Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 31 Aug 2006

To cite this article: Tsuyoshi Watabe, Kenji Kobayashi, Kazuaki Kato, Mikiji Miyata & Kazuki Sada (2005): Hierarchical Structure of Brucine Inclusion Crystals with Neutral Guest Molecules: Chiral Tapes and their Bundles, Molecular Crystals and Liquid Crystals, 440:1, 117-124

To link to this article: http://dx.doi.org/10.1080/15421400590958179

Mol. Cryst. Liq. Cryst., Vol. 440, pp. 117–124, 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590958179

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Brucine inclusion crystals with neutral guest molecules exhibit guest-dependent polymorphism due to a hierarchical structure. Chiral brucine molecules are regarded as a primary structure and assemble to form a chiral tape with a 2_1 axis as a common secondary structure. Such tapes meet together in various modes to constitute different bundles as a tertiary structure. The bundle modes are theoretically classified into eight types, which were screened by alteration of guest compounds in the volume range from 39 to 150 Å^3.

Keywords: brucine; bundle; chirality; hierarchical structure; helical tape; inclusion crystals

INTRODUCTION

Crystalline inclusion compounds have been investigated by using symmetric as well as asymmetric host compounds [1]. One of the principal advantages of the latter is that diverse assemblies can be constructed on the basis of their molecular chirality. A remarkable example is

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

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provided by bile acids and their derivatives involving a common asymmetric molecular skeleton [2]. Their crystal structures consist of rigid frameworks with hydrogen bonding networks, and exhibit a hierarchical structure based on diverse bilayered and columnar assemblies.

Brucine salts have been historically investigated as optical resolution reagents [3]. Compared to the steroids, asymmetric brucine molecules do not appear to construct a rigid host framework through hydrogen bonds. Recently, we succeeded in obtaining many crystals of brucine inclusion compounds with neutral guest molecules. It was found from their crystal structures that the host frameworks consist of chiral helical tapes with a 2_1 axis in common in spite of guest-dependent and polymorphic crystals.

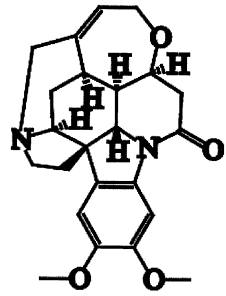
Here we describe a hierarchical structure for brucine inclusion crystals based on these chiral tapes. This hierarchical structure enables us to understand the effect of the asymmetric molecular skeleton on the host frameworks.

EXPERIMENTAL

All chemicals and solvents were commercially available and used without further purification. Brucine was recrystallized from various neutral solvents. The resulting crystals were dried on filter paper and subjected to thermogravimetric and spectroscopic analyses in order to confirm the guest components.

Crystal structures of brucine inclusion compounds were determined in the following way. X-ray single crystal diffraction data were collected on a Rigaku RAXIS RAPID diffractometer. The diffractometers used graphite-monochromatized Cu-Kα and Mo-Kα radiation. Lattice parameters were obtained by reflections for 3 oscillation images for the area detector. Direct methods were employed for the structure solution based on F^2. The structure was refined by the full-matrix least squares procedure with the program TEXSAN [4]. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions. Moreover, crystal structural data of brucine inclusion compounds were obtained from the Cambridge Structural Database (CSD) [5].

PCcavity was calculated from the volumes of the host cavity and the guest molecule [6]. The volumes of the host cavities were derived from the atomic coordinations by using a Free Volume program in the Cerius^2(version 4.0) software package [7]. The following atomic radii were adopted: hydrogen = 1.20 Å, carbon = 1.70 Å, nitrogen = 1.65 Å, oxygen = 1.60 Å, sulfur = 1.85 Å.



