Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

X-Ray Study of Asymmetric Photoreaction of 2,4,6-Triisopropyl-4′-Carboxybenzophenone

Ken Hirotsu [a], Kengo Okada [a], Hisashi Mizutani [a], Hideko Koshima [b] [c] & Teruo Matsuura [c]

[a] Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshiku, Osaka, 558, Japan

[b] PRESTO, Research and Development Corporation of Japan

[c] Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu, 520, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Ken Hirotsu , Kengo Okada , Hisashi Mizutani , Hideko Koshima & Teruo Matsuura (1996): X-Ray Study of Asymmetric Photoreaction of 2,4,6-Triisopropyl-4′-Carboxybenzophenone, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 277:1, 99-106

To link to this article: http://dx.doi.org/10.1080/10587259608046009

Mol. Cryst. Liq. Cryst., 1996, Vol. 277, pp. 99–106
Reprints available directly from the publisher
Photocopying permitted by license only

X-RAY STUDY OF ASYMMETRIC PHOTOREACTION OF 2,4,6-TRIISOPROPYL-4'-CARBOXYBENZOPHENONE

KEN HIROTSU,[1] KENGO OKADA,[1] HISASHI MIZUTANI,[1] HIDEKO KOSHIMA[2,3] AND TERUO MATSUURA[3]

[1]Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

[2]PRESTO, Research and Development Corporation of Japan.

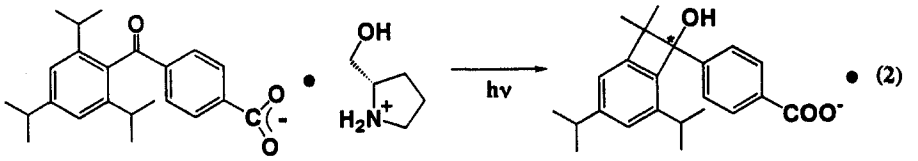
[3]Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520, Japan.

Abstract 2,4,6-Triisopropyl-4'-carboxybenzophenone was converted to the cyclobutenol derivative with the optical yield of e.e.=30% by the irradiation of its salt complex with L-prolinol. This solid state reaction proceeds without the decomposition of the crystal and the structures of the salt crystals before and after irradiation were determined using the X-ray method. In the asymmetric units of both structures, there are two independent molecules, which are related by pseudo glide plane. This pseudo symmetric arrangement of the two molecules is due to the weak chirality of L-prolinol and is responsible for the low optical yield of the reaction.

INTRODUCTION

The complexes between the chiral compounds and the prochiral ones have been used to induce an asymmetric reaction on the basis of specific interactions such as hydrogen bonds and salt bridges between the two compounds and the achiral environment in the solid state.[1-7] The photocyclization of 2,4,6-triisopropylbenzophenone to the cyclobutenol derivative by intramolecular γ-hydrogen abstraction occurs via the n-π* triplet state in the benzene solution and via the π-π* state in the solid state.[8,9] Equimolar mixture of 2,4,6-triisopropyl-4'-carboxybenzophenone and L-prolinol was recrystallized from an ethanol solution to give a chiral single crystal as the hydrogen bonded salt complex of the carboxylate anion (**1**) with the protonated L-prolinol (**2**). The irradiation of the salt complex of **1•2** gave **3•2** with the optical yield of e.e.=30%, indicating that L-prolinol acts as an ionic chiral handle although the optical yield is low (Scheme 1).[1]

The crystal structure of **1•2** was determined using the X-ray method, indicating that there are two independent salt complexes of **1•2** related by the pseudo glide plane because of the weak chirality of **2**. The photocyclization reaction of **1•2** proceeds with a slight deterioration of the salt complex crystal, resulting in the possible determination of the crystal structure of **3•2** after the irradition by a high pressure mercury lamp. In order to elucidate this asymmetric induction by comparing the crystal and molecular structure of **1•2** with that of the irradiated one (**3•2**), an X-ray crystallographic study of the salt crystal after the irradiation has been undertaken.



