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# A New Lattice Inclusion Host Involving Double-stranded Columns of Diol Molecules [1]

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# A New Lattice Inclusion Host Involving Double-stranded Columns of Diol Molecules [1]

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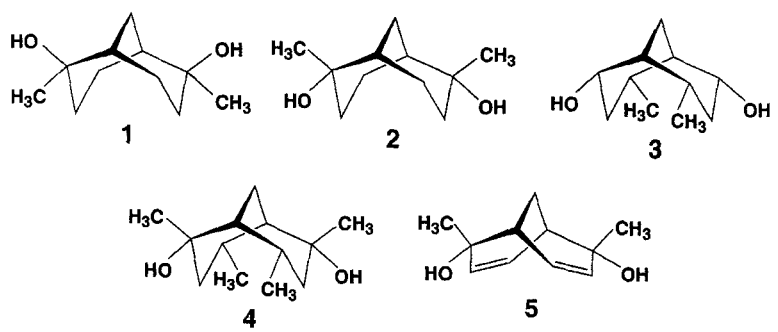
**Crystallization of dialcohol 4 from benzene yields an inclusion compound whose crystal structure [$(C_{13}H_{24}O_2)_2 \cdot (C_6H_6)$, $P2_1/c$, $a$ 7.918(2), $b$ 13.505(2), $c$ 14.924(5) Å, $\beta$ 109.30(1)°, $Z$ 2, $R$ 0.069] shows that the host molecules are present as parallel doubly-stranded columns. Each column is constructed from one strand of (+)-, and a second of (−)-, enantiomers of 4. These two chirally pure strands are linked through a continuous chain of hydrogen bonding ···O—H···O—H···O—H··· to complete the column, and the benzene guests occupy interstitial sites between the parallel columns.**

*Keywords*: Hydroxy groups; Hydrogen bonding; Dialcohols; Host–guest compounds; Crystal structure; Double-stranded structures

## INTRODUCTION

For some time we have been interested in the subtle variations of hydrogen bonding and inclusion properties observed amongst closely related $C_2$ symmetric alicyclic diols [2]. For example, the crystal structure of diol **1** contains ···H—O···H—O···H—O··· chains of hydrogen bonds surrounding threefold screw axes and this compound functions as a potent inclusion host [3]. In marked contrast, the isomeric compound **2** forms $(O—H)_4$ cycles and exhibits no inclusion properties [4].

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Recently we have discovered that diol **3** is an excellent lattice inclusion host for a wide range of guests. It encloses small organic molecules within cages built up from $(O—H)_6$ cycles of hydrogen bonds [5]. In this paper we communicate preliminary information on a further new inclusion host **4** whose molecules assemble using yet another type of hydrogen bonded synthon [6].

## RESULTS AND DISCUSSION

Racemic 2,*endo*-4,6,*endo*-8-tetramethylbicyclo [3.3.1]nonane-*endo*-2,*endo*-6-diol **4** was crystallized from benzene giving long needle-shaped crystals of the inclusion compound $(\mathbf{4})_2 \cdot (C_6H_6)$ which were suitable for X-ray analysis (Fig. 1). Numerical details of the solution and refinement of this structure are presented in Table I. Atomic parameters for the non-hydrogen atoms, and the interatomic distances and angles, are listed in Tables II and III respectively.

In the structure of $(\mathbf{4})_2 \cdot (C_6H_6)$ the hydroxy groups each form one donor and one acceptor hydrogen bond with other diols. Molecules of **4** are linked together to form linear strands containing only (+)- or only (−)-enantiomers. Pairs of strands with opposite chirality are cross-linked in an offset manner through hydrogen bonding to yield double-stranded columns (Fig. 2). Hence the opposite edges of each column are of opposite handedness. A similar type of molecular construction was noted earlier in the crystal structure of diol **5** except that, in that instance, all molecules in a given column had identical chirality [7].

