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

Hydrogen Bond 'Triple Hooks' in an Inclusion Crystal of Cholanamide with Aniline. Structural Difference of Inclusion Crystals of Cholic Acid and Cholanamide with Same Guest

Kazuki Sada [a] , Yoshiaki Matsuura [a] & Mikiji Miyata [a b]

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

[b] Material and Life Science, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka, 565, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Kazuki Sada , Yoshiaki Matsuura & Mikiji Miyata (1996): Hydrogen Bond 'Triple Hooks' in an Inclusion Crystal of Cholanamide with Aniline. Structural Difference of Inclusion Crystals of Cholic Acid and Cholanamide with Same Guest, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 276:1-2, 121-127

To link to this article: http://dx.doi.org/10.1080/10587259608039368

Mol. Cryst. Liq. Cryst., 1996, Vol. 276, pp. 121–127
Reprints available directly from the publisher
Photocopying permitted by license only

HYDROGEN BOND 'TRIPLE HOOKS' IN AN INCLUSION CRYSTAL OF CHOLANAMIDE WITH ANILINE. STRUCTURAL DIFFERENCE OF INCLUSION CRYSTALS OF CHOLIC ACID AND CHOLANAMIDE WITH SAME GUEST.

KAZUKI SADA, YOSHIAKI MATSUURA, AND MIKIJI MIYATA†*
Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11, Japan.

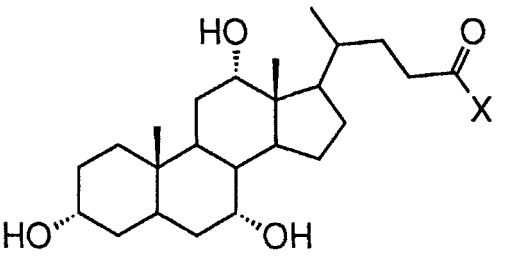
Abstract Crystal structure of an inclusion crystal of cholanamide with aniline is described. Comparison of the crystal structure with that of the cholic acid clathrate reveals both hosts have quite similar assembly mode. However, the most striking difference is hydrogen bonding. Aniline is included in host lattice of cholanamide by triple hydrogen bonds, whereas in that of cholic acid by double weak hydrogen bonds. Difference of the molecular structure between them gives raise to change the host-guest hydrogen bonding.

INTRODUCTION

Until we found channel-type inclusion compounds of cholic acid(**1**) in 1987,[1a,b] less attention had been paid in inclusion compounds of steriods other than deoxycholic acid.[2] Extensive structural studies of the inclusion compounds of **1** reveal that they have multibilayer structure with apolar channel similar to deoxylcholic acid clathrates. Less polar guest molecules such as hydrocarbons, esters, nitriles, ethers and so on are accommodated in the channel.[1] More recently, we reported cholanamide (**2**) as a new host compound that includes with a wide range of alcohols and cyclic ethers.[3a] Crystal structures of the clathrates of **2** indicates that they have similar channel structure to those of **1**. However, they have a hydrogen bond amide 'hook' on the wall of the channel to bind hydrogen bond acceptors.[3]

Comparison of inclusion behavior and crystal structures between **1** and **2** provide us

an insight for molecular design of host cavities as well as understanding of host-guest interactions. However, comparison of crystal structures of **1** and **2** with same guest molecule has been never accomplished, because their guest preference is much different. Recently, 1:1 clathrate of **1** with aniline was reported.[1g,h] This prompts us to investigate crystal structure of **2** with aniline. Here, we present crystal structure of a 1:1 complex of **2** with aniline to compare the host-guest interactions. This paper deals with difference of hydrogen bond network. Moreover, we introduce hydrogen bond 'triple hooks' in the inclusion crystals of **2**.



