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Hydrogen Bonding Networks in Bilayered Crystals Composed of Facially Amphiphilic Compounds

Mikiji Miyata [a] , Kazuki Sada [a] , Yoshitaka Yasuda [a] & Kunio Miki [b]

[a] Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu, 501-11, Japan

[b] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, 227, Japan

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HYDROGEN BONDING NETWORKS IN BILAYERED CRYSTALS COMPOSED OF FACIALLY AMPHIPHILIC COMPOUNDS

MIKIJI MIYATA, KAZUKI SADA, YOSHITAKA YASUDA
Department of Chemistry, Faculty of Engineering, Gifu University,
Yanagido 1-1, Gifu 501-11, Japan
KUNIO MIKI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Nagatsuta, Midori-ku, Yokohama 227, Japan

Abstract Highly asymmetric and facially amphiphilic compounds, cholic acid and its derivatives, form asymmetric bilayers with variable hydrogen bonding networks. The bilayers are stacked in various modes to produce dynamical inclusion crystals suitable for molecular recognition and reaction.

INTRODUCTION

Cholic acid and its derivatives (Figure 1) have fascinating structures due to the sharing of some conflicting parts, such as rigid and flexible, large and small, polar and nonpolar parts, and due to four discrete hydrogen bonding groups. In addition, they are highly asymmetric and facially amphiphilic. Studies on their molecular assemblies in the solid state could tell us various important things about a correlation between the molecular structures and assemblies.

In 1986 we found that cholic acid forms channel-type inclusion crystals with a variety of organic substances, which broke down the belief that such inclusion phenomena of bile acids are properties exclusively of deoxycholic acid and apocholic acid.[1] The discovery led us to syntheses of the inclusion compounds of cholic acid and its derivatives as well as X-ray crystallographic studies of the resulting crystals. Now we find that most of the crystals have cumulated bilayers based on the asymmetric and amphiphilic structures.

The important thing is that the bilayers are constructed by hydrogen bonds among the host compounds. Here we focus on the hydrogen bonding networks, which bring about characteristic molecular arrangements and bilayers.

THREE DIRECTIONS ON FACIALLY ASYMMETRIC MOLECULES

Cholic acid and its derivatives have three hydrogen bonding groups on one side of the rigid skeletons, which causes facially amphiphilicity. This enables us to

distinguish three directions of the molecules like animals (Figure 1).[8] Thus, hydrophilic and hydrophobic(lipophilic) sides serve as the belly and the back parts, respectively. The large skeletons and the small side chains constitute the head and the tail parts, respectively. The remaining direction is defined by the hydroxyl groups on the belly side. The right- and left-hands are the hydroxyl groups at the 12 and 7 positions, respectively.

HYDROGEN BONDING NETWORKS AND MOLECULAR ARRANGEMENTS

Figure 1 shows hydrogen bonding networks which yield various molecular arrangements. In each case, a set of four different molecules afford their different functional groups to form variable hydrogen bonding networks. For example, in the case of cholic acid (Figure 1(1)), the hydroxyl groups at the 7, 3 and 12 positions of the left, head and right parts of molecules I, II and III, respectively, and the carboxyl group of the tail part of molecule IV, construct a cyclic hydrogen bonding network.[1] This network yields a molecular arrangement in a head-to-head and tail-to-tail fashion, as compared with that of deoxycholic acid in a head-to-tail one.[9]

In the case of cholanamide (Figure 1(2)), the hydrogen bonding network among the host molecules is the same as in the case of cholic acid mentioned above, but an additional hydrogen of the amide group is used to catch a guest molecule. Especially, various kinds of alcohols are trapped into the channels.[2]

In contrast, an ester group of methyl cholate introduced a guest-dependent change in the network.[3] For example, nitrile guests cut the cyclic nework (Figure 1(3)), while alcoholic guests induced another helical network (Figure 1(4)). The hydroxyl group at the 3 position of the molecule II bridges between the intermolecular hydroxyl groups at the 7 and 12 positions in the former case, whereas the one bridges between the intramolecular groups in the latter case.

We see a completely different network in the case of 5β-petromyzonol (Figure 1(5)).[4] The molecules overlie each other on the hydrophilic sides, while the molecules closely fit together on the hydrophobic sides. Accordingly, the arrangement does not seem to yield a space for including any guest components.

We are now concentrated on determining a large amount of crystal structures of the compounds involving another skeletons, side groups and guest components.

