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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'-tetraalkyloxamide,^{1,2)} -fumaramide,^{3,4)} and -terephthalamide⁵⁾ 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.



Host $\frac{1}{2}$ 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 $\frac{1}{2}$ 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 $\frac{1}{2}$ 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.

		Host/Guest	Mp. Am (80	Cuest	Complex	Host/Guest	Mp Am/°C
Guest	Complex	ratio	mp out/ C	Guest			MP 0107 C
MeOH	needle	1:1	183-186	<i>p</i> -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>i-</i> PrOH	needle	1:1	not clear	DMSO	needle	1:1	194-198
n-BuOH	needle	1:1	not clear	CC14	needle	1:1	not clear
s-BuOH	needle	1:1	189-196	acetone	needle	1:1	not clear
<i>i</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
cyclo- hexanol	needle	1:1	153-158	pyridine	needle	1:1	not clear
ethyl- eneglyco	needle 1	1:1	not clear		needle	1:1	not clear
1,3- propaned	needle iol	1:1	not clear	benzalde- hyde	needle	2:1	not clear
1,4- butanedi	needle ol	2:1	180-182	сн ₃ соон	needle	1:1	not clear
1,5- pentaned	needle iol	2:1	not clear	$Ph \xrightarrow{Me}_{C=N}$	needle	1:1	153-155
1,6- hexanedi	needle ol	2:1	not clear	ОН			
phenol	prism	1:1	not clear	Ph $\xrightarrow{CC1}_{3}$ C = N	needle	1:1	164-166
<i>o-</i> cresol	prism	1:1	111-113	I OH			
<i>m</i> -cresol	prism	1:1	167-168				

Table 1. Inclusion Complexes of $\frac{1}{\sqrt{2}}$ with Some Guest Components^{a)}

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 $C_{38}H_{52}N_2O_2.C_6H_5OH$ (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, $\alpha = 105.06(2)$, $\beta = 92.76(2)$, $\gamma = 94.62(2)^{\circ}$, V = 1986(1) Å³, z = 2, F(000) = 720, $D_m = 1.10$ (flotation in aqueous KI), $D_c = 1.109$ g cm⁻³, Mo-K α radiation (monochromatized), $\lambda = 0.71069$ Å, $\mu = 0.64$ cm⁻¹.

A selected crystal of size 0.36 x 0.36 x 0.34 mm³ was sealed inside a 0.5 mm Lindemann glass capillary, and intensity data were collected on a Nicolet R3m diffractometer $(2\theta_{max} = 45^{\circ}, 4221 \text{ unique reflections})$ as described previously.⁶) Absorption corrections ($\mu r = 0.01$, 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 20-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-C2O 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 $R_{\rm F} = 0.104$.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 <u>a</u> pointing towards the reader, <u>b</u> downwards, and <u>c</u> from left to right. Broken lines represent O-H...O hydrogen bonds.

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