Intramolecular Migration of Bulky Substituents in the Solid State: Vinylogous Pinacol Rearrangements Induced Thermally and by Acid Catalysis

Ryo Sekiya, Kazuhiko Kiyo-oka, Tatsuro Imakubo, and Keiji Kobayashi*

Contribution from the Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan

Received March 3, 2000. Revised Manuscript Received August 10, 2000

Abstract: A vinylogous pinacol rearrangement, involving an intramolecular 1,4-migration of the bulky thienothienyl substituent and a marked change of the crystal structure, was thermally induced in the solid state for thienothienyl-substituted 9,10-dihydroxy-9,10-dihydroanthracenes, **1** and **3**∼**8**. When heated over 180 to ∼240 °C, these crystals were transformed quantitatively, accompanying dehydration, to crystals of the anthrone derivatives without wetting or melting. Diol **8**, which bears two isomeric thienothiophene rings, afforded only a single anthrone product. Compounds **1** and **8** formed a mixed crystal and its thermally induced reaction yielded two anthrone products that were attributable to intramolecular migration but afforded no anthrone derivative having the two substituents possible for the intermolecular combination. These results, along with the X-ray crystal structure of the mixed crystal, demonstrate that the rearrangement in the solid state proceeds intramolecularly. The 1,4-pinacol type rearrangements were also induced, along with the *cis*−*trans* isomerization, by cogrinding the diols with *p*-toluenesulfonic acid in a mortar at room temperature. The intramolecularity of the rearrangement was again proved by the use of the mixed crystal. The intervention of the carbocation in the solid-state grinding was ascertained by the UV/vis spectra. The time courses of the product distributions showed discrete profiles between the *trans* and *cis* diols, **1** and **3**, respectively; for the *trans* diol **1**, fast isomerization to the *cis* isomer and consecutive formation of the rearranged product via the *cis* isomer were observed. On the basis of these observations, the solid-state 1,4-rearrangement was deduced to occur preferentially via the *cis* configuration of the dihydroxy groups.

Introduction

In contrast to solid-state photoreactions which have been the subject of extensive topochemical investigation,[1] thermally induced organic reactions in the solid state have been little exploited, even over the past decade.[2] The main reason for this is that molecular crystals melt before the onset of the reaction. Thus, recent solid-state thermal reactions have been performed by cogrinding or keeping mixtures of powdered reactant and reagent.[3] In this context, new unimolecular reactions induced thermally in the solid state have only rarely been discovered.[4]

Another reason for the scarcity of unimolecular thermal reactions in the solid state is that the reactions cannot be independent of molecules situated proximately in the crystal lattices. Therefore, it is difficult to distinguish the intramolecular or intermolecular nature of solid-state rearrangement reactions topochemically.[5] Here we report novel solid-state unimolecular rearrangement reactions induced thermally in 9,10-dihydroxy-9,10-dihydroanthracene derivatives, which involve long-range intramolecular 1,4-migration of the bulky substituent. This work provides conclusive evidence for the occurrence of intramolecular thermal rearrangements in the solid state.[6] Furthermore, we demonstrate that such rearrangements are induced quite easily, along with the *cis*−*trans* isomerization of the dihydroxy substituents, by solid-state cogrinding with acid catalysis. Based on the time conversions for the *cis* and *trans* diols, the stereoselectivity of the 1,4-rearrangement due to the transannular π-participation was deduced.

(1) (a) Cohen, M. D.; Schmidt, G. M. *J. Chem. Soc.* **1964**, 1996. (b) Luty, T.; Eckhardt, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 2441.

(2) Even an old example of solid-state thermal reactions, the transformation of ammonium cyanate into urea, has been studied for more than a century. See: Dunitz, J. D.; M. Harris, K. D.; Johnston, R. L.; Kariuki, B. M.; MacLean, E. J.; Psallidas, K.; Schweizer, W. B.; Tykwinski, R. R. *J. Am. Chem. Soc*. **1998**, *120*, 13274.

(3) For recent examples of solid-state reactions induced by cogrinding, see: (a) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480−486. (b) Schmeyers, J.; Toda, F.; Boy, J.; Kaupp, G. *J. Chem. Soc., Perkin Trans. 2*, **1998**, 989. (c) Singh, N. B.; Singh, N. P.; Kumar, V. A.; Nethaji, M. *J. Chem. Soc. Perkin Trans. 2*, **1994**, 361. (d) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.

(4) The unimolecular thermal reaction in the solid state was recently reported. See: Toda, F.; Tanaka, K.; Tamashima, T.; Kato, M. *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 2724.

(5) For topochemistry in the thermally induced solid-state reactions, see: (a) Nader, F. W.; Wacker, C. -D; Irngartinger, H.; Huber-Patz, U.; Jahn, R.; Rodewald, H. *Angew. Chem., Int. Ed. Engl*. **1985**, *24*, 852. (b) Dessolin, M.; Eisenstein, O.; Goltiler, M.; Prange, T.; Sautet, P. *J. Chem. Soc., Chem. Commun.* **1992**, 132. (c) Kishan, K. V. R.; Desiraju, G. R. *J. Org. Chem*. **1987**, *52*, 4640. (d) Desiraju, G. R.; Kishan, K. V. R. *J. Am. Chem. Soc.* **1989**, *111*, 4838. (e) Naruchi, K.; Miura, M. *J. Chem. Soc., Perkin Trans. 2* **1987**, 113. (f) Diaz de Delgado, G. C.; Wheeler, A. K.; Snider, B. B.; Foxman, B. M. *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 420. (g) Goud, B. S.; Panneerselvam, K.; Zacharias, D. E.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1995**, 325. (h) Smrcina, M.; Vyskocil, S.; Hanus, V.; Polasek, M.; Langer, V.; Chew, B. G. M.; Zax, D. B.; Verrier, H.; Harper, K.; Claxton, T. A.; Kocovsky, P. *J. Am. Chem. Soc.* **1996**, *118*, 487.

(6) For the solid-state intermolecular thermal rearrangements, see: (a) Sukenik, C. N.; Bonapace, J. A. P.; Mandel, N. S.; Lau, P.−Y.; Wood, G.; Bergman, R. G. *J. Am. Chem. Soc*., **1977**, *99*, 851. (b) Menger, F. M.; Kaiserman, H. B.; Scotchie, L. J. *Tetrahedron Lett.* **1984**, *25*, 2311. (c) Dessolin, M.; Golfier, M. *J. Chem. Soc., Chem. Commun.* **1986**, 38. (d) Tasato, M. L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1593.

