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# Solid-State Photoreaction in Two-Component Molecular Crystals of Thienylacetic Acids and Aza Aromatic Compounds

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**Abstract**—A series of two-component molecular crystals of 2-thienylacetic acid (**1**) or bis(2-thienyl)acetic acid (**2**) with aza aromatic compounds such as acridine (**a**) and phenanthridine (**b**) were prepared by crystallization from the solutions of both components. Irradiation of the crystals caused photodecarboxylation and radical intermediates which give decarboxylated and condensation products. The relationship between the crystal structures and the reaction paths are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

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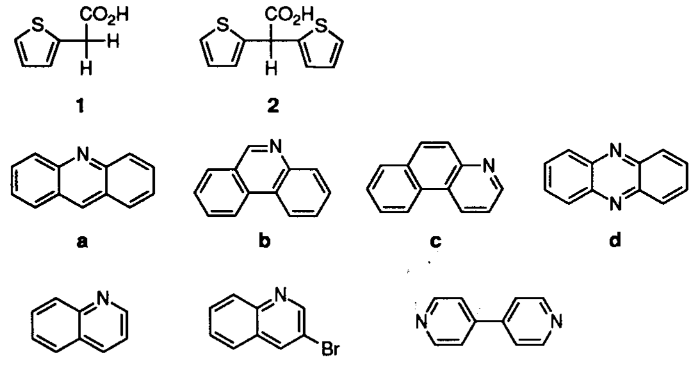
## Introduction

Solid-state photoreactions have attracted much attention from a number of organic chemists.[1–3] A large number of photoinduced electron transfer (PET) reactions are known in the solution phase.[4] We have developed solid-state bimolecular photoreactions utilizing PET in two-component molecular crystals in which the electron donor and electron acceptor species were combined.[5–7] It is well known that carboxylic acids undergo PET followed by decarboxylation when various electron acceptors are used.[8] We utilized this type of PET reaction for the two-component crystals formed from carboxylic acids and electron acceptors, and found that the solid-state photodecarboxylation usually occurred with a remarkable selectivity compared with the solution phase photodecarboxylation. These reactions comprise stoichiometrically sensitized decarboxylation in the two-component crystals of various aralkyl carboxylic acids and aza aromatic compounds;[9] photodecarboxylation and decarboxylative condensation in the CT crystals of arylacetic acids and 1,2,4,5-tetracyanobenzene through excitation of the CT bands;[10] photodecarboxylation in the two-component



Two-component molecular crystals

| | | | | | | |
|---|---|---|---|---|---|---|
| **1•a** | | | **1•d** | | | **1•g** |
| **2•a** | **2•b** | **2•c** | **2•d** | **2•e** | **2•f** | **2•g** |

**Chart 1.**

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*Keywords*: solid state bimolecular photoreactions; photodecarboxylation; two-component molecular crystals; thienylacetic acids, aza aromatic compounds.

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**Table 1.** Crystal data of the two-component crystals

| | **1·a** | **2·a** | **2·b** |
|---|---|---|---|
| *Crystal data* | | | |
| Formula | $C_{19}H_{15}NO_2S$ | $C_{33}H_{25}NO_4S_4$ | $C_{23}H_{17}NO_2S_2$ |
| $M_w$ | 321.39 | 627.80 | 403.51 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 10.190(1) | 10.037(2) | 9.815(2) |
| $b$ (Å) | 10.646(2) | 13.309(3) | 13.608(3) |
| $c$ (Å) | 7.7448(2) | 6.051(2) | 8.430(1) |
| $\alpha$ (°) | 95.28(2) | 99.22(2) | 99.79(1) |
| $\beta$ (°) | 98.65(2) | 106.98(2) | 104.62(2) |
| $\gamma$ (°) | 106.27(1) | 79.91(2) | 106.58(2) |
| $V$ (Å$^3$) | 789.3(3) | 756.0(4) | 1008.0(4) |
| $Z$ | 2 | 1 | 2 |
| $Dc$ (g cm$^{-3}$) | 1.352 | 1.379 | 1.329 |
| $F$(000) | 336.00 | 326.00 | 420.99 |
| $\mu$ (cm$^{-3}$) | 2.14 | 3.54 | 2.70 |
| *Data collection* | | | |
| Crystal size (mm) | 0.2×0.3×0.5 | 0.4×0.3×0.5 | 0.3×0.4×0.6 |
| $2\theta_{max}$ (°) | 55.0 | 50.0 | 50.0 |
| No. of reflections measured | 3831 | 2823 | 3765 |
| *Final refinement* | | | |
| No. of observations, $I>3\sigma(I)$ | 2721 | 1441 | 2348 |
| No. of variables | 186 | 161 | 257 |
| $R$ | 0.077 | 0.086 | 0.055 |
| $R_w$ | 0.128 | 0.118 | 0.080 |

crystals of *N*-phenylglycine and aza aromatic compounds;[11] enantioselective photodecarboxylative condensation in chiral crystals;[12,13] and absolute asymmetric synthesis by photodecarboxylative condensation within the chiral two-component crystal formed from diphenylacetic acid and acridine.[14]

