# Solid-State Photodecarboxylation Induced by Exciting the CT **Bands of the Complexes of Arylacetic Acids and** 1,2,4,5-Tetracyanobenzene

Hideko Koshima,\*.<sup>†,†,</sup> Kuiling Ding,<sup>†</sup> Yosuke Chisaka,<sup>†</sup> Teruo Matsuura,<sup>†</sup> Yuji Ohashi,<sup>§</sup> and Manabu Mukasa<sup>§</sup>

Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520, Japan, PRESTO, Research Development Corporation of Japan, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520, Japan, and Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

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Crystalline charge transfer complexes (3a, 3b, and 3c) of 1- and 2-naphthylacetic and 3-indoleacetic acid (1a, 1b, and 1c) with 1,2,4,5-tetracyanobenzene (2) were prepared by crystallization from the acetonitrile solutions. Irradiation of 3a and 3b gave methylnaphthalenes by decarboxylation and naphthyl(2,4,5-tricyanophenyl)methanes by subsequent dehydrocyanating condensation in the solid state. On the other hand, the photoreactivity of the crystal **3c** was low; similar photoreaction occurred only at high temperature. These solid-state reactions are induced by exciting the CT bands of **3a** and **3b**. The product selectivities were different from those of the solution photoreaction. The relationships between the photoreactivities and the crystal structures of **3a** and **3c** are discussed.

### Introduction

Photoinduced electron transfer (PET) reactions in solutions are very important, and large numbers of examples are known.<sup>1</sup> Photodecarboxylations of carboxylic acids in solutions are known to occur via PET, when acceptors such as acridine and 1,2,4,5-tetracyanobenzene (2) are present.<sup>2-8</sup> In the course of our study of the photochemistry of the mixed crystals between different organic molecules,<sup>9</sup> we found several photodecarboxylation reactions which occurred accompanying the reactivities and the product selectivities different from those of solution reactions. For instance, they are the high selective decarboxylation of the molecular crystal composed of 3-indoleacetic acid and phenanthridine,<sup>10</sup> the decarboxylating condensation retaining the initial chirality of the charge transfer (CT) crystal of (S)-(+)-2-(6methoxy-2-naphthyl)propanoic acid and  $\mathbf{2}^{11}$  and the decarboxylation of the simple polycrystalline mixtures of phenylacetic acids and 2.12 It has been thought that CT complexes give commonly no photoproduct because of the

back-electron transfer. However, Suzuki et al. reported that the CT crystals of arylolefins and bis[1,2,5]thiadiazolotetracyanoquinodimethane caused [2 + 2] photoaddition.<sup>13</sup> We describe here that the preparation and characterization of the crystalline CT complexes (3a, 3b, and 3c) of 1- and 2-naphthylacetic and 3-indoleacetic acid (1a, 1b, and 1c) with 2 and the occurrence of decarboxylation and dehydrocyanating condensation induced by exciting the CT bands. The correlations of the reactivities with the crystal structures are discussed.

## **Results and Discussion**

**Preparation and Characterization of the CT Crystals.** The CT crystals **3a–1c** were obtained by crystallizing from the equimolar solution of acids 1a-1c and tetracyanobenzene 2 in acetonitrile at room temperature. The results of full characterization by powder X-ray diffractometry (PXD), differential scanning calorimetry (DSC), solid-state <sup>13</sup>C CP-MAS NMR, IR, UV, and elemental analysis are summarized in the Experimental Section. In the case of **3a** and **3c**, the crystal structures were determined by X-ray crystallographic analysis (Figures 2 and 3).

The compositions of **3a**-**3c** are 1:1 of **1a**-**1c** and **2**. Every melting curve of **3a**–**3c** by DSC was sharp, and further heating resulted in thermal decomposition. The CT bands ( $\lambda_{width}$ ) in the solid state measured by a reflection method are 370-460 nm (3a), 370-450 nm (3b), and 370-550 nm (3c). On the other hand, the CT bands ( $\lambda_{max}$ ) in the acetonitrile solutions containing 0.05 M 1a-1c and 0.05 M 2 were observed at 378 nm (1a/2,  $\epsilon$  20), 382 nm (**1b/2**, 30), and 350 and 440 nm (**1c/2**, 40 and 25).

