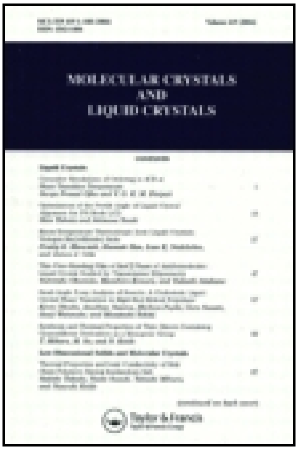

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CD Spectral Study on Chiral Arrangement and Enantioselective Reaction of Thiocoumarin in Inclusion Crystal

Koichi Tanaka [a] & Fumio Toda [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime, 790, Japan

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CD Spectral Study on Chiral Arrangement and Enantioselective Reaction of Thiocoumarin in Inclusion Crystal

Koichi Tanaka and Fumio Toda
Department of Applied Chemistry, Faculty of Engineering, Ehime University,
Matsuyama, Ehime 790, Japan

Inclusion complex formation of thiocoumarin with optically active host compound in the solid state was followed by continuous measurement of CD spectra in Nujol mull. Enantioselective photodimerization reaction of thiocoumarin in the inclusion complex was also followed successfully by using the CD spectroscopy in the solid state.

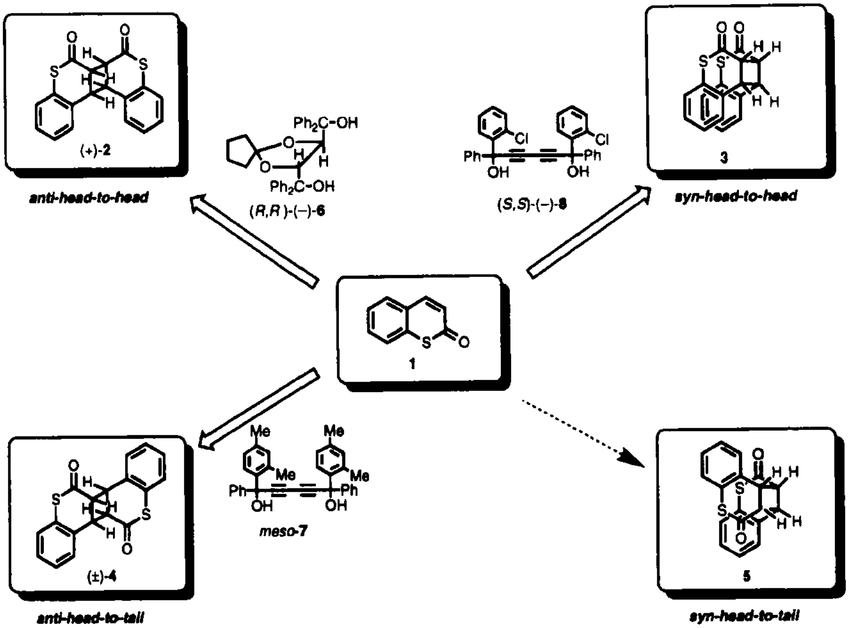
Keywords: CD spectrum; thiocoumarin; inclusion crystal; solid-state reaction

INTRODUCTION

We have found that organic molecules move and react quite easily and efficiently in the solid state and in some cases the solid-state reaction proceeds more selectively than the solution reaction.[1] Detection of molecular movement and chiral arrangement in the solid state has been carried out so far by X-ray analysis.[2] However, this method takes a long time and is limited for single crystal. Recently, we have developed a new convenient method for detecting the molecular movement and chiral arrangement of achiral molecules in the solid state by measurement of CD spectra in Nujol mull. When CD spectrum of a mixture of achiral guest, optically active host compound and liquid paraffin is measured continuously, induced CD absorption appeared and increased as the host-guest complexation proceeds. The CD spectroscopic method was also useful to follow enantioselective photoreaction in the solid state.