This paper describes the preparation of a series of thienylacetic acids and aza aromatic compounds and their solid-state and solution photoreactions.

## Results and Discussion

### Two-component molecular crystals

2-Thienylacetic acid (**1**) and bis(2-thienyl)acetic acid (**2**) were chosen as carboxylic acids and acridine (**a**), phenanthridine (**b**), benzo[*f*]quinoline (**c**), phenazine (**d**), quinoline (**e**), 3-bromoquinoline (**f**), and 4,4′-bipyridine (**g**) as aza aromatic compounds (Chart 1). Ten two-component molecular crystals were prepared by crystallization from the solutions of both components. The molar ratios of the acid and aza aromatic compounds are 1:1 for **1·a**, **2·b**, **2·c**, **2·e** and **2·f**, 2:1 for **1·d**, **1·g**, **2·a** and **2·g**, and 2:3 for **2·d**. The solvents, melting points and IR spectra are summarized in the Experimental section. The solid-state CD spectra of the crystals were measured as Nujol mulls to determine whether the crystals are chiral or not.[15,16] However, no significant solid-state CD spectra were observed for any of the 10 crystals, suggesting that these crystals are most probably achiral. Three crystals **1·a**, **2·a** and **2·b** were submitted to X-ray crystallographic analysis to confirm their achiral nature, and all were found to belong to space group $P\bar{1}$. The details of the crystal data are listed in Table 1.

Fig. 1 shows the molecular arrangement of **1·a**. The molecule of **1** is connected to **a** through O–H···N hydrogen bonding with an H1–N1 distance of 1.74 Å (Fig. 1b). The two antipodal molecular pairs are arranged centrosymmetrically in the unit cell ($P\bar{1}$, $Z=2$) (Fig. 1a). Further, these pairs are stacked in a head-to-tail manner to form a columnar structure along the *c*-axis (Fig. 1b). The acridine molecules are almost parallel with a plane-to-plane distance of 4.0 Å. Here the thiophene ring of molecule **1** is disordered, with S and C atoms coexisting at 75 and 25% occupancies, respectively.

The crystal **2·a** (Fig. 2) has a very different packing arrangement. The two molecules of **2** form a carboxy dimer in the lattice (Fig. 2a). Further, an acridine molecule is surrounded by two carboxy dimers to form an inclusion complex on the *ab* face. One of thiophene rings of molecule **2** is disordered, with S and C atoms coexisting at 60 and 40% occupancies, respectively (Fig. 2b). The acridine molecule is also disordered with the coexistence of N and C atoms at 50% occupancy. The position of the carboxy hydrogen atom could not be determined probably due to disorder.

The crystal **2·b** (Fig. 3) has a similar molecular arrangement to that of **1·a**. The molecule of **2** is connected to **b** through O–H···N hydrogen bonding with an H1–N1 distance of 1.73 Å (Fig. 3b). The two antipodal pairs are arranged centrosymmetrically in the unit cell ($P\bar{1}$, $Z=2$) (Fig. 3a). Further, the pairs are stacked in a head-to-tail manner to form a columnar structure along the *c*-axis (Fig. 3b). The phenanthridine molecules are almost parallel with a plane-to-plane distance of 3.6 Å.