Acids generally form the dimers with OH····O hydrogen bonds in the crystals.<sup>14,15</sup> The C=O bands in the IR spectra of **3a** and **3b** shifted to 1700 and 1700 cm<sup>-1</sup> from

<sup>&</sup>lt;sup>†</sup> Ryukoku University.

<sup>&</sup>lt;sup>‡</sup> PŘESTO, Research Development Corporation of Japan.

<sup>§</sup> Tokyo Institute of Technology.

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23

CN



Chemical shift, ppm

**Figure 1.** Solid state <sup>13</sup>C CP-MAS NMR spectra of a CT crystal **3a** and its components 1-naphthylacetic acid (**1a**) and 1,2,4,5-tetracyanobenzene (**2**).

1690 and 1695 cm<sup>-1</sup> of the component acids **1a** and **1b**, respectively, in spite of no change of the OH···O bands. The crystal **3c** had the C=O band at 1695 cm<sup>-1</sup> and the NH bands at 3390 cm<sup>-1</sup> which are the same as those of **1c**, and some other peaks of **3c** changed to 1490, 1425, 920, and 765 cm<sup>-1</sup> from 1480, 1405, 910, and 760 cm<sup>-1</sup> of **1c**, respectively.

Figure 1 shows the solid-state <sup>13</sup>C CP-MAS NMR spectra of **3a** and its components. The chemical shifts of the  $CH_2COOH$  carbons in **3a** are almost the same as those of **1a**, while the carbons of the naphthalene ring and molecule **2** in **3a** were considerably shifted to lower magnetic field by the  $\pi-\pi$  interaction. Thus, it reflects<sup>16,17</sup> that **3a** has an alternate stacking structure (Figure 2) different from those of the components **1a**<sup>14</sup> and **2**.<sup>18</sup> The small peaks of the spinning side bands were observed at 40–60 ppm and 190–220 ppm for **3a**, 200–220 ppm and 40–55 ppm for **1a**, and 175–185 ppm and 20–30 ppm for **2**.

The fluorescence spectral data of 3a-3c and their components in the solid state by a front face arrangement are listed in Table 1. All the fluorescence spectra of the CT crystals were quite different from those of their components. Namely, the fluorescence of the components disappeared and the broad fluorescence peaks at 487 and 481 nm of 3a and 3b, respectively, which were emitted from their CT excited states, were detected. It may be due to the smooth energy migration from the higher excited states to form the CT excited state. The crystal **3c** had no fluorescence. We also measured the emission spectrum of a solution of 1a (0.05 M) and 2 (0.05 M) in acetonitrile, which had no fluorescence despite that those of the components in acetonitrile were similar to those in the solid state, due to the low concentration of the CT complex equilibrated in the solution.

**Photoreaction of the CT Crystals.** The results of the solid-state photoreaction of the CT crystals **3a**-**3c** 

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Figure 2. Molecular packing in the crystal 3a.

Table 1.	Fluorescence	<b>Spectral Data</b>	of the CT	Crystals
3 a	and Their Com	ponents in the	Solid Sta	te

component and CT crystal		excitation (nm)	fluorescence max (nm)
1-naphthylacetic acid	1a	275	341, 355
2-naphthylacetic acid	1b	275	340, 352
3-indoleacetic acid	1c	260	317, 328
1,2,4,5-tetracyanobenzene	2	275	337, 346, 362, 378
CT crystal	3a	325	487
CT crystal	3b	325	481
CT crystal	<b>3c</b>	275	
S	chei	ne 1	



are summarized in Scheme 1 and Table 2. Irradiations of **3a** and **3b** with a xenon lamp through a UV cut filter (>390 nm irradiation) or with a high-pressure mercury lamp (>290 nm irradiation) at 15 °C gave methylnaphthalenes (**5a** and **5b**) by decarboxylation and naphthyl-(2,4,5-tricyanophenyl)methanes (**4a** and **4b**) by subsequent dehydrocyanating condensation. The product selectivities and the yields with >390 nm irradiation were comparable to those with >290 nm irradiation. These results indicate that the reaction is induced by the excitation of the CT bands and that the light energy of 290–390 nm wavelength region was effectively used for the CT excitation (Table 1). The pathway of the solid-

