Four Kinds of 2_1 Helical Assemblies with the Molecular Tilt as Well as Three-directional and Facial Chirality

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Four kinds of 2_1 helical assemblies with a right- or left-handed screw with belly- or back-inside were confirmed in cocrystals of brucine. Discrimination of the different helicities owes to the molecular tilt as well as three-directional and facial chirality of the brucine molecule.

Supramolecular chirality attracts much attention from modern research scientists because of its vital importance for treating molecular assemblies and self-organized systems.[1] The chirality of 2_1 helical assemblies in crystals still remains a challenging problem for well-understanding more than 52,000 organic crystal structures which belong to space groups with 2_1 axes.[2] This is because it has been conventionally considered that handedness of the 2_1 helical assemblies cannot be determined from a mathematical viewpoint. Namely, the 2_1 screw axis operation includes 180° rotation and translation, leading to the idea that it is impossible to distinguish right- or left-handed rotation.[3]

However, we have proposed how to define handedness of the 2_1 helical assemblies on the basis of the molecular tilt in the case of cinchona alkaloids,[4] brucine (**1**) (Chart 1),[5] and benzene,[6] as symbolized in Figure 1. In addition, we have indicated how to describe molecular and supramolecular chirality by using orthogonal three axes; head–tail(leg), belly–back, right–left, alike vertebrate animals.[5,7] Combination of the two methods may enable us to characterize reasonably a variety of 2_1 helical assemblies of asymmetric molecules. Here, we report determination of four kinds of the helicities of the assemblies on the basis of the molecular tilt as well as three-directional and facial chirality by taking **1** for instance.

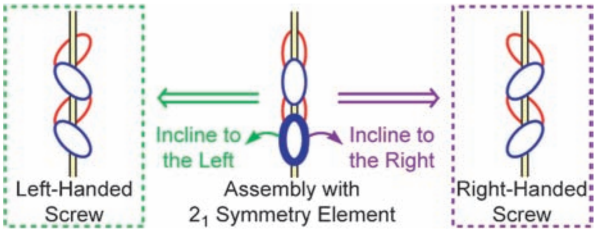

Figure 1. Definition of left- or right-handedness of 2_1 helical assemblies on the basis of the tilt of objects against a 2_1 helical axis. Yellow bars denotes the 2_1 helical axis.

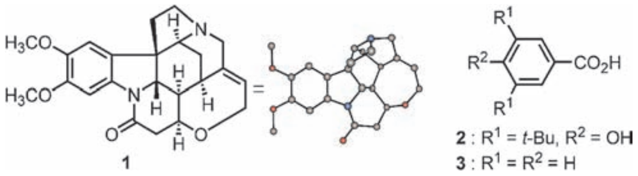

Chart 1.

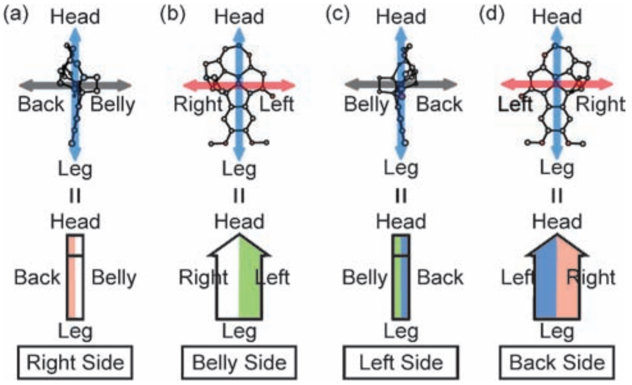

Figure 2. Views of a molecule with three-directional and facial chirality by using orthorhombic three axes: head–leg, belly–back, and right–left axes. (a) Right-side, (b) belly-side, (c) left-side, and (d) back-side views.

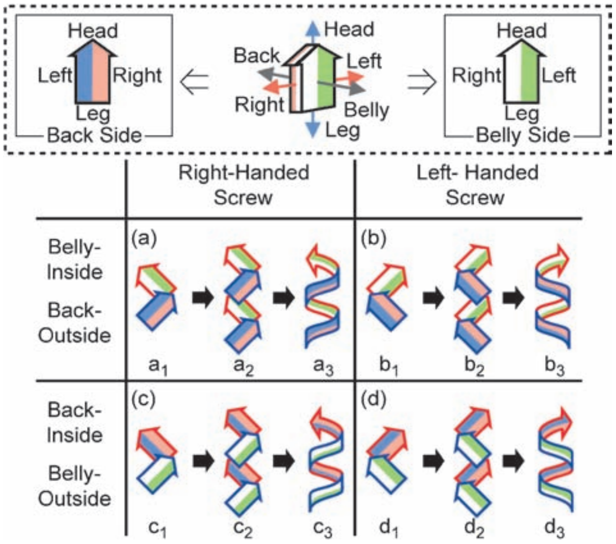

Figure 3. Schematic representation of four kinds of the helicities of the assemblies with 2_1 symmetry elements and the molecular tilt. (a) A right-handed screw with belly-inside. (b) A left-handed screw with belly-inside. (c) A right-handed screw with back-inside. (d) A left-handed screw with back-inside.