10.1021/ja000788l CCC: $19.00
Published on Web 10/06/2000

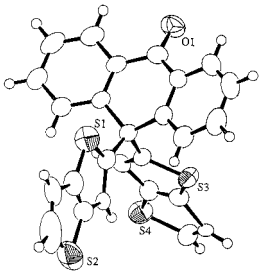
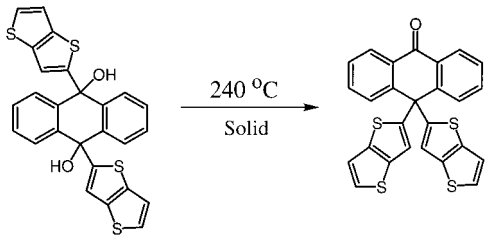


Figure 1. ORTEP view of **2**. The ellipsoids are drawn at the 50% probability level.

Results and Discussion

Thermally Induced Rearrangement. The study was based on the observation that *trans*-9,10-dihydroxy-9,10-bis(thieno-[3,2-*b*]thienyl)-9,10-dihydroanthracene (**1**) undergoes color change upon heating below melting; the melting temperature is high, over 330 °C, although around 240 °C, **1** changes to a dark brown solid. There was no sign of wetting or flowing of the solids throughout the heating process. Thermal gravimetric (TG) measurement revealed a 4% loss of weight around that temperature, indicating the elimination of water from the solid. This thermal dehydration was revealed to result in quantitative formation of 10,10-bis(thieno[3,2-*b*]thienyl)anthrone (**2**) in the solid state. The structure of **2** was deduced from the spectral data and unambiguously established by an X-ray crystallographic analysis of a single crystal obtained by recrystallization of the resulting solid from hexane−CH_2Cl_2 (Figure 1). The powder X-ray diffraction patterns produced by simulation based on the disclosed crystal structure showed excellent agreement with those of the whole sample when subjected to the thermal reaction.



1 (*trans*)
3 (*cis*) **2**

The progress of the solid-state reaction was monitored by temperature-variable FTIR spectroscopy. The spectral change was progressive. The OH-stretching bands diminished as the temperature increased, and a carbonyl peak appeared at 1658 cm^{-1} (Figure 2a).[7] Above 250 °C, the FTIR spectrum became the same as that of **2**. Corresponding to the TG, the DSC profile of **1** showed a sharp exothermic peak at 249 °C with an onset temperature of 245 °C due to the conversion of **1** to **2**.[8] The melting temperature of **2** was significantly higher (>330 °C) than the reaction temperature. All of the above observations indicate the transformation of **1** to **2** in the solid state.

Similar thermal conversions were induced in the solid state for *cis* isomer **3**[9] and other related diols, such as **4** (*trans*), **5** (*cis*), **6** (*trans*), and **7** (*cis*), to afford the corresponding anthrone derivatives. In all cases, no wetting of the crystals was detected upon visual observation by stereomicroscopy. The temperature-variable FTIR spectra, as seen in the reaction of **4** (Figure 2b), were not accompanied by a peak shift during heating, indicating again that a transient fluid phase was not involved. Diol **4** has no hydrogen bonding in its crystal structure, as revealed by X-ray analysis. Thus, the results for compound **4** imply that hydrogen bonding is not required and plays no role in promotion of the rearrangement. The marked large substituent such as the ternary condensed thiophene in **6** also undergoes solid-state rearrangement when heated to 200 °C. The occurrence of the reaction in **7** (at 150 °C), which is blocked at the 4-position of the thieno[3,2-*b*]thiophene ring by methyl substitution, indicates that the carbon atom associated with the bond cleavage forms the new carbon−carbon bond.

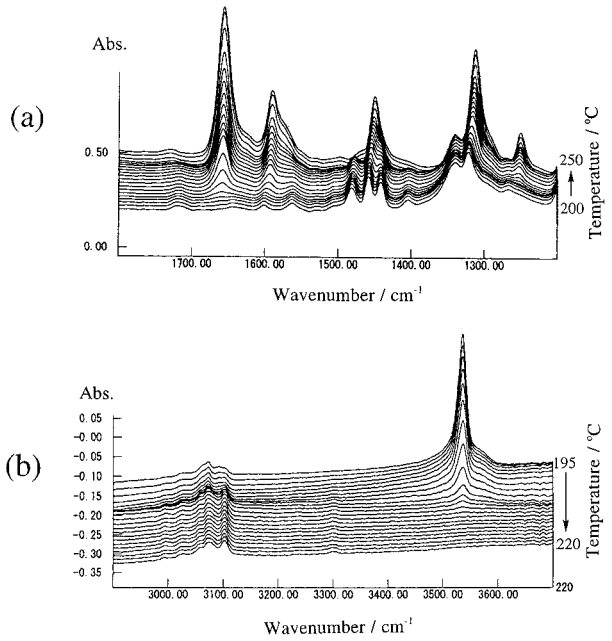
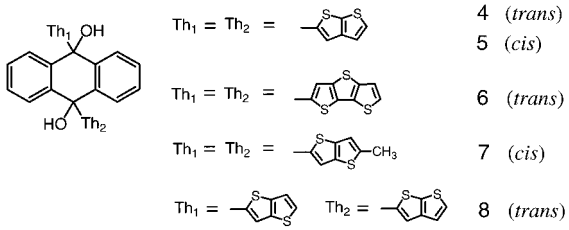


Figure 2. Temperature-dependent FTIR spectra: (a) for **1** in the 1200∼1800 cm^{-1} region, recorded by upper shift with raising the temperature from 200 to 250 °C (1 °C/min); (b) for **4** in the 3000∼3700 cm^{-1} region, recorded by downshift with raising the temperature from 195 to 220 °C (1 °C/min).



4 (*trans*)
5 (*cis*)
6 (*trans*)
7 (*cis*)
8 (*trans*)

The crystal and molecular structures of **1** and the resulting **2** are markedly different from each other. The starting crystal packs in $P\bar{1}$ (Figure 3), while it turns $P2_1/c$ after the thermal reaction. The shortest C−C distance associated with new bond formation is 4.12 Å, which corresponds to the transannular migration (Figure 3). This distance is appropriate for a topotactic process. However, because the reaction includes a marked change in the molecular and crystal structures that is ac-

(7) When the reaction was monitored by FTIR spectroscopy at a constant temperature of 200 °C, the formation of **2** as well as the disappearance of **1** exhibited linear time-conversion almost until completion. Such zero-order kinetics cannot be well-interpreted at this stage.

