

Cocrystals composed of 4,4'-(fluorene-9,9-diyl)diphenol and 6-methyl-2H-pyridone

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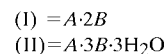
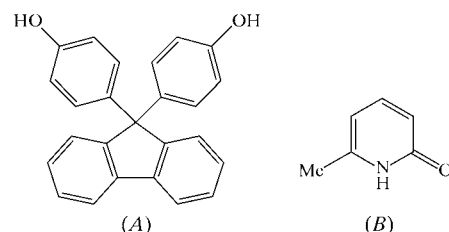
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The crystal structures of two cocrystals composed of 4,4'-(fluorene-9,9-diyl)diphenol ($C_{25}H_{18}O_2$) and 6-methyl-2H-pyridone (C_6H_7NO) are reported, namely 4,4'-(fluorene-9,9-diyl)diphenol–6-methyl-2H-pyridone (1/2), $C_{25}H_{18}O_2 \cdot 2C_6H_7NO$, (I), and 4,4'-(fluorene-9,9-diyl)diphenol–6-methyl-2H-pyridone–water (1/3/3), $C_{25}H_{18}O_2 \cdot 3C_6H_7NO \cdot 3H_2O$, (II). In both cocrystals, the mutual orientation between two 6-methyl-2H-pyridone molecules in principle enables photodimerization, yet in both cases no photodimerization occurs. In cocrystal (I) this is probably due to poor orbital overlap, while in the case of cocrystal (II) it is suggested that the lack of reaction is due to the highly complex hydrogen-bonding network that exists in the structure.

Comment

Among the numerous uses of solid inclusion compounds (Tanaka & Toda, 2002; Toda *et al.*, 2001; Toda, 1995, 1996, 1988; Toda & Tanaka, 1984), those consisting of light-stable host molecules and light-sensitive guest molecules can be used for monitoring photochemical reactions in the solid state

provided that the integrity of the single crystal is preserved throughout the reaction. The reaction of the guest molecules takes place in a cavity formed by the host; therefore, in the cases where the volume of the cavity is sufficient to accommodate the product, single-crystal-to-single-crystal transformations can occur (Lavy *et al.*, 2004; Tanaka *et al.*, 2000; Hosomi *et al.*, 2000; Tanaka, Mizutani *et al.*, 1999; Tanaka, Toda *et al.*, 1999). 4,4'-(Fluorene-9,9-diyl)diphenol (*A*) was found to be an effective clathrate host and a useful construction element to form rigid macrocyclic host compounds (Apel *et al.*, 2001). However, only two cocrystals containing *A* were found in the Cambridge Structural Database [Allen, 2002; refcodes ABUCIJ and ABUCUV (Apel *et al.*, 2001)]. We report here the structures of two new cocrystals containing *A* and the photosensitive molecule 6-methyl-2H-pyridone (*B*). These cocrystals were crystallized in an attempt to achieve single-crystal-to-single-crystal photodimerization in inclusion compounds. Cocrystal (I) (Fig. 1) crystallizes in the monoclinic space group $C2/c$. The asymmetric unit contains one molecule of *A* and two molecules of *B*. Cocrystal (II) (Fig. 2) also crystallizes in the monoclinic space group $C2/c$. In this case, the asymmetric unit contains one molecule of *A*, three molecules of *B* (*Ba*, *Bb* and *Bc*) and three water molecules.



In cocrystal (I), pairs of molecules of *B* form hydrogen-bonded dimers, as in many structures of pyridone derivatives (Lavy & Kaftory, 2006; Lavy *et al.*, 2006). Each dimer is connected *via* hydrogen bonding to two molecules of *A*, creating infinite chains (Fig. 3 and Table 1). The mutual relationship between two adjacent molecules of *B* in different chains has been examined with respect to their potential to undergo photodimerization in the solid state. The distances