### Solution and solid-state photoreactions

Herein photoreactions of **1** with **a**, and **2** with **a** or **b** were

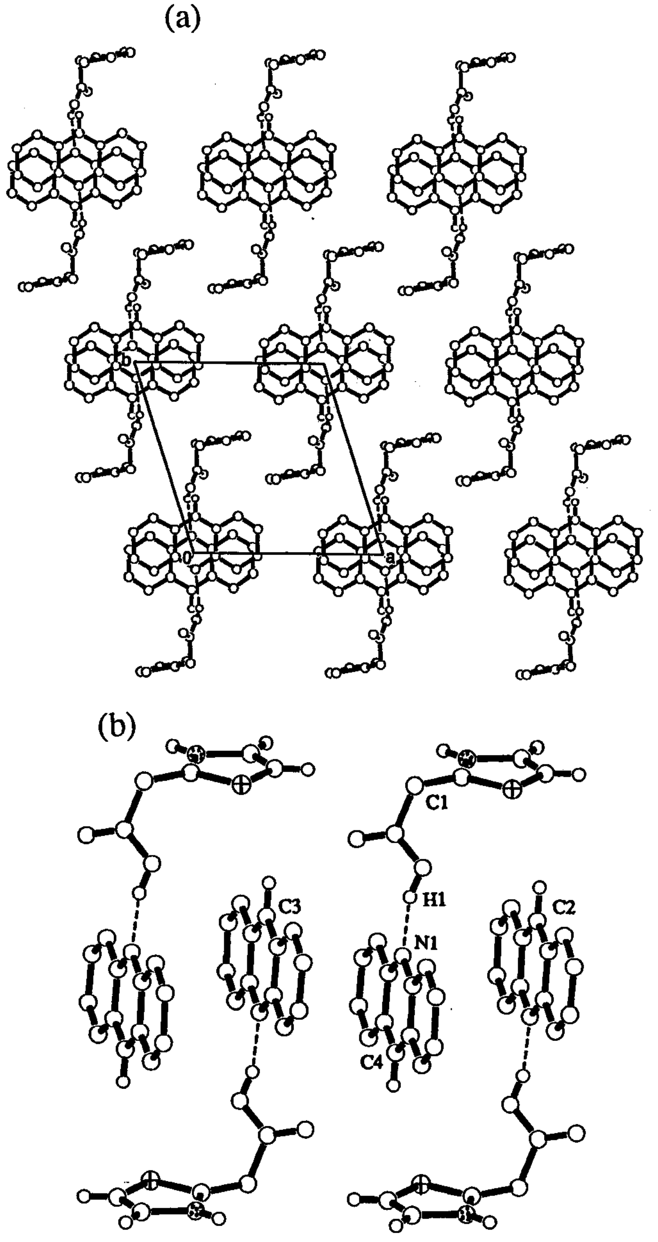


**Figure 1.** (a) Molecular arrangement and (b) reaction path in the crystal **1·a**. In (b), crossed atoms in the disordered thiophene represent the coexistence of S and C atoms with occupancies of 75 and 25%, respectively; conversely dotted atoms, 25 and 75%.

examined. Irradiation of **1** and **a** in acetonitrile under argon resulted in decarboxylation followed by radical coupling to give condensation product **3** and biacridane (**4**) as the main products with low product selectivities (Scheme 1 and Table 2, entry 5). The solid-state photoreaction of crystalline **1·a** at 15°C afforded the same products **3** and **4** as those from the solution reaction (entries 1 and 2). However, irradiation at −30°C gave **3** alone in low yields (entries 3 and 4). The poor material balance may be due to vaporization of the possible decarboxylated product 2-methylthiophene during irradiation as discussed below.

Irradiation of **2** and the aza aromatic compound **a** or **b** in acetonitrile caused similar decarboxylation to give 1,1,2,2-tetrakis(2-thienyl)ethane (**7**) as the decarboxylated dimer and the corresponding condensation product **6** or **8**, respectively (Scheme 2 and Table 3, entries 10 and 11). In contrast to the high conversion of **a** (92%), **b** was consumed only slightly (14%).

On the other hand, irradiation of the crystal **2·a** gave bis(2-thienyl)methane (**5**) as the decarboxylated product, and **6** as the condensation product (Table 3, entries 1–3). Here, the product **5** is different from the decarboxylated dimer **7** produced by the solution reaction. However, at the initial reaction stage, **5** alone was selectively obtained on irradiation at −10 and −30°C (entries 4 and 5). The low yields of **5** suggest the occurrence of side reactions. The reaction was brought about by irradiation using visible light (>400 nm) (entry 3). Therefore, this reaction can be induced by the excitation of the acridine molecule **a** at >400 nm, and **a** acts as the excited species in the crystal **2·a**.

