

Photoreactions of crystalline charge-transfer complexes

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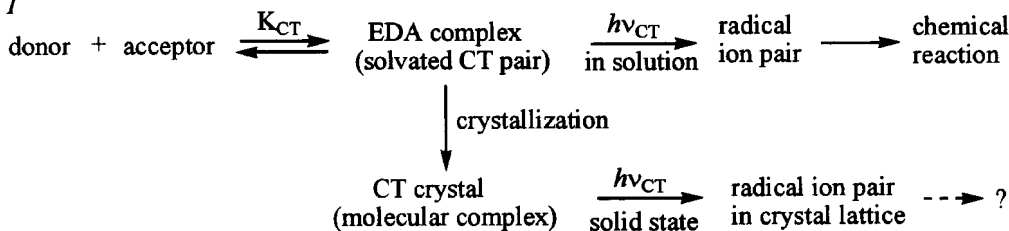
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Abstract: Bis[1,2,5]thiadiazolotetracyanoquinodimethane **1** formed stable charge-transfer (CT) crystals with arylolefins. Upon photoirradiation of these CT crystals the [2+2]-type cycloadducts **2** were produced via single electron-transfer in the solid state. In contrast to the close similarity in solution photochemistry, the solid-state reactivities were quite different for the isomeric divinylbenzenes (**DVs**). Such differences were induced by incorporating differently shaped **DV** molecules in the similar cavities formed by S •• N≡C interaction of **1**. This interaction was suggested to take an important role in maintaining the topotaxy during the cycloaddition of the *o*-**DV**•**1** CT crystal. Because of the single crystal-to-single crystal transformation as well as the predominant cycloaddition via one of the two overlaps, the crystal chirality in *o*-**DV**•**1** could be transferred as the molecular chirality in the product, thus forming the cycloadduct **2_o** in high optical yield (95% ee).

INTRODUCTION

Recently photoinduced electron-transfer (PET) reactions attract much attention in the field of organic photochemistry. Their products or reactivities are often different from those of classic photoreactions because the reactive species are not the excited molecules but the radical ions formed by single electron-transfer (SET). Photolysis of weak electron donor-acceptor (EDA) complexes in solution is a straightforward method for SET (1), so that the photoirradiation of crystalline charge-transfer complexes (CT crystal) would provide the unique opportunity to investigate the reactions of radical ions included in the highly organized crystal lattices (Scheme 1). However, there have been few reports on the photoreactivities of CT crystals although their physical properties have been thoroughly investigated due to the intriguing behaviors such as electrical conduction (2) and ferromagnetism (3).

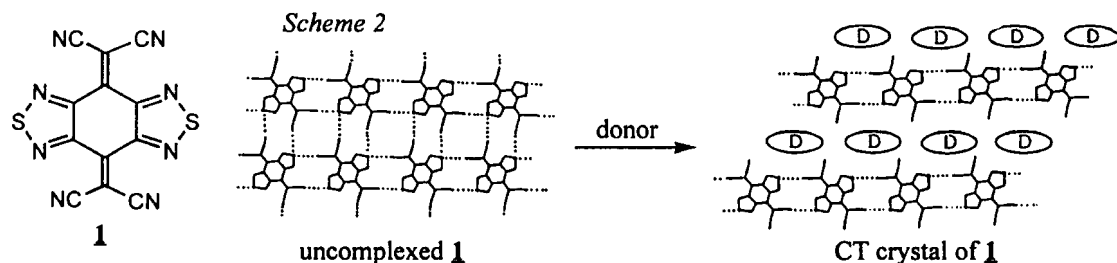
Scheme 1



It is well known that the proper packing arrangement is the governing factor in determining the reactivity and the reaction pathway in crystal (4). Thus, under the appropriate "crystal engineering" (5), CT crystals could serve as novel photoreactive species. One of the promising methods in "crystal engineering" is the usage of intermolecular interactions, and Cl •• Cl and C-H •• O contacts have often appeared in the literature (6) which induce the weakly attractive interactions of directional preference. During the course of our studies on tetracyanoquinodimethanes (TCNQs) fused with heterocycles such as **1**, it was found that the intermolecular interaction between chalcogen atoms and cyano lone pairs is also one of the sources of the directionality in crystal packing of organic molecules (7, 8).

