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Molecular Structure of the Inclusion Complex of 5-[Perfluoro(2-isopropyl-1,3-dimethyl-1-butenyl)oxy]isophthalic Acid with Ethanol

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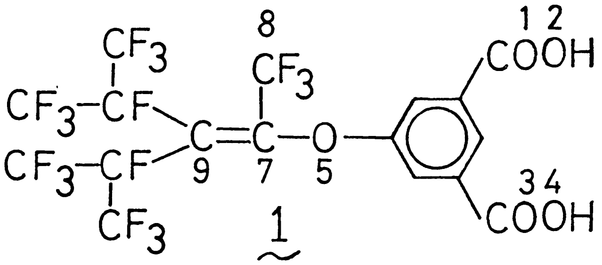
Title compound has been found to form a 2:2 crystalline inclusion complex with ethanol, and X-ray crystal structure of the complex was determined. In the structure of the complex, four intermolecular hydrogen bonds are involved between the two host and two guest molecules. By using the complexation, extraction of ethanol from aqueous solution is demonstrated.

The complexation phenomena of host and guest molecules have been studied by using X-ray analysis, and a number of acyclic host compounds which form inclusion complexes with various guest species have been reported.[1,2] Recently we found that a fluorinated compound, 5-[perfluoro(2-isopropyl-1,3-dimethyl-1-butenyl)oxy]isophthalic acid (**1**),[3] forms a crystalline inclusion complex with ethanol, and X-ray crystal structure of its 2:2 ethanol complex, featuring an interesting mode of intermolecular linkage through the four hydrogen bonds, has been determined.



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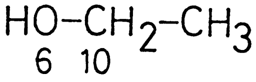

$\underset{6}{HO}-\underset{10}{CH_2}-CH_3$

We wish to briefly report physico-chemical properties and the molecular structure of the complex (**2**) of **1** and ethanol. In addition, the application of the complexation to the extraction of ethanol from aqueous solution is demonstrated.

Single crystal$^{4)}$ of **2** was prepared by recrystallization of **1** in ethanol. The complex did not show clear melting point even in a sealed capillary because of the evaporation of ethanol. Differential Thermal Analysis (DTA)$^{5)}$ showed an endothermic peak at 132 °C, where the sample weight of 7.11% decreased. These results can be interpreted by assuming the evaporation of ethanol molecule included in the crystals with the ratio of 1:1 (calcd. 7.00%) at this temperature. ^{1}H-NMR spectrum of **2** also supported the 1:1 molar ratio of host and guest molecules. ^{1}H-NMR spectra of **2** in acetone-d_6 showed a broad peak at δ=9.08 ppm in addition to those due to ethanol molecule [δ=1.10 (-CH_3) and 3.62 (-CH_2-)] and **1** [δ=7.92 (ortho) and 8.62 (para)]. This chemical shift is in the range between those due to the protons of -OH group of ethanol (δ=4.10) and -COOH groups of **1** (δ=11.40). This (δ=9.08 ppm) indicates that the protons of -OH of ethanol and -COOH of **1** exchange very rapidly. In the IR spectra, **2** showed the presence of a strongly hydrogen-bonded hydroxyl group.$^{4)}$ The mode of intermolecular linkage through the hydrogen bonds between the host and guest molecules in **2** was determined with the aid of X-ray analysis. Crystal data: $C_{19}H_{11}O_6F_{17}$, triclinic, space group P$\bar{1}$, a=7.262(2), b=9.133(3), c=18.749(5) Å, α=90.75(2), β=97.14(2), γ=94.75(2)°, V=1229.3 Å^3, Z=2, D_{cal}=1.765 g/cm^3. Structure was solved by the direct method, and refined to R=0.118 for 3906

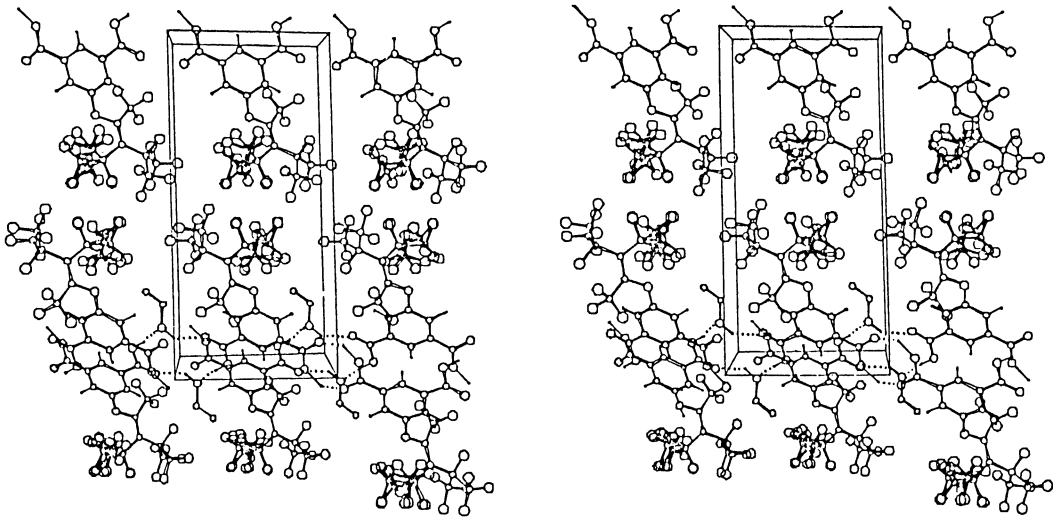

Fig. 1. Stereo view of the molecular packing of **2**. The a axis points out the plane of the paper, the b axis is horizontal, and the c axis is vertical. Hydrogen bonds are shown as broken lines.

independent reflections $[F_o>3\sigma(F_o)]$ collected on a Rigaku AFC-5 Diffractometer with Cu-Kα radiation.