(8) The calorific value of this exothermic peak is 5.5 kcal mol^{-1}. This should result from the total events, including molecular reaction, vaporization of water, and reorganization of the crystal lattices.

(9) The *cis* or *trans* configuration of a series of the diol compounds can easily be deduced from the ^1H NMR chemical shifts. The singlet signal of the thiophene ring occurs around 7.0 ppm for the *trans* isomers, but it occurs in a higher field in the range of 5.8−6.0 ppm for the *cis* isomers.

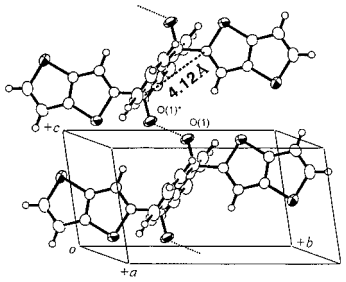


Figure 3. X-ray crystal structure of **1** (thermal ellipsoids at 50% probability). Molecules are linked by hydrogen bonding to form an infinite chain. Dotted lines indicate the relations linked by the hydrogen bonds (O ···O: 2.95 Å).

companied by 1,4-migration of the thiophene ring, a nontopochemical process is also conceivable. The topochemical principle, which states that a solid-state reaction proceeds with minimum movement of the atoms or molecular groups involved,[1] was originally proposed for solid-state photochemical reactions at ambient temperature, and its applicability to thermal reactions under these high temperatures is questionable.

It seems most likely that the reaction begins at crystal defects and/or crystal surfaces and proceeds via molecular loosening at the reaction front, followed by a unimolecular reaction and microscopic reconstruction of the crystal phase of the product. The elimination of water would be advantageous for the molecular change and reorganization,[10] because this would leave voids in the crystal lattice to provide freedom of molecular movement. The reaction is regarded as a crystal-to-crystal transformation and not a single-crystal-to-single-crystal transformation because the single crystals of **1** do not retain single crystallinity that is suited for X-ray crystallographic study.

The reaction demonstrated herein is regarded as a vinylogous pinacol rearrangement and can be referred to as a solid-state 1,4-pinacol type rearrangement.[11] The carbocation generated by the heterolytic C−O bond cleavage could be responsible for the rearrangement in a manner similar to the common pinacol rearrangement in solutions.[12] Further details of this respect will be described in a later section.

Intramolecularity. Does the solid-state 1,4-rearrangement occur intramolecularly or intermolecularly? As noted already, it is rather difficult to answer this question for a solid-state reaction. Therefore, we have utilized a mixed crystal (solid solution) of **1** and **4**. The shape and size of the thieno[3,2-*b*]-thienyl and thieno[2,3-*b*]thienyl substituents are quite similar. We found previously that compounds including thieno[3,2-*b*]-thienyl and thieno[2,3-*b*]thienyl groups as part of the molecular structure form isostructural crystals with each other.[13] Contrary to expectation, mixed crystals could not be obtained for these two compounds. Therefore, we prepared compound **8**, which bears two isomeric thienothiophenes at the 9 and 10 positions

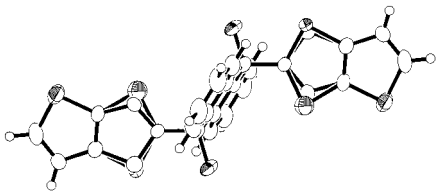
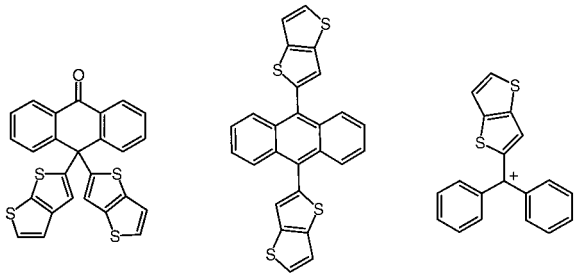


Figure 4. ORTEP view of a mixed crystal of **1** and **8** (thermal ellipsoids at 50% probability). The two isomeric thienothiophene rings are in a disordered structure.

of the dihydroanthracene ring. As anticipated, **1** and **8** yielded mixed crystals in all compositions.[14]

The X-ray crystal structure of a mixed crystal of **1** and **8** in an approximate 1:1 ratio was determined. The crystal packs in the *P*1 space group and is isostructural to that of **1.** Thus, the two isomeric thienothiophene moieties of **8** are randomly arranged, and the observed structure is reasonable as an average of the two orientations of the **8** molecules (Figure 4). When heated to over 220 °C, the mixed crystal with a 2:1 composition of **1**:**8** afforded **2** together with thieno[3,2-*b*]thienyl- and thieno-[2,3-*b*]thienyl-substituted anthrone (**9**) in a 2:1 ratio, although bis(thieno[2,3-*b*]thienyl)-substituted anthrone was not produced. If the rearrangement is an intermolecular reaction, three varieties of anthrones, including that of bis(thieno[2,3-*b*]thienyl)-substituted, should be obtained. However, this was not the case. These results indicate that even if the reaction proceeds topochemically in an ordered crystalline lattice, intermolecular migration is not involved. The solids subjected to the thermally induced reaction exhibited X-ray powder diffractions identical with those of **2**, indicating that anthrones **2** and **9** also form a mixed crystal.



9 10 11

If the noncentrosymmetric molecules of **8** are packed in random orientation with respect to the two isomeric thienothiophene substituents, the crystal of **8** can also be utilized for the determination of the intermolecular or intramolecular nature of the solid-state 1,4-rearrangement. Unfortunately, the crystal structure of **8** could not be determined by X-ray analysis because of the poor quality of its single crystals. However, the X-ray powder diffraction pattern of **8** was revealed to be superimposable on that of **1** (Figure 5). This observation strongly suggests that **8** is isostructural with **1**, giving it average centrosymmetry by virtue of disorder, although the possibility of the absence of a center of symmetry in **8** (space group *P*1) could not be ruled out. The latter case seems unlikely, because it is not conceivable that a chiral crystal would be realized only by changing the location of the two sulfur atoms in the molecular structure of **1**, which constitutes a nonchiral crystal. The thermal reaction of **8** produced only **9** and afforded no other products that were substituted by the same thienothienyl groups. Thus, the results for crystal **8** also strongly suggest that the reaction occurs

(10) For the thermal dehydration in the solid state, see: (a) Lewis, T. W.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc*. **1979**, *101*, 5717. (b) Puckett, S. A.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc*. **1976**, *98*, 787. (c) Lewis, T. W.; Deusler, E. N.; Kress, R. B.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc*. **1980**, *102*, 4659. (d) Errede, L. A.; Etter, M. C.; Williams, R. C.; Darnaner, S. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 233.

