl_3$)	1536(-5)	1341(-8)	-
DP•**3**	188-191 (acetone)	1542(-2)	1344(-4)	1649(-54)
DP•**11**	223-228dec(acetone)	1543(5)	1351(1)	1649(-72)
DP•**12**	134-137dec(acetone)	1549(1)	1343(-1)	1649(-62)

[a] In the KBr disc in cm^{-1} : ν_{as} and ν_s, the asymmetric and symmetric stretching frequencies for the nitro group; $\nu_{C=O}$, the stretching frequency for the carbonyl group. The values in parentheses refer to frequency shifts ($\Delta\nu$) from the corresponding frequencies of the pure acceptors **2** - **4**, **11** and **12**. [b] $\nu_{C\equiv N}$ [c] Reference 3.

Recrystallization of equimolar mixtures of N-alkylcarbazoles **1a**-**1h** or carbazole (**13**) and 3,5-dinitrobenzoic acid (**3**) or 3,5-dinitrobenzonitrile (**4**) from suitable solvent afforded yellowish orange crystals. Similarly, dimethoxy-N-methylcarbazoles **1i** and **1j** gave reddish brown crystals with **3**. All these crystals melted within a narrow temperature range (TABLE I) and were found to be composed of the donor and the acceptor with a 1 : 1 molar ratio on the basis of NMR and elemental analyses. Likewise, beautiful yellowish orange to reddish orange CT crystals were prepared from cocrystallization of acceptors **5**-**10** and N-alkylcarbazoles. On the other hand, attempts to obtain adduct crystals of 2,4- (**11**) or 3,4-dinitrobenzoic acid (**12**) with N-alkylcarbazoles failed. 4-(Dimethylamino)-pyridine (DP) formed yellow 1 : 1 CT crystals with **3**, **11** and **12** (TABLE I).

FT-IR spectra of the CT crystals were measured in the KBr disc. The nitro asymmetric (ν_{as}) and symmetric (ν_s) stretching frequencies and the carbonyl or cyano stretching frequency ($\nu_{C=O}$ or $\nu_{C\equiv N}$) are also listed in TABLE I. The value in parentheses refers to a shift ($\Delta\nu$) from the corresponding frequency of the pure acceptor. A negative $\Delta\nu$ indicates a red-shift and a positive $\Delta\nu$ a blue-shift. These frequency shifts may be a consequence of the CT interaction between the amine donor and the nitro acceptor[5] and

