CHEMISTRY LETTERS, pp. 1867-1870, 1985.

X-RAY CRYSTAL STRUCTURE OF A 1:1 METHANOL COMPLEX OF WINE CUP-SHAPED HOST COMPOUND N,N,N',N',N'',N''-HEXACYCLOHEXYLMETHANE TRICARBOXAMIDE

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The title novel wine cup-shaped host molecule was found to include a wide variety of guest compounds, and X-ray crystal structure of its 1:1 methanol complex was determined.

Previously, we have reported that 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (1) includes two amide molecules and forms stable 1:2 crystalline complex (Fig.1).1) This finding suggests that polyamide compound would become a host compound and includes alcohols (Fig. 1). According to this idea, we designed the title triamide host compound (2) which may have a wine cup shape. Guest molecules might be included in the cup. In fact, we found that 2 (mp 256 °C) includes a various kind of alcohols such as MeOH (ratio to 2; 1, mp of the complex in a sealed capillary; 191-201 °C), EtOH (1, 156-171), n-PrOH (1, 150-167), i-PrOH (1, 165-184), n-BuOH (1, 148-168), i-BuOH (1, 165-183), t-BuOH (1, 242-245), cyclohexanol (2, 190-230), HO(CH$_2$)$_2$OH (1, 135-190), HO(CH$_2$)$_3$OH (1, 208-230), HO(CH$_2$)$_4$OH (1, 172-230), HO(CH$_2$)$_5$OH (0.5, 165-121), HO(CH$_2$)$_6$OH (0.5, 123-141), HO(CH$_2$)$_8$OH (0.5, 160-175), and resorcinol (0.5, 203-208). It was also found that 2 includes other organic compounds such as acetone (1, 159-183), cyclohexanone (2, 180-194), γ-butyrolactone (1, not clear), dioxane (1, 162-190), DMSO (1, not clear), DMF (1, 155-162), and MeCN (2, 190-213). This excellent inclusion ability of 2 is probably due to its winw cup shape, because N,N,N',N',-tetracyclohexylmethane dicarboxamide (3, mp 184 °C) does not include any guest compound. In order to understand the reason why 2 has such a high inclusion ability, the X-Ray crystal structure of a 1:1 methanol complex of 2 was carried out.

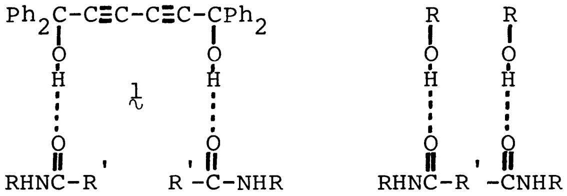


Fig. 1.

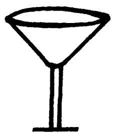
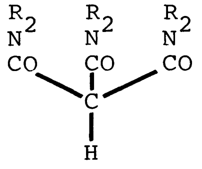
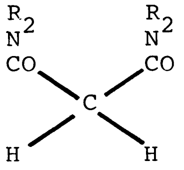


Fig. 2.



2



3

R=cyclohexyl

Crystal data of 1:1 methanol complex of 2 are as follows: colorless needles elongated along a, $C_{41}H_{71}N_3O_4$, FW=670.02, orthorhombic, space group $Pna2_1$, a= 20.93(1), b=18.26(1), c=10.549(4) Å, V = 4032(4) $Å^3$, D_m (flotation in aqueous KI) = 1.11 g cm^{-3}, Z = 4, D_c = 1.104 g cm^{-3}, Mo-$K\alpha$ radiation (graphite-monochromatized), λ = 0.71069 Å, μ = 0.65 cm^{-1}, F(000) = 1479.8.

A single crystal (0.38 x 0.36 x 0.32 mm^3) was sealed in a 0.5 mm Lindemann glass capillary and mounted on a Nicolet R3m diffractometer. The orientation matrix was determined using established procedure,[2)] and intensities ($2\theta_{max}$ = 42°, 1527 unique reflection) was collected at 22 °C using the ω-2θ variable-scan (2.02-8.37° min^{-1}) technique by two standard reflections every 125 measurements.

The structure was solved by direct phase determination guided by negative quarters.[3)] The oxygen atom of the methanol guest molecule was found to exhibit two-fold orientational disorder. In subsequent block-cascade[4)] least-squares refinement, isotopic thermal parameters were assigned to the atoms of the cyclohexyl groups and the guest molecule, and the remaining ten non-hydrogen atoms in the asymmetric unit were varied anisotropically. The 67 hydrogen atoms in the host species were generated geometrically (C-H = 0.96 Å), assigned fixed isotropic temperature factors, and allowed to ride on their respective parent carbon atoms in structure factor calculations. Convergence for 1279 observed data $[|F_o| > 2\sigma|F_o|]$ and 246 variables was reached at R = 0.086, the weighting scheme employed being $w = [\sigma^2(|F_o| + 0.002|F_o|^2]^{-1}$.[5)] Residual extremes in the final difference map lie in the range +0.36 to -0.27 eA^{-3}. All computations were performed with the SHELXTL program[6)] with atomic scattering factors taken from Ref. 7.

