

## Stoichiometrically Sensitized Decarboxylation Occurring in a Molecular Crystal Composed of Phenanthridine and 3-Indoleacetic Acid

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Irradiation of a molecular crystal between phenanthridine and 3-indoleacetic acid at  $-70\text{ }^{\circ}\text{C}$  causes decarboxylation to give 3-methylindole in high yield as the sole product; phenanthridine behaves like a stoichiometric sensitizer in the crystal.

Photodecarboxylations of organic carboxylic acids are well known as reactions induced by electron transfer.<sup>1</sup> Although a large number of photodecarboxylations in solutions have been studied by using various acceptors such as acridine and dicyanonaphthalene, the product selectivities are not necessarily high.<sup>2-7</sup> We have succeeded in achieving a high selectivity and efficiency by irradiating a molecular crystal **3** of phenanthridine **1** and 3-indoleacetic acid **2** at low temperature as a new strategy. In this communication we also report that **1** plays a role of a stoichiometric sensitizer in the crystal.

A high quality 1 : 1 single crystal **3** for X-ray crystallographic analysis was prepared by the slow evaporation of an equimolar solution of **1** and **2** in ethyl acetate at room temperature. The melting point was  $97\text{ }^{\circ}\text{C}$ , lower than those of **1** ( $106\text{ }^{\circ}\text{C}$ ) and **2** ( $169\text{ }^{\circ}\text{C}$ ). The crystal packing is shown in Fig. 1.<sup>†</sup> The space group is  $P\bar{1}$ ,  $Z = 2$  and the two planes of **1** are therefore arranged head to tail and in parallel in the unit cell. The two molecules of **2** at the top and the bottom of the *ac* face are connected at the N atoms of **1** through  $\text{OH}\cdots\text{N}$  hydrogen bonding with the  $\text{H}\cdots\text{N}$  distance of  $1.68\text{ \AA}$ . The dihedral angle of the **1** and **2** aromatic planes is  $84.84^{\circ}$ . The molecule **2** is also connected to the next **2** along the *a* axis through  $\text{NH}\cdots\text{O}=\text{C}$  hydrogen bonding with an  $\text{H}\cdots\text{O}$  distance of  $2.01\text{ \AA}$ .

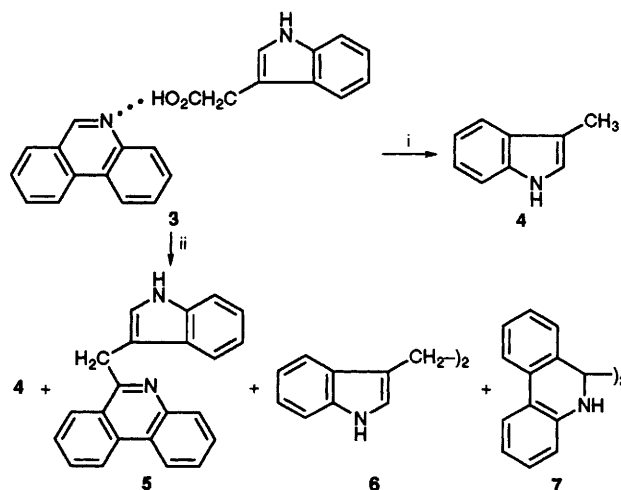
The crystal **3** (20 mg) was pulverized in a mortar and placed between two Pyrex glass plates and irradiated under argon with a 500 W xenon short arc lamp with a UV transparent filter ( $>300\text{ nm}$ ) for 3 h at  $-70$  or  $15\text{ }^{\circ}\text{C}$ , or with a 400 W high-pressure mercury lamp for 1 h at  $15\text{ }^{\circ}\text{C}$  followed by HPLC analysis. Solution photoreaction was also done on a preparative scale by the internal irradiation of an acetonitrile solution (100 ml) of **1** (5 mmol) and **2** (5 mmol) with a 100 W high-pressure mercury lamp under argon for 10 h at room temperature, followed by preparative TLC separation. The results are shown in Scheme 1 and Table 1. Reaction in

solution gave four products, 3-methylindole **4**, the coupling product **5**,<sup>‡</sup> the dimer of **4**, **6**,<sup>§</sup> and biphenanthridane **7**; the low product selectivity is due to the high mobility of the intermediate radical species in the solution. However the product selectivity of the solid-state photoreaction was very different from that of the solution reaction, with no production of **6** and **7**. Especially, irradiation of the crystal **3** at  $-70\text{ }^{\circ}\text{C}$  caused completely selective decarboxylation to give **4** alone without consumption of **1**. Scheme 2 shows the possible mechanism. The complexation of **1** and **2** occurs through the hydrogen bonding in the crystal lattice. Irradiation of the crystal induces electron transfer from **2** to **1** followed by

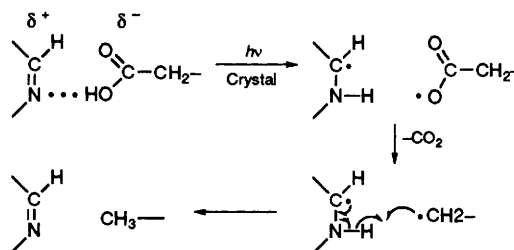
**Table 1** Solid and solution photoreactions of phenanthridine and 3-indoleacetic acid