 
 Table 2.
 Solid-State Photoreaction of the CT Crystals 3 of Acids 1 and 1,2,4,5-Tetracyanobenzene (2)

CT crystal	irrad wavelength (nm)	irrad temp (°C)	conversion (%)		yield based on consumed 1 (%)	
			1	2	4	5
3a	> 390	-70	0	0	0	0
3a	>390	-30	4	3	1	4
3a	>390	15	30	20	65	34
3a	>290	15	53	33	49	37
3b	>390	15	11	9	76	22
3b	>290	15	25	15	58	28
3c	>390	15	0	0	0	0
3c	>290	15	0	0	0	0
3c	>390	60	0	0	0	0
3c	>390	90	11	6	3	1



state photoreaction of **3a** and **3b** initiated by the excitation of the CT complex is shown in Scheme 2, which is essentially the same as that proposed by Tsujimoto et al.<sup>6</sup> The condensation products **4a** and **4b** are produced by the formation of coupled intermediate **8** of a radical •CH<sub>2</sub>Ar and an anion radical **7** followed by the elimination of a cyanide anion. The formation of **5a** and **5b** is attributed to the hydrogen transfer between a radical •CH<sub>2</sub>Ar and a radical intermediate **9**. The irradiation at -70 °C of the CT crystal **3a** did not cause any reaction. This is understandable if we consider the existence of a step requiring an activation energy, most probably the decarboxylating step.

Figure 2 illustrates the molecular packing in the crystal **3a**. The parallel and alternate stacking of the molecules **1a** and **2** with a plane to plane distance of 3.4

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Å implies that the  $\pi - \pi$  interaction has the CT character. The stacking of the **1a** and **2** planes in some orientation is similar to the CT crystal of naphthalene and **2**.<sup>19</sup> The dimeric structure of **1a** in **3a** is formed through OH---O hydrogen bonding with the H---O distance of 1.83 Å. The molecule **1a** is weakly connected to the molecule **2** in the next stacking column through OH---N with the H1---N1 distance of 3.42 Å.

It is understandable from Figure 2 that the CT excitation occurs the electron transfer from 1a to 2 along the stacking column to give the radical cation of 1a and the radical anion 7 (Scheme 2). The shortest •C-C distance between the decarboxylated radical •CH<sub>2</sub>Ar and the phenyl ring of **2** is estimated as 3.75 Å (C1–C2) from the crystal data. The distance is short enough for the radical coupling to give the intermediate 8 and subsequently to produce **4a**. Since the other •C-C distances are 4.61 Å (C1–C3), 4.62 Å (C1–C4), and 4.68 Å (C1– C5), the possibilities of the radical coupling are lower. On the other hand, the production of **5a** can be explained as follows. In spite of the slightly longer H1–C2 distance of 4.31 Å than that of C1–C2, the active radical cation 7 can abstract H<sup>+</sup> to give the intermediate **9**, from which the radical •CH<sub>2</sub>Ar abstracts the hydrogen atom subsequently to produce 5a. Accordingly, these reactions to give 4a and 5a are competitive.

On the other hand the CT crystal **3c** showed less photoreactivity. Irradiation at lower temperature than 60 °C did not cause any photoreaction and scarcely caused photoreaction even at 90 °C. The reason for the low reactivity of the crystal **3c** is most probably due to the back-electron transfer from the intermediate radicalion pair. The very slight occurrence of the photoreaction of **3c** at 90 °C may be due to the increase of the electron transfer and the increase of the thermal motion of the radicals and the molecules in the crystal **3c**.