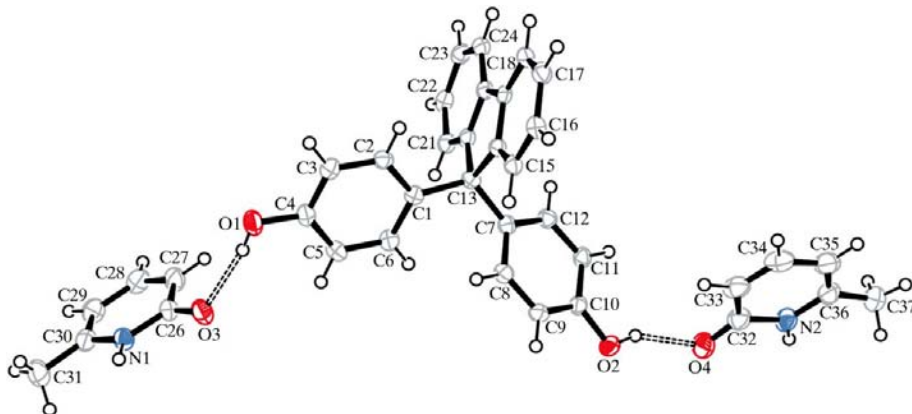


Figure 1

The asymmetric unit of cocrystal (I). Displacement ellipsoids are drawn at the 50% probability level.

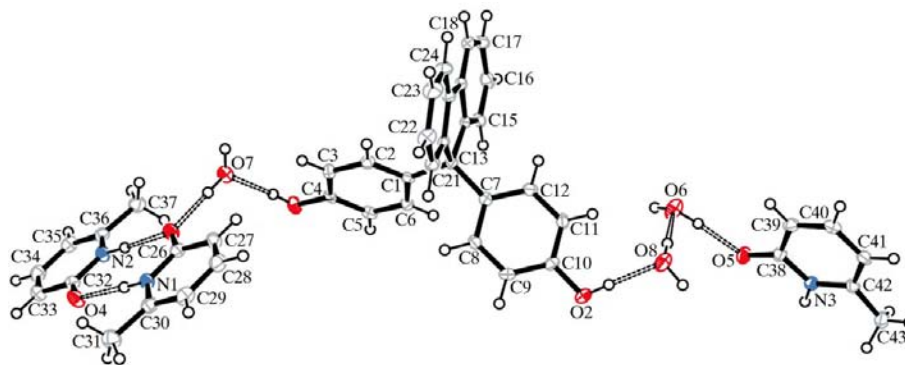


Figure 2
The asymmetric unit of cocrystal (II). Displacement ellipsoids are drawn at the 50% probability level.

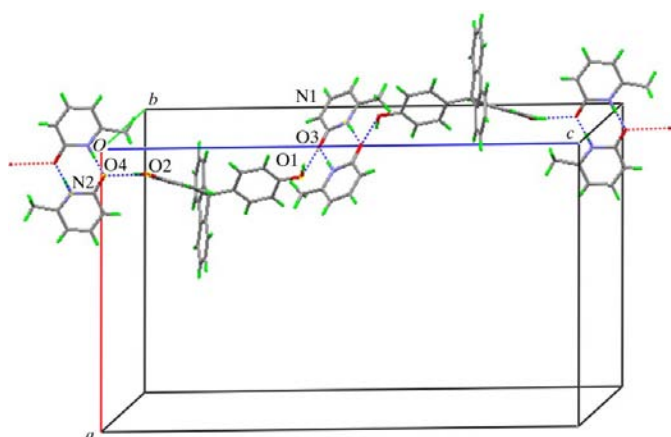


Figure 3
The hydrogen-bond network in (I) (hydrogen bonds are shown as dotted lines).

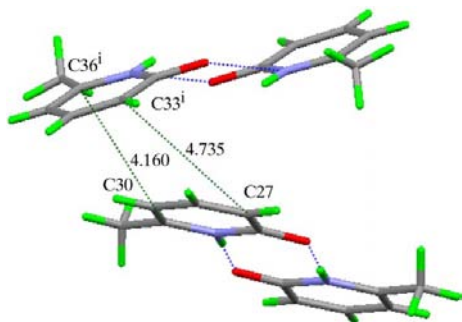


Figure 4
The mutual relationship between two adjacent dimers of 6-methyl-2H-pyridone in (I) (hydrogen bonds are shown as dotted lines). [Symmetry code: (i) $-x, y + 1, -z + \frac{1}{2}$]

between the potentially reactive atoms for a head-to-head photodimerization are 4.160 (3) Å [C30(*Ba*)...C36(*Bb*)] and 4.735 (3) Å [C27(*Ba*)...C33(*Bb*)] (Fig. 4); the former separation distance falls just within the literature limit of 4.2 Å for solid-state photodimerization (Schmidt, 1971). The angle between the mean planes of the two molecules of *B* is 39.02 (8)°, which deviates significantly from parallelism. The long distances and large angle result in poor orbital overlap efficiency, according to the definition given by Kearsley