(1) (2) (3)

Scheme 1

EXPERIMENTAL

A single crystal (0.53×0.41×0.22mm) of the salt complex was irradiated for 48 hours using a high pressure mercury lamp. The Weissenberg photograph of the irradiated crystal showed diffraction spots which can be measured using a four circle diffractometer, although some diffused diffraction spots were observed, indicating that a single crystal structure determination was possible. Diffraction intensities were measured on a Rigaku rotating anode four circle diffractometer operated at 50kV and 200mA using the $\omega/2\theta$-scan mode at room temperature. No correction was made for an absorption effect. Crystal data are listed in Table 1. The structure was solved by the direct method with the use of SHELX86.[10] A full-matrix least-squares refinement with isotropic temperature factors for nonhydrogen atoms converged to the rather high R value of 0.192. The refinement procedure was terminated at this stage, since the diffraction data are relatively poor and abnormal bond length and angles are observed around the reaction sites. All calculations except for the direct methods were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[11]

Table 1. Crystal data for the salt complex before and after irradiation

	1•2	**3•2**
Formula	$C_{28}H_{39}NO_4 \cdot H_2O$	$C_{28}H_{39}NO_4 \cdot H_2O$
F.W.	471.63	471.63
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Cell const.		
a(Å)	51.70(2)	51.486(8)
b	11.743(7)	11.73(1)
c	9.045(3)	9.127(8)
V(Å^3)	5491(4)	5512(8)
Z	8	8
*D*calc.(g/cm3)	1.14	1.14
Diffractometer	Rigaku AFC-5A	Rigaku AFC-7R
X-ray source	CuKα	CuKα
No.of independent reflctns	4381	4704
No.of reflctns used(I>3σ(I))	3043	2903
R-factor	0.068	0.192

RESULTS AND DISCUSSION

The molecular arrangements in the salt crystal (**1•2**) and the irradiated crystal (**3•2**) are shown in Figures 1a and 1b, respectively. There are two independent **1**, **2** and water molecules in the asymmetric unit and the two **1** molecules are named **1**-A and **1**-B, respectively as is shown in Figure 1a. The **1**-A and **1**-B molecules related by a pseudo glide plane parallel to *ab*-plane stack along the *b*- and *c*-axes to form the layer parallel to the *bc*-plane. One side of this layer is hydrophobic with triisopropylbenzene moieties and the other side is hydrophilic with carboxylate anions. The hydrophobic parts of the two layers face to each other nearly at a=1/4 and 3/4, making the assembly of the hydrophobic moieties of **1**-A and **1**-B. The hydrophilic parts (carboxylate anions) of the two layers are nearly at a=0 and 1/2 and interact with **2** and water molecules, forming the hydrophilic regions parallel to the *ab*-plane. The crystal structure is characterized by the alternate arrangement of the hydrophobic regions of **1** and hydrophilic regions

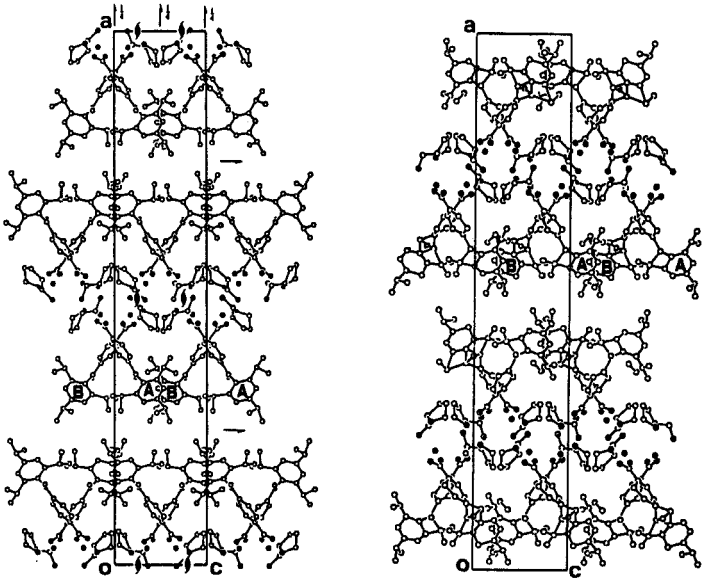


FIGURE 1 (a) View of the crystal structure of **1•2** along *b*-axis. (b) View of the crystal structure of **3•2** along *b*-axis. Oxygen and nitrogen atoms are represented by solid circles.

