

## 신규 Bis(phenylethenyl)-dicyanopyrazine계 기능성 색소의 분자간 인력에 대한 광반응성 및 물성에 대한 연구

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## Topochemical Solid State Photoreaction of Bis(phenylethenyl)-dicyanopyrazine Functional Dyes with respect to Intermolecular Interaction

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### 1. Introduction

The solid state chemistry of organic materials is of current interest with respect to their functionalities for electronics and photonics which due to the molecular stacking in aggregates.<sup>1</sup> Many functionalities of organic materials are induced from  $\pi$ -electron oriented intermolecular interactions.<sup>2</sup> Dye molecular have a large  $\pi$ -conjugated planar structure, and are thus valuable candidates for organic functional materials.<sup>3</sup>

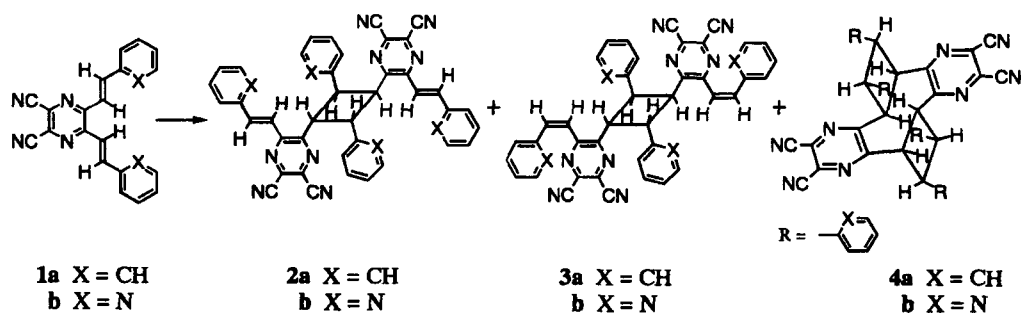
In the solid state photoreaction, so-called topochemical control are generally known in which the crystal structures and the distance between the reactive centers determine the reactivity and stereochemistry because limited motions of molecules in the crystal were proposed in comparison with those in solution.<sup>4</sup> In this paper, we intend to identify the specific lattice contraction with respect to the intermolecular  $\pi$ - $\pi$  interaction influencing on the photoreactivity and physical property of bis(phenylethenyl)-dicyanopyrazines in the solid state.

### 2. Results and Discussion

Benzene solution of **1** was irradiated by UV light at 366nm for 20h to give the mixture of **2** and **3** in 67% yield together with **4** in 33% yield, in conversion of 60%.

Thus, it was found that the molecular pair in the solution-phase photoreaction gave head-to-head(4) and head-to-tail(2 and 3) configuration, simultaneously.

Compound 1 showed crystal morphology and gave two kinds of crystals ; one is the orange colored crystal obtained from the recrystallization of 1 from the solution of hydrofuran and acetonitrile mixture (v/v = 1/1), and the other is the yellow colored crystal from benzene. They showed not only different color but also different photochemical reactions behaviors; the yellow crystal was polymerized with the irradiation however the orange one was inert. Two kinds of powdered crystal of 1 were irradiated with 366nm for 10h at room temperature, separately. The yellow colored crystal of 1 gave the insoluble photoproducts in organic solvents together with trace amounts of 2. However the orange one did not react at all.



Scheme 1.

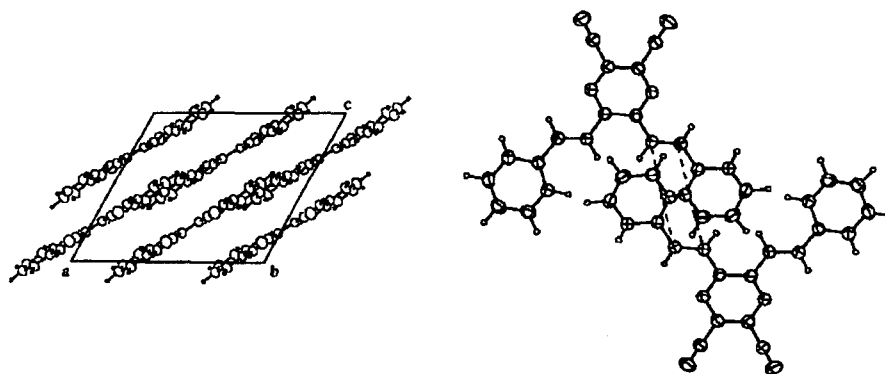
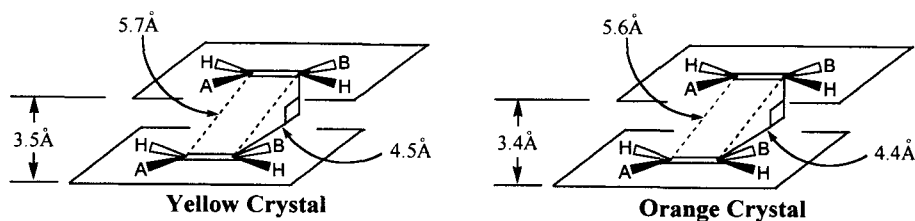


Fig. 1. The molecular and packing structure of 1 in the single crystal.

