CHEMISTRY LETTERS, pp. 1393-1396, 1987.

A Novel Host Compound with High Inclusion Ability, *N,N,N',N'*-Tetracyclohexyl-2,2'-biphenyldicarboxamide, and Crystal Structure of Its 1:1 Phenol Complex

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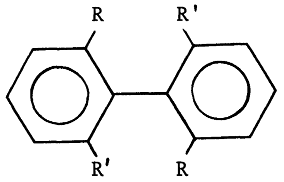
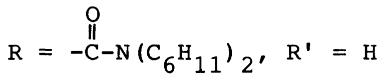
The title host compound forms crystalline inclusion complexes with a wide variety of organic guest molecules. X-Ray analysis of its 1:1 complex with phenol shows that the two molecular components are held together by a O-H···O hydrogen bond of length 2.59(1) Å.

Recently we reported that amide host compounds such as *N,N,N',N'*-tetraalkyl-oxamide,[1,2] -fumaramide,[3,4] and -terephthalamide[5] exhibit excellent inclusion properties towards alcohols. We have since tried to design analogous amide hosts which include a wide variety of organic compounds other than, or in addition to, alcohols, and finally hit upon the title host compound (**1**).

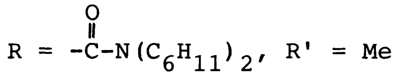
When the acid chloride prepared by the reaction of 2,2'-biphenyldicarboxylic acid with phosphorous pentachloride was treated with dicyclohexylamine in benzene, **1** was obtained in 85% yield as colorless needles, mp 208-210 °C.



1


$R = -\overset{\overset{O}{\|}}{C}-N(C_6H_{11})_2,\ R' = H$

2

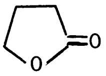
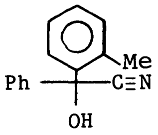
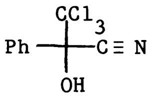

$R = -\overset{\overset{O}{\|}}{C}-N(C_6H_{11})_2,\ R' = Me$

3 1:1 complex of **1** with phenol

Host **1** forms inclusion complexes not only with alcohols but also with a wide variety of common organic compounds. Some examples of the resulting complexes are shown in Table 1. The complexes were prepared by the following methods. When **1** is soluble in a liquid guest compound, the complex was prepared by dissolving the former in the latter by heating, followed by subsequent crystallization. When **1** is not soluble in a liquid guest compound, or when the guest compound is a solid, the complex was prepared with benzene as the common solvent.

In contrast to **1**, its dimethyl derivative **2** is much more soluble in most organic solvents and does not form inclusion complexes with them. In order to rationalize this difference, we have carried out an X-ray analysis of the crystal structure of a 1:1 complex (**3**) of **1** with phenol.

Table 1. Inclusion Complexes of **1** with Some Guest Components[a]

Guest	Complex	Host/Guest ratio	Mp θm/°C	Guest	Complex	Host/Guest ratio	Mp θm/°C
MeOH	needle●	1:1	183-186	*p*-cresol	needle●	1:2	186-188
EtOH	needle●	1:1	not clear	benzene	prism	2:1	not clear
n-PrOH	needle●	1:1	not clear	DMF	needle	1:1	163-164
i-PrOH	needle●	1:1	not clear	DMSO	needle	1:1	194-198
n-BuOH	needle●	1:1	not clear	CCl_4	needle	1:1	not clear
s-BuOH	needle●	1:1	189-196	acetone	needle	1:1	not clear
i-BuOH	needle●	1:1	not clear	THF	needle	1:1	not clear
t-BuOH	needle●	1:1	182-184	dioxan	needle	1:1	not clear
cyclohexanol	needle●	1:1	153-158	pyridine	needle	1:1	not clear
ethyleneglycol	needle●	1:1	not clear		needle●	1:1	not clear
1,3-propanediol	needle	1:1	not clear	benzaldehyde	needle	2:1	not clear
1,4-butanediol	needle	2:1	180-182	CH_3COOH	needle	1:1	not clear
1,5-pentanediol	needle	2:1	not clear		needle●	1:1	153-155
1,6-hexanediol	needle●	2:1	not clear				
phenol	prism	1:1	not clear		needle●	1:1	164-166
o-cresol	prism	1:1	111-113				
m-cresol	prism	1:1	167-168				

[a] Complexes marked with ● signs were prepared with dibutyl ether as the common solvent. The others were prepared by heating a solution of **1** in the liquid guest component.

Crystal data of $C_{38}H_{52}N_2O_2 \cdot C_6H_5OH$ (**3**) are as follows: FW = 662.95, triclinic, space group $P\bar{1}$, a = 9.748(2), b = 14.467(4), c = 14.667(4) Å, α = 105.06(2), β = 92.76(2), γ = 94.62(2)°, V = 1986(1) $Å^3$, Z = 2, $F(000)$ = 720, D_m = 1.10 (flotation in aqueous KI), D_c = 1.109 g cm^{-3}, Mo-$K\alpha$ radiation (monochromatized), λ = 0.71069 Å, μ = 0.64 cm^{-1}.