Figure 2 shows stereoviews of an asymmetric and facial molecule such as **1**, where the orthorhombic three axes, such as head–leg, belly–back, and right–left axes, are defined. Faces of the molecule as well as direction of the axes are discriminated in arrows and color. As shown in Figure 3, such molecules are stacked with identical belly- or back-insides (or outsides), accompanied by the tilt, to give four kinds of bimolecular aggregates (a_1)–(d_1). The aggregates are then extended with 2_1 sym-

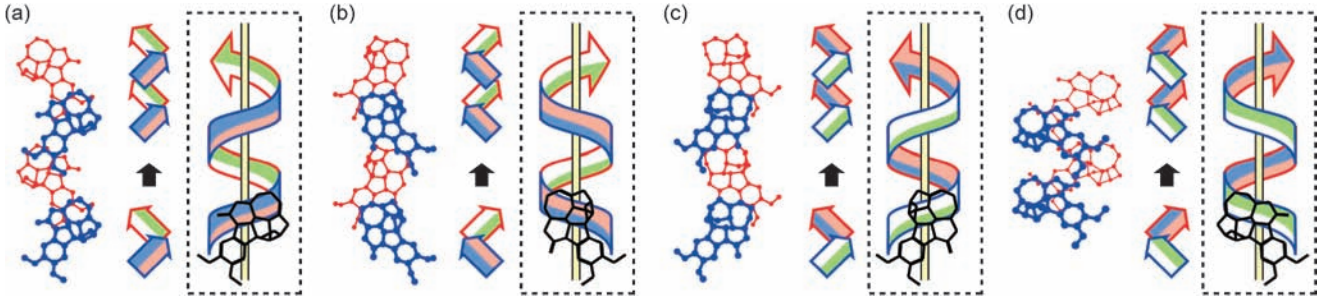

Figure 4. Views of the 2_1 helical assemblies of **1** and schematic representation of the helicities: (a) A right-handed screw with belly-inside in many cocrystals of **1**,[8] (b) A left-handed screw with belly-inside in the crystal of **1**·**2** acetone solvate,[9a] (a) A right-handed screw with back-inside in the crystal of **1**·**2** acetone solvate,[9a] (d) a left-handed screw with back-inside in the crystal of **1**·**3** hydrate.[9b] Hydrogen atoms have been omitted for clarity. Yellow bars denote 2_1 helical axes.

metry operation to yield four kinds of the 2_1 helical assemblies (a_2)–(d_2), which are briefly displayed as successive helical tapes (a_3)–(d_3). The helical arrows indicate the leg-to-head direction. In this method, we define the helical handedness of the assemblies on the basis of the molecular tilt of the head–leg axis against the crystallographic 2_1 axis. As the result, there exist at least four kinds of helical assemblies with a 2_1 axis in geometry; a right- or left-handed screw with belly- or back-inside, as schematically shown in Figure 3.

Actually, cocrystallization of **1** with various organic guests gave the four kinds of the molecular assemblies with 2_1 symmetry elements in the crystal structures. In Figure 4, the 2_1 helical assemblies, which are isolated by included guest molecules from neighbor assemblies, are shown. Figure 4a shows a typical 2_1 helical assembly in many cocrystals of **1**.[5,8] The assembly has a right-handed screw with belly-inside (back-outside), because the head–leg axis of the molecule inclines to the right against the 2_1 crystallographic axis with the belly-inside. In the similar way, the assemblies with 2_1 symmetry elements in Figures 4b, 4c, and 4d consist of a left-handed screw with belly-inside, a right-handed screw with back-inside, and a left-handed screw with back-inside, respectively.

The 2_1 helical assemblies in Figures 4b and 4c coexist in the identical crystal of brucinium 3,5-di-*tert*-butyl-4-hydroxybenzoate (**1**·**2**) acetone solvate.[9a] To our knowledge, the existence of different supramolecular isomers in the same crystal is rare.[10] On the other hand, the 2_1 helical assembly in Figure 4d lies in the crystal of brucinium benzoate (**1**·**3**) hydrate.[9b] In this way, the guest-induced supramolecular isomerism of the assemblies with 2_1 symmetry elements can be geometrically well understood by the bimolecular aggregation modes through the three-directional chirality.

In summary, we have demonstrated that the usage of the orthorhombic three axes enables us to determine four kinds of the helicities of the assemblies with 2_1 symmetry elements on the basis of the molecular tilt. Further application of this method into a wide range of 2_1 helical assemblies is now proceeding in our laboratory.

T. Watabe expresses his special thanks for the Center of Excellence (21COE) Program "Creation of Integrated Eco-Chemistry of Osaka University." This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Molecular Nano Dynamics" (No. 17034039) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Published on the web (Advance View) December 29, 2006; doi:10.1246/cl.2007.234