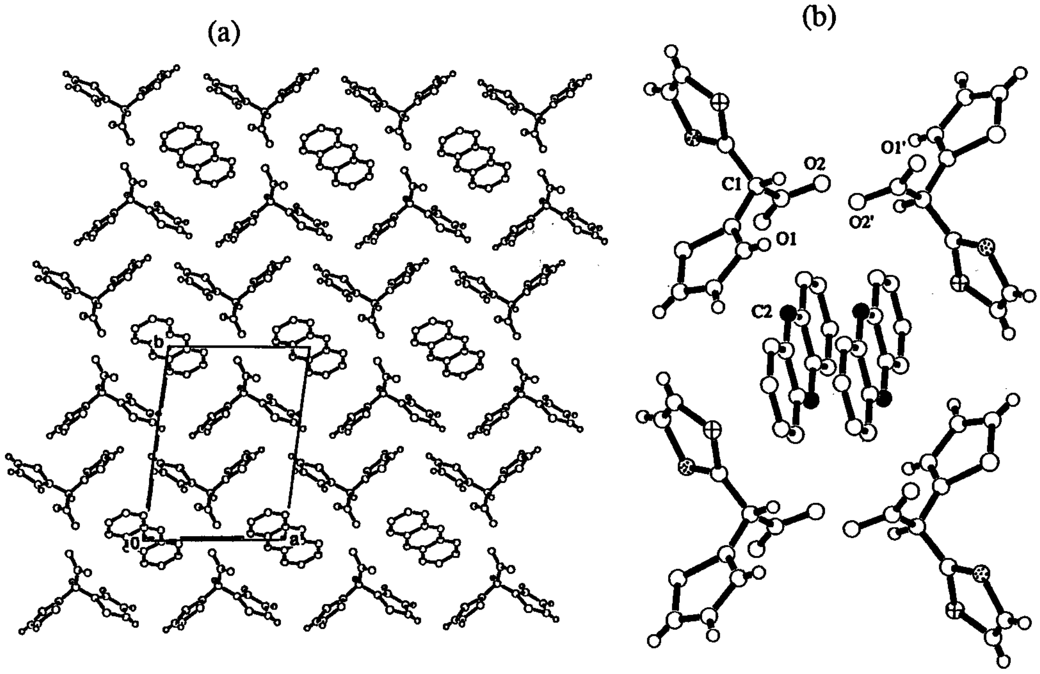


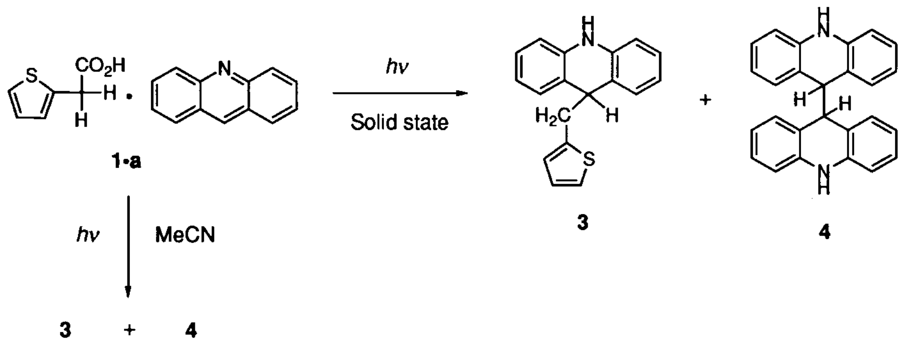
**Figure 2.** (a) Molecular arrangement and (b) reaction path in the crystal **2·a**. In (b), crossed atoms in the disordered thiophene represent the coexistence of S and C atoms with occupancies of 60 and 40%, respectively; conversely dotted atoms, 40 and 60%. Black atoms in the disordered acridine represent the coexistence of N and C atoms with occupancies of 50%.

Solid-state photoreaction of the crystal **2·b** gave **5** and **8**, similarly to those of **2·a** (entries 6 and 7). Only **5** was selectively obtained at the initial reaction stage of the irradiation under cooling (entries 8 and 9).

Scheme 3 shows the possible reaction mechanism. Irradiation of the crystal causes electron transfer from the acid to the aza aromatic compound followed by proton transfer, or conversely proton transfer followed by electron transfer, to afford carboxylate radical (**9**), and hydroacridine radical (**10**) or hydrophenanthridine radical (**11**). Next, decarboxylation of **9** produces the radical (**12**). Hydrogen abstraction can occur from the N–H of **10** or **11** by the active radical **12** leading to the formation of **5** in the crystals **2·a** and **2·b**, as opposed to the radical coupling of **12** to give **7** in solution. Radical coupling between **12** and **10**, or **12** and **11** occurs to give **3**, **6** or **8**. In the crystal **1·a**, radical coupling of **10** also can occur to produce the dimer **4**.