A selected crystal of size 0.36 x 0.36 x 0.34 mm^3 was sealed inside a 0.5 mm Lindemann glass capillary, and intensity data were collected on a Nicolet R3m diffractometer ($2\theta_{max}$ = 45°, 4221 unique reflections) as described previously.6) Absorption corrections (μr = 0.01, transmission factors 0.929 to 0.944) were applied by fitting a pseudo-ellipsoid to the azimuthal scan data of 20 strong reflections over a range of 2θ-values.7)

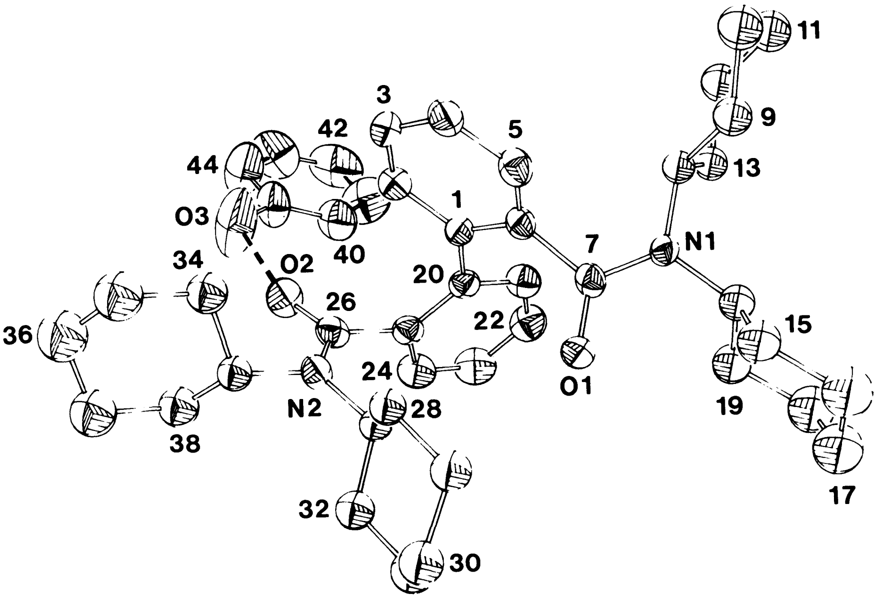


Fig. 1. Host-guest interaction and atom labelling in 3, with the O-H...O hydrogen bond represented by a broken line. Thermal ellipsoids are drawn at the 30% probalility level. Selected molecular dimensions (bond lengths in Å, torsion angles in degrees, standard deviations in parentheses): O2...O(3) 2.59(1); C1-C20 1.505(9); C6-C7 1.512(8), C25-C26 1.502(8); C7-O1 1.227(7), C26-O2 1.244(8); C7-N1, 1.347(7), C26-N2 1.344(8); N1-C8 1.479(7), N1-C14 1.482(7), N2-C27 1.484(8), N2-C33 1.480(7); C2-C1-C20-C25 -49.6(8); C1-C6-C7-O1 -60.6(8), C20-C25-C26-O2 98.1(8).

The structure was solved by direct phasing guided by negative quartets.8) In order to maintain a reasonable data-to-parameter ratio, the carbon atoms of the cyclohexyl groups were subjected to isotropic refinement, while anisotropic temperature factors were adjusted for the remaining non-hydrogen atoms in the asymmetric unit (Fig. 1). The aromatic, methylene, and methine H atoms were generated geometrically and allowed to ride on their respective parent C atoms; the phenolic proton did not show up in a difference map. All H atoms were included in structure factor calculations with assigned isotropic thermal parameters. Convergence for 3158 observed data $[|F_o| > 3\sigma(|F_o|)]$ and 322 variables was reached at $R_F = 0.104$.9) All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL package,10) the weighting function employed being $w = [\sigma^2(|F_o|) + 0.0010|F_o|^2]^{-1}$.

As illustrated in Fig. 1, the two molecular components are held together by a O-H...O hydrogen bond, so that the resulting aggregate faithfully represents the 1:1 stoichiometry of 3. The aromatic rings in the central biphenyl moiety are tilted with respect to each other, as measured by the C2-C1-C20-C25 torsion angle of -49.6(8)°. The bonding configuration at each amido N atom is planar. The two amide systems are inclined differently with respect to their respective parent aromatic rings, owing to the steric influence of the hydrogen-bonded phenol guest molecule.

The mode of molecular packing in **3** is shown in Fig. 2. It is seen that attachment of the phenol molecule to **1** makes the other amido O atom less accessible to a second incoming phenol molecule, and the introduction of *o*-methyl substituents to the biphenyl nucleus would tend to impede the approach of hydrogen-bond acceptors, thereby accounting for the lack of inclusion capability of **2**.

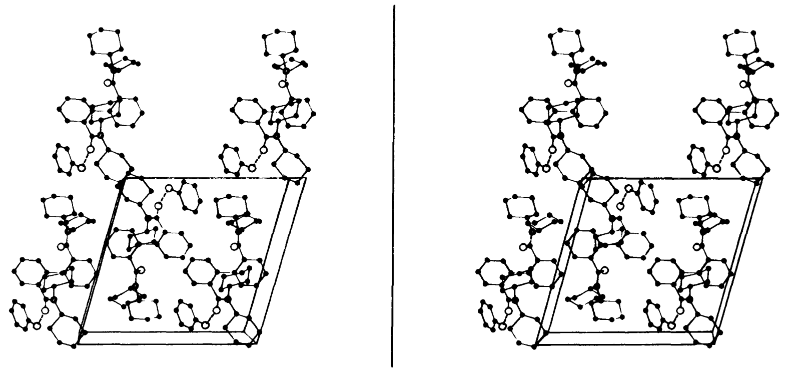


Fig. 2. Stereodrawing of the crystal structure of **3**. The origin of the unit cell lies at the upper left corner, with *a* pointing towards the reader, *b* downwards, and *c* from left to right. Broken lines represent O-H...O hydrogen bonds.

We thank the Ministry of Education, Science and Culture for Grant-in-Aid for Special Project Research (Grant No. 61134038) and the Ming Yu Cultural Foundation (Grant No. 636011000).

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(Received March 18, 1987)