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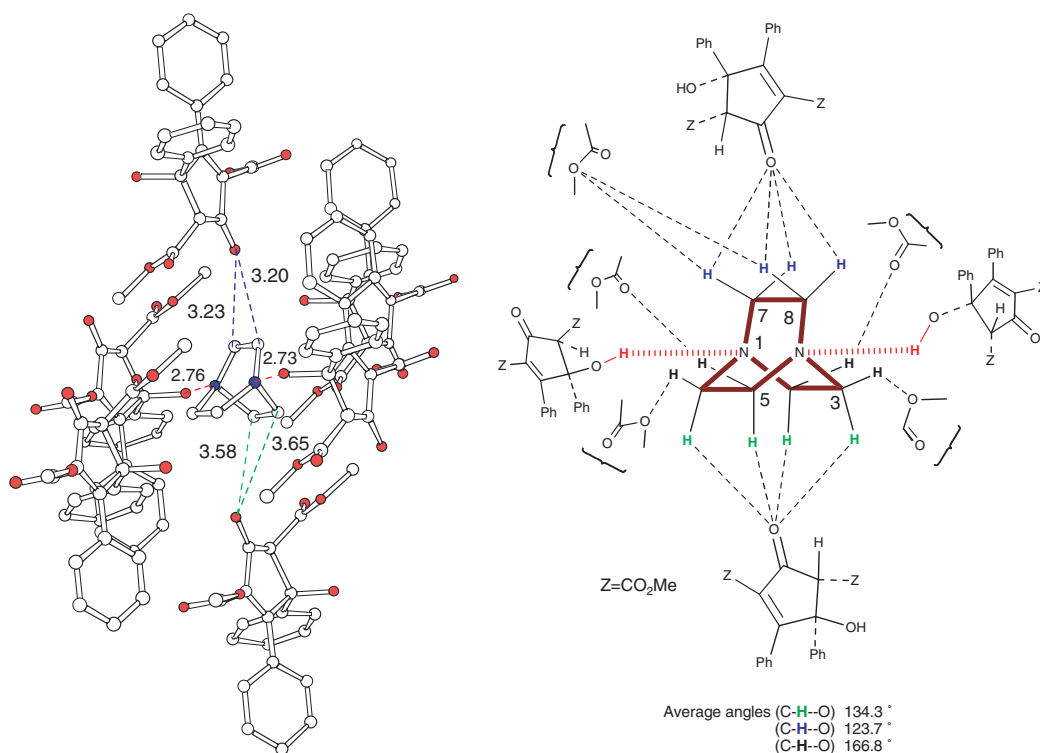


Figure 1. Packing illustration of the crystal structure of **3aa** and schematic representation of the important interactions between **1a** and **2a**. Hydrogen bonds are indicated by dashed lines: red O–H···N hydrogen bonds; blue and green tetradentate C–H···O hydrogen bond; black C–H···O hydrogen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

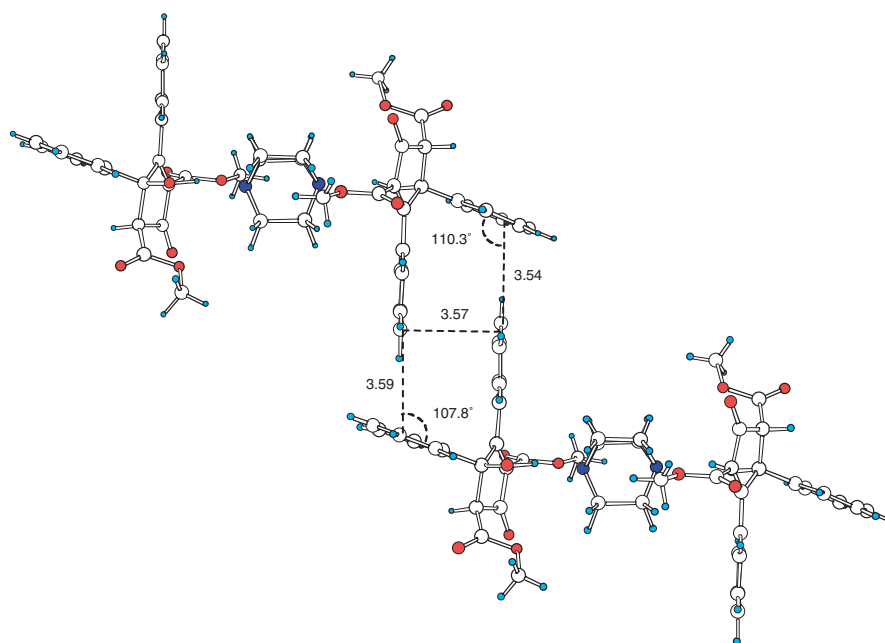


Figure 2. Host–host network between the phenyl rings through edge-to-face interactions in **3aa**.