X=OH: Cholic Acid(**1**)
X=NH_2: Cholanamide(**2**)

CRYSTAL STRUCTURE OF 2 WITH ANILINE

Recrystallization of **2** from aniline yields fine inclusion crystals. TGA and solution NMR indicate a 1:1 host:guest stoichiometry. Figure 1a shows a crystal structure of the aniline clathrate of **2**. It has multibilayer structure with molecular channel. The multibilayer structure is caused by hydrogen bonds between hydrophilic faces and van der Waals force between lipophilic ones of host molecules. This structure is quite similar to those of clathrates with 2-propanol and 1,4-dioxane. It belongs to one of the typical assembly modes of bile acids and their derivatives.[1-3]

'Triple Hooks' in the Channel

Anchor molecular shape of the host produces one-dimensional host cavity, channel, running along two-fold screw axis. In the channel, guest molecules are included. Host lattice of **2** has a hydrogen bond donor on the wall of the channel. Hydrogen bond networks and distances of the clathrates of **2** are shown in Figure 2. One amide proton of the host is free and acts as a hydrogen bond donor, because it is not used in a cycle of host-host hydrogen bonding. Accordingly, the guest molecule is caught up by the hydrogen bond 'hook'. Hydrogen bond single donors such as 1,4-dioxane are entrapped by the amide 'single

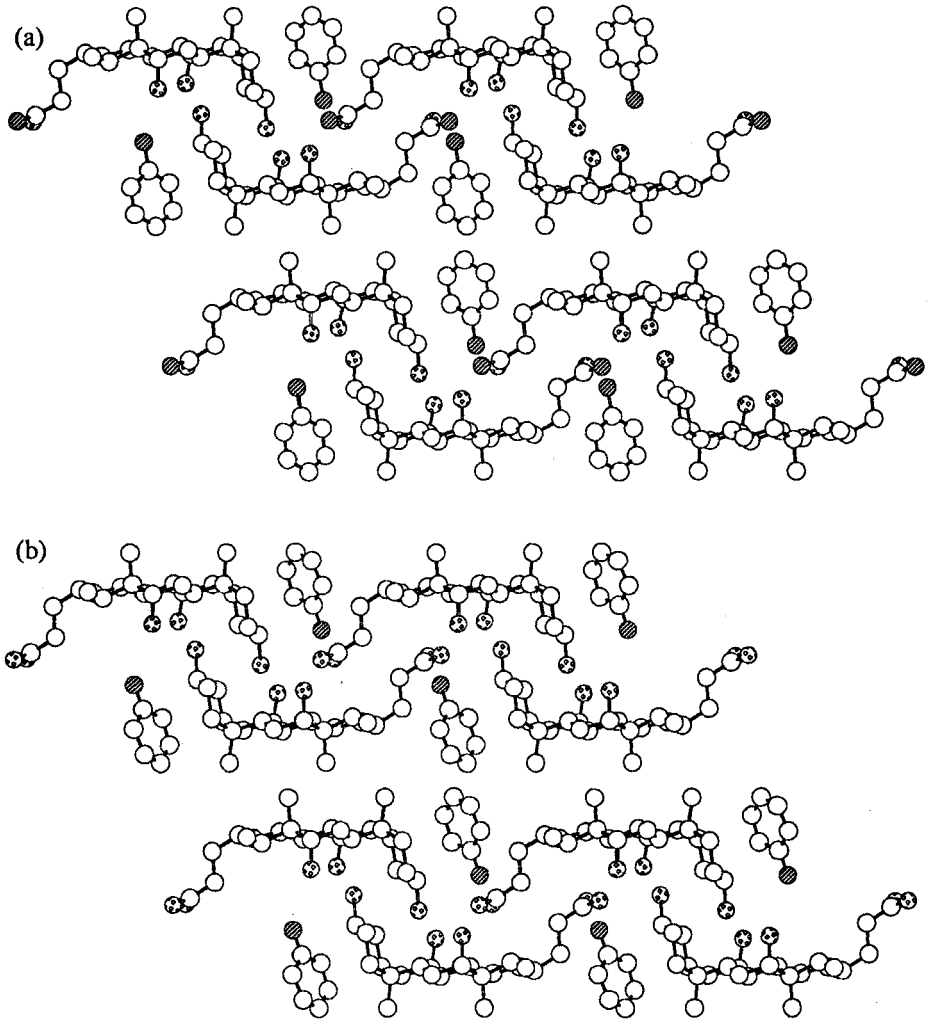


FIGURE 1 (a) Crystal structures of (a) 1:1 complex of **2** with aniline; (b) 1:1 complex of **1** with aniline.

