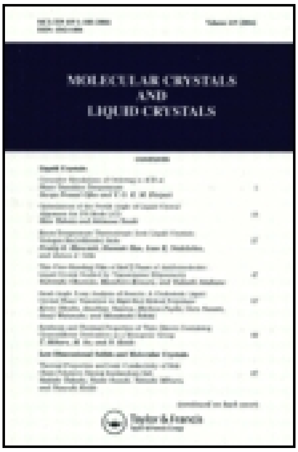

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

# A Generation of Chirality

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Version of record first published: 24 Sep 2006.

To cite this article: Koichi Tanaka, Fumio Toda, Zafra Stein & Israel Goldberg (1994): A Generation of Chirality, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 248:1, 49-52

To link to this article: http://dx.doi.org/10.1080/10587259408027162

*Mol. Cryst. Liq. Cryst.* 1994, Vol. 248, pp. 49–52
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Printed in the United States of America

# A GENERATION OF CHIRALITY

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ABSTRACT Achiral molecule of N-methyl-3,4-bis(diphenylmethylene)succimide (**1**) was found to form a chiral crystal, in which two inner phenyl groups (**a** and **a'** of **1** shown in Scheme 1) are overlapped and therefore chirality appears depending on whether **a** or **a'** is above. The chirality of **1** in the crystal was frozen by photoirradiation in the solid state to give an optically active photocyclization product (**2**).

## INTRODUCTION

On Earth, organic materials were initially produced and then living things were generated later by their complex combination and assembly. Therefore, why and how optical isomers were produced selectively or predominantly on Earth in the absence of any chiral source, is an important question, because many important biologically active compounds are optically active. Many scientists have attempted to prepare optically active compounds without using a chiral source. Most of such efforts failed and some of those which were believed to have succeeded were also clarified recently as being erroneous. Only a few results are acceptable as successful examples, but the efficiency of the generation of chirality is very low. For example, the irradiation of achiral material by a polarized light gave a chiral product, but its optical purity was very low. Furthermore, the generation of polarized light in nature is also doubtful.

An enantioselective reaction on the surface of chiral inorganic crystals such as quartz has been postulated. It is well known that chiral silicon oxide molecules form quartz whcih has a chiral surface. Neverhteless, the same question remains, of how one enantiomer of the chiral quartz can be formed predominantly. Even if this question is solved, the following question remains: is it really possible to produce optically active compounds efficiently by reaction on the surface of a chiral quartz? No such enantioselective reaction has been achieved successfully in the laboratory despite many such attempts. Some people have suggested that the initial chiral source came to Earth from space, but this avoids the same question of how the initial chiral material was generated in space.

In order to search for conditions under which chirality is generated in the absence of a chiral source, we designed a solid state reaction system in which the photoconversion of an achiral material into a chiral one occurs in the presence of a chiral source. We have finally found that some achiral compounds can be arranged in a chiral form by changing their molecular shape, for example by twisting, in the presence of optically active host compound. Photoirradiation of the host-guest inclusion crystal in which achiral molecules are arranged in a chiral form gives optically active photoreaction product.[1] When the chiral molecule can be arranged in its own crystal in a chiral form, chiral crystal of achiral molecule can be prepared. Photoreaction of the chiral crystal gives optically active product without using any chiral source. We have found that some oxoamides form chiral crystal and its photoreaction gives optically active ß-lactam derivative efficiently.[2] We now report that achiral succimide derivative, N-methyl-3,4-bis(diphenylmethylene)succimide (**1**) forms chiral crystal and its photoreaction in the solid state gives optically active photocyclization product (**2**). X-ray structure study of the chiral crystal of **1** was also carried out.

## PREPARATION OF CHIRAL CRYSTAL OF 1 AND ITS PHOTOCONVERSION TO OPTICALLY ACTIVE CYCLIZATION PRODUCT 2

3,4-Bis(diphenylmethylene)succimide (**1**) was prepared by the reaction of 3,4-bis(diphenylmethylene)cyclobutanedione (**3**)[3] with Me-$NH_2$ in $CCl_4$ in the presence of $Br_2$ according to the reported procedure (Scheme 2).[4] This reaction proceeds via the crystalline intermediate (**4**).