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 ¹H NMR spectrum of the complex in CDCl₃ exhibited an extremely wide broadening of the methyl signal of the methoxycarbonyl group on C₁

(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 C₅–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.

With piperazine (**2b**), **1a** forms stable 2:1 host–guest complex **3ab** (mp 136–137 °C, yield 90%). The X-ray analysis of the 2:1 host–guest complex (**3ab**)⁶ showed a different inclusion mode compared to the case of **3aa**, in which there are strong hydrogen bonds of two types not only between the enolic O–H hydrogen of **1a** (enol form)⁷ and the nitrogen lone pair of **2b**, but also between the N–H hydrogen and the ester carbonyl of **1a** (see Fig. 3).

As can be seen in Figure 3, the 2,5-dihydroxycyclopentadiene moieties of **2b** form a cyclic diol dimer in a face-to-face manner, stabilizing the host–host network (see also Fig. 4).

1,2-Diaminoethane (**2c**) forms a 1:1 host–guest complex (**3ac**, mp 105–108 °C, 57%) with **1a**.⁸ 1-Aza-bicyclo[2.2.2]octane (**2d**) forms an unstable 1:1 host–guest complex **3ad** (mp 118–120 °C, 71%) with **1a** in nonpolar solvents such as benzene, which gradually transformed to an equilibrium mixture during purification by recrystallization.⁹ Monoalkylamines such as triethylamine did

not form crystalline host–guest complexes with **1a** but showed yellow coloration due to the CT complex formation. Pyrazine (**2e**), dioxane (**2f**), and hexamethylenetetramine (**2g**) did not form the host–guest complexes with **1a**, indicating that 1,2-diaminoethane moieties are specifically recognized. A less electron-deficient host, 2,5-diethyl-4-hydroxy-3,4-diphenylcyclopent-2-enone (**1b**) did not act as a clathrate host.¹⁰

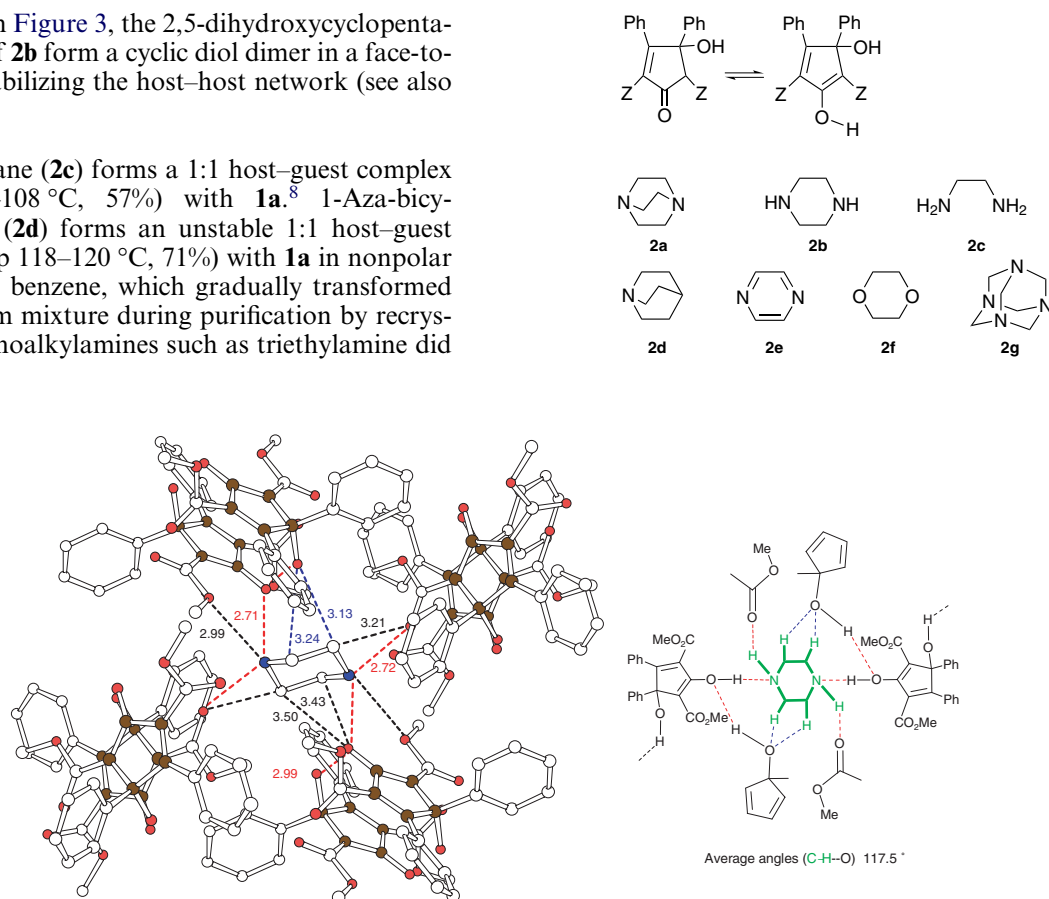


Figure 3. Packing illustration of the crystal structure of **3ab** and important interactions between **1a** and **2b**. Hydrogen bonds are indicated by dashed lines: red N–H···O, O–H···O, and O–H···N hydrogen bonds; blue lines: C–H···O hydrogen bond.