hook'.(Figure 2c)[3a]

On the other hand, there are many hydrogen bond acceptors around the hydrogen bond amide 'hook' on the surface of the channel. All four oxygen atoms of host **2** can act as hydrogen bond acceptors. However, they may be relative weak because they already take part in the cyclic host-host hydrogen bond network. Indeed, in the clathrate of 2-propanol that has one hydroxy group as a hydrogen bond donor, the alcoholic oxygen is caught by the amide 'hook'. Simultaneously, an additional hydrogen bond from the hydroxy group of the guest molecule to the oxygen atom (O12) of adjacent host molecule

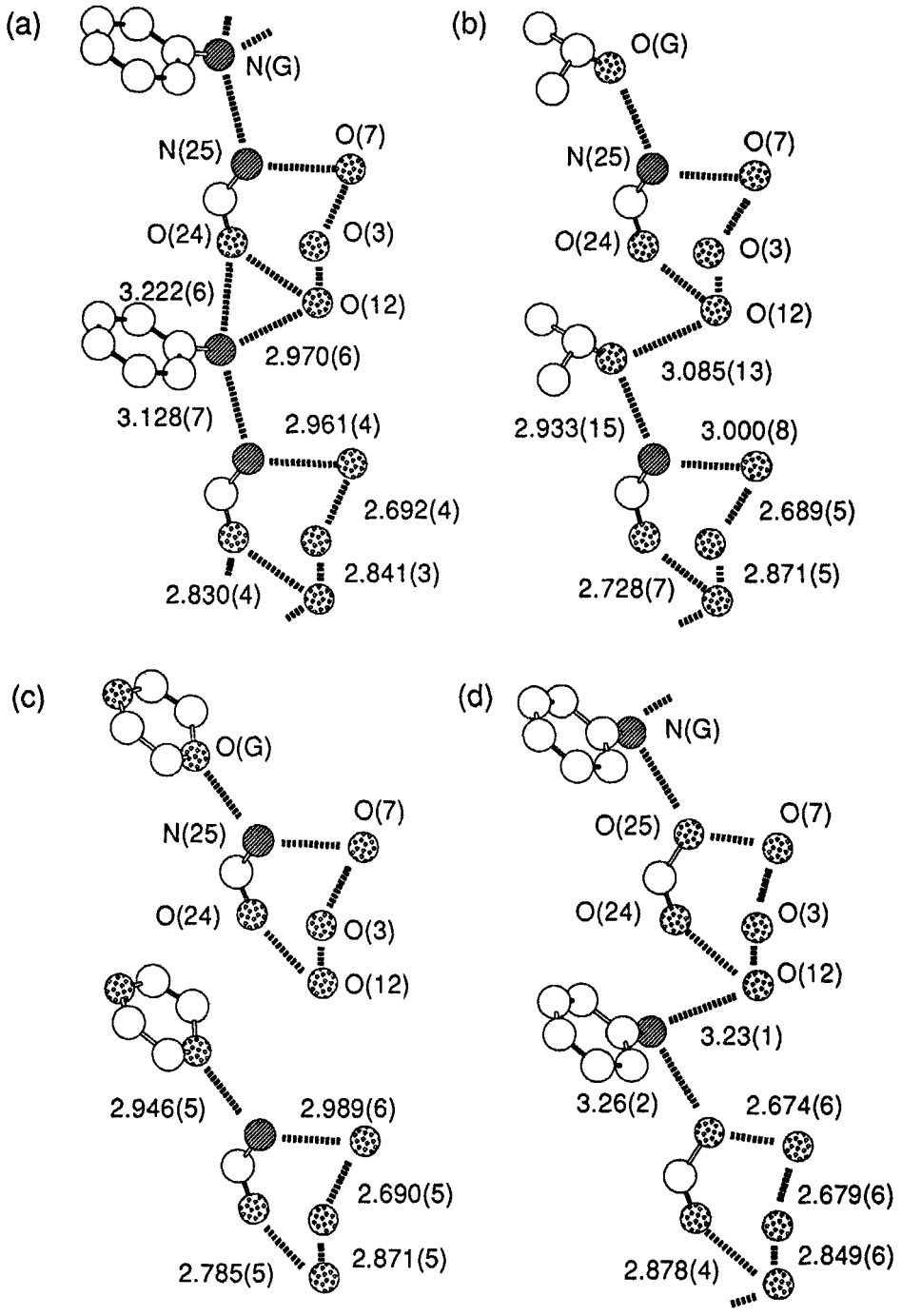


FIGURE 2 Schematic representation of hydrogen bond netwroks: (a) **2**-aniline, (b) **2**-2-propnaol, (c) **2**-1,4-dioxane, (d) **1**-aniline. Hydrogen bond length in Å and numbering scheme are shown.

is forms(Figure 2b).[3b] Therefore, 2-propanol are included in **2** by 'double hooks'. Primary amines such as aniline have one acceptor and two donors for hydrogen bonding. Three hydrogen bonds are available between host molecules and the guest in the aniline clathrate. The nitrogen atom of aniline is caught up by the host amide 'hook' and two oxygen atoms (O12 and O24) of two different neighboring host molecules are linked with the amine protons.(Figure 2a) Therefore, aniline is hold in the channel by hydrogen bond 'triple hooks'.

COMPARISON OF CRYSTAL STRUCTURE OF ANILINE CLATHRATES

Comparison of crystal structure of **1** and **2** provides us the important information of the host-guest interactions. Figure 1b shows a crystal structure of the aniline clathrate of **1**.[1g,h] They are isomorphrous. Conformation of the steroidal side chain of both hosts is identical, which is referred to gauche-type. Host arrangements are quite similar and they have same stacking manner in both lipophilic and hydrophilic layers. Moreover, orientation and location of the guest are similar in the channels.