(11) For the solid-state 1,2-pinacol rearrangement induced by acid catalysis, see: (a) Toyoshi, Y.; Nakato, T.; Okuhara, T. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 2817−2824. (b) Toda, F.; Shigemasa, T. *J. Chem. Soc., Perkin Trans. 1* **1989**, 209. (c) Kaupp, G.; Haak, H.; Toda, F. *J. Phys. Org. Chem.* **1995**, *8*, 545.

(12) (a) Rickborn, B. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 3, p 721. (b) Collins, C. J. *Q. Rev. Chem. Soc*. **1960**, *14*, 357.

(13) Hayashi, N.; Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Chem. Commun*. **1994**, 2351.

(14) Cocrystallization was ascertained by signal accumulation of the ^{1}H NMR for single crystalline samples.

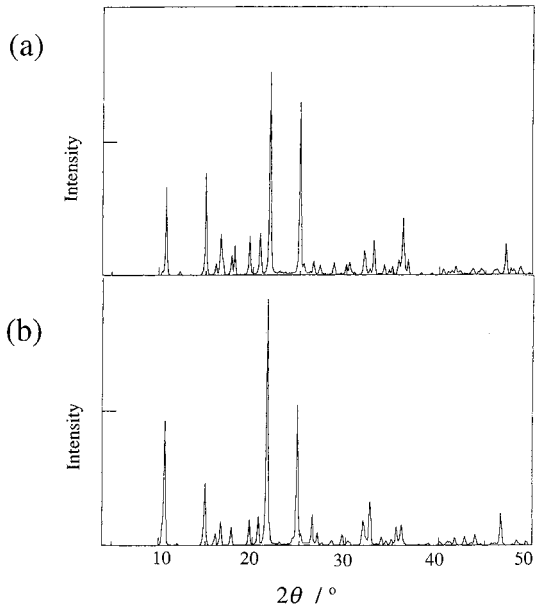


Figure 5. X-ray powder diffraction patterns: (a) **1**; (b) **8**.

intramolecularly, irrespective of whether or not a topochemical process might be involved.

Rearrangement Induced by Solid-State Cogrinding. The rearrangement was also realized in a solution by heating **1** at 230 °C for 4 h in diphenyl ether, affording **2** in quantitative yield. In the presence of *p*-toluenesulfonic acid, the rearrangement occurred within 10 min in chloroform at room temperature.[15] We then have envisaged that the acid-catalyzed 1,4-rearrangement should be induced in the solid state. Indeed, when **1** was coground with an equimolar amount of *p*-toluenesulfonic acid using a mortar and pestle for 15 min, **2** was obtained in 60% yield, along with 26% of *cis* diol **3** and a small amount of 9,10-bis(thieno[3,2-*b*]thienyl)anthracene (**10**) (7%). Grinding **1** alone did not afford any products. Table 1 summarizes the results of the reaction that was induced by cogrinding some related compounds with an equimolar amount of *p*-toluenesulfonic acid. For all cases, the solid states were retained throughout the cogrinding. The *cis* diol isomerized to the trans diol and the *trans* to the *cis*, indicating that the *cis*−*trans* equilibration took place in the presence of the acid. When the amount of *p*-toluenesulfonic acid was reduced to a 0.1 M amount of **1**, **2** was obtained in 20% yield by cogrinding both components for 30 min. A similar procedure for the *cis* isomer **3** gave rise to the formation of **2** in 72% yield.

Cogrinding of mixed crystals of **1** and **8** with *p*-toluenesulfonic acid for 20 min afforded the 1,4-rearranged products, among which there was no bis(thieno[2,3-*b*]thienyl)-substituted anthrone. Thus, again it is obvious that the rearrangement proceeds intramolecularly. The powder X-ray diffraction analysis disclosed that the ground solids of **1** and *p*-toluenesulfonic acid were in an amorphous state, which is in contrast to the solids that resulted from the thermally induced rearrangement.

Table 1. Yields (%) of the Products in the Solid State upon Cogrinding of the Diols with an Equimolar Amount of *p*-Toluenesulfonic Acid

diol	other isomer	anthrone derivative	thienothiophene-substituted anthracene
1 (*trans*)	26 (*cis*)	60 (**2**)	7 (**10**)
3 (*cis*)	3 (*trans*)	54 (**2**)	0 (**10**)
4 (*trans*)	39 (*cis*)	57	2
5 (*cis*)	2 (*trans*)	48	2

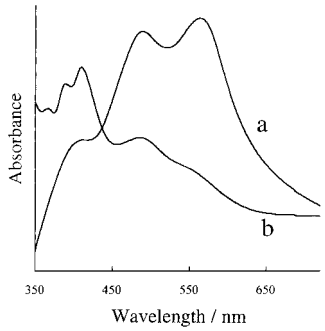


Figure 6. UV/vis absorption spectra of the carbocation as measured in a KBr pellet: (a**)** tetrafluoroborate salt of **11**; (b**)** ground solids of **3** with *p*-toluenesulfonic acid. Absorbance is plotted in arbitrary units.

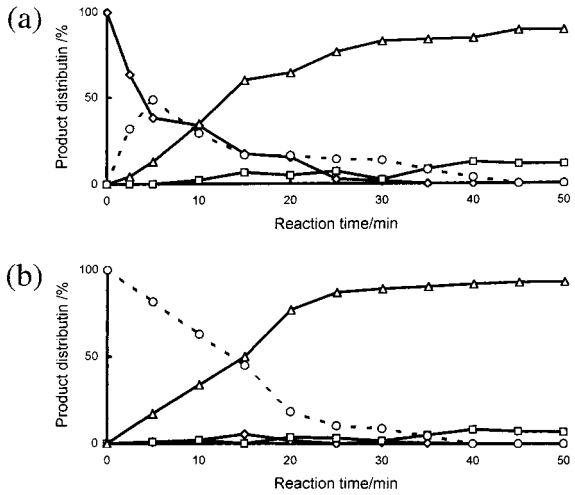


Figure 7. Time course of the reaction induced by cogrinding with *p*-toluenesulfonic acid: (a) **1** (*trans*); (b) **3** (*cis*). (−○−) **1** (*trans*); (- - ○ - -) **3** (*cis*); (△) anthrone **2**; (□) anthracene **10**.

