CHEMISTRY LETTERS, pp. 1913-1916, 1986.

Crystal Structure of a 1:1:1 Molecular Complex of (*R*)-(+)-2,2'-Dihydroxy-1,1'-binaphthyl, *N*,*N*,*N'*,*N'*-Tetra(2-butyl)terephthalamide, and Methanol

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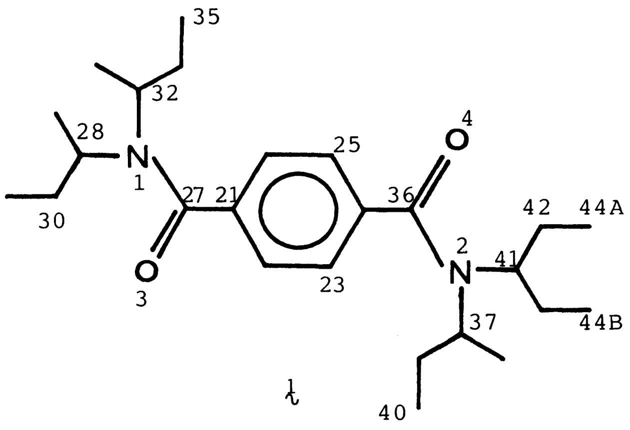
X-Ray analysis of the title complex has shown that the three molecular components are linked by hydrogen bonds to form helical chains parallel to the *a* axis. The (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl molecule adopts a transoid conformation with a torsion angle of -95(1)° about the C-C bond joining the aromatic rings.

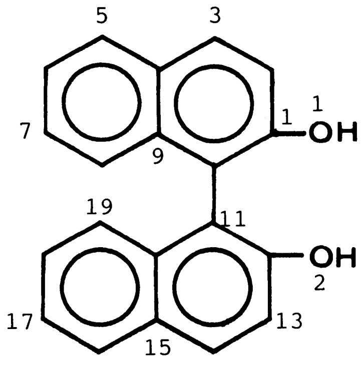
In previous papers,1-3) we have reported the formation and structural characterization of molecular complexes of amide host compounds with alcohols, which are consolidated by hydrogen bonding in the crystal lattice. We now describe the preparation and X-ray crystal structure of a new three-component complex (**3**) featuring an interesting mode of intermolecular linkage.

Complex **3** was prepared by slow evaporation of a MeOH solution of *N*,*N*,*N'*,*N'*-tetra(2-butyl)terephthalamide (**1**) and an equimolar amount of (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl [**2a**, commonly known as (*R*)-(+)-bis-β-naphthol] at room temperature; $[\alpha]_D$ +14° (MeOH, *c* 0.1), mp 170-175 °C (in a sealed capillary), IR (Nujol mull) 3150 (OH) and 1605 (CO) cm^{-1}. The 1:1:1 molar ratio was established from the NMR spectrum.

Racemic 2,2'-dihydroxy-1,1'-binaphthyl (**2b**) also forms a 1:1 complex (**4**) with **1** in MeOH; mp 171-175 °C, IR (Nujol mull) 3170 (OH) and 1590 (CO) cm^{-1}. However, **4** does not contain MeOH and its crystals are very fine hairs and hence unsuitable for X-ray analysis.



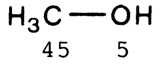
1

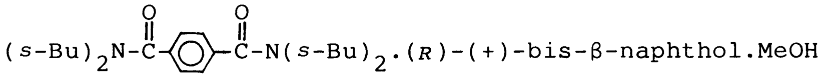


2

2a: (*R*)-(+)-compound

2b: racemic compound





$(s\text{-Bu})_2\text{N-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-C}_6\text{H}_4\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-N}(s\text{-Bu})_2\cdot(R)\text{-}(+)\text{-bis-}\beta\text{-naphthol}\cdot\text{MeOH}$

3

Crystal data of $C_{24}H_{40}N_2O_2 \cdot C_{20}H_{14}O_2 \cdot CH_4O$ (3) are as follows: $F.W. = 706.96$, orthorhombic, space group $P2_12_12_1$, $a = 11.546(5)$, $b = 14.696(4)$, $c = 24.508(9)$ Å, $V = 4158(2)$ Å^3, $Z = 4$, $D_c = 1.129$, $D_m = 1.14$ g cm^{-3} (flotation in KI/H_2O), Mo-$K\alpha$ radiation (monochromatized), $\lambda = 0.71069$ Å, $\mu = 0.68$ cm^{-1}, $F(000) = 1528$.

A single crystal of size 0.42 x 0.40 x 0.40 mm^3 was sealed in a 0.5 mm Lindemann glass capillary. The intensities fell off rapidly with increasing Bragg angle, and data ($2\theta_{max} = 42°$, 2183 unique reflections) were collected and processed as described previously.$^{4)}$

The structure was solved by performing a tangent refinement using random starting phases$^{5)}$ for reflections with $|E| > 1.6$. Owing to the unfavorable data-to-parameter ratio, the C atoms of bis-amide 1 were varied isotropically, while the remaining non-hydrogen atoms in the asymmetric unit (see structural formulas for atom numbering) were subjected to anisotropic refinement. The unequal arms of a *s*-butyl group in 2a exhibited two-fold disorder; in the adopted model, a terminal methyl C atom was represented by C(44A) and C(44B) in a site occupancy ratio of 7:3. All H atoms were generated geometrically and included in structure factor calculations with assigned isotropic thermal parameters, except those belonging to the MeOH molecule and four C atoms [C(42), C(43), C(44A), and C(44B)] of the disordered *s*-butyl group. Convergence for 1929 observed data [$|F_o| > 3\sigma|F_o|$]