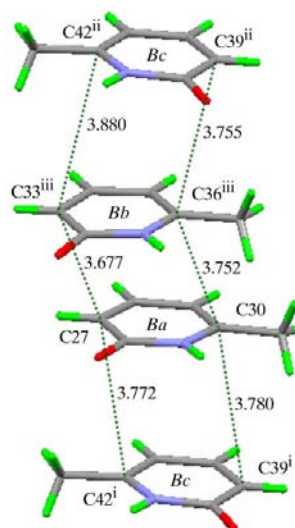


Figure 5
The mutual relationship between *B* molecules in cocrystal (II). [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x + 1, -y + 1, z - \frac{1}{2}$; (iii) $-x + 2, -y + 1, -z$.]

(1987). Nonetheless, a single crystal of (I) was irradiated for 15 h, after which there was no evidence of photodimerization having occurred.

In cocrystal (II), the three methylpyridone molecules in the asymmetric unit are arranged in an antiparallel manner. The methyl group of molecule *Ba* faces in the opposite direction to that of *Bc* but has the same direction as the methyl group of *Bb* (Fig. 5). The structure consists of a complex hydrogen-bonded network (Fig. 6 and Table 2), with pairs of methylpyridone molecules forming hydrogen-bonded dimers, which are stacked in parallel above one another. Each methylpyridone dimer is hydrogen bonded to two water molecules, one on each side of the dimer. In turn, each water molecule is also hydrogen bonded to the host molecule *A* and another water molecule in an adjacent layer. For a possible head-to-tail photodimerization, the distances between potentially reacting atoms in the case of reaction between molecules *Ba* and *Bc* are 3.773 (3) Å [C27(*Ba*)...C42(*Bc*)] and 3.780 (3) Å [C30(*Ba*)...C39(*Bc*)], and the distances between potentially reacting atoms in the case of head-to-tail reaction between molecules

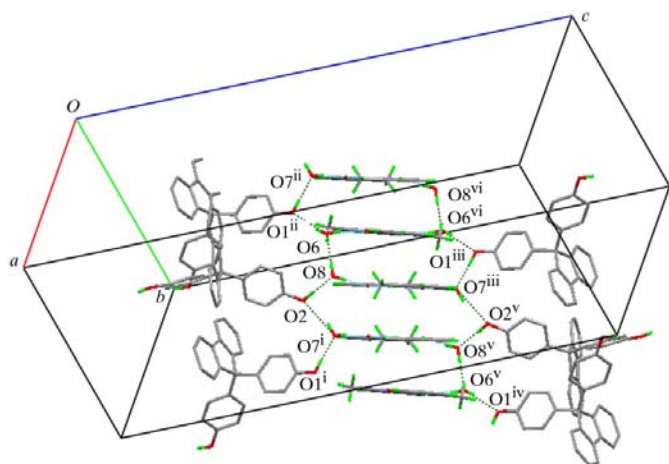


Figure 6

The hydrogen-bond network in cocrystal (II) (hydrogen bonds are shown as dotted lines). [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x, -y + 2, z + \frac{1}{2}$; (v) $-x + 1, -y + 2, -z + 1$; (vi) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

Bb and Bc are 3.879 (3) Å [$C33(Bb) \cdots C42(Bc)$] and 3.755 (3) Å [$C36(Bb) \cdots C39(Bc)$]. The distances between potentially reacting atoms in the case of head-to-head reaction between Ba and Bb are 3.752 (3) Å [$C30(Ba) \cdots C36(Bb)$] and 3.677 (3) Å [$C27(Ba) \cdots C33(Bb)$]. In principle, all of these distances enable photodimerization; however, no photodimerization occurred after irradiation of a single crystal of (II) for 17 h.

In the case of (I), we believe that the unfavourable orientation of two 6-methyl-2H-pyridone molecules with respect to each other for photodimerization explains the lack of reaction. However, in the case of (II) the situation is different. The mutual orientation between the potentially reacting molecules in (II) would seem to permit photodimerization in a manner seen previously (Lavy & Kaftory, 2007). We suggest that the complex hydrogen bonding described above prevents photodimerization, as any such reaction would require disruption of the hydrogen-bonding network, which is probably energetically unfavourable.