The outer faces of the double-stranded columns of **4** are hydrophobic since all the hydroxy groups are situated in the centre of the column. The benzene guest molecules occupy regions of space between four neighboring diol columns (Figs. 3 and 4). There does not appear to be any specific supramolecular

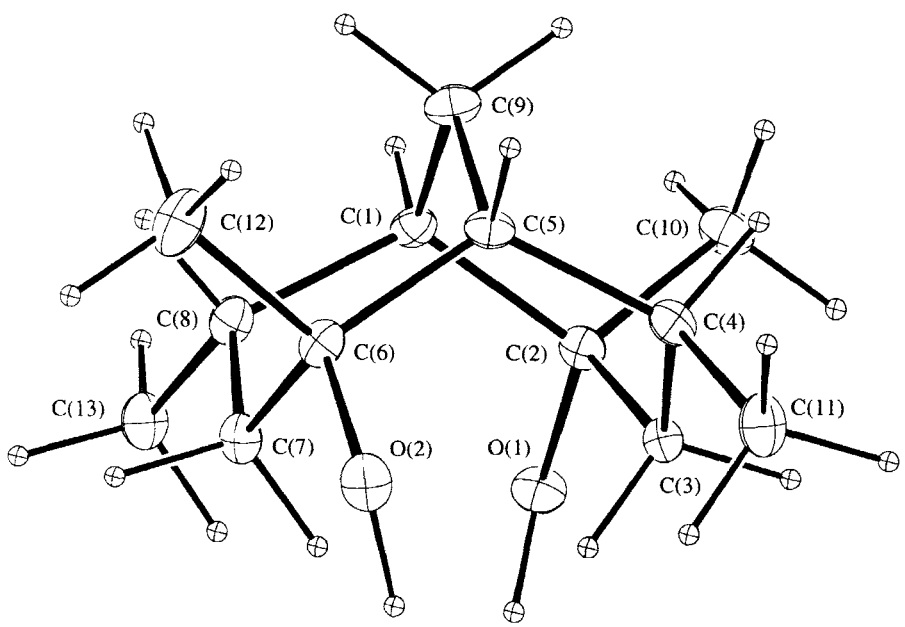


FIGURE 1 Crystallographic numbering system used for the diol **4** in the structure $(\mathbf{4})_2 \cdot (C_6H_6)$.

TABLE I Numerical details of the solution and refinement of the structure $(4)_2 \cdot$(benzene)

| | |
|---|---|
| Formula | $(C_{13}H_{24}O_2)_2 \cdot (C_6H_6)$ |
| Formula mass | 502.8 |
| Space group | $P2_1/c$ |
| $a$/Å | 7.918(2) |
| $b$/Å | 13.505(2) |
| $c$/Å | 14.924(5) |
| $\beta$/° | 109.30(1) |
| $V$/Å$^3$ | 1506.2(7) |
| $T$/°C | 21(1) |
| Z | 2 |
| $D_{calc.}$/g cm$^{-3}$ | 1.11 |
| $\lambda$/Å | MoK$\alpha$, 0.7107 |
| $\mu$/mm$^{-1}$ | 0.066 |
| Scan mode | $\theta/2\theta$ |
| $2\theta_{max}$/° | 50 |
| No. of intensity measurements | 2654 |
| Criterion for observed reflection | $I/\sigma(I) > 3$ |
| No. of independent obsd. reflections | 1182 |
| No. of reflections ($m$) and variables ($n$) in final refinement | 1182<br>152 |
| $R = \Sigma m\|\Delta F\|/\Sigma m\|F_o\|$ | 0.069 |
| $R_w = [\Sigma m_w\|\Delta F\|^2/\Sigma m_w\|F_o\|^2]^{1/2}$ | 0.115 |
| $s = [\Sigma m_w\|\Delta F\|^2/(m-n)]^{1/2}$ | 1.74 |
| Crystal decay | 1 to 0.86 |

synthon operating between host and guest, rather just a summation of many weak hydrophobic interactions.

Our preliminary studies on the new diol host **4** indicate that it forms rather similar lattice inclusion compounds with a number of other guest molecules. The structures of these new materials are currently under investigation.

## EXPERIMENTAL SECTION

### Crystal Structure Solution and Refinement

Reflection data were recorded by using an Enraf Nonius CAD4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromated molybdenum radiation ($\lambda$ 0.7107 Å). Data were not corrected for absorption, as the absorption coefficient was very small. Reflections with $I > 3\sigma(I)$ were considered observed. The structure was determined

