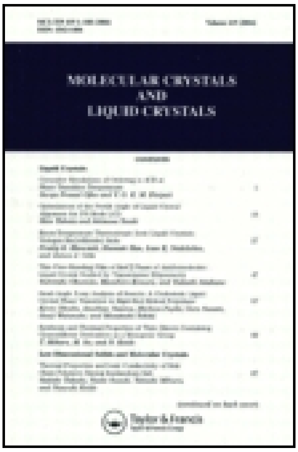

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Solid-State Photosolvolysis of Clathrate Crystals Including Ethanol as a Guest Component

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SOLID-STATE PHOTOSOLVOLYSIS OF CLATHRATE CRYSTALS INCLUDING ETHANOL AS A GUEST COMPONENT

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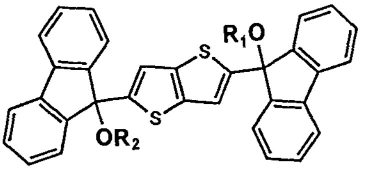
Abstract A simple bimolecular photosubstitution at a saturated carbon atom of the host by the guest molecule has been observed in the clathrate crystals which are composed of 9-fluorenyl substituted thienothiophenes as a host component and include ethanol as a guest species. Based on the X-ray analyses, topochemical characteristics of this novel solid-state photosolvolysis are discussed.

INTRODUCTION

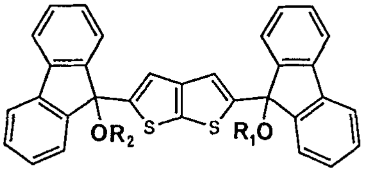
A variety of solid-state photoreactions have been reported up to now.[1] However, no photosubstitution at a saturated carbon atom in the solid-state has yet been known. This is due to the difficulty of preorganization of the reactive partners within the favorable distance in the crystalline state. In solution, photosolvolysis is common as photosubstitution at a tetrahedral carbon atom.[2] We demonstrate here the first solid-state bimolecular photosubstitution, that should be designated as "solid-state photosolvolysis", encountered in host-guest clathrate crystals of the host compounds that have recently been explored in this laboratory.[3]

INCLUSION PROPERTIES

Bis(9-hydroxyfluoren-9-yl)thieno[3,2-b]thiophene **1** is a photoreactive compound[4] and acts as an excellent host for a variety of guest compounds to form clathrate crystals.[3] We have now prepared a new host compound **2** as an isomer of host **1**. In spite of the structural similarity, host **2** showed rather different inclusion properties from those of host **1** (Table 1).



1; R_1=H, R_2=H
3; R_1=H, R_2=Et
4; R_1=Et, R_2=Et



2; R_1=H, R_2=H
5;R_1=H, R_2=Et
6; R_1=Et, R_2=Et

TABLE I Host : guest ratios of crystalline inclusion compounds of host **1** and host **2**.

guest	acetone	DMSO	dioxane	EtOH	n-PrOH	CH_2Cl_2
host **1**	1:2	1:2	1:2	1:2	1:2	1:0
host **2**	4:1	1:2	1:1	2:1	1:2	2:1

SOLID-STATE PHOTOLYSIS

Finely powdered (**1**)$(EtOH)_2$ crystals were irradiated by means of a high-pressure mercury lamp at ambient temperature for 24 h. The photoproducts were chromatographed on a silica gel column to give monoether **3** and diether **4**. The product distribution and conversion were determined on the basis of the ^{1}H-NMR integrations to be 49, 38, and 13%, respectively, for **3**, **4** and unreacted **1**. The solid-state formation of the ethers is conclusive, since the mass spectra of the solid sample after irradiation exhibited the molecular-ion peaks ascribable to **3** and **4**. Similar photosubstitutions were also observed in $(\mathbf{2})_2$(EtOH) crystals, wherein the products are monoether **5** (31%) and diether **6** (6%).

CRYSTAL STRUCTURES AND TOPOCHEMISTRY

In (**1**)$(EtOH)_2$ crystals,[5] there are two crystallographically independent (**1**)$(EtOH)_2$ units which are linked by the intermolecular host-host hydrogen bonds to lead an infinite chain. To each of the OH groups of the host compound an ethanol molecule is hydrogen-bonded (Figure 1). Thus, attack by the ethanol molecules is to take place from the same side as the OH group leaves. The interatomic distances between the ethanol oxygen atom and the fluorenyl 9-carbon atom are 3.65 and 3.86 Å (Table II), being favorable distances for displacement.

The X-ray powder diffraction studies revealed that the irradiated solids at 60% conversion retain still a crystalline lattice, although it is not identical with that of the starting (**1**)$(EtOH)_2$ crystals.