Brucine

RESULTS AND DISCUSSION

Hierarchical Structure of Brucine Inclusion Crystals

Recrystallization of brucine from over one hundred and fifty neutral organic compounds, such as alcohols, ketones, esters, aromatic compounds and so on, afforded over thirty kinds of inclusion crystals. So far, twentyfive examples of single crystal data were obtained from these, and four more were obtained from the Cambridge Structural Database (CSD) [8]. We carried out a comparative study of these crystal structural data. Although their molecular assemblies seem to have various patterns of host frameworks in appearance, it was found that the crystals have a hierarchical structure, as schematically shown in

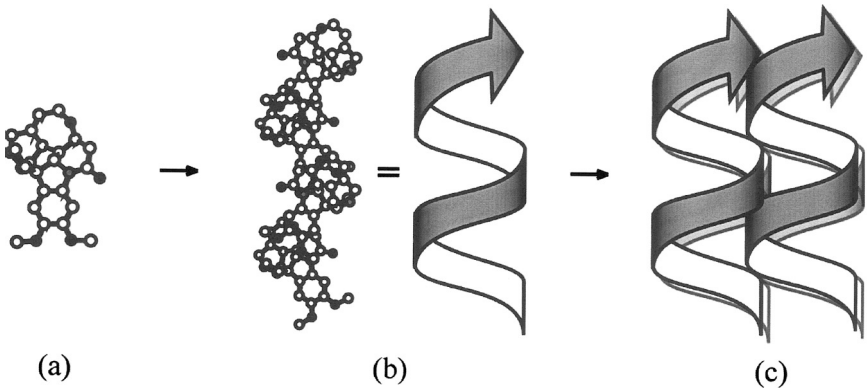


FIGURE 1 Hierarchical structure of brucine crystals. (a) primary structure: molecular structure, (b) secondary structure: chiral helical tape, (c) tertiary structure: bundle structure of the chiral helical tapes.

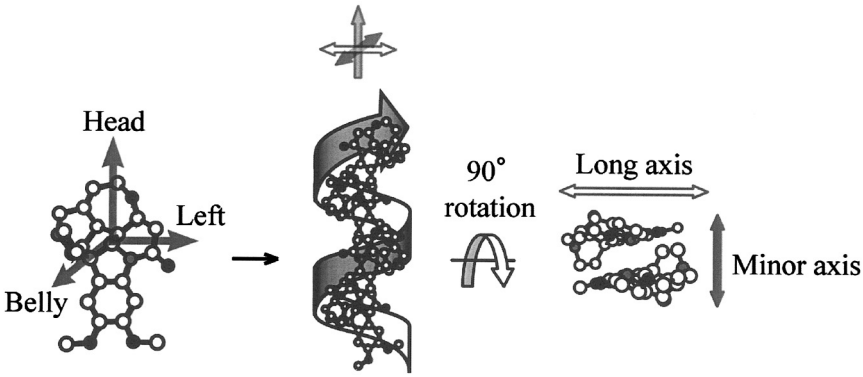


FIGURE 2 Defined directions of the brucine molecule and the chiral helical tape.

Figure 1. This structure is considered to have primary, secondary and tertiary structures, as in the case of proteins. Thus, a conformationally fixed molecule of brucine (Fig. 1(a)) serves as a primary structure. The molecules make a chiral and helical tape (Fig. 1(b)) and a bundle of the tapes (Fig. 1(c)) in all the crystal structures.

The common unit in Figure 1(b) is termed as "a helical tape", because the tape consists of a helical molecular assembly with a crystallographic 2_1 axis. The tape is displayed with an arrow to distinguish directions, as shown in Figure 2. Thus, a brucine molecule has an asymmetric structure with three distinguishable axes; *head* and *foot*, *belly* and *back*, as well as *right* and *left*. Therefore, the arrow indicates the *foot*-to-*head* direction, which is consistent with the crystallographic 2_1 axis. In addition, the tape has distinguishable long and minor axes, as can be seen from a rotation of the tape through 90 degrees.