This was also the case for **3**. The noncrystallinity of the resulting solids indicates that the process is not topotactic.

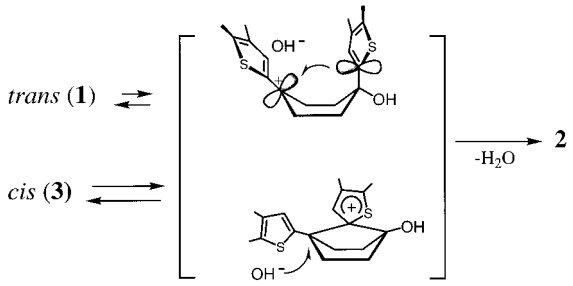
The intervention of carbocation as an intermediate was supported by the solid-state UV/vis spectra. The absorption bands at 488 nm and ca. 563 nm developed in the early stage of cogrinding of **1** and **3** with *p*-toluenesulfonic acid, respectively, and these bands then faded on further grinding or on standing. These bands are characteristic of a triphenylmethyl-type tertiary carbocation, because the tetrafluoroborate salt of diphenylthienothienylcarbocation (**11**) that was prepared as a reference compound also exhibits two bands at 490 and 560 nm (Figure 6). The 9,10-dication intermediate would be responsible for the formation of **10**, but we cannot argue further mechanistic details at this stage. The most plausible explanation is the intervention of compound **1** as a reducing agent for the dication, because thienothiophene compounds such as **1** act as electron donors.[16] It should be noted that 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene afforded no rearranged products either in the solid state or in solution. The incorporation of the thiophene ring in the substrate 1,4-diol compounds is essential for promotion of the 1,4-pinacol type rearrangement.

Figure 7 shows the time courses of the product distribution from **1** (*trans*) and **3** (*cis*) when these were coground with *p*-toluenesulfonic acid, respectively, for 1 h. The most significant feature was the transient increase of the *cis* (**3**) when the *trans*

(15) During the preparation of this manuscript, a paper reporting similar 1,4-rearrangements in liquid phase was published: Smet, M.; van Dijik, J.; Dehaen, W. *Tetrahedron* **1999**, *55*, 7859.

(16) Tanaka, M.; Kobayashi, K. *Chem. Commun*. **1998**, 1965.

Scheme 1



(**1**) was ground: the *trans* isomer underwent fast isomerization to the *cis* isomer and the anthrone **2** was formed consecutively via the *cis* isomer. These observations can be interpreted rationally by assuming the π-participation in the carbocation intermediate generated as a common intermediate for the *cis*−*trans* isomerization and the 1,4-rearrangement. In *cis* isomer **3**, the π-electrons of the thienothiophene ring are transannularly well-placed to interact with the developing carbocation to yield the thiophene analogue of the phenonium ion, which leads ultimately to the1,4-rearranged product (Scheme 1). Thus, cis isomer **3** rearranges more easily than *trans* isomer **1**. Recombination of the hydroxide ion on the backside of the π-participation yields the *cis* isomer, and this path would be kinetically faster than an attack from the other side to yield the *trans* isomer. For the *trans* isomer, the generation of the carbocation and its return to the original configuration are both kinetically less favorable than those for the *cis* isomer. Therefore, the isomerization to the *cis* isomer is enhanced at the early stage of the reaction, but, finally, the 1,4-rearrangement accompanied by the dehydration is achieved, splitting irreversibly from the common carbocation intermediate.

As already noted, the 1,4-rearrangement was induced only in the thiophene compounds and not in the 9,10-diphenyl derivatives. These observations also support the π-participation or the involvement of the thiophene analogue of the phenonium ion, because there is a much greater tendency for thiophene, particularly at the α-position, to be displaced by incoming groups than there is in the benzene series. Furthermore, the sulfur-heterocycles could stabilize the carbocation intermediate by charge delocalization.[17]

Concluding Remarks

We have demonstrated the thermally induced solid-state reaction which is accompanied by significant change of the molecular and crystal structures. The rearrangement was proved to be an intramolecular process that uses the mixed crystal (solid solution). In the mixed crystal, the random occupation of molecules of the two different compounds realizes all possible combinations of the intermolecular relation, which is similar to that of a solution. This approach could be widely used to distinguish intramolecular or intermolecular phenomena in the crystalline state. We have, furthermore described that, along with the *cis*−*trans* isomerization, the acid-catalyzed rearrangement takes place quite easily and retains the solid state when coground. This rearrangement proceeds intramolecularly. The *cis* isomer of the diols was shown to be more reactive for the 1,4-rearrangement than the *trans* isomer. These results were rationalized in terms of the π-participation of the carbocation intermediate that was generated in the solid state.

(17) Abarca, B.; Asensio, G.; Ballesteros, R.; Varea, T. *J. Org. Chem.* **1991**, *56*, 3224.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL α-500 spectrometer. UV/vis spectra were recorded on a Jasco V-570 spectrometer. Mass spectra were measured on a JEOL JMS-600H machine under electron impact at 70 eV. FTIR was measured on a JASCO FT/IR-350 spectrometer. The temperature-variable FTIR measurements were carried out employing a micro FTIR spectrometer (JASCO MFT-2000). A single-crystal sample was placed between two KBr plates, and a temperature controller (Mettler EP82−HT) was set up on the XY stage of the spectrometer. The temperature was increased at 1 °C/min and the IR spectrum was measured at each 1 °C or 2 °C increment. The X-ray powder diffraction analysis was conducted on a Rigaku RAD-C X-ray diffractometer using monochromatic Cu *K*α radiation (λ = 1.5418 Å). The differential scanning calorimetry (DSC) traces were recorded on a Seiko SS-5200 DSC at a scanning rate of 5 °C min^{-1} from 40 to 280 °C. All solvents used in this work were purified using normal methods.