TABLE II Atomic parameters for the non-hydrogen atoms in the structure $(4)_2 \cdot (C_6H_6)$. The suffix B indicates the benzene guest molecule

| Atom | $x$ | $y$ | $z$ | $(U_{11}+U_{22}+U_{33})/3$ |
|---|---|---|---|---|
| O(1) | 0.3671(4) | 0.5107(3) | 0.4067(2) | 0.052(1) |
| O(2) | 1.0148(4) | 0.5378(3) | 0.4106(3) | 0.060(1) |
| C(1) | 0.4675(6) | 0.5923(4) | 0.2847(3) | 0.044(1) |
| C(2) | 0.4286(6) | 0.4937(4) | 0.3261(3) | 0.043(1) |
| C(3) | 0.5860(6) | 0.4244(4) | 0.3599(3) | 0.041(1) |
| C(4) | 0.6994(6) | 0.4180(4) | 0.2960(3) | 0.045(1) |
| C(5) | 0.7500(6) | 0.5209(4) | 0.2700(3) | 0.043(1) |
| C(6) | 0.8660(6) | 0.5904(4) | 0.3473(4) | 0.045(1) |
| C(7) | 0.7646(6) | 0.6366(4) | 0.4086(4) | 0.046(1) |
| C(8) | 0.5751(6) | 0.6721(4) | 0.3533(4) | 0.048(1) |
| C(9) | 0.5697(6) | 0.5716(4) | 0.2141(3) | 0.054(2) |
| C(10) | 0.2700(6) | 0.4421(4) | 0.2515(4) | 0.061(2) |
| C(11) | 0.8522(7) | 0.3440(4) | 0.3340(4) | 0.065(2) |
| C(12) | 0.9443(7) | 0.6707(4) | 0.3014(5) | 0.074(2) |
| C(13) | 0.4853(7) | 0.7200(4) | 0.4179(4) | 0.057(2) |
| C(1)B | 0.0891(18) | 0.5860(7) | 0.0060(6) | 0.153(5) |
| C(2)B | −0.0597(19) | 0.5824(8) | 0.0306(5) | 0.149(6) |
| C(3)B | −0.1489(8) | 0.4964(13) | 0.0246(5) | 0.149(5) |
| C(4)B | −0.0891(18) | 0.4140(7) | −0.0060(6) | 0.153(5) |
| C(5)B | 0.0597(19) | 0.4176(8) | −0.0306(5) | 0.149(6) |
| C(6)B | 0.1489(8) | 0.5036(13) | −0.0246(5) | 0.149(5) |

TABLE III Interatomic distances (Å) and angles (°), including dimensions associated with the hydrogen bonding. The suffix B indicates the benzene guest molecule

| | | | |
|---|---|---|---|
| O(1)–C(2) | 1.457(5) | C(4)–C(11) | 1.527(7) |
| O(2)–C(6) | 1.432(5) | C(5)–C(6) | 1.535(7) |
| C(1)–C(2) | 1.542(6) | C(5)–C(9) | 1.554(7) |
| C(1)–C(8) | 1.536(7) | C(6)–C(7) | 1.535(6) |
| C(1)–C(9) | 1.551(6) | C(6)–C(12) | 1.520(7) |
| C(2)–C(3) | 1.506(6) | C(7)–C(8) | 1.531(6) |
| C(2)–C(10) | 1.542(6) | C(8)–C(13) | 1.520(7) |
| C(3)–C(4) | 1.514(6) | C(1)B–C(2)B | 1.346(5) |
| C(4)–C(5) | 1.531(7) | | |
| O(1)···O(2)[a] | 2.833(4) | O(1)···O(1)[b] | 2.898(4) |
| O(2)···O(2)[c] | 2.939(4) | | |
| C(2)–C(1)–C(8) | 118.6(4) | C(4)–C(5)–C(9) | 105.3(4) |
| C(2)–C(1)–C(9) | 109.5(4) | C(6)–C(5)–C(9) | 110.5(4) |
| C(8)–C(1)–C(9) | 106.3(4) | O(2)–C(6)–C(5) | 110.5(4) |
| O(1)–C(2)–C(1) | 111.1(4) | O(2)–C(6)–C(7) | 106.7(4) |
| O(1)–C(2)–C(3) | 106.6(3) | O(2)–C(6)–C(12) | 106.4(4) |
| O(1)–C(2)–C(10) | 104.6(4) | C(5)–C(6)–C(7) | 113.3(4) |
| C(1)–C(2)–C(3) | 114.7(4) | C(5)–C(6)–C(12) | 109.2(4) |
| C(1)–C(2)–C(10) | 108.9(4) | C(7)–C(6)–C(12) | 110.5(4) |
| C(3)–C(2)–C(10) | 110.3(4) | C(6)–C(7)–C(8) | 114.7(4) |
| C(2)–C(3)–C(4) | 114.9(4) | C(1)–C(8)–C(7) | 111.7(4) |
| C(3)–C(4)–C(5) | 111.6(4) | C(1)–C(8)–C(13) | 116.7(4) |
| C(3)–C(4)–C(11) | 111.4(4) | C(7)–C(8)–C(13) | 111.8(4) |
| C(5)–C(4)–C(11) | 116.6(4) | C(1)–C(9)–C(5) | 107.9(3) |
| C(4)–C(5)–C(6) | 120.4(4) | C(2)B–C(1)B–C(6)B | 120.0(0) |
| C(2)–O(1)···O(2)[a] | 129.6(4) | C(2)–O(1)···O(1)[b] | 116.3(4) |
| O(1)[b]···O(1)···O(2)[a] | 113.6(3) | C(6)–O(2)···O(2)[c] | 118.5(4) |
| C(6)–O(2)···O(1)[d] | 130.7(4) | O(1)[d]···O(2)···O(2)[c] | 110.4(3) |