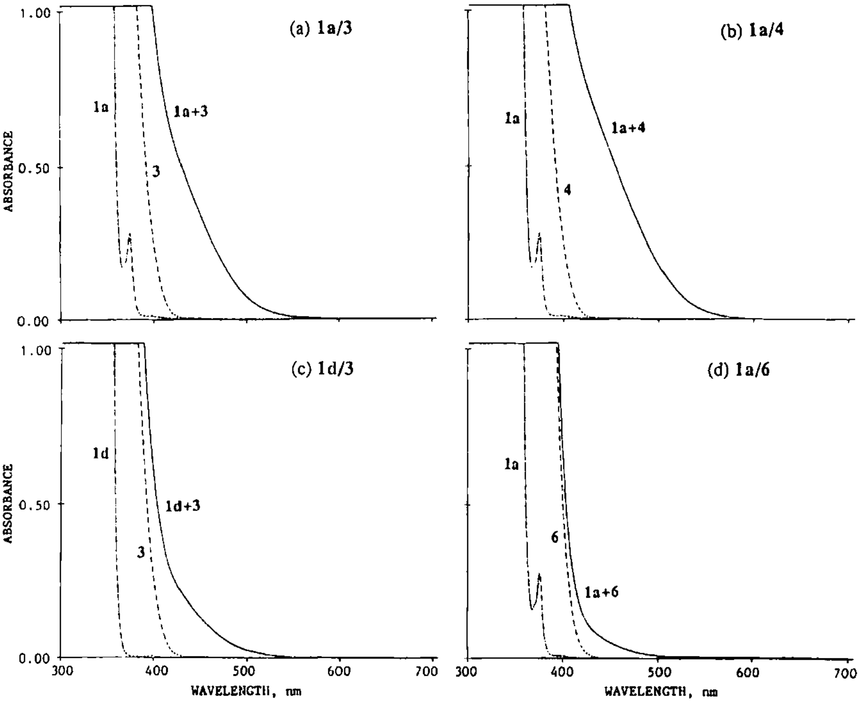


FIGURE 1. The UV-VIS absorption spectra in acetonitrile: donor (**1a** or **1d**), 2.5 x 10^{-2} M; acceptor (**3**, **4**, or **6**), 2.5 x 10^{-2} M; path length, 1 cm.

additionally of the C—H•••O hydrogen bonding interaction between the alkylamino and the nitro groups.[6]

The UV-VIS absorption spectra for a solution containing 2.5 x 10^{-2} M each of the donor and the acceptor in acetonitrile were measured. A CT band was clearly visible in all cases, as exemplified by the mixtures **1a** + **3**, **1a** + **4**, **1d** + **3** and **1a** + **6** (FIGURE 1). The intensities of the CT band for a series of N-alkylcarbazoles **1a** -**1h** were nearly equal except **1d**, where it was considerably weaker: compare (a) and (c) in FIGURE 1. The diffuse reflectance spectra for the CT crystals **1a•3**, **1i•3** and **1j•3** were measured and the presence of the CT band in the solid state was confirmed (FIGURE 2).

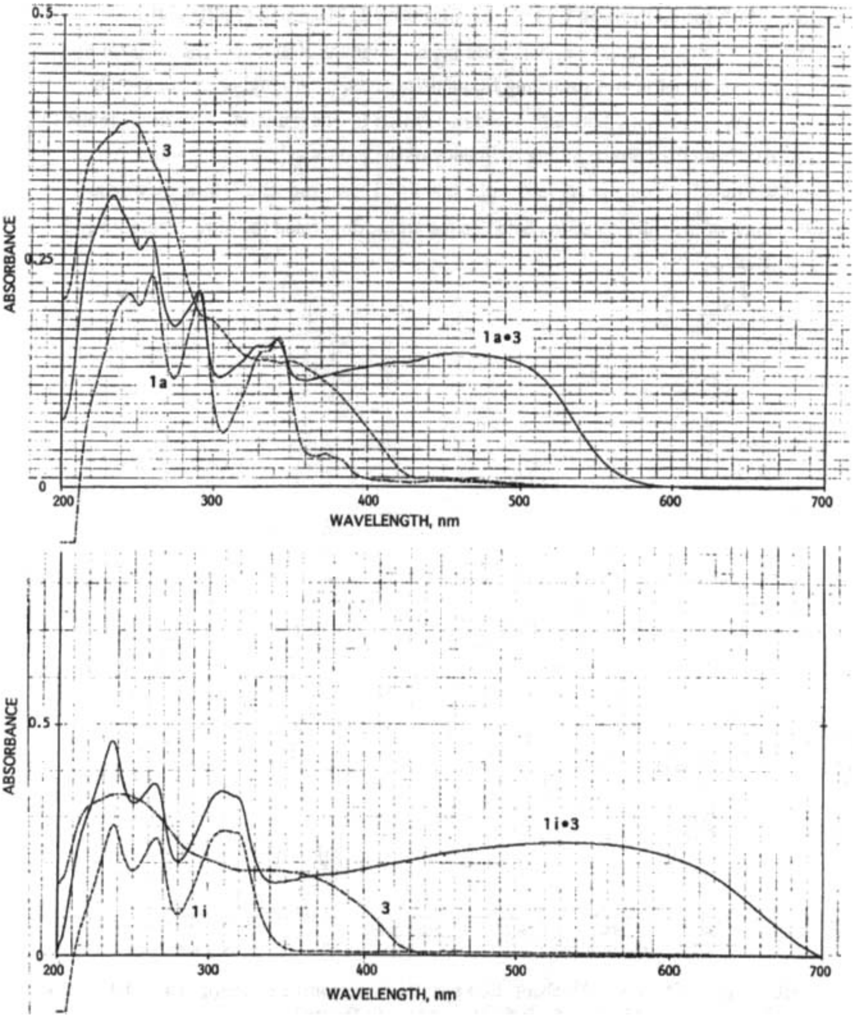
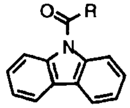
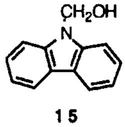