It should be noted that the crystal structure of 3c (Figure 3) is somewhat different from that of **3a**. The molecular packing in the crystal of 3c also has parallel and alternate stacking structures of 1c and 2 molecules with a plane-to-plane distance of 3.4 Å. The stacking of the phenyl rings of **1c** and **2** generates the  $\pi - \pi$  interaction and the CT character. The molecules of 1c stack head to tail in the same column, different from the case of the crystal 3a having head-to-head arrangement of 1a (Figure 2). Two molecules of 1c in the adjacent columns form the dimer structure through OH---O hydrogen bonding with the H---O distance of 1.70 Å. The molecule **1c** has two other weak interactions to the molecule **2**. One is the very weak hydrogen bonding in the same stacking column through NH---N with the H2---N2 distance of 3.82 Å. Another one is the weak hydrogen bonding to the the molecule 2 in the next column through OH---N with the H1---N1 distance of 3.07 Å. The C•−C distances between the decarboxylated radical •CH<sub>2</sub>Ar, if it is formed, and the phenyl ring of 2 (Figure 3) are estimated to be 4.50 Å (C1-C2), 5.09 Å (C1-C3), 5.34 Å (C1-C4), 5.39 Å (C1-C5), and 5.61 Å (C1-C6), which are considerably longer than those in the crystal 3a (Figure 2).

For a comparison, photoreactions of the solutions of 1a-1c (0.05 M for 1a and 1b and 0.1 M for 1c) and 2 (0.05 M) in acetonitrile were carried out by irradiating the wavelength region of >290 nm or >390 nm at 15 °C.



Figure 3. Molecular packing in the crystal 3c.

 Table 3.
 Photoreaction of Acids 1 with

 1,2,4,5-Tetracyanobenzene (2) in Acetonitrile

mixture of	irrad wavelength	irrad time	conversion (%)		yield based on consumed 1	
<b>1</b> and <b>2</b>	(nm)	(h)	1	2	4	6
1a/2	> 390	24	40	4	2	37
1a/2	>290	4	90	79	81	6
1a/2 <sup>a</sup>	>290	5	100	91	84	4
1b/2 <sup>a</sup>	>290	24	100	90	62	10
1c/2 <sup>a</sup>	>290	30	74	76	47	0

<sup>a</sup> Photoreaction in preparative scale.

Similar photocondensation to the solid state occurred to give **4a**–**4c** as the main products, and in this case, the aldehydes 6a-6c were produced in low yields (Scheme 1 and Table 3). The reactivity of 1c with 2 was lower than those of 1a and 1b with 2. It should be emphasized that no formation of the decarboxylated products 5a-5cwas observed in the solution photoreaction. A similar observation has been found in the photoreaction of a 1:1 molecular crystal composed of 1c and phenanthridine,<sup>10</sup> in which the solid-state photoreaction gave 5c as the sole product, while the photoreaction in acetonitrile gave several products including a small amount of 5c. The excitation by the irradiation at >390 nm of the solution of 1a and 2 hardly caused the condensation reaction, giving 4a in only 2% yield. The reason for the ineffectiveness is probably the low concentration of the CT complex **3a** equilibrated in the solution.

The quantum yields ( $\Phi$ ) for the photoreaction of the CT crystals **3a** and **3b** at 300–330 nm irradiation were

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Table 4. Quantum Yields of Solid-State Photoreaction of the CT Crystals 3 and Solution Photoreaction of Their Components Acids 1 and 1,2,4,5-Tetracyanobenzene (2)<sup>a</sup>

	$\Phi$ in CT crystal		$\Phi$ in ace	tonitrile <sup>a</sup>
CT crystal of <b>1</b> and <b>2</b>	4	5	4	6
3a 3b	0.10 0.06	0.043 0.034	0.05 0.23	0.17 0.10

 $^a$  Irradiation wavelengths were 300–330 nm and >450 nm.  $^b$  0.005 M 1 and 0.005 M 2.