Synthesis of *Trans*- and *Cis*-9,10-bis(thieno[3,2-*b*]thienyl)-9,10-dihydroxy-9,10-dihydroanthracene (1) and (3). Thieno[3,2-*b*]thiophene (13.99 g, 0.10 mol) was added to a solution of lithium diisopropyl amide (0.11 mol) in THF (500 mL) at 0 °C under argon. After stirring under reflux for 1 h, the reaction mixture was cooled to room temperature and anthraquinone (5.20 g, 25 mmol) was added. The mixture was refluxed for 5 h and poured into saturated NH_4Cl aqueous solution and extracted with dichloromethane. The organic phase was washed with brine, dried, and concentrated. The residue was chromatographed on silica gel eluting with CH_2Cl_2−hexane to yield 4.55 g of *trans* diol **1** (37%) and 4.14 g of *cis* diol **3** (34%). Other diol compounds were prepared according to a similar procedure and are characterized as follows. **1 (*trans*)**: ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 2H), 7.03 (s, 2H), 7.19 (d, J = 5.3 Hz, 2H), 7.31 (d, J = 5.3 Hz, 2H), 7.39 (dd, J = 3.2, 6.0 Hz, 4H), 7.73 (dd, J = 3.4, 6.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 73.7, 118.2, 119.5, 126.8, 127.7, 129.0, 138.4, 139.1, 140.0, 154.5; IR (KBr) 702.0, 761.7, 1077.1, 1106.0, 1324.9, 3451.0 cm^{-1}; MS *m*/*z* 488 (M^+), 470. Calcd for $C_{26}H_{16}O_2S_4$: C, 63.90; H, 3.30; S, 26.25. Found: C, 63.76; H 3.49; S, 26.16. **3 (*cis*)**: mp 209−212 °C; ^{1}H NMR ($CDCl_3$) δ 3.00 (s, 2H), 5.93 (s, 2H), 6.89 (d, J = 5.3 Hz, 2H), 7.04 (d, J = 5.3 Hz, 2H), 7.56 (dd, J = 3.3, 5.7 Hz, 4H), 8.09 (dd, J = 3.3, 5.7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 73.1, 118.8, 119.1, 125.3, 127.3, 128.6, 137.2, 139.4, 140.1, 150.5; IR (KBr) 739.6, 1108.9, 1168.7, 1347.0, 1449.2, 3324.7 cm^{-1}; MS *m*/*z* 488 (M^+), 470. Calcd for $C_{26}H_{16}O_2S_4$: C, 63.90; H, 3.30; S, 26.25. Found: C 63.80; H, 3.56; S, 26.09.

***Trans*-9,10-bis(thieno[2,3-*b*]thienyl)-9,10-dihydroxy-9,10-dihydroanthracene (4).** ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 2H), 6.94 (s, 2H), 7.08 (d, 2H, 5.3 Hz), 7.27 (d, 2H, 5.3 Hz), 7.38 (dd, 4H, 3.2 Hz, 5.9 Hz), 7.74(dd, 4H, 3.2 Hz, 5.9 Hz); ^{13}C NMR ($CDCl_3$) δ 73.74, 118.65, 120.10, 127.46, 127.61, 128.92, 137.19, 140.09, 145.83, 155.48; IR (KBr) 640.3, 703.8, 776.8, 811.9, 986.4, 1331.61, 1446.7, 3530.1 cm^{-1}; MS *m*/*z* 488 (M^+) 470. Calcd for $C_{26}H_{16}O_2S_4$: C, 63.90; H, 3.30; S, 26.25. Found: C, 63.76; H, 3.49; S, 26.16.

***Cis*-9,10-bis(thieno[2,3-*b*]thienyl)-9,10-dihydroxy-9,10-dihydroanthracene (5).** ^{1}H NMR ($CDCl_3$) δ 2.99 (s, 2H), 5.90 (s, 2H), 6.42 (d, 2H, 5.2 Hz), 6.91 (d, 2H, 5.2 Hz), 7.56 (dd, 4H, 3.4 Hz, 5.8 Hz), 8.10 (dd, 4H, 3.4 Hz, 5.8 Hz); ^{13}C NMR ($CDCl_3$) δ 73.14, 119.39, 119.58, 125.23, 126.69, 128.59, 136.03, 140.16, 144.67, 148.73; IR (KBr) 655.7, 748.3, 834.0, 1003.8, 1023.1, 1078.0, 1109.8, 1173.3, 1322.9, 1467.6, 3477.0 cm^{-1}; MS *m*/*z* 488 (M^+), 470. Calcd for $C_{32}H_{30}N_2O_4S_4$ (as a 1:2 DMF solvate): C, 60.54; H, 4.76; N, 4.41; S, 20.20. Found: C, 60.49; H, 4.75; N, 4.47; S, 20.31.

***Trans*-9,10-bis(dithieno[3,2-*b*;2′,3′-*d*]thienyl)-9,10-dihydroxy-9,10-dihydroanthracene (6).** ^{1}H NMR ($CDCl_3$) δ 2.98 (s, 2H), 7.07 (s, 2H), 7.25 (d, 2H, 5.2 Hz), 7.33 (d, 2H, 5.2 Hz), 7.41 (dd, 4H, 3.4 Hz, 5.8 Hz), 7.76 (dd, 4H, 3.4 Hz, 5.8 Hz);^{13}C NMR (THF-d_8) δ 73.55, 119.80, 121.54, 126.44, 128.71, 129.67, 131.88, 141.49, 141.61, 141.69, 157.60; IR (KBr) 604.6, 700.0, 767.5, 825.4, 892.9, 983.5, 1089.6, 1186.0, 1359.6, 1443.5, 3405.7 cm^{-1}; MS *m*/*z* 600 (M^+), 582. Calcd for $C_{30}H_{16}O_2S_6$: C, 59.97; H, 2.68; S, 32.02. Found: C, 59.57; H, 2.94; S, 31.93.

