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A novel clathrate host allowing structural adjustment during the inclusion of 1,2-diaminoethanes

Koki Yamaguchi, Saori Nakatomi, Yasuyuki Yoshitake and Kazunobu Harano*

Graduate School of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-hon-machi, Kumamoto 862-0973, Japan

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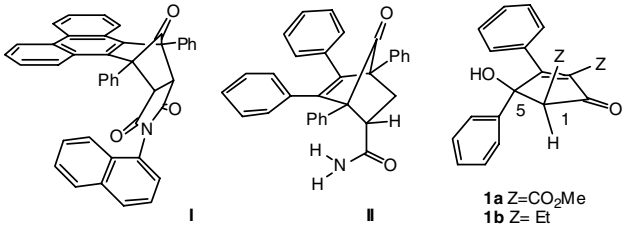
Abstract—Dimethyl 5-hydroxy-2-oxo-4,5-diphenylcyclopent-3-ene-1,3-dicarboxylate (**1a**) forms relatively stable inclusion complexes with compounds having 1,2-diaminoethane moiety.

Recently, we reported that the Diels–Alder (DA) adducts (**I**) of phencyclone and *N*-arylmaleimides act as non-hydroxylic clathrate hosts (clathrands), which include aromatic guests.[1a] On the other hand, the DA adducts (**II**) of tetracyclone and some 2-alkenoic acids or 2-alkenamides serve as hydroxylic clathrate hosts[1b] showing inclusion ability toward alcohols, ethers, and ketones.[1c]



The X-ray analyses of the inclusion compounds showed that the complexes are stabilized by C–H··O hydrogen bond[2] and edge-to-face interaction (aromatic CH–π hydrogen bond)[3] besides strong O (or N)–H··O hydrogen bond between the host and guest.

In this letter, we wish to show that a cyclopentadienone precursor (**1a**) acts as an efficient clathrate host for recognition of molecules bearing 1,2-diaminoethane moiety.

When 1,4-diazabicyclo[2.2.2]octane (**2a**) (0.046 g) was added to a suspension of dimethyl 5-hydroxy-2-oxo-4,5-diphenylcyclopent-3-ene-1,3-dicarboxylate (**1a**) (0.25 g) in benzene (1.5 mL), the solid immediately dissolved with change of color (colorless → yellow) to give pale yellow precipitates (**3aa**) (mp 131–132 °C, yield 26% in MeCN and 69% in benzene). The ^{1}H NMR spectrum showed that **3aa** is a stable 2:1 host–guest complex. The structure of **3aa** was established by the single crystal X-ray analysis (Fig. 1),[4] showing that the guest molecule is included as two rotational isomers[5] around the axis through the two nitrogen atoms of **2a**.

As shown in Figure 1, both nitrogen atoms of **2a** are hydrogen bonded to the hydroxy groups of the host molecules. Four ethano-bridge hydrogens (C_7–C_8) of **2a** form tetradentate C–H··O hydrogen bonds with the enone–carbonyl oxygen of an adjacent host molecule. The >C=O··C_7 and >C=O··C_8 distances are 3.20 and 3.23 Å, respectively. On the other hand, four hydrogens of the hexahydropyrazine moiety (N_1–C_6) also make weak tetradentate C–H··O hydrogen bonds with the enone–carbonyl oxygen of another host molecule. The residual four hydrogens are also linked to the oxygen atoms of the methoxycarbonyl groups of the hosts by C–H··O hydrogen bonds. Thus, all of the hydrogen atoms of **2a** make C–H··O hydrogen bonds with the oxygen atoms of the host molecules. Inspection of the packing diagram of **3aa** indicates that the host–host network is stabilized by the edge-to-face interactions between the phenyl rings of host molecules (see Fig. 2). The host

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* Corresponding author. Tel.: +81 96 371 4573; fax: +81 96 371 4639; e-mail: harano@gpo.kumamoto-u.ac.jp