Although these reaction processes inevitably lead to alteration of the crystal lattice, the reaction paths at the initial reaction stage can be discussed on the basis of the distances estimated from the crystallographic data. In the crystal **1·a** (Fig. 1b), hydrogen abstraction should be a higher priority than radical coupling because of the shorter C1–H1 distance (3.18 Å) for hydrogen abstraction than the C1–C2 or C1–C3 radical coupling distances of 5.18 or 5.72 Å, respectively. Probably the reason why 2-methylthiophene (derived from hydrogen abstraction) was not obtained is its vaporization during the irradiation (Table 2, entries 3 and 4). The relatively high yields of radical coupling products **3** and **4** can be explained by the considerable decomposition of the initial crystal structure of **1·a** at the high conversions (100 and 65%) of **1** and **a**, respectively (entry 2).

The crystal **2·a** has an inclusion complex structure (Fig. 2).



**Scheme 1.**

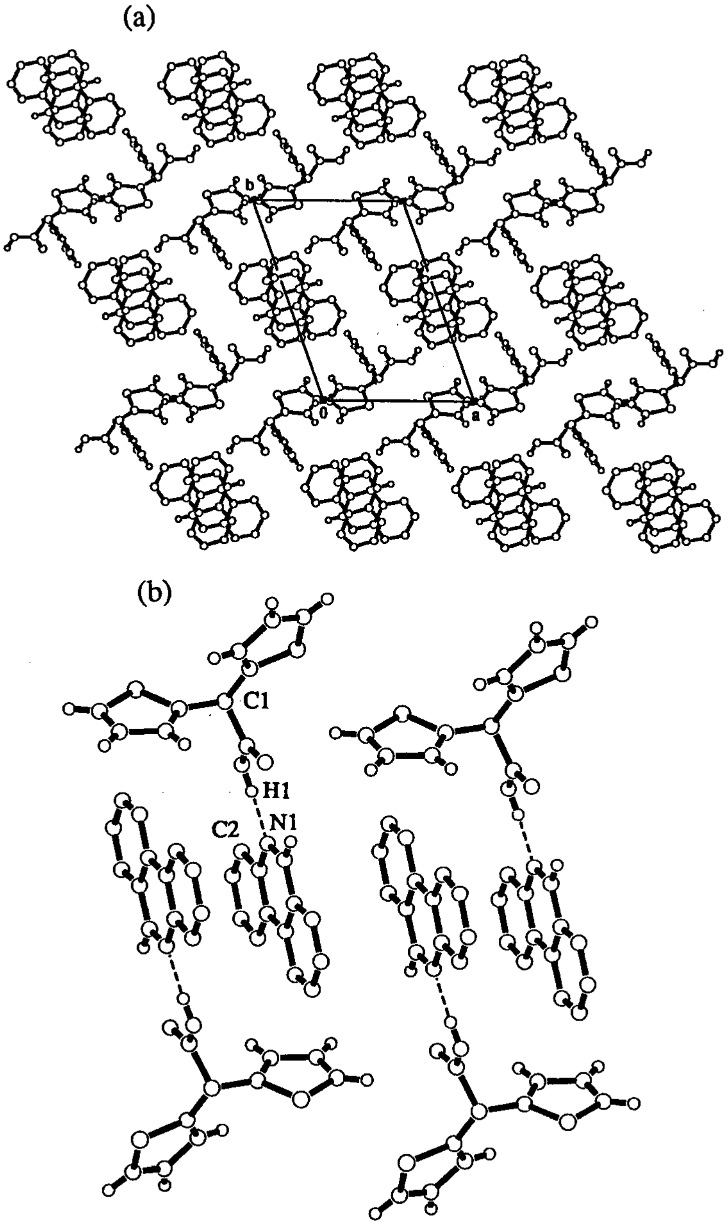


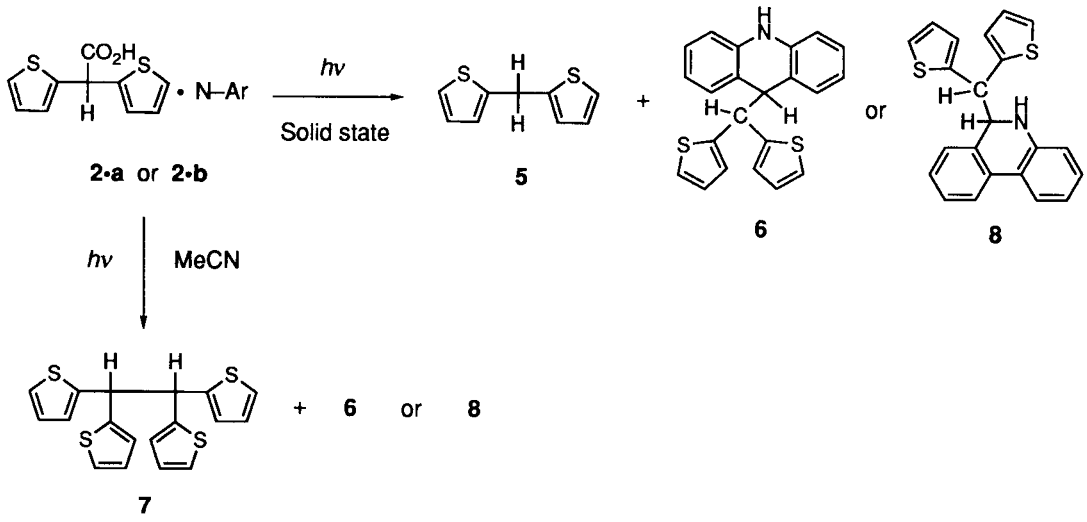
**Figure 3.** (a) Molecular arrangement and (b) reaction path in the crystal **2·b**.

The two molecules of **2** should form a carboxy dimer from the O1···O2′ distance of 3.10 Å and also hydrogen bonding to the acridine molecule from the O1···N(C2) distance of 2.97 Å (Fig. 2b). Here the N atom is disordered, with the