Most characteristic difference between them is hydrogen bonding. Figure 2d indicates hydrogen bond scheme of the aniline clathrate of **1**.[1g,h] Carboxyl host **1** has no more hydrogen bond donors, because one carboxyl proton is used in a host-host hydrogen bond cycle. However, amide host **2** has one amide proton as the hydrogen bond 'hook' as discussed above. Accordingly, **1** can not form any hydrogen bonds from a host to a guest in this channel-type structure. In the lipophilic channel, weak hydrogen bond acceptors or apolar guest molecules are easily included. However, in the aniline clathrate, there are two weak host-guest hydrogen bonds. Two oxygen atoms (O12 and O25) on the surface of the channel act as hydrogen bond acceptors for two amine protons of aniline. Consequently, aniline is included in the lattice of **1** by hydrogen bond 'double hooks' from the guest to the host as well as by steric fitness between host cavities and guest molecules.

The amide host **2** with aniline forms the triple hydrogen bonds, whereas the carboxy host **1** forms the double hydrogen bonds. We think that the hydrogen bond from amide nitrogen to aniline in **2** is most important among the host-guest interactions. This hydrogen bond not only contributes to host-guest binding itself, but also enable to the nitrogen atom of aniline to contact closely to oxygen atoms on the surface of the channel. As a result, the hydrogen bonds from aniline to host in **2** are much shorter than those in **1**. Accordingly, host lattice **2** binds aniline much more strongly than **1**.

CONCLUDING REMARKS

Host-host hydrogen bonds of **2** are unchanging. However, host-guest hydrogen bonds are dependent on hydrogen ability of guest molecules. 1,4-Dioxane, 2-propanol, and aniline are included in **2** by single, double and triple hydrogen bonds. In order to understand the host-guest interactions of **2**, it is necessary to investigate crystal structures of both clathrates with other strong hydrogen bond donors and acceptors such as amides, acids, diols and so on.