FIGURE 2. The diffuse reflectance spectra in MgO for the CT crystals **1a•3** and **1i•3**, the donors (**1a** and **1i**), and the acceptor (**3**).

Solid-state photolyses of the above CT crystals were carried out with a 400-W high-pressure mercury lamp through Pyrex (>280 nm). Before irradiation, the crystals were ground into powders in a mortar and 30 mg of the powder was spread between two Pyrex plates. This was placed in our special photolysis vessel[7] and photolyzed at 4 °C for 5 h under a nitrogen or argon atmosphere. The solid photolysate was dissolved in acetone and was separated by preparative TLC (silica gel, CH_2Cl_2/hexane or AcOEt/hexane).



14a, R = H 14b, R = Me 14c, R = Et
14d, R = Pr 14e, R = iPr 14f, R = Bu
14g, R = pentyl



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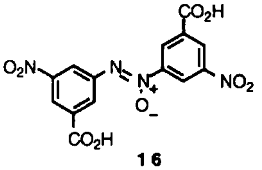

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TABLE II. Photoreactivities of Several Charge-Transfer Crystals in the Solid State.

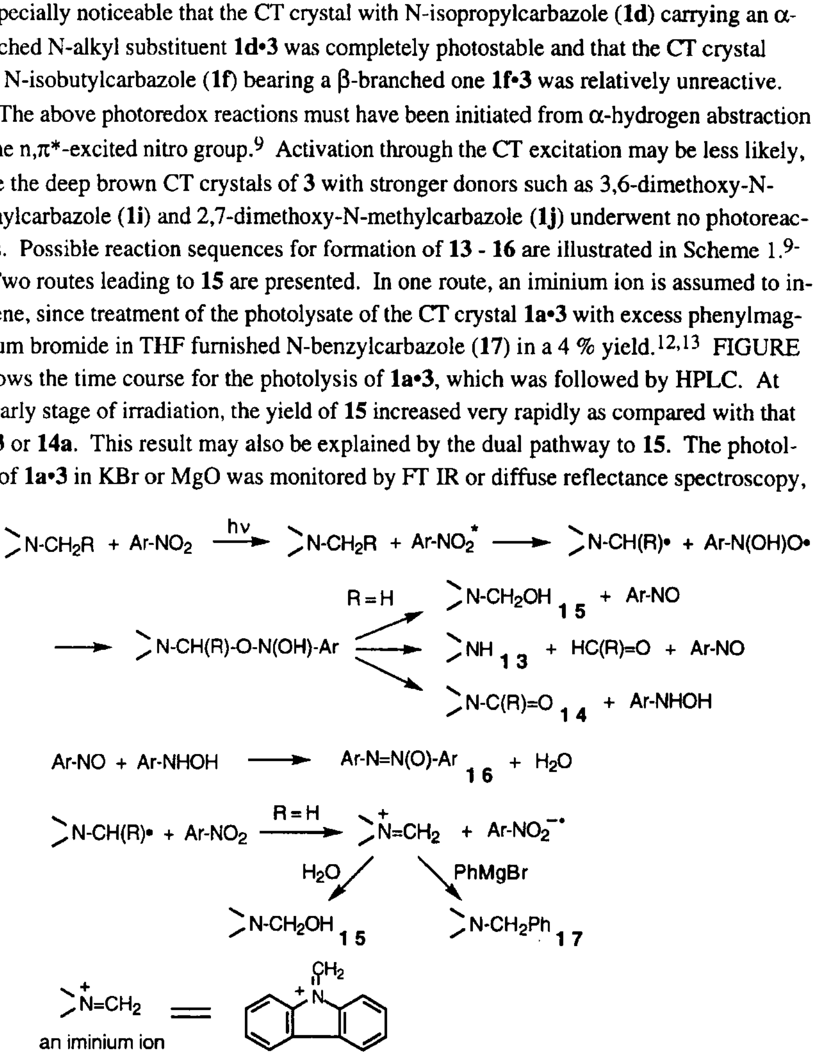
CT crystals	products, %[a]			
	13	14	15	13+14+15
1a•3	5	**14a**,19	30[b]	54
1b•3	9	**14b**,4	-[c]	13
1c•3	11	**14c**,6	-[c]	17
1d•3		no reaction		0
1e•3	10	**14d**,5	-[c]	15
1f•3	5	**14e**,3	-[c]	8
1g•3	17	**14f**,7	-[c]	24
1h•3	8	**14g**,7	-[c]	15
1i•3		no reaction		0
1j•3		no reaction		0
13•3		no reaction		0
1a•4	5	**14a**,3	11[c]	19
1b•4		no reaction		0
1d•4		no reaction		0
1a•2[d]	8	**14a**,10	25[e]	43