N and C atoms coexisting at 50% occupancies. The active radical **12** abstracts the carboxy hydrogen to give **5** alone at the initial reaction stage, but the distance for hydrogen abstraction is not known because the position of the carboxy hydrogen atom could not be found in the crystal data analysis. Radical coupling with the C1–C2 radical distance (4.98 Å) gives **6**.

**Table 2.** Photoreaction of 2-thienylacetic acid and acridine in crystalline state and in solution

| Entry | Irradiation | | | Conversion (%) | | Corrected yield (%) | |
|---|---|---|---|---|---|---|---|
| | (°C) | Lamp | (h) | **1** | **a** | **3** | **4** |
| *Solid state* | | | | | | | |
| 1 | 15 | Hg | 0.1 | 83 | 18 | 23 | 30 |
| 2 | 15 | Hg | 0.5 | 100 | 65 | 52 | 48 |
| 3 | −30 | Xe | 2 | 33 | 3 | 12 | – |
| 4 | −30 | Xe | 5 | 51 | 4 | 8 | – |
| *MeCN soln.* | | | | | | | |
| 5 | rt | Hg | 4 | 81 | 100 | 44 | 45 |

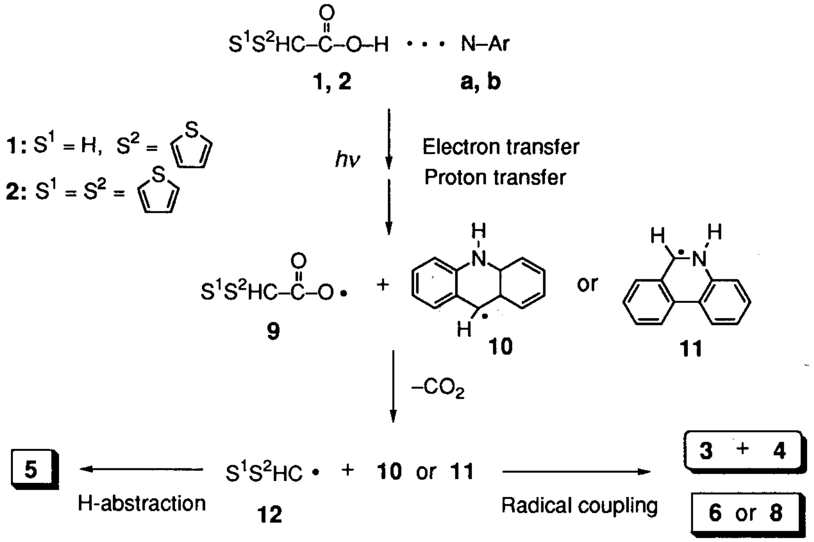
In the case of crystal **2·b** (Fig. 3b), hydrogen abstraction by the radical **12** occurs across the shortest C1–H1 distance (3.14 Å) at the initial reaction stage under cooling (Table 3, entries 8 and 9). Radical coupling also occurs upon irradiation at 15°C between a neighboring radical pair **12** and **11**, which is derived from a hydrogen bonding pair with the C1–C2 distance (5.27 Å) in the starting crystal (entries 6 and 7).



