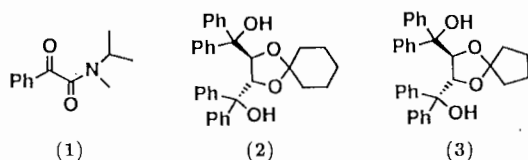


06-Crystallography of Organic Compounds

PS-06.02.08 STRUCTURES OF ISOMORPHOUS CLATHRATE COMPOUNDS OF α -OXAMIDE. By D.Hashizume*, H.Uekusa, Y.Ohashi, Department of Chemistry, Tokyo Institute of Technology, Japan, and R.Matsukawa, K.Miyamoto, and F.Toda, Department of Applied Chemistry, Ehime University, Japan.

The powdered sample of α -oxamide(1) is transformed to β -lactam on exposure to visible light. When it forms host-guest clathrate compounds with various host molecules, many different products are made. Recently new host molecules (2) and (3) were prepared. These molecules easily made host-guest clathrate crystal with (1), which are abbreviated to (2-1) and (3-1), respectively.



They were isomorphous to each other as shown Table 1. And the crystal structure of (2-1) is shown in Fig. 1. Two intermolecular hydrogen bonds were observed between carbonyl groups of (1) and hydroxyl groups of two host molecules (Fig. 2). The conformation of (1) was almost the same in both crystals. And the primary carbon of isopropyl group of (1) is close to α -carbonyl group and their distances were 2.875(6)Å, 2.86(1)Å and 3.194(6)Å, 3.194(9)Å for carbon-carbon and carbon-oxygen, respectively. After irradiation of visible light, β -lactam and furan derivative were obtained from each crystal. However, the ratio of β -lactam and furan derivative is different between two crystals. Further study is in progress.

Table 1. Crystal data.

Crystal	(2-1)	(3-1)
a/Å	9.469(4)	9.434(3)
b/Å	34.358(2)	34.056(3)
c/Å	10.4616(5)	10.404(2)
β /°	94.798(3)	94.87(2)
V/Å ³	3391.4(3)	3331(1)
Z	2	2
S.G.	P2 ₁	P2 ₁

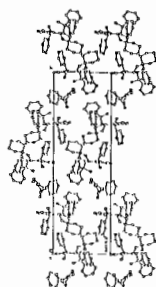


Fig. 1. Crystal structure of (2-1). And (3-1) is isomorphous for it.

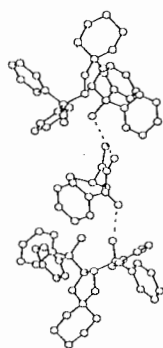


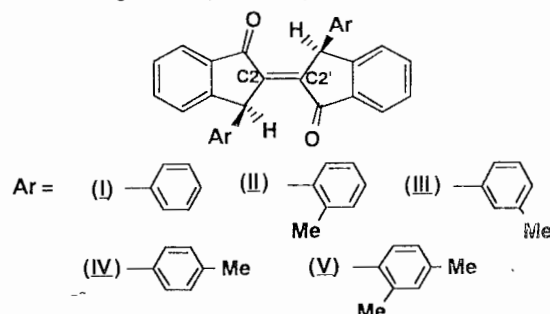
Fig. 2. Hydrogen bonds between oxygen of carbonyl groups of α -oxamide and hydroxy groups of host molecules.

PS-06.02.09 CRYSTAL AND MOLECULAR STRUCTURES OF PHOTOCROMIC BIINDENYLIDENE DERIVATIVES. By K. Okada*, K. Hosomi, K. Hirotsu, T. Higuchi, K. Tanaka† and F. Toda†, Department of Chemistry, Faculty of Science, Osaka City University, †Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Japan

Trans-syn-biindenylidene derivatives (Fig.1 I~IV) exhibit intense or weak photochromism, the reversal change of color from yellow to red purple upon exposure to light. The photocoloration in the present study is observed only in crystalline state and was found to be a formation of stable triplet biradicals by powder pattern ESR spectrum (Scheme I).

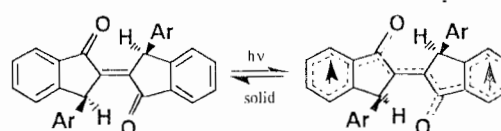
In order to elucidate the relationship between crystal structures and photochromic behavior, a series of compounds (Fig.1) was synthesized with a range of substituents (Ar) and subjected to X-ray diffraction analyses.

Fig.1 *trans-syn*-biindenylidene derivatives



Each derivative has roughly the same shape with an approximate two-fold axis passing through the central C=C bond and two parallel substituents (Ar) vertical to the chromophore. However, the chromophores take significantly different conformations (Type I and Type II in Fig.2). Type I is characterized by the bending of the chromophores at C2 and C2' atoms, resulting in the curved forms of the chromophores, and Type II is characterized by the twist of the indenylidene rings around the central C=C bond (Fig.2).

Scheme I



Interestingly, the chromophores stack face-to-face in all photochromic crystals (I~IV), while no such stacking was formed in the derivative V which does not show the photochromic effect. The crystals composed of the parallel stacking of Type I and Type II molecules show intense and weak photocoloration, respectively. These results indicate that the photochromic behavior of *trans-syn*-biindenylidene derivatives might be controlled through the effect of the substituents (Ar groups) of chromophores on the crystal packing and the molecular conformation.

Fig.2 face-to-face stacking of Type I (left) and Type II (right) molecules