MOLECULAR PACKING AFFECTED BY S •• N≡C CONTACTS

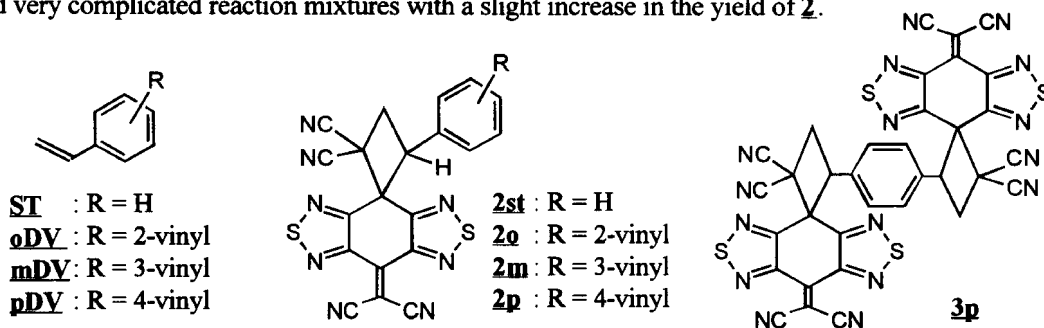
In the crystal of **1** short atomic contacts of S •• N≡C (3.04 Å) connect the molecule with four neighbors, thus forming a nearly coplanar "sheet-like" network. The atomic charges estimated by ab initio calculation (STO-3G) were in accord with the assumption that such contacts stabilize the crystalline state electrostatically. Similar short contacts as well as the infinite network formation in crystal were also observed in its selenium congeners by Se •• N≡C interaction (7) or other related molecules possessing chalcogen atoms and dicyanomethylene moieties (9).



Because **1** (E_{red} , -0.02 V vs SCE) is strong electron acceptors like TCNQ itself (E_{red} , +0.18 V) it formed EDA complexes in solution as well as stable CT crystals with a variety of electron donors. One of the important features of this molecule is the recognition properties during the CT crystal formation. As in the case of uncomplexed **1**, S \cdots N=C interaction also connects the molecules of **1** in the CT crystals with aromatic hydrocarbons, thus forming linear "ribbon-like" networks as shown in Scheme 2. Between the two "ribbons" are formed inclusion cavities. Donors with the different shapes are incorporated in the similar cavities, thus the thermodynamic stability of CT crystals differs for the isomeric aromatic hydrocarbons. In this way, complexations of **1** with the isomer mixtures of disubstituted benzenes exhibited the high *p*-derivative selectivity (7). These results prompted us to explore the CT excitation reactions of the molecular complexes of **1** (10) in the anticipation that such inclusion cavities could work as the unique reaction centers in the solid-state reactions. Arylolefins are suitable electron donors because of the sufficient donating properties as well as the versatile reactivities at the vinyl groups in their cation radicals (11).

CT EXCITATION REACTIONS OF **1** AND ARYLOLEFINS IN SOLUTION AND IN THE SOLID STATE

It was previously found that the [2+2]-type cycloaddition between **1** and styrene (**ST**; E_{ox} , +1.90 V) or divinylbenzenes (**DVs**) occurred via SET to give the adducts **2** upon CT excitation ($\lambda > 450$ nm) in MeCN. The numbers of vinyl groups or their substituting positions had little effect on the photoreactivity of EDA complexes. Although the regioisomer could not be isolated from the reaction mixtures, the yields of **2** were as low as 10% after 5 h-irradiation, showing their very low reactivities in solution. Such inefficiency may be partly due to the small association constants (K_{CT} , 0.85-1.5 dm³ mol⁻¹ in MeCN at 20 °C) for the above mentioned EDA complexes. However, the similar photolyses in the presence of large excess donors produced very complicated reaction mixtures with a slight increase in the yield of **2**.



On the other hand, when a water suspension of the finely powdered **ST**·**1** crystal was irradiated within the CT band the regioselective cycloaddition occurred smoothly giving the same adduct **2st** as a sole product. The apparent reactivity in the solid state is much higher than that in solution because **2st** was obtained in good yield (71%) within a shorter irradiation period (1 h) with longer wavelength light ($\lambda > 505$ nm). In the case of *o*-**DV** (E_{ox} , +1.82 V) the solid-state photoreactivity is much more prominent, the adduct **2o** was isolated in 84% upon irradiation for 15 min with much lower energy light ($\lambda > 540$ nm). These results clearly show that the cycloaddition via SET actually occurs even in the solid state upon irradiation of CT crystals, and the characteristic features in the solid state may be the higher reaction efficiency than in solution as well as the formation of the sole product under the topochemical control by the crystal lattice.