measured by the thin-layer technique reported by Ito et al.<sup>20</sup> (Table 4). The  $\Phi$  values for **4a** and **5a** were comparable to those of **4b** and **5b**, respectively. We also measured the  $\Phi$  values for **4** and **6** in the acetonitrile solution of **1** (0.005 M) and **2** (0.005 M) with the usual merry-go-round technique as shown in Table 4. The  $\Phi$  values for **4a** and **4b** in the solid state are comparable for those in the solution. Relatively high  $\Phi$  values for **6a** and **6b** formation in acetonitrile compared to the final preparative yields of **6a** and **6b** (Table 3) are attributable to their facile production at the early stage of the photoreaction. The formations of **6a** and **6b** are ascribed to result from the participation to the cation-radical species of water present in the solvent acetonitrile.

In conclusion, the CT excitation of the CT crystals between 1- and 2-naphthylacetic acid and 1,2,4,5-tetracyanobenzene causes decarboxylation and subsequent dehydrocyanating condensation to give the methylnaphthalenes and the naphthyl(2,4,5-tricyanophenyl)methanes.

## **Experimental Section**

General Procedure. <sup>1</sup>H NMR spectra were measured on a 60 MHz JEOL PMX-60 spectrometer with tetramethylsilane as an internal standard. Solid-state <sup>13</sup>C CP/MAS NMR spectra were taken on a Bruker MSL-200 spectrometer by using glycine as an external standard. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer and a JASCO FT/IR-8300 spectrophotometer. UV and fluorescence spectra were measured on a Shimadzu UV-3100 spectrophotometer and RF-5000 spectrofluorophotometer, respectively. Powder X-ray diffractograms (PXD) were taken on a Rigaku Geigerflex by using Cu-target X-ray tube equipped with RAD-C system. X-ray crystallographic data were obtained using a Rigaku AFC7R diffractometer with graphite-monochromated Mo K $\alpha$ radiation and analyzed by teXsan. Differential scanning calorimetry (DSC) was done on a Rigaku Thermoflex TAS-200 DSC8230D, and melting points (mp) were not corrected. Elemental analysis was carried out with a Yanaco CHN Corder MT-5. HPLC with a photodiode array detector were used for determining the products on a Waters HPLC system. All the reagents were commercially available.

**Preparation of CT Crystals.** CT crystals **3a**–**3c** were prepared by dissolving 1:1 molar mixtures of **1a**–**1c** and **2** in acetonitrile by gentle heating followed by crystallizing at room temperature and filtering. The CT crystals were characterized by PXD, DSC, solid-state <sup>13</sup>C CP-MAS NMR, IR, UV, fluorimetry, and elemental analysis. The PXD patterns of **3a**–**3c** were different from those of the components, indicating the formation of new compounds. Some of the results are shown in the text, Figure 1, and Table 1.

**3a**: yellow needle crystal; mp 219 °C dec 242 °C; <sup>13</sup>C CP-MAS NMR 180, 124–136, 116, 37 ppm; IR (KBr) 3400–2400, 1700 cm<sup>-1</sup>; UV 370–460 nm (CT band). Anal. Calcd for  $C_{22}H_{12}N_4O_2$  (1:1): C, 72.51; H, 3.33; N, 15.38. Found: C, 72.62; H, 3.42, N, 15.28.

**3b**: yellow needle crystal; mp 212 °C dec 239 °C; <sup>13</sup>C CP-MAS NMR 180, 127–135, 116, 38 ppm; IR (KBr) 3400–2400, 1700 cm<sup>-1</sup>; UV 370–450 nm (CT band). Anal. Calcd for  $C_{22}H_{12}N_4O_2$  (1:1): C, 72.51; H, 3.33; N, 15.38. Found: C, 72.83; H, 3.45; N, 15.35.

**3c**: red yellow crystal; mp 212 °C dec 228 °C; <sup>13</sup>C CP-MAS NMR 182, 111–135, 107, 30 ppm; IR (KBr) 3390, 3300–2400, 1695 cm<sup>-1</sup>; UV 370–450, 370–550 nm (CT bands). Anal. Calcd for  $C_{20}H_{11}N_5O_2$  (1:1): C, 67.98; H, 3.14; N, 19.82. Found: C, 67.66, H, 3.31; N, 20.08.