The structure of 1:1 methanol complex of 2, as adequately described by its molecular formula, is illustrated in Fig. 3 together with numbering of the stoms. The hydroxyl group of the methanol molecule is disordered over two sites of equal occupancy [O(4) and O(5)], forming donor hydrogen bonds of 2.76(1) and 2.71(1) Å to O(2) and O(1), respectively. The host molecular structure conforms closely to idealized C_3 symmetry (see torsion angles in the legend of Fig. 3), despite the fact that only two of its three carbonyl groups interact with the guest species.

A stereo view of the crystal packing is shown in Fig. 4. It is structurally feasible that replacement of methanol by other mono- or di-hydroxy guest components may generate a series of analogous inclusion complexes. The propeller-like geometry of **2**, with hydrophobic groups constituting the blades and hydrophilic groups close to its core, appears to be particularly favorable for guest inclusion, and we are currently engaged in the design and synthesis of related host compounds.

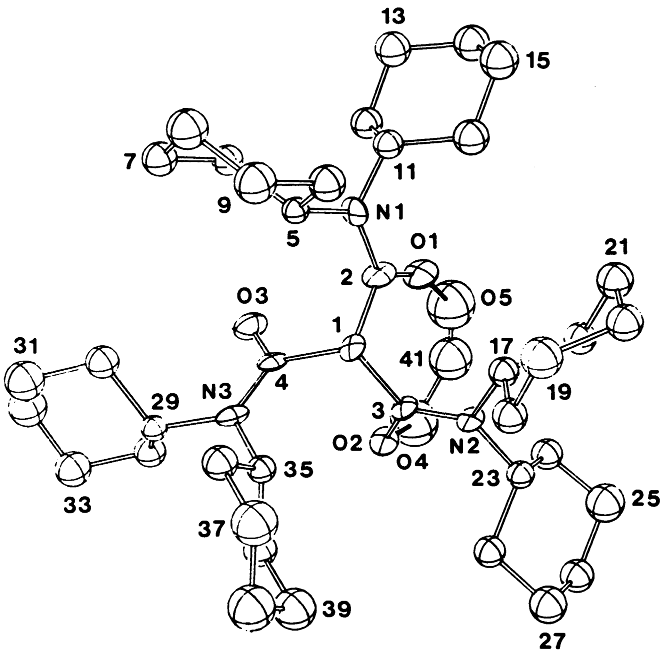


Fig. 3. Perspective view of the structure of 1:1 methanol complex of **2**. The solid lines represent hydrogen bonds involving the disordered hydroxyl group of the methanol molecule. Selected bond length ($\sigma \approx 0.1$ Å) and torsion angles ($\sigma \approx 1°$): C(1)-C(2), 1.53; C(1)-C(3), 1.58; C(1)-C(4), 1.56; O(1)-C(2), 1.21; O(2)-C(3), 1.21; O(3)-C(4), 1.21; N(1)-C(2), 1.39; N(2)-C(3), 1.35; N(3)-C(4), 1.37Å; C(1)-C(2)-N(1)-C(5), -9; C(1)-C(3)-N(2)-C(17), -8; C(1)-C(4)-N(3)-C(35), -9; C(1)-C(2)-N(1)-C(11), 170; C(1)-C(3)-N(2)-C(23), 179; C(1)-C(4)-N(3)-C(29), 174; C(2)-N(1)-C(5)-C(6), -122; C(3)-N(2)-C(17)-C(22), -123; C(4)-N(3)-C(35)-C(40), 116; C(2)-N(1)-C(11)-C(12), 71; C(3)-N(2)-C(23)-C(24), 68; C(4)-N(3)-C(29)-C(34), 64°.

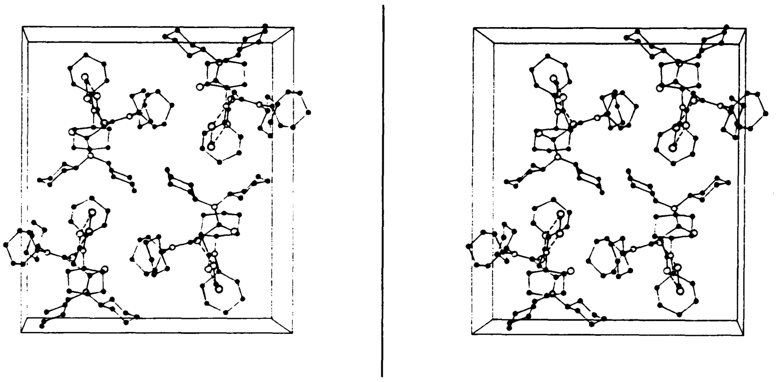


Fig. 4. Stereodrawing of the molecular packing. The orign of the unit cell lies at the upper left corner, with a pointing downwards, b from left to right, and c towards the reader. Note that both disordered sites of the hydroxyl group are included, and the hydrogen bonds appear as broken lines.

The authors thank the Ministry of Education, Science and Culture for Grant-in-Aid for Special Project Research (Grant No. 59212030) and the Ming Yu Cultural Foundation (Grant No. 636011000).

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(Received September 18, 1985)