Local microenvironmental concentration of ethanol sorrounding the OH groups of the host is lower for $(\mathbf{2})_2(EtOH)$ crystals[6] than that of (**1**)$(EtOH)_2$. There are two crystallographically independent host molecular A and B in $(\mathbf{2})_2(EtOH)$. The two hydroxyl groups of A are directed to the same side and make a cyclic dimer unit A-A by the hydrogen bonds. The OH groups of another host B adopt an *anti* orientation and one of there groups in participating in the A-A unit by forming hydrogen bond through a guest ethanol molecule (Figure 2).

Remarkably, in the case of $(\mathbf{2})_2(EtOH)$, the solid state photoreaction does not lead to collapse of the host crystal lattice; the X-ray powder diffraction pattern of 30% conversion crystals is entirely identical with that of the starting clathrate crystals.

Diether **6** is formed, although the non-hydrogen-bonded distance between the atoms that are forming the bond, is as long as 5.06 Å (Table II). We could introduce a topochemical factor characteristic for the solid-state substitution reaction; In crystal lattices the to-be-sustituted carbon atom should be held, through the reaction process, in minimal deformation from its initial tetrahedral geometry. In Table II the bond angles formed by the ethanol oxygen, the fluorenyl carbon, and the hydroxyl oxygen are listed. The bond formation between the 5.06 Å distance is associated with the small distortion(15.3°) of the tetrahedral reaction center, making the displacement by the ethanol possible.[7]

At this early stage we assume that an ionic intermediate is involved in the solid-state photosustitutions, as suggested for the photolysis of 9-fluorenol and their derivatives.

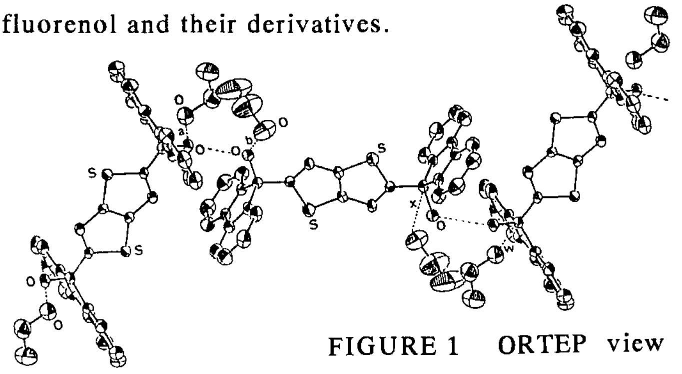


FIGURE 1 ORTEP view of (**1**)$(EtOH)_2$

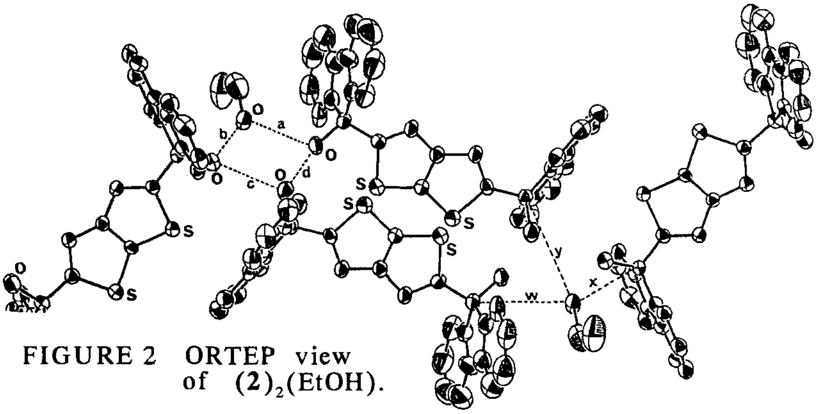


FIGURE 2 ORTEP view of $(\mathbf{2})_2(EtOH)$.

TABLE II. Interatomic distances between the host and guest molecules and the angles formed by (H)O—C--O(Et).

	(H)O--O(Et)	C---O(Et)	(H)O—C---O(Et)
$(\mathbf{1})(EtOH)_2$	2.71 (a) Å	3.65 (w) Å	39.8 °
	2.82 (b)	3.86 (x)	35.4
$(\mathbf{2})_2(EtOH)$	2.83 (a)	3.73 (w)	41.8
	2.70 (b)	3.74 (x)	35.8
		5.06 (y)	15.3
	2.94 (c)		
	2.94 (d)		

For the explanation of a-d and x-y, see Figures 1 and 2.

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5. Crystal Data of $(\mathbf{1})(EtOH)_2$, $C_{36}H_{32}O_4S_2$, monoclinic, $P2_1/a$; a=17.403(3), b=20.654(4), c=8.695(1) Å, β=99.73(1)°, V=3080.4(9)Å ^{3}, Z=2, d_c=1.278 g/cm^3, R=0.069, R_w=0.080.
6. Crystal Data of $(\mathbf{2})_2(EtOH)$, $C_{66}H_{46}O_5S_4$, monoclinic, $P2_1/c$; a=24.359(3), b=13.793(2), c=15.508(1) Å, β=99.728(8)°, V=5135(1) Å ^{3}, Z=2, d_c=1.355 g/cm^3, R=0.089, R_w=0.131.
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