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# INCLUSION PROPERTIES OF N,N,N',N'-TETRAISOPROPYLOXAMIDE AND CRYSTAL STRUCTURE OF ITS 1:1 COMPLEX WITH 1-METHYLNAPHTHALENE

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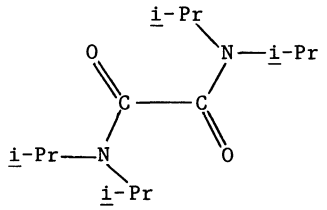
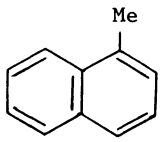
N,N,N',N'-Tetraisopropyloxamide forms crystalline inclusion complexes with a variety of aromatic compounds, and X-ray analysis of its 1:1 complex with 1-methylnaphthalene showed that the aromatic guest molecules are stacked in columns parallel to the b axis.

For some time we have directed our efforts to the study of host molecules possessing at least one hydroxyl group[1] and utilization of their inclusion properties in the isolation,[2] optical resolution,[3] and stereoselective photoreaction[4] of various guest species. We now wish to report that N,N,N'N'-tetraisopropyloxamide (1) forms crystalline inclusion complexes with a variety of aromatic guest molecules such as benzene, m- and p-xylenes, phenol, m- and p-cresols, 1-methylnaphthalene (2), etc., suggesting that hydrogen bonding plays no part in the construction of the host lattice.



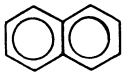
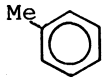
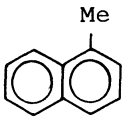
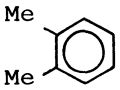
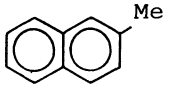
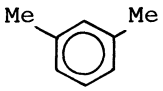
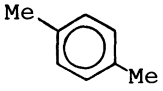
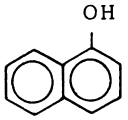
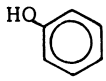
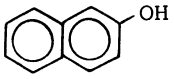
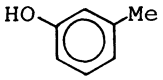
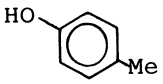
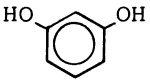

1




2

Host 1 (mp 102-103 °C) was synthesized from oxalyl chloride and diisopropylamine according to the literature procedure.[5] Preparation of the 1:1 complex (3) of 1 with 2 is given as a typical example. When a solution of equimolar amounts of 1 (1.28 g, 5 mmol) and 2 (0.71 g, 5 mmol) in hexane (10 ml) was kept at room temperature for 6 h, 3 was deposited as colorless prisms (1.79 g, 90%). Complex 3 suffers from surface decomposition in air and may be separated into its components by silica gel column chromatography using $CCl_4$ as a solvent.

Table 1. Inclusion complexes of 1 with various aromatic guest species

| Guest | Form of crystals | Mp/°C | Guest | Form of crystals | Mp/°C |
|---|---|---|---|---|---|
|  | needles | 40-45 |  | prisms | 102-103 |
|  | needles | 55-65 |  | prisms (3) | 83-85 |
|  | needles | 54-63 |  | prisms | 49-53 |
|  | needles | 34-48 | | | |
|  | needles | 47-64 |  | prisms | 145-147 |
|  | needles | 113-116 |  | prisms | 157-159 |
|  | needles | 99-103 | | | |
|  | prisms | 83-86 |  | needles | 190-194 |

When the guest component is a liquid, the corresponding inclusion complex is readily obtained by recrystallization of 1 from the liquid. All complexes studied and their melting points are listed in Table 1. As determined by $^1$H NMR spectroscopy, the host/guest ratio in this series of complexes is generally 1:1.

In order to place our understanding of the inclusion properties of 1 on a sound footing, we have chosen to determine the crystal structure of 3, which hopefully may provide useful clues towards the design of new host systems.

Crystal data of $C_{14}H_{28}N_2O_2 \cdot C_{11}H_{10}$ (3) are as follows: FW = 398.58, monoclinic, space group C2/c, a = 42.91(1), b = 6.815(2), c = 27.219(3) Å, β = 110.08(1)°, V = 7476(3) Å$^3$, Z = 12, $D_c$ = 1.062, $D_m$ (flotation in aqueous KI) = 1.065 g cm$^{-3}$, Mo-Kα radiation (graphite-monochromatized), λ = 0.71069 Å, μ = 0.62 cm$^{-1}$, F(000) = 2615.59.