However, these features are not always true as exemplified by the photoreactions of *m*-**DV** (E_{ox} , +1.83 V) and *p*-**DV** (E_{ox} , +1.51 V). The time course of the solid-state reaction of the *m*-**DV**·**1** crystal indicated that the adduct formation became sluggish with the progress of reaction, and the yield of adduct **2m** reached the maximum value (ca. 45%) after 5 h-irradiation. Such an incomplete conversion of *m*-**DV**·**1** to **2m** is due to the crystal-to-amorphous transformation, which was indicated by the changes of X-ray powder diffraction patterns. On the other hand, the *p*-**DV**·**1** crystal was found to be photoinert at the initial stage whereas the prolonged irradiation caused the cycloaddition of defect-accelerated type. The 1:2 adduct **3p** was also formed as a secondary product from **2p** although the similar multi-addition has never occurred upon CT excitation of other CT crystals or EDA complexes in solution.

PACKING ARRANGEMENT IN ISOMERIC DV•1 CT CRYSTALS AND THE STRUCTURE-REACTIVITY RELATIONSHIP

The solid-state reactivities are quite different from those in solution and largely changed for the isomeric **DV•1** CT crystals. In order to account for such variation in reactivity X-ray structural analyses of the three isomeric **DV•1** crystals were carried out. None of them crystallizes isomorphously to each other, yet their molecular arrangements exhibit several common features. The striking similarity is the formation of "ribbon-like" networks by S •• N=C interaction (Fig. 1). Between the two "ribbons" are formed inclusion cavities as predicted in Scheme 2. Perpendicular to these arrangements are formed one-dimensional mixed columns in which the donor and the acceptor molecules are repeated alternately. Because the differently shaped **DV** isomers are incorporated in the similar cavities, the face-to-face overlapping patterns in the columns are changed significantly. By considering the resulting differences in the molecular overlaps as well as the degree of close packing of donors in the cavities, the variation in the solid-state reactivity can be accounted for as follows.

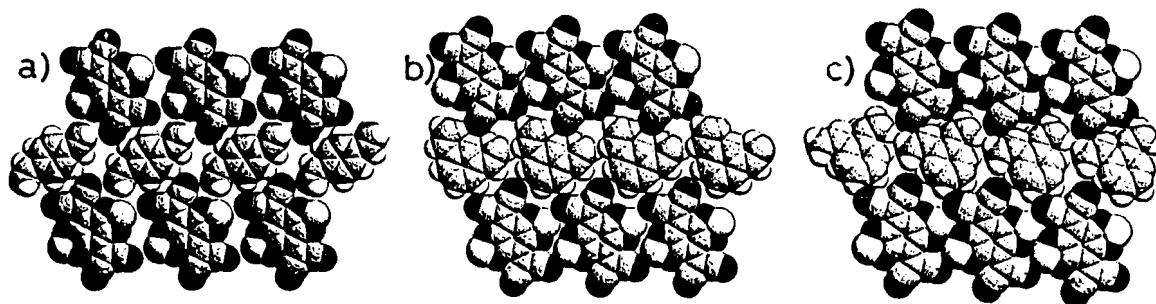


Fig. 1 Space-filling representation of packing arrangements in a) *p*-**DV•1**, b) *m*-**DV•1**, and c) *o*-**DV•1** CT crystals. Please note the unoccupied free space in the cavity of *p*-**DV•1** and the close packing in *m*-**DV•1**.

Two olefinic parts are arranged unfavorably for the cycloaddition in the overlap of the *p*-**DV•1** crystal, which may result in the initial photoinertness of this crystal. However, the "ribbon" network is looser than in others (distances for S •• N=C contacts: 3.49 Å in *p*-**DV•1**; 3.23 and 3.25 Å in *m*-**DV•1**; 3.14 and 3.43 Å in *o*-**DV•1**), so that the large space is left unoccupied in the cave as can be seen in Fig. 1a. These features of the packing arrangement might allow the in-plane rotation of *p*-**DV** in the cavity, resulting in the cycloaddition of defect-accelerated type upon prolonged irradiation. In contrast, the incomplete conversion of *m*-**DV•1** to **2m** seems related with the closer packing of *m*-**DV** in the cavity. Although the reactive two double bonds are arranged favorably in the molecular overlap, formation of an adduct molecule would disturb the neighboring overlap because the large atomic motion is required with the progress of cycloaddition in *m*-**DV•1**. Such a process would gradually disintegrate the crystal lattice to make the solid unreactive.

