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 °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.[1] Although a large number of photodecarboxylations in solutions have been studied by using various acceptors such as aciridine and dicyanonaphthalene, the product selectivities are not necessarily high.[2–7] 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 °C, lower than those of **1** (106 °C) and **2** (169 °C). The crystal packing is shown in Fig. 1.† 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 OH···N hydrogen bonding with the H···N distance of 1.68 Å. The dihedral angle of the **1** and **2** aromatic planes is 84.84°. The molecule **2** is also connected to the next **2** along the *a* axis through NH···O=C hydrogen bonding with an H···O distance of 2.01 Å.

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 nm) for 3 h at −70 or 15 °C, or with a 400 W high-pressure mercury lamp for 1 h at 15 °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**,‡ the dimer of **4**, **6**,§ 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 °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

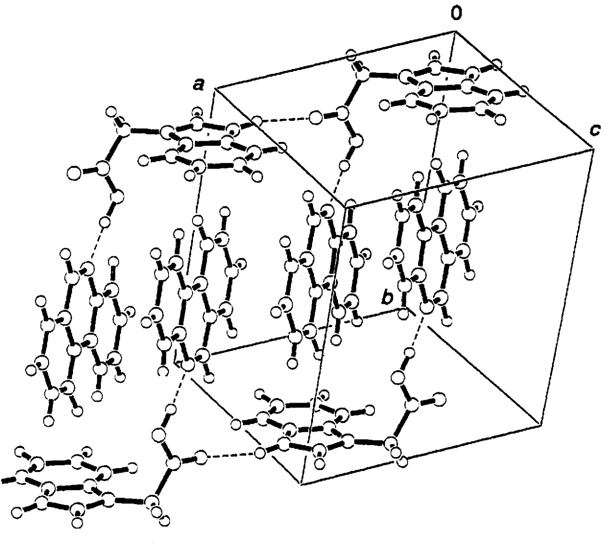
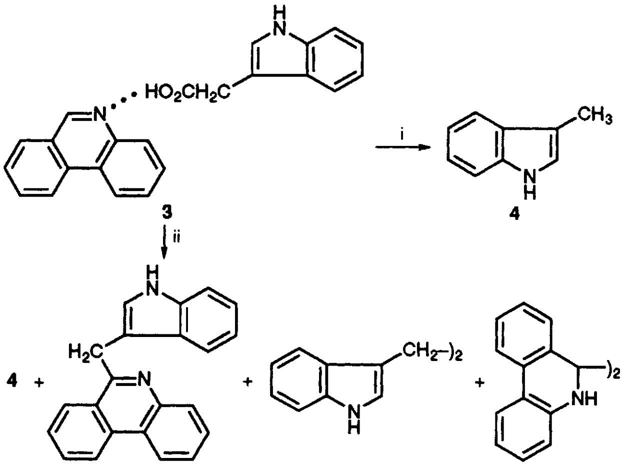


Fig. 1 A packing view of the molecular crystal between phenanthridine and 3-indoleacetic acid

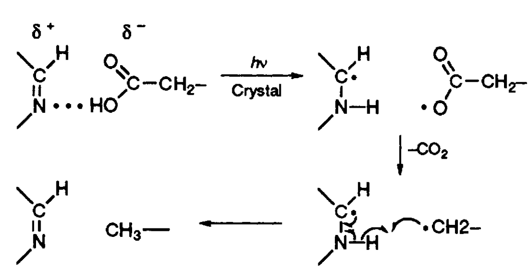
Table 1 Solid and solution photoreactions of phenanthridine and 3-indoleacetic acid

State on irrad. (Temp.)	Irrad. lamp	Conversion (%) 1	2	Yield based on consumed 2 (%) 4	5	6	7
Crystal 3 (−70 °C)	*a*	0	23	92	0	0	0
Crystal 3 (15 °C)	*a*	14	62	69	13	0	0
Crystal 3 (15 °C)	*b*	20	91	77	10	0	0
MeCN solution (room temp.)	*b*	74	69	18	29	21	56[c]

[a] Xe lamp with a UV transparent filter. [b] Hg lamp. [c] Yield based on consumed **1**.



Scheme 1 *Reagents and conditions*: i, *hν*, crystal, −70 °C; ii, *hν*, MeCN



Scheme 2

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 $N\underline{H}{\cdots}\underline{C}H_2$ and $H\underline{C}{\cdot}{\cdots}\underline{C}H_2$ 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 crystallograpic data of **3**. At −70 °C, the distance of 3.2 Å is short enough for hydrogen abstraction by the active $\cdot CH_2-$ 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 °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.

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Footnotes

† *Crystal data* for **3**: $C_{23}H_{18}O_2N_2$, M = 354.41, triclinic, space group $P\bar{1}$, a = 8.5082(5), b = 13.407(1), c = 8.4683(9) Å, α = 103.018(7), β = 106.269(6), γ = 81.260(6), V = 899.4(1) Å^3, Z = 2, D_c = 1.309 g cm^{-1}, $F(000)$ = 372.00, (Mo-Kα) = 0.84 cm^{-1}. 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 °C (from MeCN); UV λ_{max}(MeCN) 221 (log ε 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^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.90–8.67 (m, 13H), 6.60–6.73 (m, 1H), 4.80 (d, J = 2.0 Hz, 2H). Analysis calculated for $C_{22}H_{16}N_2$: 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 °C (from MeCN); UV λ_{max}(MeCN) 225 (log ε 4.86), 282 nm (4.11); IR (KBr), 3400, 3050, 2940, 2900, 2850, 1614, 1454, 1420, 1334, 1220, 1090, 744 cm^{-1}; ^{1}H NMR ([^{2}H]$_8$ THF) δ 9.73 (s, broad, 2H), 6.83–7.67 (m, 10H), 3.10 (s, 4H). Analysis calculated for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.63; H, 6.33; N, 10.90%.

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