[a] Yields are based on the initial amount of the starting materials. A significant amount of the starting materials remained unreacted. [b] 3,3'-Dinitroazoxybenzene-5,5'-dicarboxylic acid **16**, which was isolated as the dimethyl ester, was also produced in a 5 % yield. [c] The corresponding azoxybenzene was isolated in a low yield (NMR and mass spectral analyses). [d] Reference 3. [e] 3,3'-Dinitroazoxybenzene 23 %.

As summarized in TABLE II, photoreactions occurred in many cases and the α-position of the N-alkylcarbazole was oxidized to produce carbazole (**13**), N-acylcarbazole (**14**) and N-(hydroxymethyl)carbazole (**15**). In addition, after treatment of the photolysate of **1a•3** with excess Me_3SiCHN_2 in MeOH/benzene/hexane, the dimethyl ester of an azoxybenzene **16** was isolated in a low yield (5 %).[8] As already reported,[3] the photolysis of the adduct crystal **1a•2** gave the corresponding azoxybenzene in a much higher yield (23 %). It is probable that the solid melted partly during the photolysis of **1a•2** because of its low melting point (49 °C, TABLE I) and thus the chances of encounter between a nitrosobenzene and a phenylhydoxylamine intermediate increased.

For the CT crystals of **3** with a series of N-alkylcarbazoles **1a-1h**, the reaction proceeded most readily for **1a** (the total yield for **13** - **15**, 54 %), then the total yields decreased in going from **1a** to the other carbazoles having longer alkyl chains (**1b-1h**). It is especially noticeable that the CT crystal with N-isopropylcarbazole (**1d**) carrying an α-branched N-alkyl substituent **1d•3** was completely photostable and that the CT crystal with N-isobutylcarbazole (**1f**) bearing a β-branched one **1f•3** was relatively unreactive.

The above photoredox reactions must have been initiated from α-hydrogen abstraction by the n,π*-excited nitro group.[9] Activation through the CT excitation may be less likely, since the deep brown CT crystals of **3** with stronger donors such as 3,6-dimethoxy-N-methylcarbazole (**1i**) and 2,7-dimethoxy-N-methylcarbazole (**1j**) underwent no photoreactions. Possible reaction sequences for formation of **13** - **16** are illustrated in Scheme 1.[9-11] Two routes leading to **15** are presented. In one route, an iminium ion is assumed to intervene, since treatment of the photolysate of the CT crystal **1a•3** with excess phenylmagnesium bromide in THF furnished N-benzylcarbazole (**17**) in a 4 % yield.[12,13] FIGURE 3 shows the time course for the photolysis of **1a•3**, which was followed by HPLC. At the early stage of irradiation, the yield of **15** increased very rapidly as compared with that of **13** or **14a**. This result may also be explained by the dual pathway to **15**. The photolysis of **1a•3** in KBr or MgO was monitored by FT IR or diffuse reflectance spectroscopy,



Scheme 1. A tentative mechanism for the solid-state photolysis.

respectively, but unfortunately the intermediates for **13** - **15** were not clearly detectable.