Stereoselective Photodimerization of Thiocoumarin in Inclusion Crystal

It has been reported that photoirradiation of thiocoumarin **1** in solution and in the solid state gives *anti-head-to-head* dimer (±)-**2** (mp 239-240 °C)[3] and *syn-head-to-head* dimer **3** (mp 215-217 °C)[4], respectively. Recently, we have found that photodimerization reaction of thiocoumarin can be controlled by using host compounds. For example, when a mixture of thiocoumarin **1** and optically active host compound (*R*, *R*)-(-)-**6**[5] in butyl ether was kept at room temperature for 12 hr, a 1:1 inclusion complex (mp 106-108 °C) was obtained as colorless needles. The 1:1 complex gave *anti-head-to-head* dimer (+)-**2** (mp 254-255 °C) of 100% ee {$[\alpha]_D$+182 °(*c* 0.02, $CHCl_3$)} in 73% yield upon photoirradiation in the solid state. The optical purity of **2** was determined by HPLC on the chiral stational phase Chiralpak AS with using hexane-EtOH (95:5) as an eluent. (-)-**2** of 100% ee was also obtained when the host compound (*S*, *S*)-(+)-**6** was used



instead of (*R*,*R*)-(-)-**6**. Racemic *anti-head-to-tail* dimer **4** (mp 166-168 ℃) was obtained selectively by photoirradiation of 1:2 complex (colorless needles, mp 115-118 ℃) of **1** with the host compound *meso*-**7**[6] in 69% yield. Achiral *syn-head-to-head* dimer **3** was also obtained by photoirradiation of the 1:2 complex (colorless needles, mp 130-131 ℃) of **1** with (*S*,*S*)-(-)-**8**[7] in 74% yield.

CD Spectral Study

We found that CD spectroscopy in Nujol mull is an excellent method not only for detecting the chiral molecular arrangement but also for following the molecular movement in the solid state.

Mixing of powdered thiocoumarin **1** and optically active host compound (*R*,*R*)-(-)-**6** in Nujol mull at room temperature for 1 hr gave their 1:1 complex which was identical with the authentic sample prepared by recrystallization. The inclusion complexation of **1** and (-)-**6** was followed by continuous measurement of CD spectra in Nujol mull. CD spectra of a mixture of (-)-**6** (3 mg), **1** (1 mg) and liquid paraffin (30 mg) were measured every 30 min for 1 hr (Fig. 1 (A)). The CD spectra were measured on a Jasco J-720 spectropolarimeter with using quartz windows. Although a mixture of **1** and (-)-**6** in Nujol mull did not show clear CD absorption initially, induced CD absorptions of (-)-Cotton effect at around 250 and 320 nm appeared and increased as the complexation proceeds. When (+)-**6** was used instead of (-)-**6**, a mirror imaged CD spectra appeared (Fig.1 (B)). This shows that molecules of achiral **1** move and form inclusion complex with (-)-**6** in the solid state and two molecules of **1** are arranged in chiral positions to each other through hydrogen bond between carbonyl oxygen of **1** and OH group of (-)-**6** (Fig. 3).

The enantioselective photodimerization reaction of thiocoumarin **1** in the inclusion complex was also followed by measurement of CD spectra of a photo-exposed mixture of the 1:1 complex (5 mg) and liquid paraffin (30 mg). CD absorptions of (-)-Cotton effect at around 260 and 320 nm of **1** in the inclusion complex disappeared and new CD absorptions of (+)-**2** at around 270 and 330

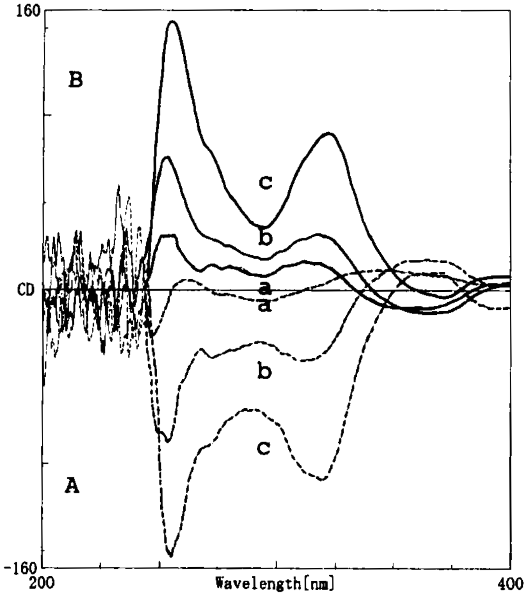


FIGURE 1 CD spectra of a mixture of (-)-**6** (A) or (+)-**6** (B), **1** and liquid paraffin after a) 0, b) 30 and c) 60 min.