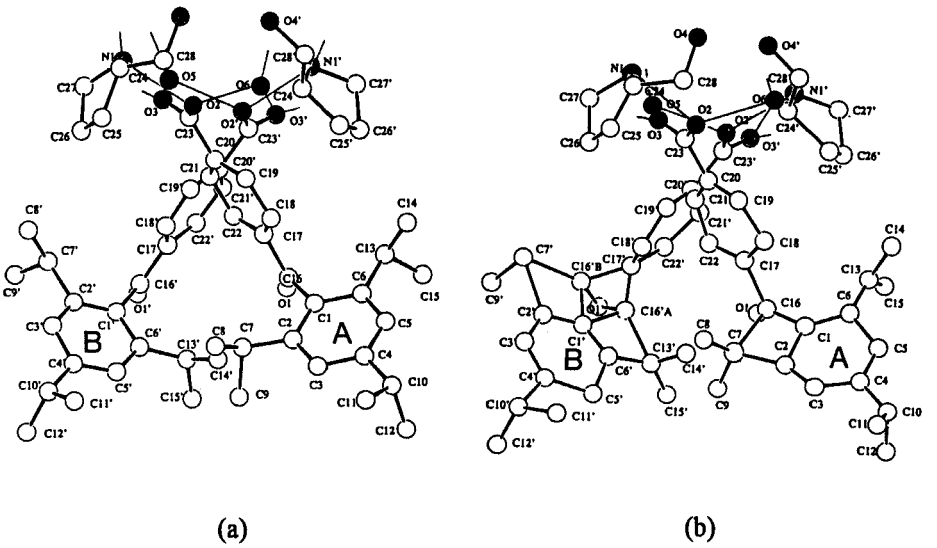


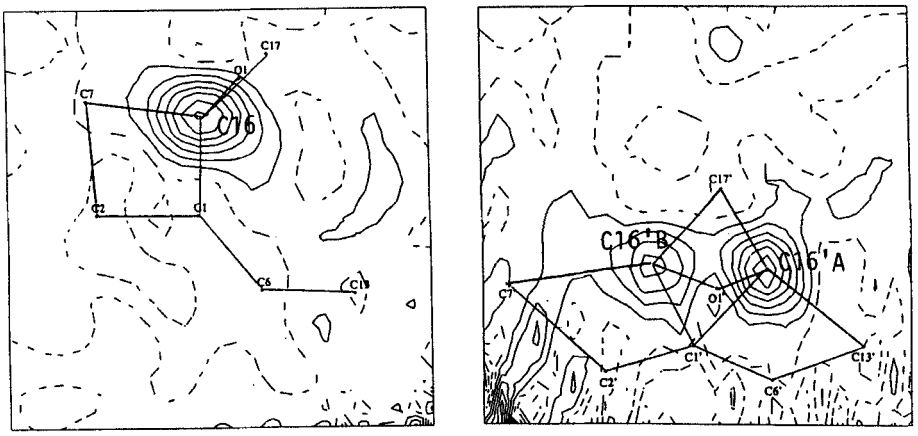
FIGURE 2 (a) Molecular structures of two independent salt complexes in **1•2** crystal. (b) Molecular structures of two independent complexes in **3•2** crystal. Hydrogen bonds are represented by thin lines.

(COO^- anions of **1**, **2** and water molecules). Although the origins of the unit cells are different in Figures 1a and 1b, these figures show that the crystal structure after the irradiation (Figure 1b) is quite similar to that of **1•2**. Especially, almost the same interactions are observed in the interface between the hydrophobic regions and in the hydrophilic region in the crystal structures of **1•2** and **3•2**. This reflects the progress of the photocylization reaction without the decomposition of the crystal. The formation of the cyclobutenol ring observed in Figure 1b clearly shows that **1**-A and **1**-B were converted to **3**-A and **3**-B, respectively, by the irradiation of the **1•2** single crystal.