**Scheme 2.**

**Table 3.** Photoreaction of bis(2-thienyl)acetic acid and aza aromatic compounds in solid state and in solution

| Entry | Components | Irradiation | | | Conversion (%) | | Corrected yield (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | (°C) | Lamp | (h) | **2** | **a** or **b** | **5** | **7** | **6** | **8** |
| *Solid state* | | | | | | | | | | |
| 1 | **2·a** | 15 | Hg | 0.5 | 96 | 92 | 25 | | 76 | |
| 2 | **2·a** | 15 | Xe | 1 | 74 | 12 | 24 | | 63 | |
| 3 | **2·a** | 15 | Xe (>400 nm) | 1 | 62 | 12 | 27 | | 75 | |
| 4 | **2·a** | −10 | Xe | 1 | 26 | 7 | 30 | | – | |
| 5 | **2·a** | −30 | Xe | 4 | 15 | 5 | 39 | | – | |
| 6 | **2·b** | 15 | Hg | 0.5 | 100 | 23 | 63 | | | 40 |
| 7 | **2·b** | 15 | Xe | 1 | 37 | 12 | 59 | | | 23 |
| 8 | **2·b** | −10 | Xe | 1 | 10 | 11 | 72 | | | – |
| 9 | **2·b** | −30 | Xe | 1 | 7 | 4 | 56 | | | – |
| *MeCN soln.* | | | | | | | | | | |
| 10 | **2**+**a** | rt | Hg | 5 | 100 | 92 | | 13 | 65 | |
| 11 | **2**+**b** | rt | Hg | 9 | 89 | 14 | | 49 | | 50 |



**Scheme 3.**

## Experimental

### General procedures

$^1$H-NMR spectra were measured on a JEOL JNM-GSX270 spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a Horiba FT/IR-210 spectrophotometer. Melting points 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.

### Preparation of two-component molecular crystals

The two-component molecular crystals investigated here incorporate 2-thienylacetic acid (**1**) and bis(2-thienyl)acetic acid (**2**) as the acid components and aza aromatic compounds such as acridine (**a**), phenanthridine (**b**), benzo[*f*]quinoline (**c**), phenazine (**d**), quinoline (**e**), 3-bromoquinoline (**f**), and 4,4′-bipyridine (**g**) as electron acceptors (Chart 1). The starting acid compound **2** was synthesized by condensation of chloral and thiophene followed by alkaline treatment.[17,18] Ten two-component molecular crystals were prepared by crystallization from the solutions of both components:

**1·a**: yellow prisms; 1:1; mp 68–71°C (from MeCN); IR (KBr) 3057, 1697 cm$^{-1}$;
**1·d**: yellow needles; 2:1; mp 71–73°C (from MeCN); IR (KBr) 1716 cm$^{-1}$;
**1·g**: brown prisms; 2:1; mp 75–78°C (from MeCN); IR (KBr) 3091, 1691 cm$^{-1}$;
**2·a**: brown prisms; 2:1; mp 80–83°C (from AcOEt); IR (KBr) 3088, 1701 cm$^{-1}$;
**2·b**: brown prisms; 1:1; mp 67–68°C (from AcOEt); IR (KBr) 3103, 1718 cm$^{-1}$;
**2·c**: brown prisms; 1:1; mp 85–88°C (from AcOEt); IR (KBr) 3101, 1713 cm$^{-1}$;
**2·d**: yellow needles; 2:3; mp 112–116°C (from MeCN); IR (KBr) 3093, 1705 cm$^{-1}$;
**2·e**: brown prisms; 1:1; mp 73–76°C (from AcOEt); IR (KBr) 3097, 1709 cm$^{-1}$;
**2·f**: brown prisms; 1:1; mp 66–68°C (from AcOEt); IR (KBr) 3107, 1720 cm$^{-1}$;
**2·g**: brown prisms; 2:1; mp 93–95°C (from MeCN); IR (KBr) 3105, 1701 cm$^{-1}$.

### Preparative photoreaction in solutions

Common procedure: a solution (100 ml) of a thienylacetic acid (5 mmol) and an aza aromatic compound (5 mmol) was internally irradiated with a 100-W high-pressure mercury lamp under argon bubbling at room temperature. The reaction mixture was filtered to separate a precipitate of **4**, **6** or **8** and then the solution was submitted to preparative TLC (silica gel plate).