Table 2. Crystallographic Data for Compounds **1**, **2**, **4** and the Mixed Crystal of **1** and **8**

compound	diol **1**	mixed **1**, **8**	anthrone **2**	diol **4**
formula	$C_{26}H_{16}O_2S_4$	$C_{26}H_{16}O_2S_4$	$C_{26}H_{14}OS_4$	$C_{26}H_{16}O_2S$
formula wt	488.65	488.65	470.64	488.65
crystal sytem	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	*Pbca* (no. 61)
a/Å	8.681(3)	8.708(2)	11.510(1)	16.921(8)
b/Å	10.847(2)	10.856(2)	9.1965(6)	22.237(9)
c/Å	6.1595(9)	6.1420(9)	20.402(4)	11.281(4)
α/deg	97.66(1)	97.83(2)	90	90
β/deg	106.37(2)	106.40(1)	98.66(1)	90
γ/deg	76.51(2)	76.27(2)	90	90
V/Å^3	539.7(2)	539.6(2)	2135.0(4)	4244(2)
Z	1	1	4	8
D_{calc}/gcm^{-3}	1.503	1.504	1.464	1.529
μ(Mo *K*α), cm^{-1}	4.63	4.63	4.62	4.71
no. of reflections measured	2462	3160	3731	6821
no of reflections with $I > 3\sigma(I)$	2086	1973	2739	2626
no. of parameters	146	154	344	290
R	0.038	0.056	0.065	0.056
R_W	0.032	0.048	0.070	0.066
GOF	5.710	3.035	1.520	1.869

***Cis*-9,10-bis(5-methyl-2-thieno[3,2-*b*]thienyl)-9,10-dihydroxy-9,10-dihydroanthracene (7).** mp 210−215 °C; ^{1}H NMR (THF-d_8) δ 2.38 (d, 6H, 0.61 Hz), 2.99 (s, 2H), 5.84 (s, 2H), 6.55 (d, 2H, 0.61 Hz), 7.54 (dd, 4H, 3.4 Hz, 5.8 Hz), 8.09 (dd, 4H, 3.4 Hz, 5.8 Hz); ^{13}C NMR ($CDCl_3$) δ 16.08, 73.06, 117.70, 119.02, 126.46, 128.20, 136.41, 139.69, 141.97, 142.43, 152.35; IR (KBr) 740.5, 818.6, 1006.6, 1126.2, 1636.3, 3443.3 cm^{-1}; MS *m*/*z* 516 (M^+), 498. Calcd for $C_{29}H_{22}O_2S_4Cl_2$ (as a CH_2Cl_2 solvate): C, 57.89; H, 3.69; S, 21.32. Found: C, 58.05; H, 3.78; S, 21.54.

***Trans*-9-thieno[2,3-*b*]thienyl-10-thieno[3,2-*b*]thienyl-9,10-dihydroxy-9,10-dihydroanthracene (8).** ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 1H), 2.90 (s, 1H), 6.94 (s,1H), 7.03 (s, 1H), 7.08 (d, J = 5.3 Hz, 1H), 7.19 (d, J = 5.3 Hz, 1H), 7.28 (d, J = 5.3 Hz, 1H), 7.32 (d, J = 5.3 Hz, 1H), 7.39 (m, 4H), 7.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 73.5, 73.6, 118.3, 118.6, 119.6, 120.1, 126.7, 127.6, 127.7, 127.8, 128.9, 129.0, 137.3, 138.4, 139.2, 140.0, 140.2, 146.8, 154.4, 155.5; IR (KBr) 705.8, 765.6, 1077.0, 1108.9, 1324.9, 3459.0 cm^{-1}; MS *m*/*z*, 488 (M^+), 470. Calcd for $C_{26}H_{16}O_2S_4$: C, 63.90; H, 3.30; S, 26.25. Found: C, 63.67; H, 3.39; S, 26.49.

Solid-State Thermolysis. Compound **1** (3.1 g, 6.3 mmol) was heated to 250 °C on a hot plate equipped with a thermometer under a stereomicroscope to yield **2** (2.92 g, 6.2 mmol) in quantitative yield. An analytically pure sample was obtained by recrystallization from CH_2Cl_2−hexane. The solid-state thermal reactions of **3**∼**8** were conducted in a similar procedure as described for **1**. Compound **3** became fluid around 210 °C and then immediately solidified to give anthrone **2**. Therefore, **3** was heated at 180 °C for 30 min, resulting in the formation of **2** in the solid state without melting. The reaction of **7** was also carried out at 180 °C.

Cogrinding. A mixture of **1** (100 mg, 0.2 mmol) and *p*-toluenesulfonic acid (34 mg, 0.2 mmol) was coground for 20−60 min using an agate mortar and a pestle. For product analysis, the mixture was occasionally ground, although to obtain the time conversion, grinding was continued almost up to the completion of the reaction. The reacted solids were quenched with $NaHCO_3$ solution prior to the NMR analysis in order to avoid the acid-catalyzed reaction in solution upon dissolution of the coground solids. Analytically pure products were obtained by gel permeation chromatography (GPC).

10,10-Bis(thieno[3,2-*b*]thienyl)-9,10-dihydroanthracene-9-one (2). Product from **1** and **3**: mp >330 °C; ^{1}H NMR ($CDCl_3$) δ 6.97 (s, 2H), 7.13 (d, J = 5.2 Hz, 2H), 7.33(d, J = 5.2 Hz, 2H), 7.52−7.55 (m, 2H), 7.58−7.61 (m, 4H), 8.33 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 119.5, 121.2, 121.3, 127.4, 127.7, 128.4, 129.9, 131.1, 133.0, 137.6, 139.7, 147.0, 152.6, 183.4; IR (KBr) 636.4, 712.6, 762.7, 933.4, 1320.0, 1456.0, 1658.5 cm^{-1}; MS *m*/*z* 470 (M^+). Calcd for $C_{26}H_{14}OS_4$: C, 66.35; H, 3.00; S, 27.25. Found: C, 66.13; H, 3.06; S, 27.43.

10-(Thieno[2,3-*b*]thienyl)-10-(thieno[3,2-*b*]thienyl)-9,10-dihydroanthracene-9-one (9). Product from **8**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 6.94 (s, 1H), 6.97 (s, 1H), 7.09 (d, J = 5.3 Hz, 1H), 7.12 (d, J = 5.1 Hz, 1H), 7.28 (d, J = 5.1 Hz, 1H), 7.33 (d, J = 5.3 Hz, 1H), 7.54 (m, 2H), 7.60 (m, 4H), 8.33 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 54.11, 116.7, 116.9, 118.9, 119.4, 125.2, 126.9, 127.2, 127.3, 128.9, 129.8, 134.0, 138.4, 138.9, 140.2, 145.9, 146.5, 153.6, 156.1, 183.3; IR (KBr) 642.2, 722.2, 1319.1, 1455.0, 1596.8, 1657.5 cm^{-1}; MS *m*/*z* 470 (M^+). Calcd for $C_{26}H_{14}OS_4$: C, 66.35; H, 3.00; S, 27.25. Found: C, 66.24; H, 3.13; S, 27.08.