The way to make the bundle from the tapes is theoretically interpreted as follows. Figure 3(a) shows four possible combinations, Modes 1–4, of four tapes with respect to the direction. In Mode 1, the directions of helical tapes are parallel in both long and minor axes. The directions are antiparallel in the long axis and parallel in the minor axis for Mode 2, while the directions of helical tapes are parallel in the long axis and antiparallel in the minor axis for Mode 3. In Mode 4, the directions of helical tapes are antiparallel in both long and minor axes. On the other hand, Figure 3(b) shows phase lags between the tapes with a 2_1 axis. The modes *in* and *out of* phase are termed as **A** and **B**, respectively. The combinations of the direction modes (Modes 1–4) and phase modes (*in* and *out of* phase) generate 8 kinds of bundle

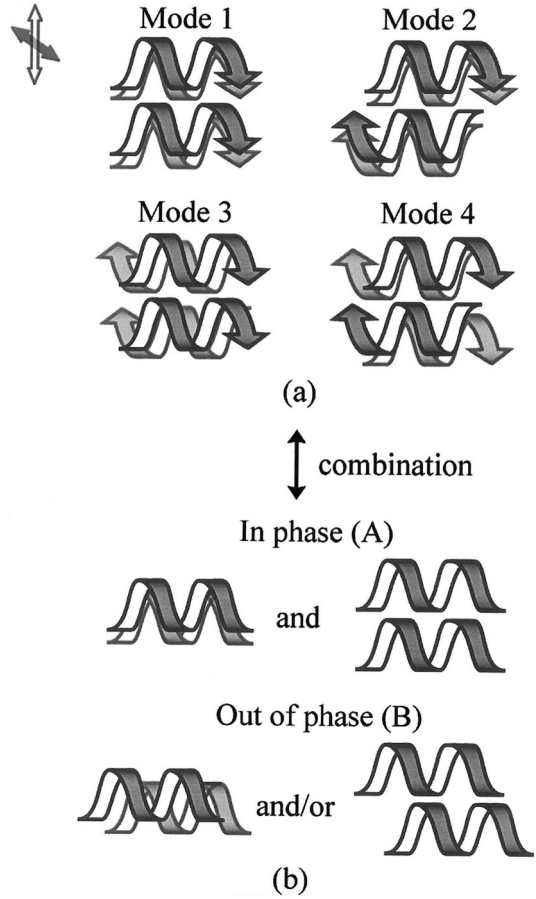


FIGURE 3 Theoretical classification of the bundle structures. (a) four kinds of direction modes based on combinations of the four chiral tapes, (b) phase modes based on lags between the chiral helical tapes.

modes of the tape assemblies; **Mode 1A**, **Mode 1B**, **Mode 2A**, **Mode 2B**, **Mode 3A**, **Mode 3B**, **Mode 4A** and **Mode 4B**. In fact, four assembly modes were observed, as shown in Figure 4. Each assembly mode has an individual shape of inclusion space, which fits the corresponding guest components.

Relation between the Assembly Modes and Guest Volumes

As described above, brucine exhibits guest-dependent polymorphism. We previously demonstrated that packing coefficients of the host

TABLE 1 Relation between Guest Molecules and Bundle Modes of Brucine

Guest molecule	Bundle mode	*PCcavity*	Guest volume
Guest free	Mode 1A		
Methanol	Mode 2B	64.7	38.9
Ethanol/Water*	Mode 2B	72.5	55.6/17.5
1-Propanol	Mode 3A	57.9	73.4
2-Methyl-1-propanol	Mode 3A	60.9	90.3
2-Methyl-2-propanol	Mode 3A	59.6	89.5
2-Methyl-2-butanol	Mode 3A	73.1	106.8
3-Methyl-1-butanol	Mode 3A	78.1	107.7
3-Methyl-2-butanol	Mode 3A	72.6	107.2
3,3-Dimethyl-2-butanol	Mode 3A	73.9	125.1
2,4-Dimethyl-3-pentanol	Mode 3A	69.7	134.9
Tetrahydrofurfuryl alcohol	Mode 3A	64.9	98.1
2-Methylcyclohexanol	Mode 3A	61.7	124.5
Tetrahydropyran-2-methanol	Mode 3A	76.5	117.5
Cyclooctanol	Mode 3A	69.9	133.7
Benzene	Mode 3A	64.3	83.4
Fluorobenzene	Mode 3A	67.3	88.4
Aniline	Mode 3A	73.9	95.8
Anisole	Mode 3A	73.0	110.4
1,2-Methylenedioxybenzene	Mode 3A	68.9	102.8
Pyridine	Mode 3A	61.3	80.0
1-Methylnaphthalene/Water	Mode 1B	76.9	142.4/17.5
1-Methoxynaphthalene/Water	Mode 1B	70.5	148.5/17.5
6-Hexanolactone	Mode 3A	62.2	91.7
2-Methylcyclohexanone	Mode 3A	69.1	117.5
DMSO/Water	Mode 2B	63.0	69.4/17.5