Symmetry operators
[a] $-1+x, y, z$.
[b] $1-x, 1-y, 1-z$.
[c] $2-x, 1-y, 1-z$.
[d] $1+x, y, z$.

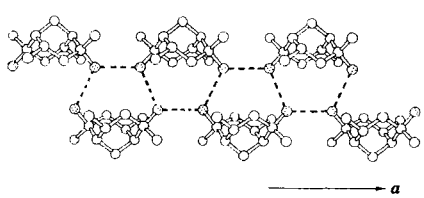


FIGURE 2 Part of a double-stranded column of diol molecules in the crystal structure of $(\mathbf{4})_2 \cdot (C_6H_6)$. The two parallel, but offset, strands are constructed from molecules of opposite chirality. Oxygen atoms are designated by stippling and hydrogens are omitted. Hydroxy group hydrogen bonding is indicated using dashed lines.

by direct phasing (SIR92 [8]) and Fourier methods. Hydrogen atoms of the hydroxy groups were disordered over two positions with equal occupancy, both of which resulted in

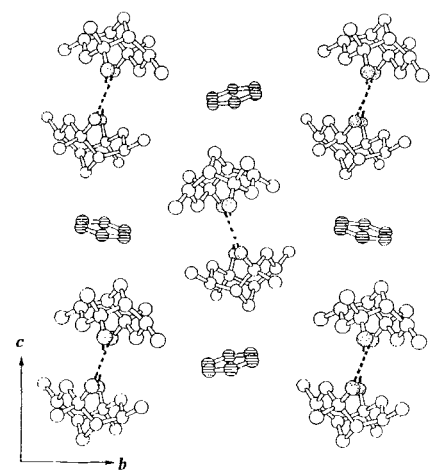


FIGURE 3 Projection view of $(\mathbf{4})_2 \cdot (C_6H_6)$ in the *bc* plane showing a slice through the doubly-stranded columns of **4** molecules and benzene guests. The carbon atoms of the guests are hatched.

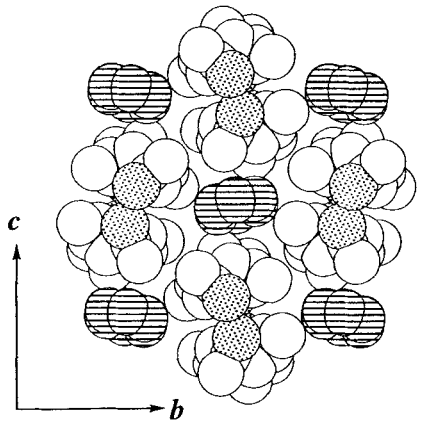


FIGURE 4 Similar view of $(\mathbf{4})_2 \cdot (C_6H_6)$ to that in Figure 3, but using space filling representation to show how the benzene guests pack between four neighboring diol columns.

hydrogen bonding. The hydrogen atoms were positioned along the O···O vectors at a distance of 1.0 Å. Other hydrogen atoms were included in calculated positions. The benzene guest was located around a centre of symmetry and was refined as a rigid group. Positional parameters for the other non-hydrogen atoms were refined anisotropically using full-matrix least squares [9]. The thermal motion of the benzene molecule was described by a 12 parameter TL group (where T is the translation tensor and L is the libration tensor). Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [10], and a DEC Alpha AXP workstation was used for calculations.

Supplementary data available: ORTEP plot showing the crystallographic numbering system used, hydrogen atom coordinates, torsional angles, and structure factors.

### *Acknowledgement*

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### *References*

[1] This paper celebrates the 67th birthday of Fumio Toda and his outstanding contributions to organic solid state chemistry. *A guest never forgets the host who had treated him kindly*, Homer. (9th century BC). *Odyssey*, 15.
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