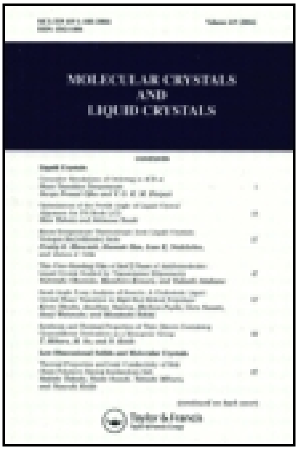

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Multi-Stage Crystalline State Racemization of a Bulky Chiral Group

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To cite this article: Yoshii Sam , Yuji Ohashi , Yoshifusa Arai & Yoshiaki Ohgo (1992): Multi-Stage Crystalline State Racemization of a Bulky Chiral Group, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 219:1, 149-152

To link to this article: http://dx.doi.org/10.1080/10587259208032127

Mol. Cryst. Liq. Cryst. 1992, Vol. 219, pp. 149–152
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Printed in the United States of America

MULTI-STAGE CRYSTALLINE STATE RACEMIZATION OF A BULKY CHIRAL GROUP

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(Received August 19, 1991; in final form December 2, 1991)

Abstract A chiral dimethoxycarbonylethyl group in a cobaloxime complex with pyridine as an axial base ligand revealed crystalline-state racemization by X-ray exposure or visible light, whereas those of complexes with (S)- and (R)-phenylethylamines and propylamine showed no change. Such differences can be explained by the size of the reaction cavity for the dimethoxycarbonylethyl group and the packing mode of the groups in each crystal.

Keywords: Crystalline State Reaction, Racemization, Cobaloxime Complexes, X-ray structure analysis

INTRODUCTION

The chiral dimethoxycarbonylethyl (dmce) group in a cobaloxime complex with diphenylmethylphosphine (dpmp) as an axial base ligand has been found to be racemized by X-ray or visible light without degradation of crystallinity. The racemization process consists of two stages; conformational change and inversion of the chiral group, which was ascertained by stepwise structure analyses. An unstable structure was observed at the intermediate stages[1].

In order to examine the reaction process more precisely, the chiral dmce cobaloxime crystals with four different axial base ligands, pyridine, (S)-, (R)-phenylethylamine and propylamine, have been prepared and the reactivities have been investigated.

RESULTS AND DISCUSSION

The crystallographic data are summarized in Table I.

TABLE 1 Crystal data

	1	**2**	**3**	**4**	**5**
a/Å	16.137(2)	14.942(2)	9.125(1)	9.803(3)	13.690(3)
b/Å	18.529(3)	=a	15.820(2)	15.544(3)	24.894(9)
c/Å	7.801(2)	10.174(3)	9.348(1)	9.267(3)	9.399(2)
α/°	90.0	90.0	90.0	90.0	90.0
β/°	97.25(2)	90.0	102.57(1)	117.24(2)	108.00(2)
γ/°	90.0	120.0	90.0	90.0	90.0
V/Å^3	2313.9(9)	1969.9(7)	1317.0(1)	1255.4(7)	3046.(2)
Z	4	3	2	2	4
Space Group	$P2_1$	$P3_2$	$P2_1$	$P2_1$	$P2_1$

