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

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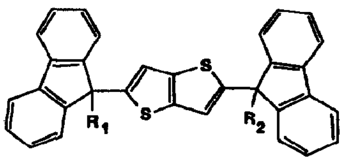
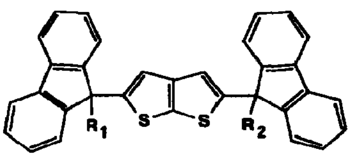
Abstract: The guest ethanol molecules in the clathrate crystals reacted photochemically with the diol host compounds, bis(9-hydroxyfluoren-9-yl)thieno[3,2-b]- and [2,3-b]-thiophenes, to cause photosubstitutions in the solid-state.

Organic photoreactions in the crystalline state have become the current subject of active research and a number of solid-state photoreactions have been reported up to now.[1] However, simple bimolecular photosubstitution at a saturated carbon atom has not yet been known in the solid state. This is due to the difficulty of preorganization of the reactive partners within the favorable distance in the crystalline state and also to the situation that most of photosubstitutions at a tetrahedral carbon atom known to date are photosolvolyses.[2] We demonstrate here the first solid-state photosubstitution that was realized in host-guest clathrate crystals including a solvent species as a guest component.[3] The reaction may be designated as *solid-state photosolvolysis*.

In spite of the structural similarity, isomeric bis(9-hydroxyfluoren-9-yl)thienothiophenes **1** and **2** showed rather different inclusion properties as host compounds.[4] Upon recrystallization from ethanol **1** afforded the clathrate crystal with a host-guest molar ratio of 1 : 2, whereas for **2** a host-guest ratio of 2:1 was obtained.



1: R_1 = OH, R_2 = OH
3: OH OEt
4: OEt OEt



2: R_1 = OH, R_2 = OH
5: OH OEt
6: OEt OEt

Grinded (**1**)(EtOH)$_2$ crystals were irradiated by means of a high-pressure mercury lamp at ambient temperature for 6 h. The photoproducts were chromatographed on a silica gel column to give monoether **3** (43%) and diether **4** (21%) along with unreacted **1** (36%).[5]

The solid-state formation of the ethers is conclusive, since the mass spectra of the irradiated solid sample exhibited the molecular-ion peaks ascribable to **3** and **4** at m/e 528 and 556, respectively. Similar photosubstitutions were also observed in (**2**)$_2$(EtOH) crystals, wherein the products after 4 h irradiation are monoether **5** (36%) and diether **6** (7%).

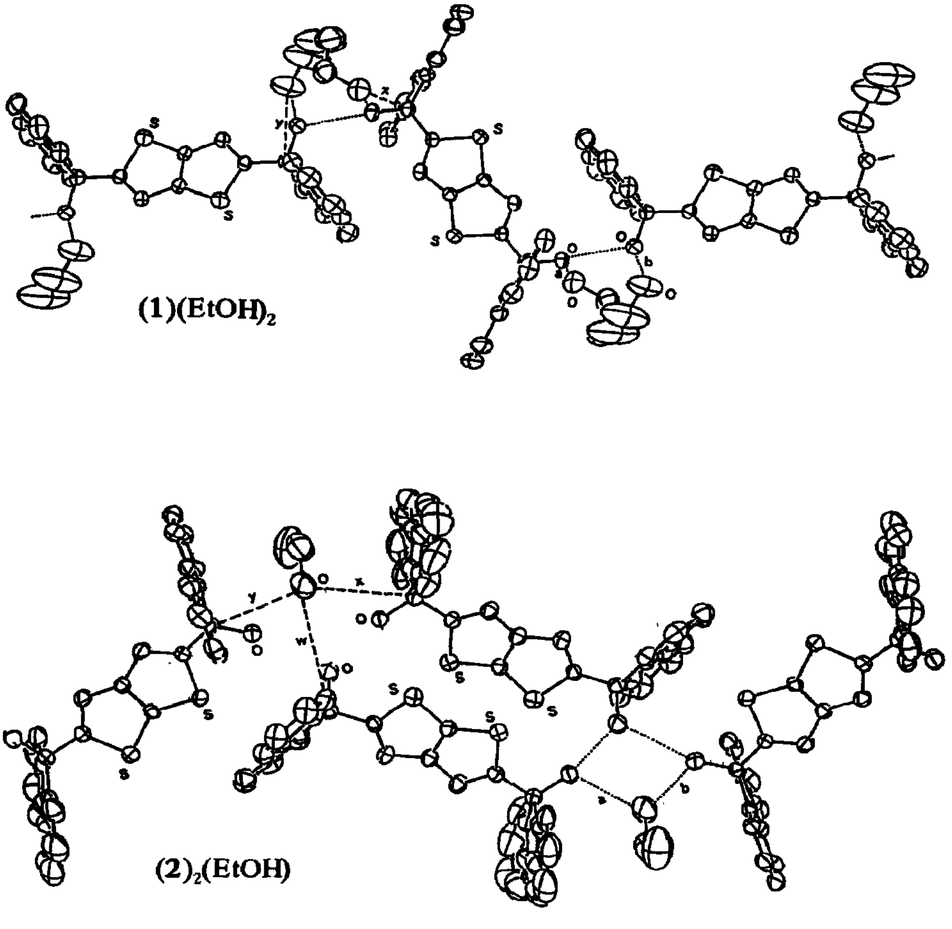


Figure 1. ORTEP view of (**1**)(EtOH)$_2$ and (**2**)$_2$(EtOH) crystals. Dotted lines a and b indicate the relation linked by the hydrogen bond between the host and the guest and broken lines x, y and w indicate the direction of the new-bond formations: For (**1**)(EtOH)$_2$, a=2.71, b=2.82, x=3.65, y=3.86 Å. For (**2**)$_2$(EtOH), a=2.83, b=2.70, x=3.73, y=3.74, w=5.06 Å.