On the other hand, the high reaction efficiency in *o*-**DV•1** can be accounted for by the fact that the cycloaddition occurred without significant change of the crystal matrix formed by **1**. Transformation of *o*-**DV•1** to **2o** was proven to be one of the rare examples of the single crystal-to-single crystal reactions (12). Thus, we could analyze the crystal structure after photoirradiation of the single crystal of *o*-**DV•1**. Direct comparisons of molecular arrangements are very indicative of the detailed sequence of this reaction. Although the two different overlaps (type-1 and -2) are repeated alternately along the mixed column, only type-2 is conducive to the photoreactivity in the significant magnitude (Fig. 2). The cycloaddition via type-1 forms (*S*)-**2o**, whereas (*R*)-**2o** is formed via type-2. Via the mirror images of these two overlaps (type-1m and -2m) are formed the antipodes, (*R*)- and (*S*)-**2o**, respectively. The fact that the reaction proceeds predominantly via type-2 (and type-2m) indicates that the product molecules in a columnar stack would have the same ab-

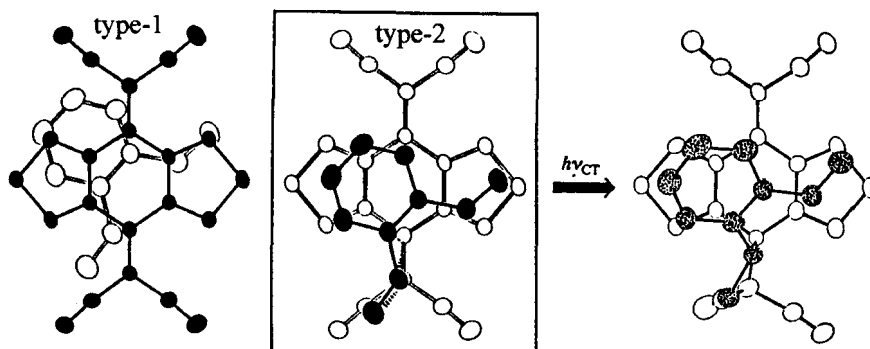


Fig. 2 Schematic illustration of the formation of adduct **2o** via the overlap of type-2 in *o*-**DV•1** CT crystal.

solute configuration. Furthermore, because of its adoption of the chiral space group, no mirror images are present in the same single crystal of *o*-DV•**1**. Thus, a certain single crystal having type-1 and -2 overlaps would form (*R*)-**2o** as a major stereoisomer whereas the adduct with (*S*)-configuration would be obtained from another single crystal having only type-1m and -2m overlaps. These conditions meet the requirements to realize the "absolute asymmetric synthesis (13)" in which the chiral molecules are produced from achiral substrates by using the crystal chirality as a sole asymmetric source. In fact, when carefully prepared single crystals were irradiated at -70 °C and analyzed piece by piece, some specimens showed (+)- and some showed (-)-optical rotation. Yet, in both cases the values of enantiomeric excess were as high as 95%.

CONCLUSION

The results described in this article clearly show that CT crystals serve as novel photoreactive substances. In the favorable cases the apparent reactivities are much higher than in solution, suggesting that the intimate arrangement of donor and acceptor is quite suitable for SET upon CT excitation. The similar [2+2]-type cycloaddition was also induced in the solid state when *o*-methoxystyrene, *o*-methylstyrene, or indene was used as a donor (14). Of course, the proper molecular arrangement is not always attained in the CT crystal of **1**, so that there are also a lot of unreactive CT crystals such as stilbene, acenaphthylene, and benzo[b]-furan complexes. In spite of some difficulty to find the appropriate combinations of donor and acceptor that may form the reactive crystals, very intriguing behaviors such as the "absolute asymmetric synthesis" are endowed by conducting the PET reaction in the solid state. By searching for reactions other than the [2+2]-type cycloaddition and/or by using another intermolecular interaction to control the packing arrangement in crystal will be provided the chance to explore this undeveloped category of photochemistry.

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