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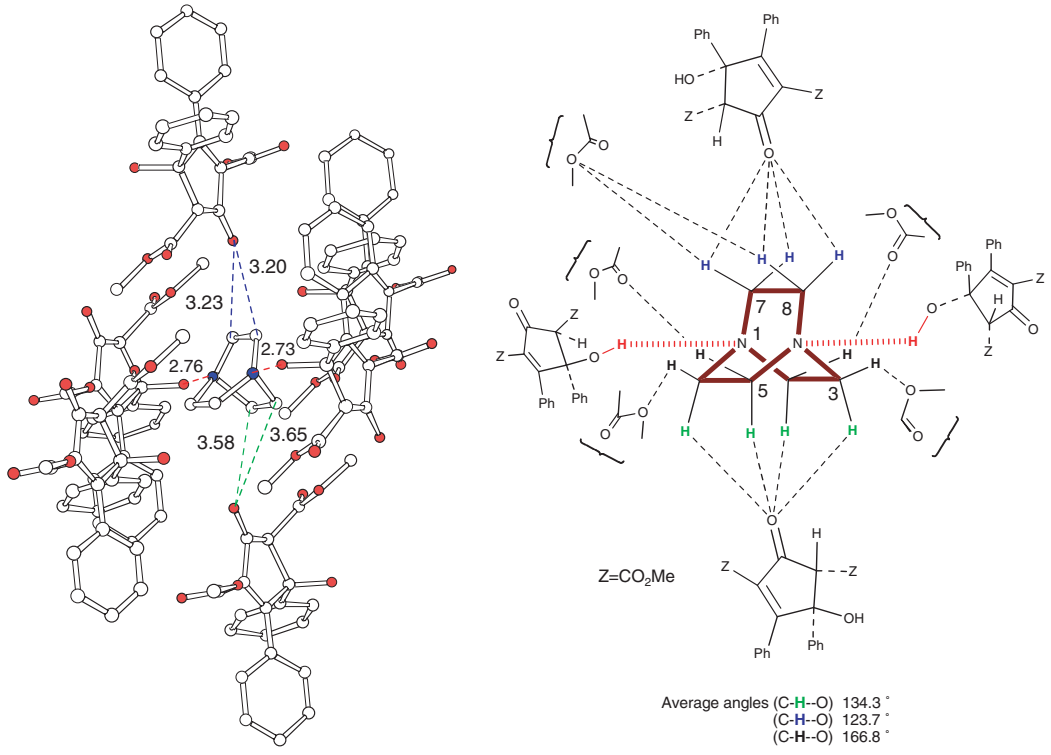

Figure 1. Packing illustration of the crystal structure of **3aa** and schematic representation of the important interactions between **1a** and **2a**. Hydrogen bonds are indicated by dashed lines: red O–H··N hydrogen bonds; blue and green tetradentate C–H··O hydrogen bond; black C–H··O hydrogen bond.

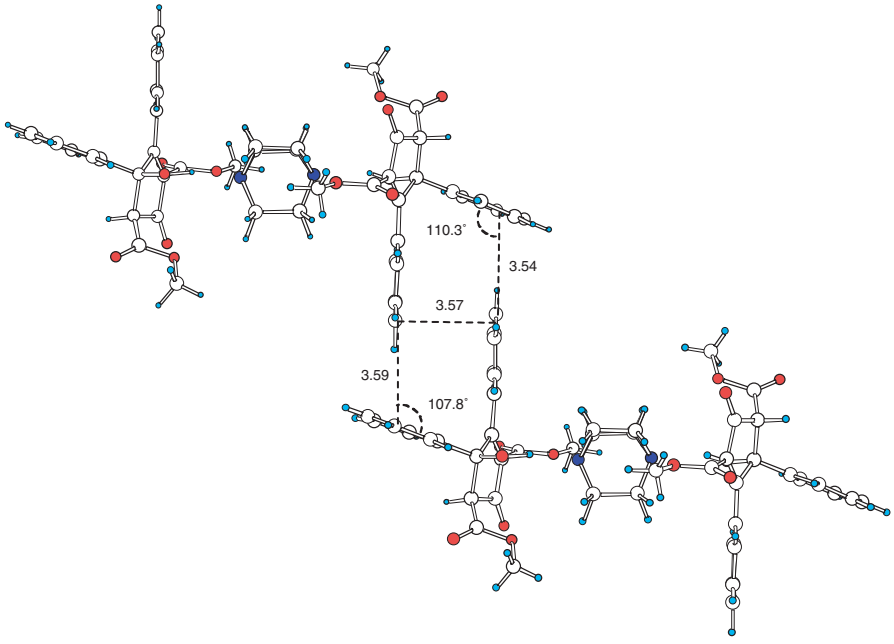

Figure 2. Host–host network between the phenyl rings through edge-to-face interactions in **3aa**.

effectively recognizes the guest, indicating that the three-dimensional structural feature of the host molecule is very suitable for the recognition of **2a**.

The two O–H··N hydrogen bonds are probably retained in solution. The ^{1}H NMR spectrum of the complex in $CDCl_3$ exhibited an extremely wide broadening of the methyl signal of the methoxycarbonyl group on C_1 (see **1a**), indicating the presence of restricted rotation of the methoxycarbonyl group due to the interference of the bulky guest molecule hydrogen bonded to the C_5–OH group. The visible absorption spectrum of the reaction mixture showed the appearance of a new absorption band near 400 nm (shoulder), suggesting the charge-transfer (CT) complex formation between the host and guest.