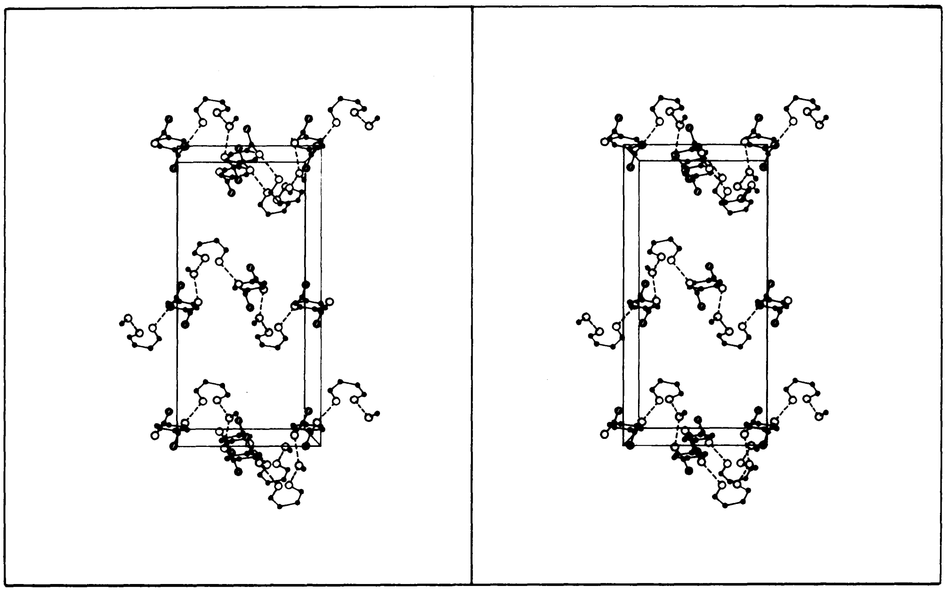
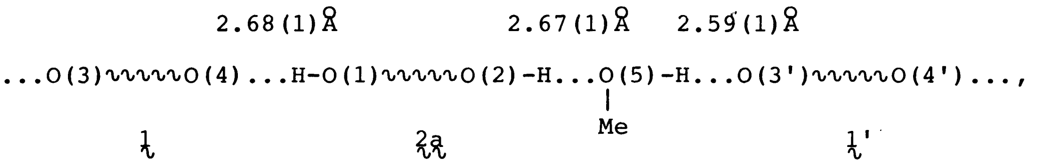


Fig. 1. Stereodrawing of the molecular packing in **3**. For clarity, all *s*-butyl groups of **1** and most aromatic C atoms of **2a** have been omitted, so that the latter moiety appears like 1,4-butanediol. Hydrogen bonds are shown as broken lines. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader, and *c* downwards.

and 371 variables was reached at 0.097.[6)] All computations were performed with the SHELXTL package,[7)] the weighting function employed being $w = [\sigma^2(|F_o|) + 0.0005|F_o|^2]^{-1}$.

In the crystal structure of **3**, the three kinds of molecular components are alternately linked by O-H...O hydrogen bonds to form helical chains parallel to the *a* axis (Fig. 1). The mode of linkage along each chain is of the type:



$$\underset{\mathbf{1}}{\cdots O(3)\sim\sim\sim\sim O(4)}\overset{2.68(1)\,\text{Å}}{\cdots} \underset{\mathbf{2a}}{H\text{-}O(1)\sim\sim\sim\sim O(2)}\text{-}H\overset{2.67(1)\,\text{Å}}{\cdots}\underset{\text{Me}}{\underset{|}{O(5)}}\text{-}H\overset{2.59(1)\,\text{Å}}{\cdots}\underset{\mathbf{1'}}{O(3')\sim\sim\sim\sim O(4')}\cdots,$$

where the wavy lines represent relevant molecular skeletons, and bis-amide **1'** is generated from **1** by the 2_1 screw operation ($\frac{1}{2} + x$, $-\frac{1}{2} - y$, $-z$). In the molecular skeleton of **1**, the central aromatic ring and the amide moieties are each planar, their relative orientations being gauged by the torsion angles O(3)-C(27)-C(21)'-C(22) = -114(2)° and O(4)-C(36)-C(24)-C(25) = 109(2)°. As measured by the torsion angle τ [C(1)-C(10)-C(11)-C(12) = -95(1)°] about the inter-ring C(10)-C(11) bond [1.490(13) Å] joining the two β-naphthol moieties, molecule **2a** in the present complex adopts the transoid conformation, in contrast to the cisoid conformation [τ = -78.2(2)° and inter-ring C-C = 1.492(2) Å] observed for **2a** in its 1:1 complex with (*R*)-(+)-methyl *m*-tolyl sulfoxide.$^{4)}$

We thank the Ministry of Education, Science, and Culture of Japan (Grant No. 56460040) and the Ming Yu Cultural Foundation (Grant No. 636011000) for financial support.

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(Received September 12, 1986)