**Solid-State Photoreaction.** Twenty mg of the CT crystal pulverized in a mortar was placed between two Pyrex glass plates and irradiated with a 400 W high-pressure mercury lamp (>290 nm irradiation) or a 500 W xenon short arc lamp with a UV cut filter (>390 nm irradiation) under argon at 15 °C for 24 h. The irradiated sample was methylated with CH<sub>2</sub>N<sub>2</sub> followed by HPLC analysis (C<sub>18</sub> column, methanol–water). The results are shown in Scheme 1 and Table 2.

**Photoreaction in Solutions.** Ten mL of the acetonitrile solution containing 0.05 M **1a** and 0.05 M **2** in a Pyrex test tube was irradiated under argon with a 400 W high-pressure mercury lamp for 4 h at 15 °C or with a 500 W xenon short arc lamp through a UV cut filter for 24 h at 15 °C. The irradiated solutions were analyzed by HPLC.

For a commom procedure in preparative scale, a solution of 1a-1c (5 mmol or 10 mmol for 1c) and 2 (5 mmol) in 100 mL of acetonitrile was internally irradiated with a 100 W high-pressure mercury lamp under argon at room temperature. The mixture was submitted to filtration and preparative TLC (silica gel plate) separations. The results are shown in Scheme 1 and Table 3 together with the HPLC analysis.

**1a with 2.** After irradiation of a solution containing **1a** (931 mg) and **2** (891 mg) for 5 h, evaporation of the solvent followed by filtration gave 1144 mg of a condensation product **4a**, which was recrystallized from acetonitrile to yield white crystals: mp 197–198.5 °C; <sup>1</sup>H-NMR (CD<sub>3</sub>CN)  $\delta$  8.28 (s, 1H), 7.16–8.00 (m, 8H), 4.73 (s, 2H); IR (KBr), 3100, 3050, 2230, 1580, 1560, 1490, 915, 796, 776 cm<sup>-1</sup>; UV  $\lambda_{max}$  (MeCN) 222.8 (log  $\epsilon$  5.14), 259.4 nm (4.53). Anal. Calcd for C<sub>20</sub>H<sub>11</sub>N<sub>3</sub>: C, 81.89; H, 3.78; N, 14.33. Found: C, 82.07; H, 4.01; N, 14.39. The filtrate was submitted to preparative TLC (benzene as an eluent) to give an additional 83 mg of **4a** and 28 mg of 1-naphthaldehyde **6a** as an oil, and the <sup>1</sup>H-NMR and IR spectra are consistent with those of an authentic sample. The recovery of **2** was 9%.

**1b with 2.** After irradiation of a solution of **1b** (931 mg) and **2** (891 mg) for 24 h and evaporation of the solvent, 640 mg of **4b** was obtained by filtration and recrystallization from acetone to give white crystals: mp 210.5–211 °C; 'H-NMR (acetone- $d_6$ )  $\delta$  8.50 (s, 1H), 8.20 (s, 1H), 7.67–7.93 (m, 4H), 7.30–7.60 (m, 3H), 4.53 (s, 2H); IR (KBr) 3100, 3040, 2950, 2230, 1595, 1540, 1505, 1488, 1380, 1360, 920, 900, 865, 830, 798, 754 cm<sup>-1</sup>; UV  $\lambda_{max}$  (MeCN) 214.0 (log  $\epsilon$  4.93), 225.8 nm (5.08). Anal. Calcd for C<sub>20</sub>H<sub>11</sub>N<sub>3</sub>: C, 81.89; H, 3.78; N, 14.33. Found: C, 81.80; H, 3.96; N, 14.24. The filtrate was submitted to preparative TLC (benzene as an eluent) to give further 274 mg of **4b** and 78 mg of 2-naphthaldehyde **6b**, the melting point, <sup>1</sup>H-NMR, and IR spectral data of which were identical to those of an authentic sample. The recovery of **2** was 10%.