1: py(243K, before irradiation); 2: (S)-pea; 3: (R)-pea; 4: pa; 5: dpmp

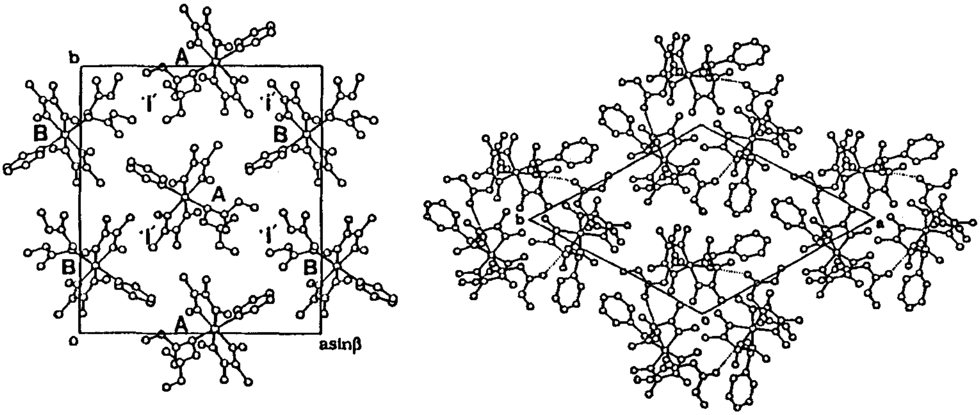
Molecular and crystal structures

The crystal structure of the pyridine complex (py), 1, along the c axis is shown in Fig.1(a). There are two molecules related by pseudo-inversion center (i') in an asymmetric unit. The structure is very similar to the reactive dpmp complex. However the crystalline-state racemization was not observed at room temperature. The crystal was warmed to 358K and exposed to X-ray about two weeks. Considerable decrease in intensities of h0l reflections with h+k=2n+1 was observed. This means that the n-glide plane appeared and the pseudo-inversion center changed to a crystallographic one. Although the structure of the irradiated crystal was disordered, the crystal may be fully racemized and would take an ordered structure after complete irradiation, as observed in the irradiated crystal of dpmp complex.

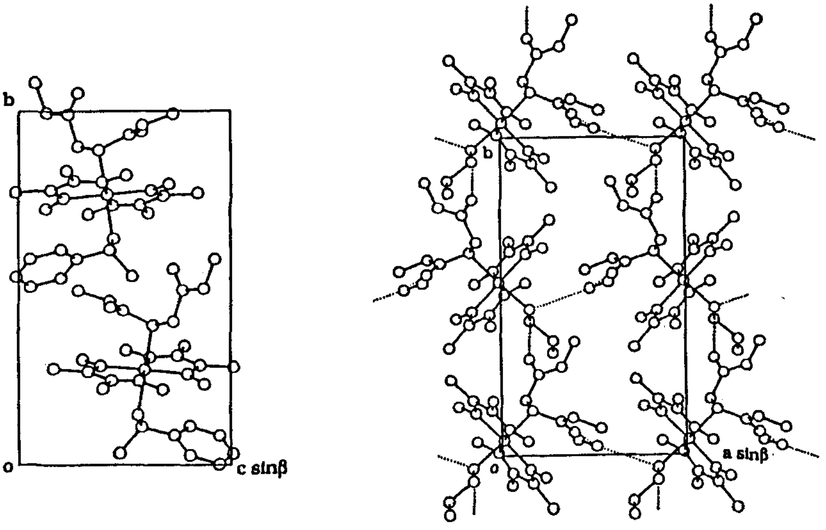
The crystal of (S)-phenylethylamine complex ((S)-pea), 2, belongs to the space group $P3_2$ and has one molecule in an asymmetric unit. The crystal structure viewed along the c axis is shown in Fig.1(b). The carbonyl oxygen atom of the dmce group is hydrogen bonded to the neighboring molecule. The crystal showed no crystalline-state racemization at room temperature.

(R)-phenylethylamine complex ((R)-pea), 3 is a diastereomer of (S)-pea. The space group is $P2_1$. The crystal structure viewed along the a axis is shown in Fig.1(c). No short contact was observed. This crystal was also non-reactive at room temperature.

The structure of propylamine complex (pa), 4 contains a solvent molecule (methanol) in an asymmetric unit. The oxygen atom of methanol is linked to the oxygen and nitrogen atoms of pa molecules and forms a hydrogen bond network.



(a) py, 1 (b) (S)-pea,2



(c) (R)-pea,3 (d) pa,4

FIGURE 1 Crystal structures of four complexes

Reactivity and cavity size

In order to explain why the above crystals were non-reactive at room temperature and why the py crystal was racemized only at high temperatures, the cavity for the dmce group in each crystal was drawn and its volume was calculated in the same way as reported earlier[2]. The volumes of the cavities of four crystals and the dpmp complex are listed in Table II. Since the py and dpmp crystals have two independent molecules, A and B, their cavities were calculated individually. For the dpmp crystal only the B molecules were inverted to the opposite configuration whereas the A molecules remained unaltered. The cavity volumes of the dmce groups of the above four crystals are significantly smaller than that of the B dmce group of the dpmp complex. This can account for the non-reactivity of the above crystals at room temperature. Although the cavity volume of the B dmce group of the py complex at 358K has not yet been calculated, the cavity should have enough space to change the configuration.

In dpmp and py crystals, two dmce groups are found to face each other around a pseudo inversion center. Such a packing mode may be essential for inversion of the bulky dmce group.

TABLE II Cavity volume

Base	volume/Å^3	
pa	34.6	non-reactive, include H-bonds
(R)-pea	37.6	non-reactive
(S)-pea	45.7	non-reactive, include H-bonds
py A	37.6	non-reactive
py B	45.0	non-reactive
dpmp A	42.1	non-reactive
dpmp B	56.8	reactive

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