10,10-Bis(thieno[2,3-*b*]thienyl)-9,10-dihydroanthracene-9-one. Product from **4** and **5**: mp >300 °C. ^{1}H NMR ($CDCl_3$) δ 6.94 (s, 2H), 7.10 (d, 2H, 5.3 Hz), 7.28 (d, 2H, 5.3 Hz), 7.54 (m, 2H), 7.60 (m, 4H), 8.32 (d, 2H, 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 53.81, 120.10, 121.81, 127.60, 127.69, 128.39, 129.81, 131.13, 133.06, 137.88, 145.04, 146.93, 153.51, 183.43; IR (KBr) 641.2, 727.0, 810.9, 933.4, 1319.1, 1454.1, 1595.8, 1657.5 cm^{-1}; MS *m*/*z* 470 (M^+). Calcd for $C_{26}H_{14}OS_4$: C, 66.35; H, 3.00; S, 27.25. Found: C, 66.24; H, 3.12; S, 27.08.

10,10-Bis(dithieno[3,2-*b*;2′,3′-*d*]thienyl)-9,10-dihydroanthracene-9-one. Product from **6**: mp 236−239 °C; ^{1}H NMR ($CDCl_3$) δ 7.02 (s, 2H), 7.25 (d, 2H, 5.0 Hz), 7.33 (d, 2H, 5.0 Hz), 7.56 (m, 2H), 7.63 (m, 4 H), 8.35 (d, 2H, 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 55.11, 120.61, 125.50, 126.31, 127.82, 128.53, 129.70, 130.85, 131.15, 131.40, 133.16, 139.66, 141.42, 146.74, 151.09, 183.26; IR(KBr) 601.7, 720.3, 892.9, 931.5, 1317.1, 1360.5, 1453.1, 1596.8, 1663.3 cm^{-1}; MS *m*/*z* 582 (M^+). Calcd for $C_{30}H_{14}OS_6$: C, 61.83; H, 2.42; S, 33.01. Found: C, 62.30; H, 2.17; S, 32.68.

10,10-Bis(5-methylthieno[3,2-*b*]thienyl)-9,10-dihydroanthracene-9-one. Product from **7**: mp 204−206 °C; ^{1}H NMR ($CDCl_3$) δ 2.53 (d, 6H, 0.9 Hz), 6.48 (d, 2H, 0.9 Hz), 6.85 (s, 2H), 7.51 (m, 2H), 7.57 (m, 4H), 8.31 (dd, 2H, 0.9 Hz, 7.0 Hz);^{13}C NMR ($CDCl_3$) 16.29, 53.38, 117.29, 121.21, 127.55, 128.20, 129.83, 131.08, 132.93, 135.75, 139.31, 142.45, 147.22, 150.63, 183.53; IR (KBr) 719.3, 768.5, 811.9, 931.5, 1188.9, 1317.1, 1453.1, 1597.7, 1665.2 cm^{-1}; MS *m*/*z* 498 (M^+). Calcd for $C_{28}H_{18}OS_4$: C, 67.43; H, 3.65; S, 25.72. Found: C, 67.26; H, 3.69; S, 26.02.

9,10-Bis(thieno[3,2-*b*]thienyl)anthracene (10). mp >340 °C; ^{1}H NMR ($CDCl_3$) δ 7.43 (m,8H), 7.49 (d, 2H, 5.5 Hz), 8.01 (dd, 4H, 3.4 Hz, 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 119.50, 121.75, 125.93, 126.67, 126.86, 130.43, 131.36, 139.17, 140.15, 140.77; IR (KBr) 639.3, 713.5, 768.5, 789.7, 813.8, 1168.7, 1438.6; MS *m*/*z* 454 (M^+). Calcd for $C_{26}H_{14}S_4$: C, 68.72; H, 3.09; S, 28.19. Found: C, 68.49; H, 2.73; S, 29.01.

Diphenyl(thieno[3,2-*b*]thienyl)carbonium tetrafluoroborate (11) (BF_4). To a solution of diphenylthieno[3,2-*b*]thienylcarbinol (1.44 g, 4.46 mmol) in 6 mL of propionic unhydride cooled by ice bath, 1.5 mL of tetrafluoroboric acid was added. The mixture was stirred for 30 min at 0 °C to give a red solution. The resulting solution was cooled at −15 °C and the deep red crystals of (**11**)(BF_4) were recrystallized: mp 183−184 °C; ^{1}H NMR ($CDCl_3$) δ 7.63 (m, 2H), 7.71 (m, 5H), 7.77

(m, 1H), 7.92 (m. 2H), 8.67 (d, 1H, 5.19 Hz), 8.78 (s, 1H); IR (KBr) 704.9, 796.0, 1032.2, 1083.8, 1334.0, 1470.9, 1586.2, 3099.1 cm^{-1}. Calcd for $C_{19}H_{13}BF_4S_2$: C, 58.17; H, 3.35; S, 16.35. Found: C, 57.90; H, 3.41; S, 16.37.

X-ray Crystal Structure Determinations. Intensity data for **1**, **4**, and a mixed crystal of **1** and **8** were collected on a Rigaku AFC-5S diffractometer using graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) at room temperature. For **2**, intensity data were collected on a Rigaku R-AXIS-II imaging plate area detector using graphite-monochromated Mo *K*α radiation (λ = 0.71069 Å) at room temperature. The crystallographic data are summarized in Table 2. The crystal structure was solved by direct methods using the SIR88[18] (for **1**, **2**, and the mixed crystal of **1** and **8**) and SAPI 91[19] (for **4**) program packages and refined by the full-matrix least-squares using the TEXSAN program package.[20] The mixed crystal was refined as a 1:1 composition of **1** and **8**. Non-hydrogen atoms other than the disordered atoms were refined anisotropically. The disordered atoms in the mixed crystal were refined isotropically. All of the hydrogen atoms were calculated geometrically except those of the hydroxy groups and the disordered atoms.

Acknowledgment. This work was financially supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No 10146101) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **1**, **2**, **4**, and the mixed crystal (**1**+**8**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA000788L

(18) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterro, D. *J. Appl. Crystallogr*. **1989**, *22*, 389.

(19) Fan, H.-F. *Structure Analysis Program with Intelligent Control*; Rigaku Corp.: Tokyo, 1991.

(20) *Single-Crystal Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX, 1995.