The X-ray powder diffraction patterns of both irradiated clathrates, along with their intensities, were almost identical with those of the starting clathrate crystals, indicating the crystalline phase is retained throughout the photoreaction. The X-ray structural analysis revealed that an ethanol molecule is hydrogen-bonded to each of the OH groups of the host molecules.[6] If a topochemical reaction is presumed, the attack of 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 indicate that 3.65 and 3.86 Å in (**1**)(EtOH)$_2$ as well as 3.73 and 3.74 Å in (**2**)$_2$(EtOH) are topochemically favorable distances for displacement (Figure 1).

For the formation of diether **6** from (**2**)$_2$(EtOH), however, local microenvironmental concentration of ethanol surrounding the OH groups of host **2** is not enough; the bond formation between the non-hydrogen-bonded distance as long as 5.06 Å is required (Figure 1). This distance appears to be quite long for topochemical solid-state reactions and therefore to indicate that the formation of **6** is not a topochemical process. For the formation of **3**, **4** and **5** it seems also likely that non-topochemical character is dominant, since the time dependence of the product distribution, as followed by the NMR analysis, revealed the presence of an induction period; there must be speccical sites at which reaction occurs preferentially.[7] In line with this observation, the photosolvolysis was fast in the finely grinded clathrate solids, in which the defect sites are increased, but was quite slow in a single crystal.

At this early stage we assume that an ionic intermediate is involved in these solid-state photosolvolyses, as suggested for the photosolvolysis of 9-fluorenol[8] and thienylmethanol derivatives[9] in alcohol, since no hydroxyl radical-derived products were observed. In line with the solid-state photoreaction of (**1**)(EtOH)$_2$, the photolysis of **1** in an ethanol solution for 1 h resulted in efficient solvolysis to give corresponding diether **4** almost quantitatively.[10] The present results may serve as prototypes for mechanistic studies of molecular contacts in solution reaction. Further experiments are in progress.

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References and Notes

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3. There has been a relevant example that the crystalline host-guest complexes have been employed to accomplish the solid-state photoreaction between two different compounds, i. e. intermolecular hydrogen abstractions. See, (a) R. Poporitz-Biro, C. P. Tang, H. C. Chang, M. Lahav, L. Leiserowitz, *J. Am. Chem. Soc.*, **1985**, 107, 4043; (b) C. P. Tang, H. C. Chang, R. Popovitz-Biro, F. Frolow, M. Lahav, L. Leiserowitz, R. K. McMullen, *J. Am. Chem. Soc.*, **1985**, 107, 4058.
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5. The product distributions were determined on the basis of the ^{1}H NMR integrations.

   ^{1}H NMR data (270 MHz, CDCl$_3$). **3**: δ 7.7-7.2 (m, 16H), 6.78 (s, 1H), 6.70 (s, 1H), 3.09 (q, J=7.0 Hz, 2H), 2.6 (broad s, 1H), 1.09 (t, J=7.0 Hz, 3H). **4**: δ 7.7-7.2 (m, 16H), 6.69 (s, 2H), 3.08 (q, J=7.0 Hz, 4H), 1.08 (t, J=7.0 Hz, 6H). **5**: δ 7.7-7.2 (m, 16H), 6.60 (s, 1H), 6.49 (s, 1H), 3.08 (q, J=7.0 Hz, 2H), 2.63 (broad s, 1H), 1.10 (t, J=7.0 Hz, 3H). **6**: δ 7.7-7.2 (m, 16H), 6.43 (s, 2H), 3.07 (q, J=7.0 Hz, 4H), 1.09 (t, J=7.0 Hz, 6H).

   The definite evidence for the existence of water in the irradiated solids could be obtained neither by IR nor by NMR. The maximum conversion is attained within 6 h. During this period the yields of both **3** and **4** increase with irradiation, but further irradiation brings about neither significant changes of the product distribution nor the increase of the diether.
6. X-ray crystal structure determinations. (**1**)(EtOH)$_2$: P2$_1$/a, a=17.403(3) Å, b=20.654(4) Å, c=8.695(1) Å, β=99.73(1)°, V=3080.4(9) Å^3, Z=2, R=0.074, R$_w$=0.074. (**2**)$_2$(EtOH): P2$_1$/c, a=24.359(3) Å, b=13.793(2) Å, c=15.508(1) Å, β=99.728(8)°, V=5135(1) Å^3, Z=2, R=0.094, R$_w$=0.107. Details of the structures have been deposited at the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, England.
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10. In dichloromethane, however, **1** undergoes photochemical transformation to a quinonoid compound. See, Y. Mazaki, S. Murata, K. Kobayashi, *Tetrahedron Lett.*, **1991**, 32, 4367.

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