CHANGE OF INCLUSION SPACES AND MOLECULAR RECOGNITION

Molecular graphics can describe the channels in size, shape and chirality.[6] Usually

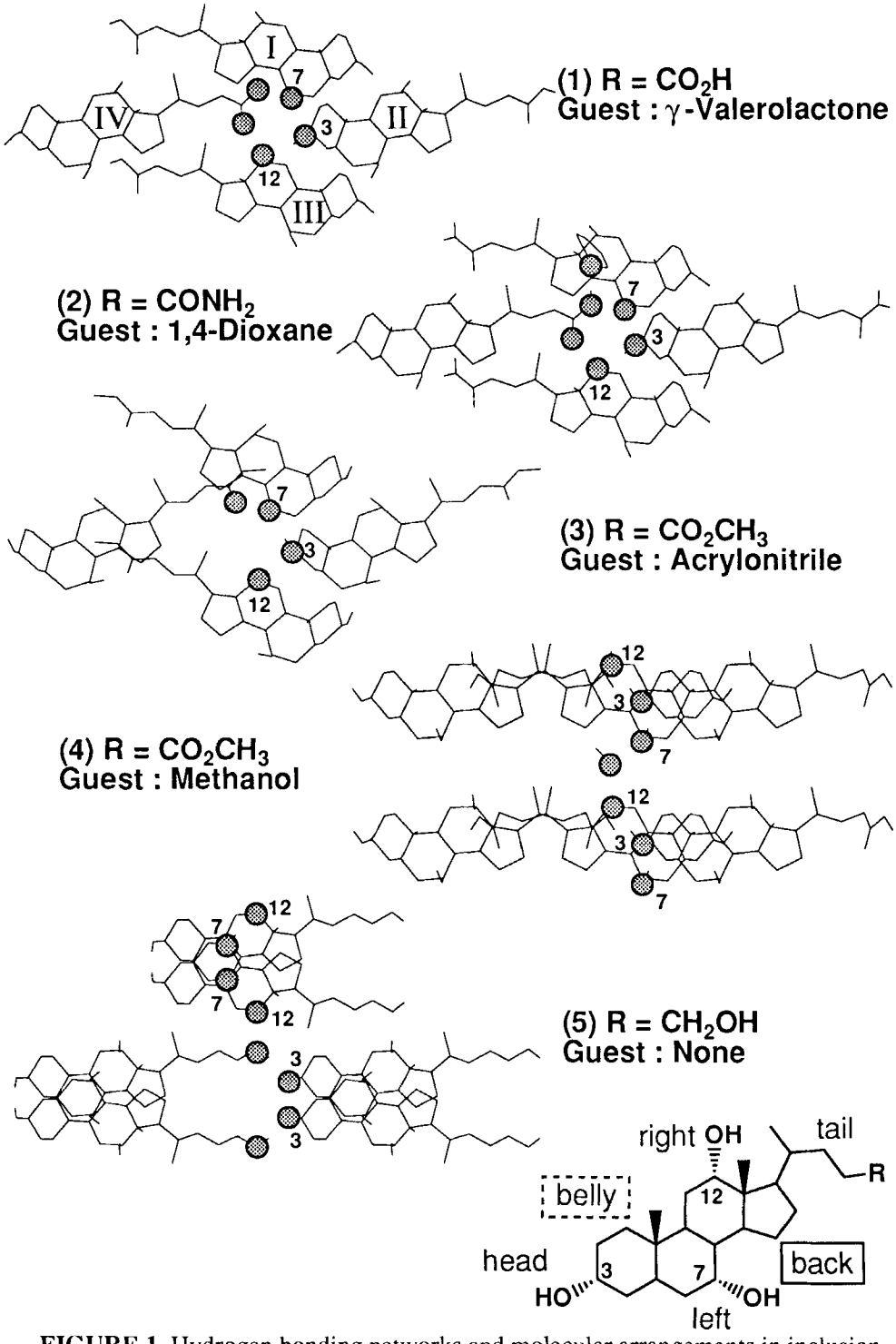

FIGURE 1. Hydrogen bonding networks and molecular arrangements in inclusion crystals composed of cholic acid and its derivatives.

slidings of the bilayers bring about channel-like spaces for including guest components. In the case of the cyclic networks, two kinds of side pockets lie on the channel walls. The one locates between the tail parts, and the other locates between the shoulder parts of the skeletons. Therefore, some changes of the conformations and positions of the tails can lead to any small or large changes of the inclusin spaces in shape and size.

CONCLUDING REMARKS

Cholic acid and its derivatives are the molecules having highly valuable information among isomers which amount to more than one billion. The assemblies constructed by variable hydrogen bondings have guest-dependent dynamical structures[5] suitable for molecular recognition[6] and polymerization reaction.[7] This flow of the information reminds us of biopolymers such as proteins, where hydrgen bondings play important roles. We consider that even molecules having intermediate molecular weights can possess significant information and express it.[8]

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