Solid-state photolyses of the other CT crystals were likewise examined. Their photoreactivities changed considerably, depending on the donors and acceptors employed. These results will be reported elsewhere.

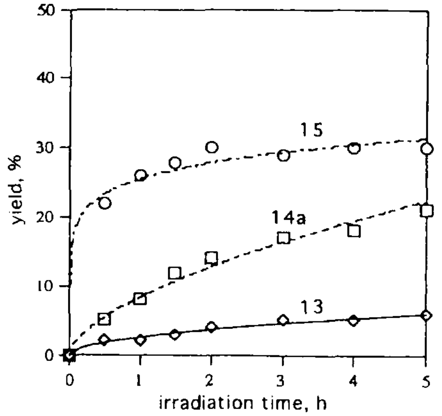
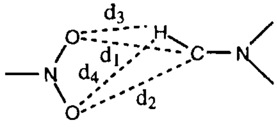


FIGURE 3. Time course for the solid-state photolysis of the CT crystal **1a•3**

Photolyses of solutions containing 2.5-5 x 10^{-2} M each of donor and acceptor in 10 mL of acetonitrile were similarly carried out at >280 nm. In contrast to the solid-state photolyses summarized in TABLE II, photoreactions in acetonitrile solution were very inefficient. Only low yields of **15** (5 %), **13** (trace) and **14a** (1 %) were produced from photolysis of a mixture of **1a** and **3**. In other cases, essentially no photoproducts were detectable by NMR and HPLC. The observed much higher photoreactivities in the solid state than in solution may have ensued from molecular recognition processes in the crystallization, where the donor N-CH group and the acceptor nitro group tend to be juxtaposed by the C—H•••O interactions.[6]

From the above result that the reaction is much more efficient in the solid state than in solution, it is suggested that the nitro group is in the vicinity of the alkylamino group in the solid state. Furthermore, according to Scheme 1, both of the oxygen atoms of the nitro group must be close to the N-α-carbon of the carbazole molecule (at least, for the formation of **13** and **14**). FIGURE 4 (A) and (B) display the crystal packing for the photoreactive crystal **1a•3** and the photoinert crystal **1d•3**, respectively.[14] The C•••O distances between the carbazole N-α-carbon and the nitro oxygens nearby (d_1 and d_2) and the corresponding H•••O distances between the hydrogen on the carbazole N-α-carbon and the nitro oxygens (d_3 and d_4) are specified.



The C•••O distance for the most reactive CT crystal **1a•3** (the total product yield 54 %) is as short as 3.28 Å (d_1 = 3.28, d_2 = 3.69 Å) at the most favorable nitro-N-alkyl arrangement. The corresponding H•••O distance is 2.61 Å (d_3 = 2.61, d_4 = 3.09 Å), which is well within the reported critical distance for the hydrogen-abstraction reaction to occur, i.e., 2.72 Å (the van der Waals sum of the hydrogen and oxygen atoms).[15] For the photoinert CT crystal **1d•3**, the C•••O and H•••O distances are considerably longer (d_1 = 3.67, d_2 = 3.70, d_3 = 2.85 and d_4 = 3.43 Å). Therefore, the photoreactivities of these two CT crystals may be understood by considering the d_1 - d_4 values.