The triisopropylbenzoylbenzoate molecules **1**-A and **1**-B, and the corresponding cyclobutenol products **3**-A and **3**-B are shown in Figures 2a and 2b, respectively. The hydrogen bonded salt of **1**-A and O5(H_2O) are related by a pseudo mirror plane (actually the pseudo glide plane) to that of **1**-B and O6(H_2O). This pseudo achiral arrangement is attributed at least in part to the weak chirality of the protonated L-prolinol (**2**), because the hydrogens on the nitrogen atom protrude from both sides of the pyrrolidine ring, resulting in the possible formation of the symmetric hydrogen bonds/salt bridges of N1-H---O2 and N1'-H---O2'. Each carboxylate anion in **1**-A, **1**-B, **3**-A and **3**-B are involved four hydrogen bonds and fixed tightly in the crystal. Two pseudo symmetric hydrogen bonding networks are formed in the following way: H-N1-H→O2←H-O6(←H-N1')-H→O3'←H-O4', H-N1'-H→O2'←H-O5(←H-N1)-H→O3←H-O4'.

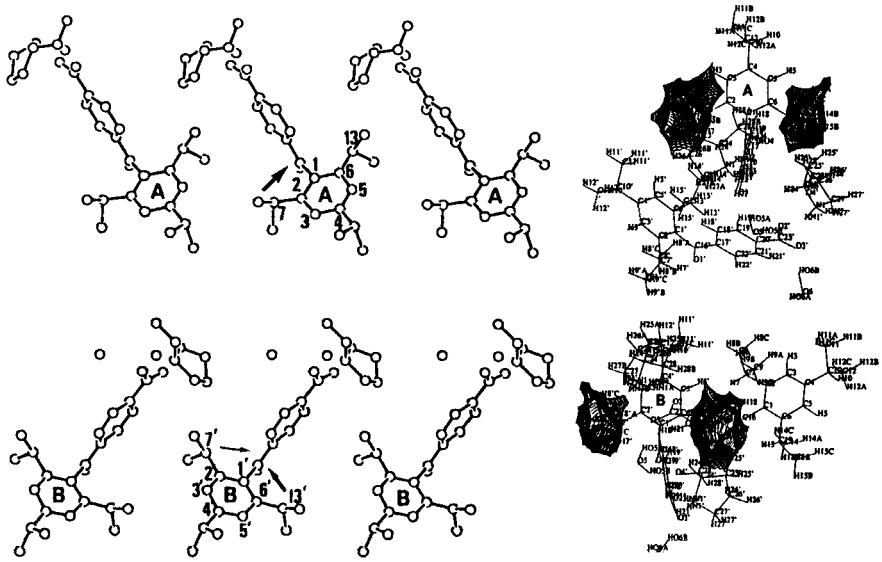
The molecular conformation of **1**-A is quite similar to that of **1**-B with the 4-carboxybenzoyl planes (planar within 0.09Å in 1-A and 0.14Å in 1-B) of **1**-A and **1**-B forming angles of 85.0°and 85.5° with the triisopropyl benzene plane, respectively. The molecular structure of **3**-A showed that the cyclization reaction occurred on one side (C7 isopropyl group) of the molecule to give *R*-**3** by reference to the known absolute configuration of L-prolinol, although the **1**-A molecule has an approximate Cs symmetry. Interestingly, in the case of **3**-B, which is situated in the nearly identical crystallographic environment with that around **3**-A, the reaction occurred on both sides of the molecule with the different proportion to give the mixture of *R*-**3** and *S*-**3**.

The omit difference Fourier map phased with all atoms except C16 was calculated (Figure 3a), showing a one electron density peak corresponding to C16 with no other



(a) plane defined by C1, C2 and C6 (b) plane defined by C1', C7' and C13'

FIGURE 3 (a) Omit difference Fourier map phased with all atoms of **3**-A except C16. (b) Omit difference Fourier map phased with all atoms of **3**-B except C16'A and C16'B.