ACKNOWLEDGEMENTS

This work was supported by Grants-in-Aid for Scientific Research from Ministry of Education, Science and Culture, Japan, and by the Ciba-Geigy Foundation (Japan) for the Promotion of Science. We thank Mr. M. Shibakami at the National Institute of Material and Chemical Research, Japan for supplying us the crystal data for **1** with aniline.

REFERENCES AND NOTES

† Present address: Material and Life Science, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan.

1 (a) M.Miyata, M.Shibakami, W.Goonewardena, and K.Takemoto, Chem.Lett., 605 (1987); (b) K.Miki, A.Masui, N.Kasai, M.Miyata, M.Shibakami, and K.Takemoto, J.Am.Chem.Soc., 110, 6594 (1988); (c) M. Miyata, M. Shibakami, and K. Takemoto, J.Chem.Soc., Chem.Commun., 655 (1988); (d) K.Miki, N.Kasai, M.Shibakami, K.Takemoto and M.Miyata, J.Chem.Soc., Chem.Commun., 1757 (1991); (e) M.Miyata, K.Sada, S.Hori, and K.Miki, Mol.Cryst.Liq.Cryst., 219, 71 (1992); (f) M. Miyata, K. Sada, K. Hirayama, Y. Yasuda, and K. Miki, Supramol. Chem, 2, 283 (1993); (g) M.R.Caira, L.R.Nassimbeni, and J.L.Scott, J.Chem.Soc.,Chem.Commun., 613 (1993); (h) M.Shibakami and A.Sekiya, J.Chem.Soc.,Chem.Commun., 429 (1994); (i) M.R.Caira, L.R.Nassimbeni and J.L.Scott, J.Chem.Soc., Perkin Trans.2, 623, 1403 (1994); (j) K.Nakano, K.Sada, and M.Miyata, Chem.Lett., 137, (1994); (k) J.L.Scott, J.Chem.Soc., PerkinTrans.2, 495 (1995); (l) M. Shibakami, M. Tamura, and A. Sekiya, J.Am.Chem.Soc., 117, 4499 (1995); (m)K.Nakano, K.Sada and M.Miyata, J.Chem.Soc.,Chem.Commun., 953 (1995).

2 (a) E.Giglio, in Inclusion Compounds, edited by J.L.Atwood, J.E.D.Davies and D.D.MacNicol, (Academic Press, London, 1984) Vol.2, Chapt.7, pp.207-229; (b) K.Padmanabhan, K.Venkatesan and V.Ramamurthy, Can.J.Chem., 62, 2025 (1984); (c) E.Giglio, F.Mazza and L.Scaramuzza, J.Inclu.Phenom., 3, 437 (1985); (d)

R.Popovitz-Biro, C.P.Tang, H.C.Chang, M.Lahav and L.Leiserowitz, J.Am.Chem.Soc., 107, 4043 (1985); (e) C.P.Tang, H.C.Chang, R.Popovitz-Biro, F.Frolow, M.Lahav, L.Leiserowitz and R.K.McMullan, J.Am.Chem.Soc., 107, 4058 (1985); (f) L.R.Nassimbeni, M.L.Niven, D.A.Stuart and K.J.Zemke, J.Crystallogr.Spectrosc.Res., 16, 557 (1986); (g) H.C.Chang, R.Popovitz-Biro, M.Lahav, and L.Leiserowitz, J.Am.Chem.Soc., 109, 3883 (1987); (g) S.Cerrini, G.Pochetti, F.Gallese and E.Possagno, Acta Cryst., C49, 1087 (1993).

3 (a) K.Sada, T.Kondo, M.Miyata, T.Tamada, and K.Miki, J.Chem.Soc.,Chem.Commun., 753 (1993); (b) K.Sada, T.Kondo, M.Miyata, and K.Miki, Chem. Mater. 6, 1103 (1993).