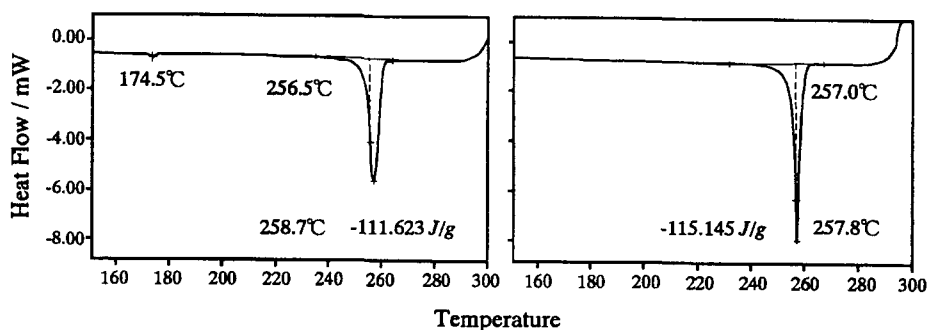
The X-ray crystal analyses revealed the planar and layered packing structure (Fig. 1). Each molecule is oriented in the same line of direction in the

plane, and the nearest next lines are oriented in the reverse direction.

Even though the distances between the planes are calculated in  $3.5\text{\AA}$ , the intermolecular distance of the reactive centers in upper and lower molecules to give the photodimer was calculated as  $5.7\text{\AA}$ , and consequently, **2** could be obtained from the results of the lattice slipping in ca.  $4.5\text{\AA}$  in the crystal structures under photoirradiation(**Fig. 2**). On the other hand, the orange crystal of **1** was photostable and the X-ray crystal analysis revealed that the orange one was contracted in only crystallographic *c*-axis by  $0.11\text{\AA}$  in comparison with that of yellow crystal. Thus, the distance between the reactive double bond in the orange crystal is  $5.6\text{\AA}$ , which are closer than yellow crystal. At the low temperature, both crystals were shrunken with similar way. However, the lattice contraction of orange crystal was smaller than that of yellow one, respectively, which means the crystal lattice of orange one was more strongly packed by the enhanced intermolecular  $\pi$ - $\pi$  interaction. Consequently, in the orange crystal, the enhanced intermolecular interaction makes more packed crystal structure than yellow one which can interrupt the molecular movement for the photoreaction.



**Fig. 2.** The molecular arrangement of ethylene units in the yellow and orange crystal of **1**.



**Fig. 3.** Thermal properties of yellow(Left) and orange(Right) crystals of **1**

Interestingly, the yellow crystal of **1** was changed to orange one by heating to 174.5°C. This morphological transformation occurred like dominoes, which was started from one terminal point of the yellow crystal and the color change was propagated to the other end of the crystal, completely. It is well confirmed by the differential scanning calorimetry; orange crystals showed a sharp endothermic peak at 257.8 °C, but yellow one showed a broad peak at 258.7 °C, respectively, and another small peak at 174.5°C(Fig. 3). A small peak at 174.5°C in the yellow crystal indicates the endothermic lattice contraction from the yellow crystal to orange one. However, none of such transition point of orange crystal was observed. This small endothermic peak shows that the crystal structure of yellow one is less stable than that of orange one, and the energy gap between two phase is small. Consequently, the lattice in the yellow one starts to transform with orange one from the one side at 174.5 °C, and this phase transition spread out into the whole crystal.

### 3. Conclusion

Compound **1** showed the crystal morphology to give the yellow and orange colored single crystals. Photoreaction of the yellow crystals gave photodimer and polymer, but the orange was inert. The morphological transformation from the yellow crystals to orange one was occurred and this phenomenon was well confirmed by the X-ray crystal analyses and the differential scanning calorimetry (DSC). Selective topochemical photocycloaddition of **1** and their morphological lattice transformation were well explained from the points of the lattice contraction and the dynamic movement of the crystal lattice.

### 4. References

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