Recrystallization of **1** from acetone formed chiral crystal as orange hexagonal plates (**A**, converts to crystal **C** by heating at 260 °C) and two racemic crystals as orange rectangular plates (**B**, mp 302 °C) and yellow rectangular plates (**C**, mp 297 °C). These can easily be separated by picking up. In one piece of **A** crystal, for example, (+)-**1** molecules are pucked and (-)-**1** molecules are pucked in another piece of **A** crystal. These chiral crystals are tentatively named as (+)-**A** and (-)-**A** crystal, respectively. The chirality of **1** in the crystal **A** was proven by photoirradiation of the crystal to give the optically active photocyclization product **2**. For example, irradiation of powdered (+)-**A** crystal (50 mg) by 100W high-pressure Hg-lamp for 50 h gave (+)-**2** of 64% ee (50 mg, 100% yield, mp 285-287 °C, $[\alpha]_D$ +102° (c 0.05, $CHCl_3$)). Similar irradiation of (-)-**A** crystal gave (-)-**2**. The optical purity was determined by HPLC on the chiral solid phase, Chiralpak AS.

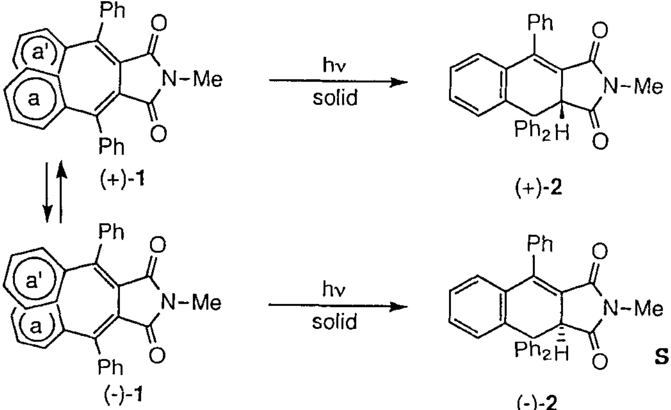
The chirality of 1 in crystal is probably attributed to the steric prohibition of an interconversion between the two phenyl rings **a** and **a'** (Scheme 1). Namely, **1** is a simple chiral helicene, although the chirality appears only in the crystalline state. Nevertheless, the chirality of the helicene can be transfered to the stable **2** by photoreaction. This is an example of the generation of chirality.[5,6]

Photoirradiation of crystals **B** and **C** gave racemic 2. In these racemic crystals, (+)-**1** and (-)-**1** molecules would be pucked in a 1:1 ratio. Interconversion among the three crystals **A**, **B**, and **C** and that between (+)-**A** and (-)-**A** crystals occur easily. By heating at 260 °C, **A** is converted to **C**. Addition of one piece of (+)-**A** crystal as seed crystal during the recrystallization of **C** (100 mg) from acetone (20 ml) gave (+)-**A** (66 mg), **B** (15 mg), and **C** crystal (10 mg).

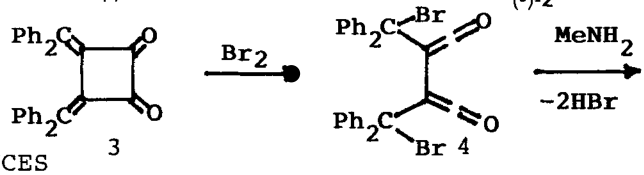
Addition of one piece of (-)-**A** crystal during the recrystallization of (+)-**A** crystal (50 mg) from acetone gave (-)-**A** (23 mg), **B** (4 mg), and **C** crystal (8 mg).

X-ray structure study of the chiral crystal **A** supported that the chirality of **1** is attributed to the steric prohibition of an interconversion between the phenyl rings **a** and **a'** in crystal.

Interestingly, however, when the Me group of **1** is substituted with H and other alkyl group such as Et, nPr, nBu, and $PhCH_2$, no chiral crystal is formed. The formation of chiral crystal of the succimide is very sensitive to the substituent on the nitrogen atom.



**Scheme 1**



**Scheme 2**

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