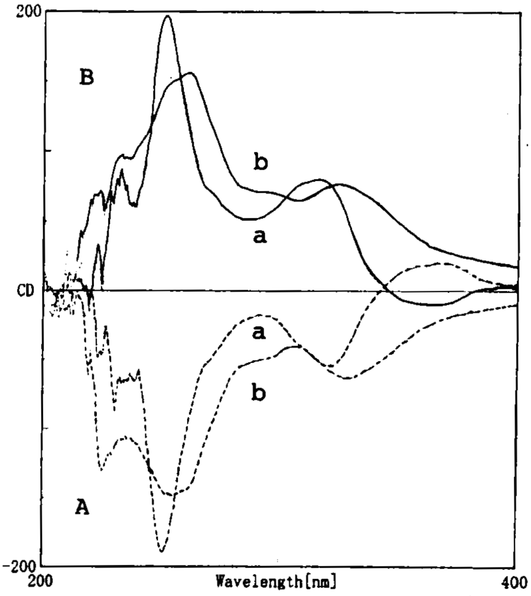


FIGURE 2 CD spectra of 1:1 complex of **1** with (-)-**6** (A) or (+)-**6** (B) a) before and b) after photoirradiation for 5 min.

nm appeared after 5 min irradiation (Fig. 2(A)). Mirror imaged CD spectra were also obtained when (+)-**6** was used instead of (-)-**6** (Fig. 2(B)).

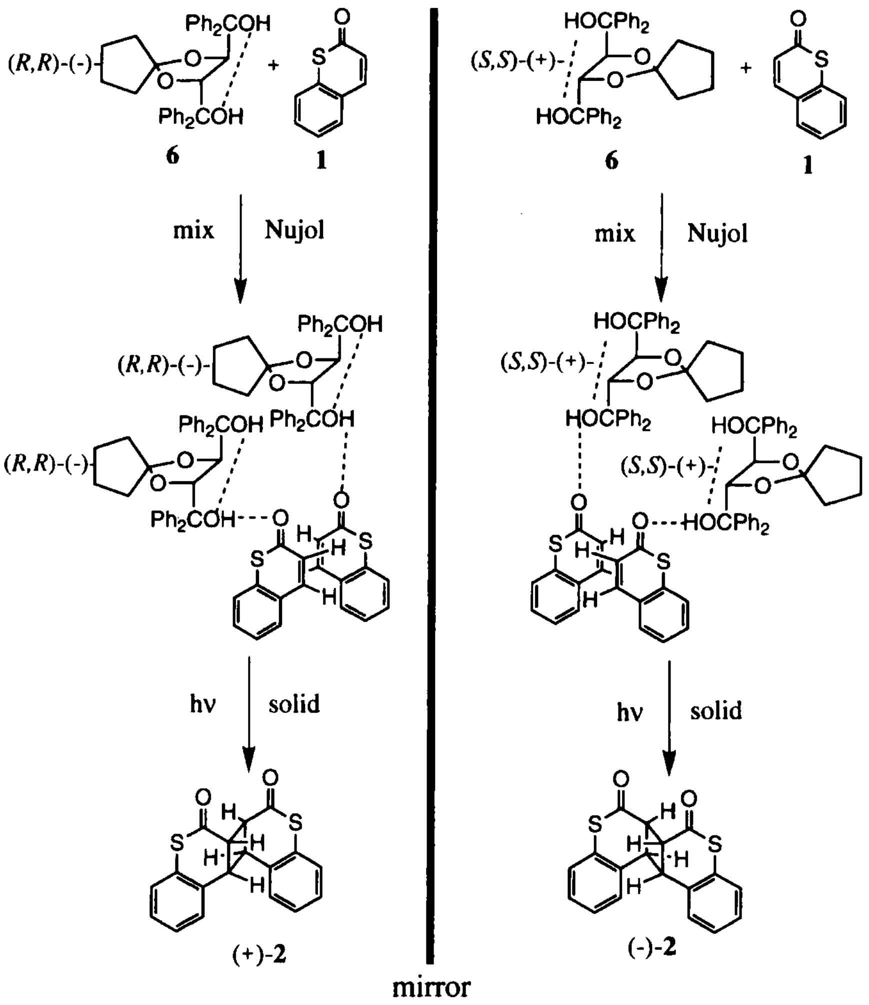


FIGURE 3 Schematic illustration of the chiral arrangement and enantioselective photodimerization of **1** in the solid state.

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