CHEMISTRY LETTERS, pp. 113-116, 1986.

INCLUSION PROPERTIES OF N,N,N',N'-TETRACYCLOHEXYLFUMARAMIDE AND CRYSTAL STRUCTURE OF ITS 1:1 MOLECULAR COMPLEX WITH ETHANOL

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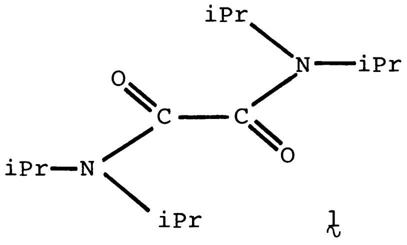
The title host compound forms crystalline inclusion complexes with a wide variety of alcohols. X-Ray analysis of its 1:1 ethanol complex showed that the crystal comprises a packing of a hydrogen-bonded guest···host···guest aggregate and a discrete host molecule, each of which occupy a different crystallographic center of symmetry.

In a previous paper, we reported that N,N,N',N'-tetraisopropyloxamide (**1**) forms inclusion complexes with a wide variety of aromatic compounds, and that the guest species is surrounded by four isopropyl groups and two carbonyl oxygen atoms belonging to neighboring host molecules in the crystalline state.¹⁾ The poor inclusion ability of **1** in regard to alcohols is probably due to steric crowding of isopropyl groups around the carbonyl groups, which prevents the close approach of guest molecules for hydrogen bond formation in the solid complex. This prompted us to design the title compound (**2**) which has a _trans_-ethylene linkage as a spacer, and we subsequently confirmed that it exhibits excellent inclusion properties towards a wide variety of alcohols (Table 1).



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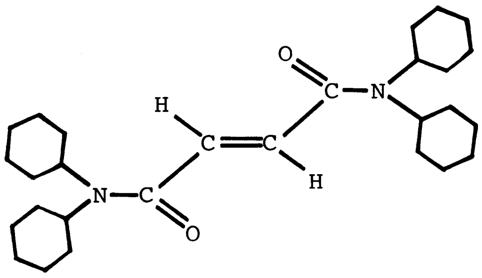
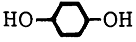
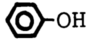
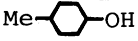


2

Host **2** (mp 206-208 °C) was synthesized from fumaroyl chloride and dicyclohexylamine according to the literature procedure.[2)] Preparation of the 1:1 complex of **2** with ethanol (**3**) is given as a typical example. Host **2** (1 g) was dissolved in ethanol (5 ml) by heating, and the resulting solution was kept at room temperature for 3 h to give **3** as colorless prisms in 95% yield. When the guest compound is a solid of high melting point, the complex was prepared by using acetone or benzene as a solvent. The host/guest ratio was determined by ^1H NMR spectroscopy.

Table 1. Inclusion complexes of **2** with various alcohols[a)]

Alcohols	Host/Guest ratio	Alcohols	Host/Guest ratio
MeOH	1:3	$HO(CH_2)_6OH$	2:1
EtOH	1:1	$HO(CH_2)_8OH$	2:1
nPrOH	1:1		2:1
iPrOH	1:2	(*E*)-$HOCH_2CH=CHCH_2OH$	2:1
iBuOH	1:1	$HO(CH_2)_2O(CH_2)_2OH$	2:1
tBuOH	1:2		1:2
s-pentanol	1:1	o-cresol	1:2
3-hexenol	1:1	m-cresol	1:2
$HC\equiv CCH_2OH$	1:1	p-cresol	1:2
	1:1	picric acid	1:2
$HO(CH_2)_2OH$	2:1	α-naphthol	1:2
$HO(CH_2)_4OH$	2:1	β-naphthol	1:2
$HO(CH_2)_5OH$	2:1	resorcinol	1:2

a) All complexes do not show clear melting point.

Crystal data of $(C_6H_{11})_2NOCCH=CHCON(C_6H_{11})_2\cdot C_2H_5OH$ (**3**) are as follows: FW = 488.75, triclinic, space group $P\bar{1}$, $\underline{a}$ = 9.861(1), $\underline{b}$ = 11.787(4), $\underline{c}$ = 13.598(5) Å, α = 88.09(2), β = 86.04(2), γ = 72.75(2)°, $\underline{V}$ = 1505.7(7) $Å^3$, $\underline{D}_m$ (flotation in aqueous KI) = 1.08 g cm^{-3}, $\underline{Z}$ = 2, $\underline{D}_c$ = 1.078 g cm^{-3}, Mo $\underline{K}\alpha$ radiation (graphite-monochromatized λ = 0.71069 Å), μ = 0.64 cm^{-1}, F(000) = 539.92.

A single crystal (0.36 x 0.34 x 0.30 mm^3) was enclosed in an ethanol atmosphere inside a 0.5 mm Lindemann glass capillary. Intensities ($2\theta_{max}$ = 42°, 2828 unique reflections) were collected at 22 °C on a Nicolet R3m diffractometer, and data processing and structure solution followed procedures as previously described.[3)]

The unit cell of **3** contains two independent host molecules, **3A** and **3B**, centered at Wyckoff positions 1(*a*) [0,0,0] and 1(*g*) [0,1/2,1/2], respectively. The oxygen atom of the ethanol guest molecule was found to be disordered over two sites [O(3) and O(4)] of unequal occupancy [0.72(2) and 0.28(2), respectively]. In blocked-cascade[4)] least-squares refinement, the O and N atoms of the host molecules were varied anisotropically, the other non-hydrogen atoms isotropically, and all H atoms except those of the ethanol molecule included in structure factor calculations with assigned isotropic thermal parameters. Convergence for 2345 observed data $[|F_o| > 3\sigma|F_o|]$ and 166 variables was reached at R = 0.119, the weighting scheme employed being $w = [\sigma^2(|F_o|) + 0.0018|F_o|^2]^{-1}$.[5] All computations were performed with the SHELXTL package[6] with atomic scattering factors taken from Ref. 7.