*Crystal structural data from CSD.

cavity (*PCcavity*), the ratio of the volume of the guest compounds to the host cavities, is a useful parameter for screening polymorphic crystals of cholic acid and its derivatives [9]. In this connection, we calculated the *PCcavity* of brucine inclusion crystals in the same way.

Table 1 illustrates that the bundle modes of helical tapes depend on the guest components. Figure 5 shows a correlation between the guest volumes and *PCcavity*, and a correlation between the bundle modes and the guest volumes. It can be seen from this figure that the modes depend on the volumes of neutral guest molecules, providing a mechanism for formation of the guest-dependent polymorphic crystals of brucine. In this manner, the host frameworks of brucine may be predictable with respect to the volumes of guest compounds.

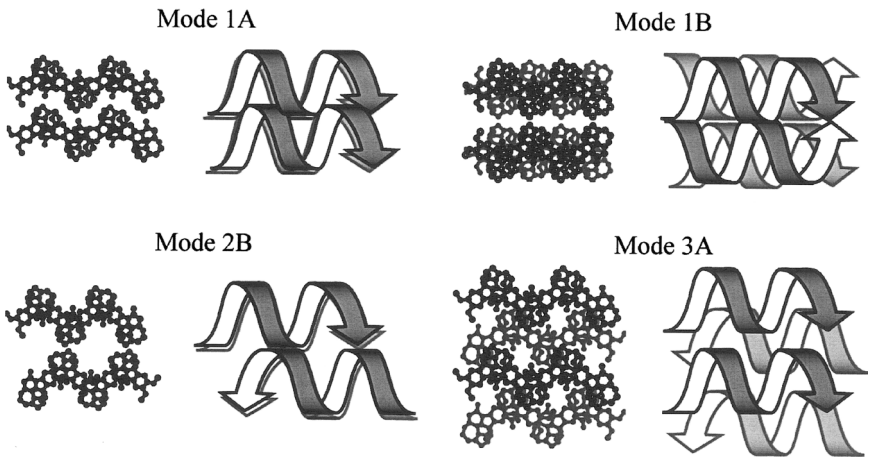


FIGURE 4 Bundle structures of brucine inclusion crystals on the basis of combinations of direction and phase modes.

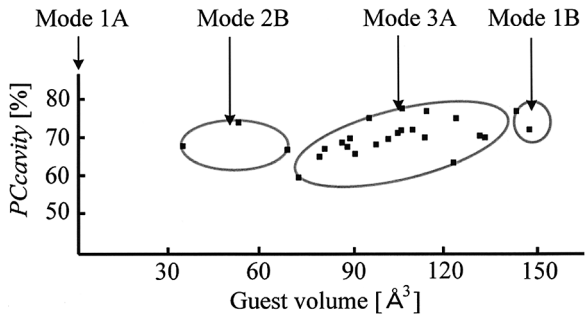


FIGURE 5 Correlation between *PCcavity* and bundle structures in brucine inclusion crystals.

CONCLUSION

We demonstrated that the chiral and helical tape serves as a common structural unit in brucine inclusion crystals with neutral guest compounds. The tapes combine together to afford various bundles, whose modes were theoretically classified into eight types. The alterations of the guest molecules enabled us to observe the four bundle modes among them. The concept of such a hierarchical structure may be applied to comprehensive inclusion crystals.

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