The molecular structure of **2** has a disordered perfluoro-dimethylbutenyl group, and the accurate structure could not be obtained. however, the mode of host and guest interaction was elucidated. A stereo view of the molecular packing is shown in Fig. 1. As shown in Fig. 2, two guest molecules are linked by hydrogen bonds between two -OH groups and two -COOH groups of two host molecules. Consequently, two host and two guest molecules are binded to one another, forming a twelve-membered cyclic hydrogen bondings. The mode of the hydrogen bonding observed for **2** is in contrast with those observed for the dimerized benzoic acid.$^{8)}$ In the structure of **2**, each molecule is located around the inversion center which is at the center of a twelve-membered ring.

The most striking fact is that the **1** forms a complex with ethanol but not with methanol. Since isophthalic acid did not form a complex with either methanol or ethanol, perfluoroalkoxyl group may take an important role to form the crystalline complexes with ethanol. However, we can not understand the reason why the **1** does not form an inclusion crystalline complex with methanol.

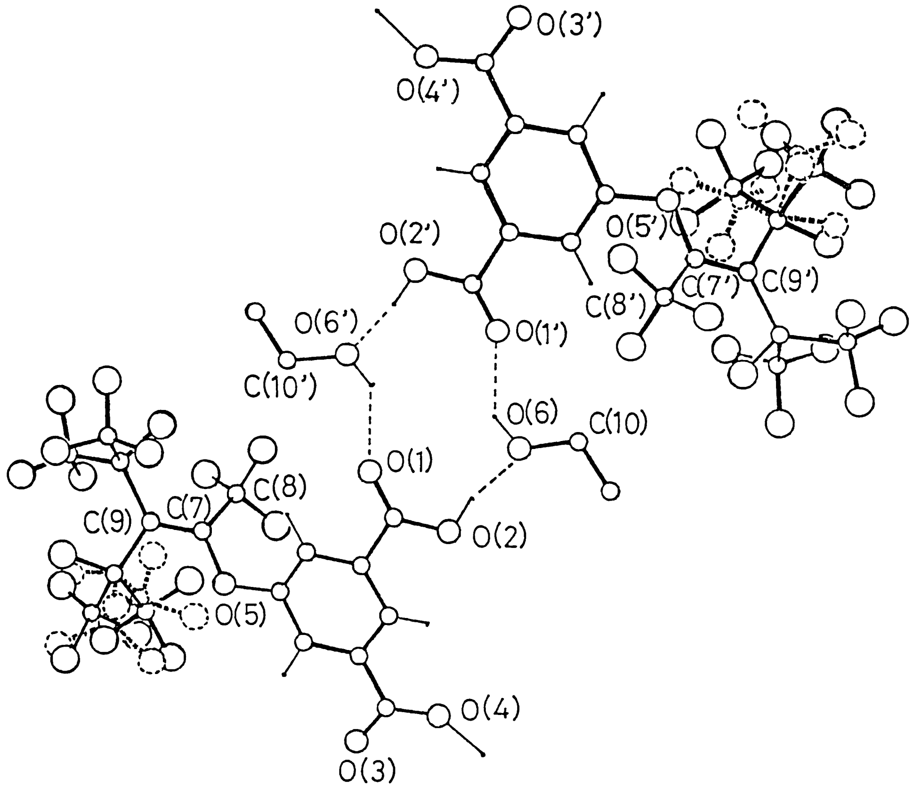

Fig. 2. Host-guest interaction and atom labelling, with the OH----O hydrogen bonds indicated by broken solid lines.

The compound **1** can be used for an extraction of ethanol from aqueous solution: In a 70 % ethanol solution (30 ml, equivalent to 365 mmol ethanol), **1** (6.1 g, 10 mmol) was dissolved by heating at 70 °C, and the solution was kept at room temperature for 24 hr, yielding **2** (5.9 g, 9 mmol, 90 % based on **1**). By heating **2** at 132 °C, anhydrous ethanol (0.4 g) was obtained. The recovered **1** can be used again.

References

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3) Trade name of **1** is FTERGENT 501A of NEOS company: Physico-chemical constants of **1**; white powder; ^{1}H-NMR (60 MHz) (acetone-d_6) δ:11.40 (2H, s), 8.51 (1H, s), 7.83 (2H, s); ^{19}F-NMR (57 MHz) (axetone-d_6) (ppm)$^{6)}$ 55.2 (3F, d, J_{FF}=62 Hz), 70.3 (6F, s), 71.3 (6F, d, J_{FF}=32 HZ), 165.2 (2F, m)$^{7)}$; IR (in KBr) (cm^{-1}) 3600-2500 (OH), 1725-1700 (=C=O), 1400-1100 (CF).

4) Colorless crystal; ^{1}H-NMR (60 MHz) (acetone-d_6) δ:9.08 (3H, broad), 8.62 (1H, s), 7.92 (2H, s), 3.62 (2H, q), 1.10 (3H, t); IR (in KBr) (cm^{-1}) 3600-2500 (OH), 3460 (strong, due to hydrogen bonding), 1725 (=C=O), 1704 (=C=O), 1400-1100 (CF).

5) The spectra were measured under the condition of heating ratio of 10 °C/min..

6) ^{19}F-NMR spectra being obtained in the presence of $CFCl_3$ as an internal standard and peak center positions being given in ppm upfield from $CFCl_3$.

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