(a) (b)

FIGURE 4 (a) Stackings of 1-A and 1-B molecules along c-axis. (b) Cavities of o-isopropyl groups on C2, C6, C2' and C6'.

significant peak around C16. Thus, almost 100% asymmetric induction (*R*-**3**) was attained for this case, although the elongation of the peak and abnormal bond lengths and angles around C7 may depict the partial existence of 1-A. The omit difference Fourier map phased with the all atoms except C16'A and C16'B was calculated (Figure 3b) showing the two resolved peaks corresponding to C16'A and C16'B with the ratio of peak height=2(*S*-**3**):1(*R*-**3**). The **3**-B molecule in Figure 2b is the superposition of *S*-**3** and *R*-**3**, which causes the anomalous bond distances and angles around C16'A, C13', C16'B and C7' and one missing methyl group on C7'. The optical yield of e.e. was simply calculated to be (1+1/3-2/3)/2=33%, which closely agrees with 30% as determined by chiral HPLC.

Why is only *R*-**3** formed in **3**-A, and *S*-**3** is dominant in **3**-B? The stacking of **1**-A molecules along the *c*-axis is nearly identical with the mirror image of that of **1**-B molecules (Figure 4a). The environment around the *o*-isopropyl groups on C2 and C6' is quite different from that on C2' and C6. The cavities of the *o*-isopropyl groups on C2, C6, C2' and C6' were calculated to be 20.8Å^3, 17.8Å^3, 17.6Å^3 and 22.9Å^3, respectively, as shown in Figure 4b.[12] This result is consistent with the preferential reaction on the sides of C2 in **1**-A and of C6' in **1**-B. However, the asymmetric induction (33%) of **3** is due to the cyclization reaction on the side of C2' of **1**-B. At the present time, the reason for this asymmetric induction cannot be reasonably explained. The *o*-isopropyl groups on C6 in **1**-A and C2' in **1**-B interact somewhat differently with the pyrrolidine rings of **2**, which are located between the *o*-isopropyl groups and *p*-carboxybenzene rings, suggesting that this might induce the asymmetry of 2, because other interactions are quite similar to these two isopropyl groups.

Acknowledgment

This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas, No. 06242101and 06242218, from the Ministry of Education, Science and Culture.

REFERENCES

1. H. Koshima, A. Maeda, N. Masuda. T. Matsuura, K. Hirotsu, K. Okada, H. Mizutani, Y. Ito, T. Y. Fu, J. R. Scheffer and J. Trotter, Tetrahedron Asymmetry, 5, 1415 (1994).
2. A. D. Gudmundsdottir and J. R. Scheffer, Tetrahedron Lett., 31, 6807 (1990).
3. A. D. Gudmundsdottir and J. R. Scheffer, Photochem. Photobiol., 54, 535 (1991).
4 R. Jones, J. R. Scheffer, J. Trotter and J. Yang, Tetrahedron Lett., 33, 5481 (1992).
5. A. D. Gudmundsdottir, J. R. Scheffer and J. Trotter, Tetrahedron Lett., 35,1397 (19 94).
6. F.Toda, H. Miyamoto, K. Takeda, R. Matsugawa and N. Maruyama, J. Org. Chem., 58, 6208 (1993).
7. F. Toda, H. Miyamoto and S. Kikuchi, J. Chem. Soc., Chem. Commun., 1995, 621.
8. Y. Ito, H. Nishimura, Y.Umehara, Y. Yamada, M. Yone and T. Matsuura, J. Am. Chem. Soc., 105,1590 (1983).
9. Y. Ito and T. Matsuura, Tetrahedron Lett., 29 3087 (1988).
10. A. G. M. Sheldrick, SHELX-86 in Crystallographic Computing 3(Eds G. M. Sheldrick, C. Kruger and R. Goddard) Oxford University Press. pp.175-189 (1985).
11. teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).
12. Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada and Y. Ohgo, J. Am. Chem. Soc., 103, 5805 (1981).