Irradiation of **1** (711 mg) and **a** (895 mg) in MeCN for 4 h gave **3** (604 mg) and **4** (420 mg) in 44 and 47% yields, respectively.

**3**: mp 195–196°C (from MeCN); $^1$H NMR ($CDCl_3$) $\delta$ 7.07–7.13 (m, 3H), 6.97 (dd, $J$=7.5, 1.2 Hz, 2H), 6.80–8.86 (m, 3H), 6.71 (dd, $J$=7.5, 1.2 Hz, 2H), 6.35 (d, $J$=2.7 Hz, 1H), 6.01 (s, 1H), 4.22 (t, $J$=6.9 Hz, 1H), 3.05 (d, $J$=6.9 Hz, 2H); IR (KBr) 3375 cm$^{-1}$. Anal. Calcd for $C_{18}H_{15}NS$: C, 77.94; H, 5.45; N, 5.05. Found: C, 77.87; H, 5.53; N, 4.95.

**4**: mp 211–212°C (from THF). The IR spectrum and elemental analysis of **4** were consistent with those of the authentic sample.[7]

Irradiation of **2** (1121 mg) and **a** (895 mg) in MeCN for 5 h gave **6** (1303 mg) and **7** (268 mg) in 65 and 13% yields, respectively.

**6**: mp 206–208°C (from MeCN); $^1$H NMR (DMSO-$d_6$) $\delta$ 9.15 (s, 1H); 6.82–6.85 (m, 4H), 6.73 (s, 2H), 6.70 (s, 4H), 6.49–6.58 (m, 4H), 4.55 (d, $J$=8.4 Hz, 1H), 4.39 (d, $J$=8.4 Hz, 1H); IR (KBr) 3373 cm$^{-1}$. Anal. Calcd for $C_{22}H_{17}NS_2$: C, 73.49; H, 4.77; N, 3.90. Found: C, 73.55; H, 4.82; N, 4.08.

**7**: mp 161–164°C (from MeCN); $^1$H NMR ($CDCl_3$) $\delta$ 7.08–7.10 (m, 4H), 6.78–6.82 (m, 8H), 5.14 (d, $J$=10.5 Hz, 2H); IR (KBr) no NH. Anal. Calcd for $C_{18}H_{14}S_4$: C, 60.29; H, 3.94. Found: C, 60.23; H, 3.94.

Irradiation of **2** (1121 mg) and **b** (895 mg) in MeCN for 9 h gave **7** (520 mg) and **8** (145 mg) in 26 and 7% yields, respectively.

**8**: mp 206–208°C (from MeCN); $^1$H NMR (DMSO-$d_6$) $\delta$ 8.12 (d, $J$=7.5 Hz, 4H), 7.97 (d, $J$=7.5 Hz, 4H), 7.76–7.85 (m, 6H), 6.45 (d, $J$=7.5 Hz, 1H), 6.30 (d, $J$=7.5 Hz, 1H), 5.57 (s, 1H); IR (KBr) 3375 cm$^{-1}$. Anal. Calcd for $C_{22}H_{17}NS_2$: C, 73.49; H, 4.77; N, 3.90. Found: C, 73.77; H, 4.91; N, 4.12.

### Solid-state photoreaction

A crystal (20 mg) was pulverized in a mortar, placed between two Pyrex glass plates, and irradiated under argon with a 400-W high-pressure mercury lamp (>290 nm irradiation), or a 500-W xenon short arc lamp with a UV cut filter (>400 nm irradiation) or without filter (>290 nm irradiation). The irradiated sample was filtered and the solution was treated with $CH_2N_2$ followed by HPLC analysis. The results are shown in Schemes 1 and 2, and Tables 2 and 3.

### X-Ray crystallographic analysis

Three crystals of **1·a**, **2·a** and **2·b** were submitted to X-ray structure analysis. Data collections were performed on a Rigaku AFC5R automatic four-circle X-ray diffractometer with a graphite-monochromated Mo K$\alpha$ ($\lambda$=0.71069 Å) radiation. Absorption corrections were applied. No degradation of the crystal by X-ray was ascertained in all cases by repeated monitoring of the three representative reflections every 150 reflections. These structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Atomic parameters were refined by the full-matrix least-squares method at the final stage. All the calculations were carried out on teXsan crystallographic software package, Molecular Structure Corporation. The crystal data are listed in Table 1.

## Acknowledgements

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