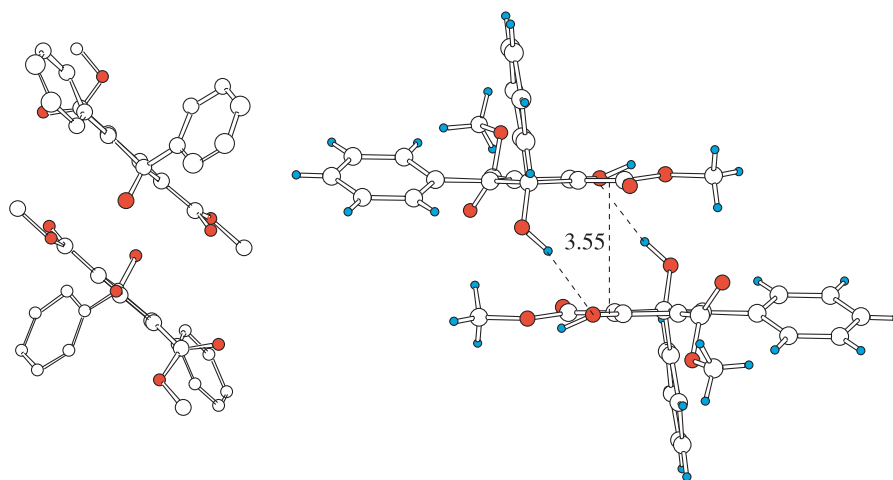


Figure 4. Host–host interaction between the 2,5-dihydroxycyclopentadiene moieties through cyclic O–H···O hydrogen bonds in **3ab**.

The present host molecule is considered to have induced-fit-type binding ability toward 1,2-ethanediamines, regardless of the type of the diamines, in which two $>\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds between the $\text{C}_5\text{-OH}$ and diamines play a leading role in recognition of the 1,2-diaminoethane moiety. With primary and secondary 1,2-diaminoethane, the host molecule isomerizes to the enol form acting as hydrogen-bond donor towards the diamines. In both cases, the conformational flexibility of the methoxycarbonyl groups plays an important role for the effective accumulation of the weak $\text{C}-\text{H}\cdots\text{O}$ interactions between host and guest.

We are currently investigating the inclusion behavior of more electron-deficient host having 4,5-dipyridin-2-yl groups and the crystallographic analyses of the inclusion complexes.

Supplementary data

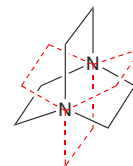
The procedure of single-crystal X-ray analyses, ORTEP drawings and NMR data for **3aa** and **3ab** are available. With this article and can be found, in the online version, at doi:10.1016/j.tetlet.2004.12.085.

X-ray crystallographic data: Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 255495 and 221324. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or deposit@ccdc.cam.ac.uk].

References and notes

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- Crystal Data of **3aa**; $\text{C}_{24}\text{H}_{24}\text{NO}_6$, $M = 422.46$. triclinic, space group $P1$, $a = 9.842$ (3), $b = 15.123$ (4), $c = 8.221$ (3) Å, $\alpha = 100.54$ (3), $\beta = 113.02$ (2), $\gamma = 96.42$ (2)°, $V = 1084.2$ (7) Å³, $D_c = 1.294$ gcm⁻³, $D_o = 1.290$ gcm⁻³, $Z = 2$, $R = 0.099$, $R_w = 0.100$. CCDC reference number 255495.
- The disorder of **3aa** is schematically shown below. The line drawing with numbering sequence is shown in the supplementary data.



- Crystal Data of **3ab**; $\text{C}_{23}\text{H}_{23}\text{NO}_6$, $M = 409.44$. monoclinic, space group $P21/c$, $a = 14.323$ (6), $b = 13.443$ (8), $c = 10.689$ (4) Å, $\beta = 92.90$ (3)°, $V = 2055$ (1) Å³, $D_c = 1.323$ gcm⁻³, $D_o = 1.308$ gcm⁻³, $Z = 4$, $R = 0.081$, $R_w = 0.131$. CCDC reference number 221324.
- The distances and angles of the enol moiety are shown in the supplementary data.
- The IR spectra (nujol) of **3ab** and **3ac** suggest that the host transforms to the enol form. The NMR spectral patterns closely resemble to that of **3aa**, indicating that the structure in solution is different from the crystal structure.
- The preliminary experiment shows that K_{assoc} is 44.8 M⁻¹.
- A referee pointed out that the β -ketoester moiety is important for the inclusion ability.