TABLE III summarizes the C•••O distances d_1 and d_2 for a series of CT crystals. The d_1/d_2 set where both of the two oxygen atoms of the nitro group are near to the N-α-carbon atom of the carbazole molecule (i.e., the most favorable nitro-N-alkyl arrangement) are listed together with the d_1/d_2 set of the shortest d_1 distance. From inspection of these

d_1 and d_2 distances, the solid-state photoreactivities of **1c•3** and **1e•3** are expected to be intermediate between those of **1a•3** and **1d•3**. The observed total yields of products (**13** + **14** + **15**) for these CT crystals are in agreement with this prediction. Along the same line of discussion, the CT crystal **1f•3** should be completely photoinert, though it was found to possess a low photoreactivity. These results led us to conclude that a correlation exists between the solid-state photoreactivities of the present CT crystals and their C•••O

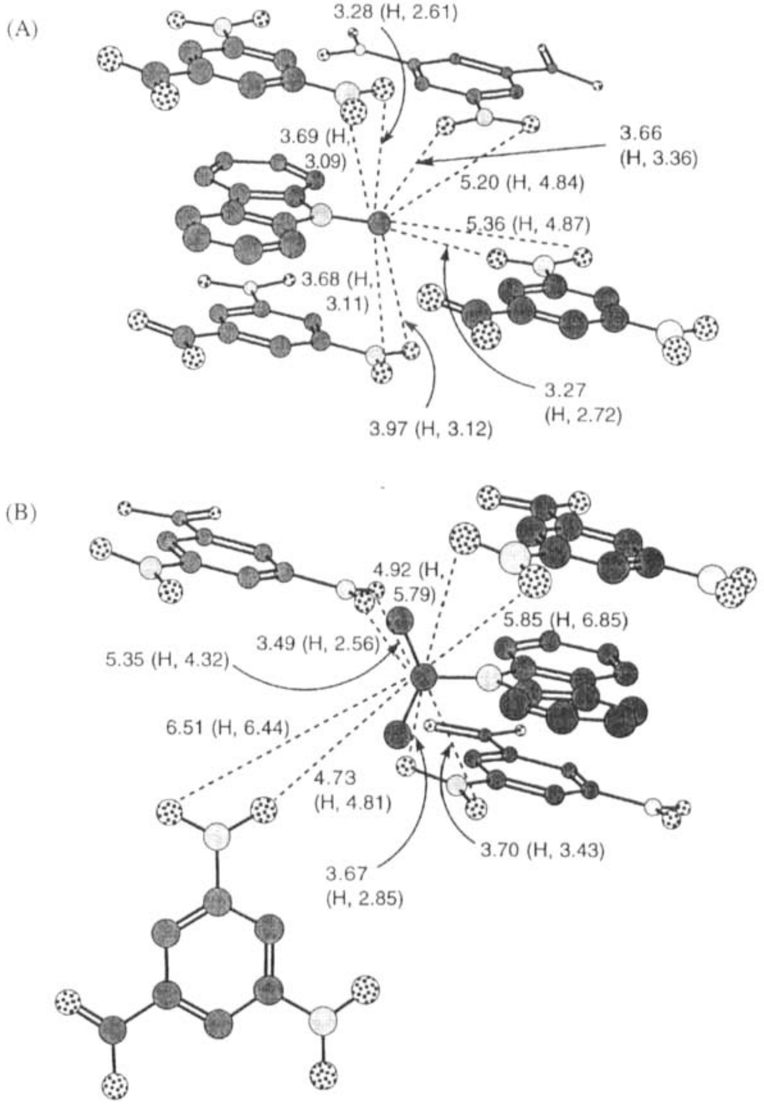


FIGURE 4 Crystal structures of the charge-transfer crystals **1a•3** (A) and **1d•3** (B): the figures in Å. Hydrogens are removed for clarity.

TABLE III. The C•••O Distances, d_1 and d_2.

CT crystals	d_1, d_2 (Å)[a]	d_1, d_2 (Å)[b]	total yield (%)[c]
1a•3	3.28, 3.69	3.27, 5.36	54
1b•3	The carbazole moiety is disordered.		13
1c•3	3.36, 3.72	same as left	17
1d•3	3.67, 3.70	3.49, 5.35	0
1e•3	3.35, 3.68	same as left	15
1f•3	4.30, 4.49	3.75, 5.10	8

[a] The d_1/d_2 set, where both of the two nitro oxygen atoms are near to the carbazole N-α-carbon atom (the most favorable nitro-N-alkyl arrangement). [b] The d_1/d_2 set, where the distance between one of the two nitro oxygen atoms and the carbazole N-α-carbon atom is the shortest of all. [c] The total yield of **13**, **14** and **15** (TABLE II).

distances as a whole, although the correlation is not perfectly parallel. However, detailed effects of the CT interaction on the solid-state photoreactivity are yet to be studied.