Both major and minor sites [O(3) and O(4), respectively] of the hydroxyl group are capable of forming donor hydrogen bonds [2.81(1) and 2.70(1) Å, respectively] with the O(1) atom of host molecule **3A** (Fig. 1). Figure 2 clearly shows that **3** comprises a packing of trimeric $C_2H_5OH\cdots$**3A**$\cdots C_2H_5OH$ aggregates and discrete **3B** units, which occupy the corners of the unit cell and the centers of the (100) faces, respectively. The centrosymmetric host molecules **3A** and **3B** have very similar dimensions and adopt virtually the same configuration in the crystal lattice: the central ethylenic double bond is conformationally *s-cis* with respect to both carbonyl functions, and the bonding configuration about each N atom is planar, so that π delocalization extends over the entire backbone of the molecule.

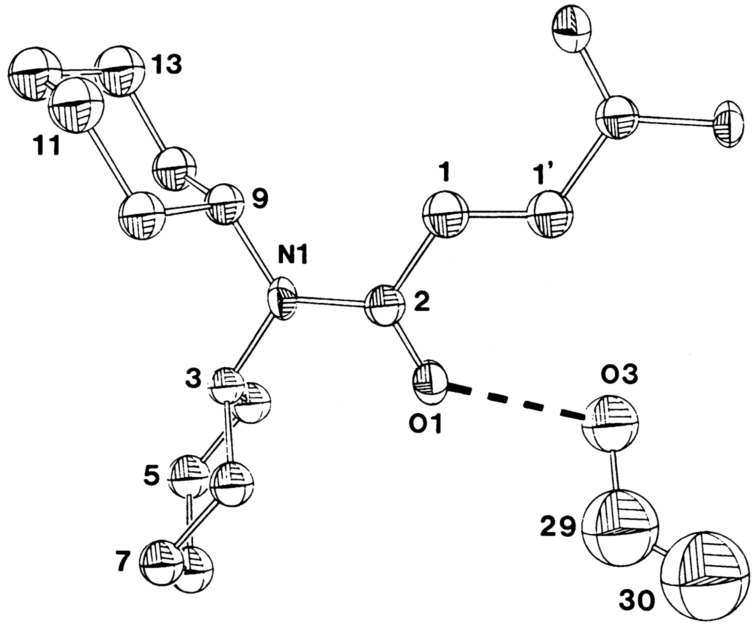


Fig. 1. Host-guest interaction and atom labelling in **3**, with the hydrogen bond represented by a broken solid line. Selected bond distances (σ∿0.1 Å) and bond angles (σ∿0.6°) with the corresponding values for the uncomplexed host molecule **3B** enclosed in parentheses: C1-C1', 1.32(1.30); C1-C2, 1.48(1.47); O1-C2, 1.24(1.22); N1-C2, 1.35(1.38); N1-C3, 1.49(1.46); N1-C9, 1.47(1.48); C1'-C1-C2, 123.2(120.2); C1-C2-O1, 119.3(119.6); C1-C2-N1, 118.6(120.2); O1-C2-N1, 122.1(119.6), C2-N1-C3, 119.3(117.6); C2-N1-C9, 123.1(123.4); C3-N1-C9, 117.6(118.5).

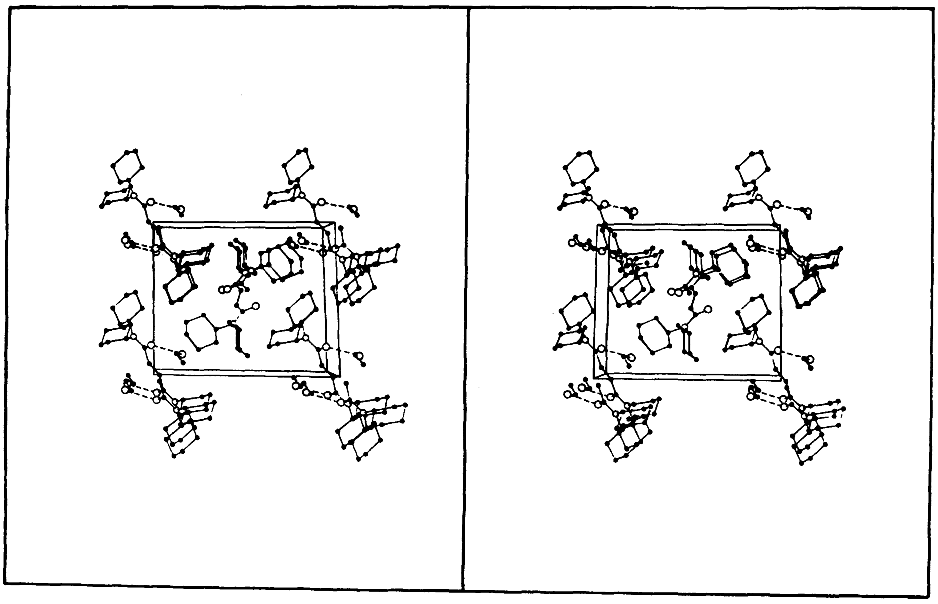


Fig. 2. Stereodrawing of the molecular packing in **3**. The origin of the unit cell lies at the upper left corner, with a pointing towards the reader, b downwards, and c from left to right. For clarity the less populated site of the disordered hydroxyl group has been excluded, and the hydrogen bonds appear as broken lines.

We 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 October 14, 1985)