State on irradiation (Temp.)	Irradiation lamp	Conversion (%)		Yield based on consumed <b>2</b> (%)			
		<b>1</b>	<b>2</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
Crystal <b>3</b> ( $-70\text{ }^{\circ}\text{C}$ )	<i>a</i>	0	23	92	0	0	0
Crystal <b>3</b> ( $15\text{ }^{\circ}\text{C}$ )	<i>a</i>	14	62	69	13	0	0
Crystal <b>3</b> ( $15\text{ }^{\circ}\text{C}$ )	<i>b</i>	20	91	77	10	0	0
MeCN solution (room temp.)	<i>b</i>	74	69	18	29	21	56 <sup>c</sup>

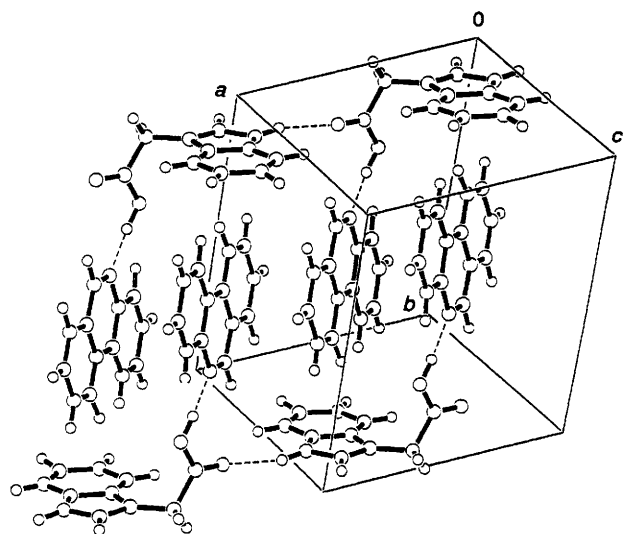
<sup>a</sup> Xe lamp with a UV transparent filter. <sup>b</sup> Hg lamp. <sup>c</sup> Yield based on consumed **1**.



**Scheme 1** Reagents and conditions: i,  $h\nu$ , crystal,  $-70\text{ }^{\circ}\text{C}$ ; ii,  $h\nu$ , MeCN



**Scheme 2**



**Fig. 1** A packing view of the molecular crystal between phenanthridine and 3-indoleacetic acid

proton transfer to the N atom of **1** and decarboxylation to give the two radical species. Although these processes inevitably lead to the alternation of the crystal lattice composed of **1** and **2**, probably the radical species can move little in their lifetimes. The  $\text{NH}\cdots\text{CH}_2$  and  $\text{HC}\cdots\text{CH}_2$  distances between the two radical species (Scheme 2) are thought to be approximately 3.2 and 5.3 Å, which are values estimated from the crystallographic data of **3**. At  $-70^\circ\text{C}$ , the distance of 3.2 Å is short enough for hydrogen abstraction by the active  $\cdot\text{CH}_2$ -radical from the N-H, resulting in the formation of **4** and the regeneration of **1**. This indicates that **1** behaves like a sensitizer, acting only in one cycle, *i.e.* a stoichiometrical sensitizer. In the case of irradiation at  $15^\circ\text{C}$  the coupling product **5** can be also produced in low yield, probably because of a larger thermal motion of the radical species. In conclusion, molecular crystals between two different organic substances can be useful for accomplishing controlled and selective sensitized reactions.

One of the authors (K.D.) is a guest researcher from Zhengzhou University, China.

Received, 9th June 1994; Com. 4/03500C

#### Footnotes

† Crystal data for **3**:  $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2$ ,  $M = 354.41$ , triclinic, space group  $P\bar{1}$ ,  $a = 8.5082(5)$ ,  $b = 13.407(1)$ ,  $c = 8.4683(9)$  Å,  $\alpha = 103.018(7)$ ,  $\beta = 106.269(6)$ ,  $\gamma = 81.260(6)$ ,  $V = 899.4(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.309$  g cm<sup>-3</sup>,  $F(000) = 372.00$ , (Mo-K $\alpha$ ) =  $0.84$  cm<sup>-1</sup>. Of the 4123 reflections collected, 3023 data were used for the structure analysis; 245

parameters were refined anisotropically by full-matrix least-squares analysis to give  $R = 0.052$  and  $R_w = 0.042$ . Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Spectral data for **5**: mp  $201.5$ – $204.0^\circ\text{C}$  (from MeCN); UV  $\lambda_{\text{max}}$ (MeCN) 221 (log  $\epsilon$  4.76), 248 (4.69), 329 (3.43), 343 nm (3.36). IR (KBr) 3230, 3065, 2935, 1608, 1580, 1520, 1452, 1366, 1350, 1224, 1104, 762, 738, 728, 720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.90–8.67 (m, 13H), 6.60–6.73 (m, 1H), 4.80 (d,  $J = 2.0$  Hz, 2H). Analysis calculated for  $\text{C}_{22}\text{H}_{16}\text{N}_2$ : C, 85.69; H, 5.23; N, 9.08. Found: C, 85.78; H, 5.46; N, 9.08%.

§ Spectral data for **6**: mp  $263$ – $265^\circ\text{C}$  (from MeCN); UV  $\lambda_{\text{max}}$ (MeCN) 225 (log  $\epsilon$  4.86), 282 nm (4.11); IR (KBr), 3400, 3050, 2940, 2900, 2850, 1614, 1454, 1420, 1334, 1220, 1090, 744 cm<sup>-1</sup>; <sup>1</sup>H NMR ([<sup>2</sup>H]<sub>8</sub> THF)  $\delta$  9.73 (s, broad, 2H), 6.83–7.67 (m, 10H), 3.10 (s, 4H). Analysis calculated for  $\text{C}_{18}\text{H}_{16}\text{N}_2$ : C, 83.04; H, 6.19; N, 10.76. Found: C, 82.63; H, 6.33; N, 10.90%.

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