Among the thirteen charge-transfer crystals for which we were successful in determining the crystal structures, four were found to have a non-centrosymmetric space group (TABLE IV). Thus, their efficiencies for second harmonic generation (SHG) were measured by the powder method, using a 1064 nm Nd-YAG laser. Unfortunately, however, their SHG efficiencies were very small: **1c•3** = 0.04, **1a•7** = 0.04, **1a•4** = 0.05 and DP•**3** = 0.1 relative to a SHG signal of urea. Furthermore, these crystals suffered a considerable change in color after several hundreds of the laser shots. At this stage, we can not judge whether this system is promising for fabrication of SHG-active materials.

ACKNOWLEDGMENT

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8. Dimethyl ester of **16**: mp 115-122 °C; NMR ($CDCl_3$, 200 MHz) δ 9.38 (1 H, t, J = 2.2 Hz), 9.36 (1 H, q, J = 2.0 Hz, J' = 1.6 Hz), 9.31 (1 H, q, J = 2.1 Hz, J' = 1.5

Hz), 9.11 (1 H, q, J = 2.1 Hz, J' = 1.4 Hz), 9.05 (1 H, q, J = 1.9 Hz, J' = 1.6 Hz), 8.93 (1 H, q, J = 2.1 Hz, J' = 1.4 Hz), 4.07 (3 H, s), 4.03 (3 H, s); MS m/e (rel intensity) 404 (17, M+), 388 (9), 361 (5), 180 (63), 167 (100).

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13. When a photolysate of **1a•3** was dissolved in methanol instead of acetone and the solution was allowed to stand overnight, N-methoxymethylcarbazole (**18**) was obtained at the expense of **15**. This result, however, does not prove the iminium ion intervention, since **15** was quantitatively converted into **18** in a methanol solution.
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TABLE IV Crystal Data

		a, Å	b, Å	c, Å	α°	β°	γ°	Z	Dx,g/cm^3	R
1a•3	triclinic $P\bar{1}$	8.408	15.762	6.991	91.88	99.87	81.58	2	1.45	0.057
1b•3	monoclinic $P2_1/n$	7.037	17.579	15.807	-	93.72	-	4	1.39	0.158
1c•3	monoclinic Cc	10.098	13.570	29.744	-	92.01	-	8	1.35	0.067
1d•3	monoclinic $P2_1/a$	8.506	29.535	8.567	-	108.05	-	4	1.34	0.049
1e•3	triclinic $P\bar{1}$	16.722	16.783	8.415	102.38	92.32	109.90	4	1.36	0.059
1f•3	monoclinic $P2_1/c$	8.211	31.920	8.437	-	106.55	-	4	1.36	0.058
1a•6	monoclinic $P2_1/c$	8.149	16.836	28.157	-	95.87	-	8	1.41	0.065
1a•7	orthorhombic $P2_1ab$	18.765	28.649	7.086	-	-	-	8	1.41	0.061
1a•4	orthorhombic $P2_12_12_1$	8.339	27.604	7.817	-	-	-	4	1.38	0.069
1b•4	monoclinic $P2_1/a$	16.227	6.982	17.435	-	107.30	-	4	1.37	0.079
DP•3	orthorhombic $P2_12_12_1$	13.762	18.620	5.886	-	-	-	4	1.77	0.045
DP•11	triclinic $P\bar{1}$	8.774	12.287	7.693	107.42	105.79	76.99	2	1.48	0.045
DP•12	monoclinic $P2_1/n$	8.101	7.736	24.214	-	95.74	-	4	1.47	0.047