A single crystal (0.42 x 0.40 x 0.34 mm$^3$) was sealed in a 0.5 mm Lindemann glass capillary and mounted on a Nicolet R3m diffractometer. Intensities ($2\theta_{max}$ = 40°, 2933 unique reflections) were collected at 22 °C using the ω-2θ variable scan

(2.02-8.37° $min^{-1}$) technique monitored by three check reflections.

The structure was solved by direct phase determination. The asymmetric unit comprises 1½ diamide host (1) and 1½ 1-methylnaphthalene (2) guest molecules. In other words, there exist two independent host molecules, 1A and 1B, one of which (1B) is located at Wyckoff position 4(e) of $C_2$ symmetry. Likewise one (2B) of the two crystallographically distinct guest molecules (2A and 2B) occupies the centrosymmetric site 4(b) and therefore exhibits two-fold disorder of its substituent methyl group. In subsequent refinement, the 27 non-hydrogen atoms which belong to the diamide molecules were varied anisotropically, the other non-hydrogen atoms isotropically, and 6 tertiary plus 10 aromatic H atoms geometrically generated and included in structure factor calculations with assigned isotropic thermal parameters. Convergence for 2248 observed data [$|F_o| > 3\sigma|F_o|$] and 313 variables was reached at $R = 0.144$.[6] All computations were performed with the SHELXTL program package,[7] and the weighting scheme employed was $w = [\sigma^2(|F_o|) + 0.003|F_o|^2]^{-1}$.

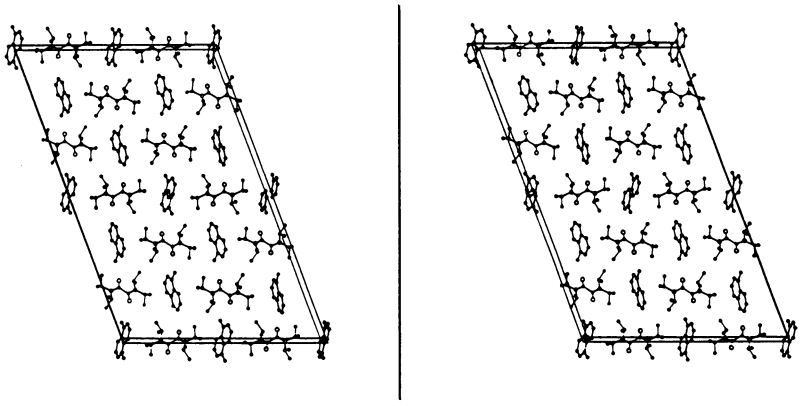


Fig. 1. Stereodrawing of the molecular packing in 3. The origin of the unit cell lies at the lower left corner, with a pointing from left to right, b away from the reader, and c slanting upwards. Note that guest molecules 2B appear as both 1,5-dimethylnaphthalene (apparent center of symmetry introduced by statistical disorder) and toluene (half molecule) in this drawing.

Host molecules 1A and 1B adopt similar configurations in the crystal lattice: the O-C-C-O torsion angles are 92(1) and -93(1)°, respectively, so that the two planar amide moieties in each molecule behave as separate π systems with virtually no conjugation across the central C-C bond [1.55(2) and 1.51(2) Å, respectively].

The packing diagram of 3 (Fig. 1) shows that all molecules lie mainly in the ($\bar{4}02$) and (006) planes, with those of type B concentrated in the (002) planes.

Both A- and B-type guest molecules are accommodated in channels parallel to the b axis. There is no evidence of any significant interaction between host and guest other than dispersion forces. The open nature of the host lattice, as well as the inherent conformational flexibility of 1 (namely rotation about the central C-C and outer C-N single bonds), readily account for the versatility of the latter in host/guest complexation. Further structural studies and the molecular design of related host system are in progress.

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6) The atomic co-ordinates for this work are available on request from the Cambridge Crystallographic Data Centre. A table of structure factors is available from the last author.

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