Experimental

The component substances were purchased from Sigma. The cocrystals were obtained from ethyl acetate solutions of mixtures of the components (typical quantities 0.005 g). The solution was left to evaporate at room temperature and, after a week, crystals were obtained. Two types of crystals were found in the same vial and were selected by their different morphological forms.

Cocrystal (I)

Crystal data

$C_{25}H_{18}O_2 \cdot 2C_6H_7NO$
 $M_r = 568.65$
 Monoclinic, $C2/c$
 $a = 17.480$ (4) Å
 $b = 11.114$ (2) Å
 $c = 29.698$ (6) Å
 $\beta = 93.894$ (8)°
 $V = 5756$ (2) Å³

$Z = 8$
 $D_x = 1.312$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 120$ (2) K
 Prism, colourless
 $0.30 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART 6K CCD
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1998)
 $T_{min} = 0.975, T_{max} = 0.992$

23891 measured reflections
 5129 independent reflections
 3823 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.056$
 $\theta_{max} = 25.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.147$
 $S = 1.16$
 5129 reflections
 390 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.31$ e Å⁻³
 $\Delta\rho_{min} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H1A \cdots O3	0.84	1.89	2.672 (2)	155
O2–H2A \cdots O4	0.84	1.89	2.646 (2)	149
N1–H1B \cdots O3 ⁱ	0.88	1.88	2.755 (2)	174
N2–H2B \cdots O4 ⁱⁱ	0.88	2.18	2.940 (2)	145

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x, -y - 1, -z$.

Cocrystal (II)

Crystal data

$C_{25}H_{18}O_2 \cdot 3C_6H_7NO \cdot 3H_2O$
 $M_r = 731.82$
 Monoclinic, $C2/c$
 $a = 14.432$ (4) Å
 $b = 14.665$ (5) Å
 $c = 35.675$ (10) Å
 $\beta = 90.133$ (14)°
 $V = 7550$ (4) Å³

$Z = 8$
 $D_x = 1.288$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.35 \times 0.25 \times 0.15$ mm

Data collection

Bruker SMART 6K CCD
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1998)
 $T_{min} = 0.970, T_{max} = 0.987$

24437 measured reflections
 6729 independent reflections
 5287 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.048$
 $\theta_{max} = 25.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.113$
 $S = 1.28$
 6729 reflections
 515 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0401P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.005$
 $\Delta\rho_{max} = 0.25$ e Å⁻³
 $\Delta\rho_{min} = -0.21$ e Å⁻³

The water H atoms in (II) were found in a difference Fourier map and then freely refined. All other H atoms were positioned geometrically (aromatic C–H = 0.95 Å, N–H = 0.88 Å, methyl C–H = 0.98 Å and O–H = 0.84 Å) and refined using a riding model [$U_{iso}(H) = 1.2U_{eq}(\text{aromatic C and N})$ and $1.5U_{eq}(\text{methyl C and O})$].

For both cocrystals, data collection: *SMART-NT* (Bruker, 2000); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997b).

Table 2
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O7	0.84	1.84	2.680 (2)	174
O2—H2A...O8	0.84	1.77	2.605 (2)	178
O6—H6A...O5	0.95 (3)	1.80 (3)	2.738 (2)	170 (2)
O6—H6B...O1 ⁱ	0.88 (3)	2.11 (3)	2.962 (2)	165 (3)
O7—H7A...O3	0.92 (3)	1.80 (3)	2.708 (2)	168 (3)
O7—H7B...O2 ⁱⁱ	0.86 (3)	2.20 (3)	3.020 (3)	161 (3)
O8—H8A...O6	0.91 (3)	1.87 (3)	2.778 (3)	175 (2)
O8—H8B...O4 ⁱⁱⁱ	0.90 (3)	1.79 (3)	2.685 (2)	174 (3)
N1—H1B...O4	0.88	1.88	2.755 (2)	179
N2—H2B...O3	0.88	1.93	2.805 (2)	176
N3—H3B...O5 ⁱⁱ	0.88	1.90	2.777 (2)	176

Symmetry codes: (i) $-x + 1, y, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{3}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3045). Services for accessing these data are described at the back of the journal.

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