**1c with 2.** After irradiation of a solution containing **1c** (1755 mg) and **2** (891 mg) for 30 h, concentration of the solution to ~20 mL gave 569 mg of **4c** as yellow needles: mp 251–254 °C (with decomposition, from MeCN); <sup>1</sup>H-NMR (CD<sub>3</sub>CN)  $\delta$  8.23 (s, 1H), 7.87 (s, 1H), 6.90–7.57 (m, 6H), 4.37 (s, 2H); IR (KBr) 3370, 3100, 3050, 2920, 2240, 1594, 1540, 1488, 1450, 1424, 1335, 1100, 920, 748, 600 cm<sup>-1</sup>; UV  $\lambda_{max}$  (MeCN) 221.6 (log  $\epsilon$  4.96), 250.8 (4.29), 281.0 nm (3.92). Anal. Calcd for C<sub>18</sub>H<sub>10</sub>N<sub>4</sub>: C, 76.58; H, 3.57; N, 19.85. Found: C, 76.53; H, 3.73; N, 19.83. The filtrate was submitted to preparative TLC (hexane–ethyl acetate, 1:1, as an eluent) to give an additional 407 mg of **4c**. A trace of 3-indolealdehyde **6c** was also produced. The recoveries of **1c** and **2** were 26% and 24%, respectively.

**Determination of Quantum Yield.** Quantum yield was determined in a thin-film state basically by the procedure reported by Ito et al.<sup>20</sup> The crystalline thin film was prepared by addition of a small amount of acetone (0.5 mL) containing 0.05 mmol of the CT crystals in a Pyrex tube ( $180 \times 17$  i.d. mm) and by evaporation of the solvent with a vacuum rotary

<sup>(20)</sup> Ito, Y.; Matsuura, T.; Fukuyama, K. Tetrahedron Lett. 1988, 29, 3087.

## Solid-State Photodecarboxylation

evaporator. The film was irradiated on a merry-go-round apparatus with a 400 W high-pressure mercury lamp through a potassium chromate filter (light transmission, 300–330 nm and >450 nm) under argon at 15 °C. The irradiation was stopped at a small conversion (<10%) and the products formed were analyzed by HPLC. Photocyclization of 2,4,6-triisopropylbenzophenone in benzene ( $\Phi_{CB} = 0.52$ ) was used as an actinometer. Quantum yields for the reactions in acetonitrile were also measured simultaneously with the usual merry-goround technique. The results are listed in Table 4.

**X-ray Crystallographic Analysis of the CT Crystals.**<sup>21</sup> **3a**: triclinic;  $P\overline{1}$ ; a = 7.890(7) Å, b = 16.786(8) Å, c = 7.007(3) Å,  $\alpha = 93.91(4)^{\circ}$ ,  $\beta = 96.43(5)^{\circ}$ ,  $\gamma = 90.39(6)^{\circ}$ ; V = 919.9(10) Å<sup>3</sup>; Z = 2. The structure was solved by direct method (MULTAN88) and refined by the full-matrix least-squares procedure to R = 0.072 and  $R_w = 0.053$  for 1566 independent observed reflections [ $I > 3.00\sigma(I)$ ] of total 3504 reflections with  $2\theta \le 50.0^{\circ}$ . **3c**: monoclinic;  $P2_1/n$ ; a = 9.145(4) Å, b = 16.425(4) Å, c = 11.903(3) Å,  $\beta = 102.31(2)^{\circ}$ ; V = 1747.0(9) Å<sup>3</sup>; Z = 4. The structure was solved by direct methods (SHELXS-86) and refined by the full-matrix least-squares procedure to R = 0.053 and  $R_w = 0.071$  for 2758 independent observed reflections [ $I > 1.50\sigma(I)$ ] of total 4423 reflections with  $2\theta \le 55.0^{\circ}$ .

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<sup>(21)</sup> The authors have deposited atomic coordinates for **3a** and **3c** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.