#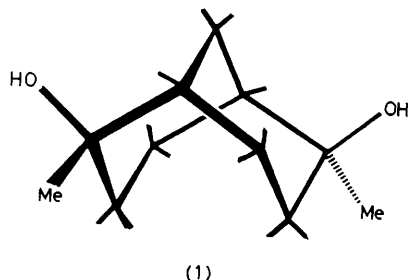 Helical Canal Inclusion Complexes Formed by a Bicyclic Diol; X-Ray Crystal Structure of exo-2, exo-6-Dihydroxy-2,6-dimethylbicyclo-[3.3.1]nonane–Ethyl Acetate Inclusion Complex

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Summary An X-ray crystal structure determination shows that, as a consequence of helices of hydrogen bonds, crystalline exo-2,exo-6-dihydroxy-2,6-dimethylbicyclo-[3.3.1]nonane comprises a network of separate helical canals, lined only with hydrocarbon hydrogen atoms, which trap a variety of guest molecules.

The crystal structure† reveals a trigonal network of diol molecules linked by hydrogen bonds, as shown in projection in Figure 1. All hydrogen bonds occur along narrow channels, parallel to the needle axis of the crystal, and are related by crystallographic threefold screw axes. As a

exo-2,exo-6-Dihydroxy-2,6-dimethylbicyclo[3.3.1]non-ane (1), prepared by hydration of 2,6-dimethylenebicyclo-[3.3.1]nonane[1] using Brown's mercuric acetate procedure,[2] crystallises from ethyl acetate as long trigonal needles with elemental analysis consistent with the composition diol (1):ethyl acetate = 3:1. The presence of guest ethyl acetate in this solid was confirmed by i.r. (mull) and $^{13}$C n.m.r. [$(CD_3)_2SO$ solution] spectroscopy.
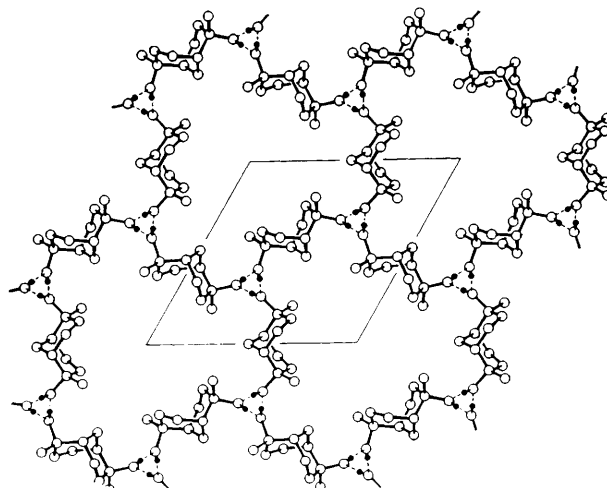
Figure 1. Projection view, parallel to the threefold screw axes, of the diol host network: the filled circles and dotted lines represent OH hydrogen atoms and hydrogen bonds respectively. Hydrocarbon hydrogen atoms are omitted.
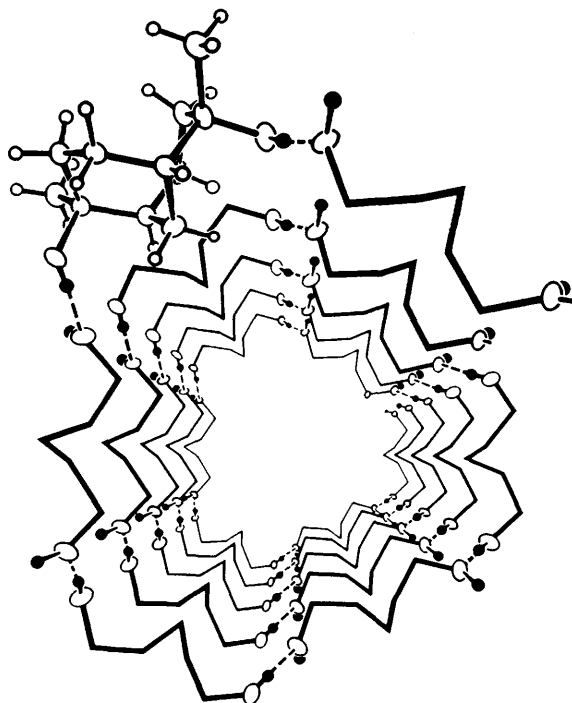
(1)

FIGURE 2. Perspective view of the helical sequence of hydrogen bonded diol molecules in one canal: all except one diol molecule are represented diagrammatically as the bridge linkage of the two OH groups.

result of this hydrogen bonding there exists another set of wide and open helical canals,[3] each of which also possesses crystallographic threefold screw symmetry. Figure 2 shows, diagrammatically and in exaggerated perspective, the double helix (pitch $2c$) of hydrogen-bonded diol molecules which constitute one such canal. It is significant that the canal is lined only with saturated hydrocarbon hydrogen atoms (not marked on Figure 1). The channel defined by the van der Waals boundaries of these hydrogen atoms is approximately triangular, side ca. 6·3 Å, in cross-section.

The ethyl acetate guest is strongly disordered in its location in the canal, and contributes only to low-angle $X$-ray scattering. Nevertheless, forcing conditions (dynamic vacuum at 60 °C) are required to remove ethyl acetate. Similar crystalline inclusion complexes occur with guests as diverse in functionality and shape as chloroform, toluene, dioxan, and acetone. Further study of the scope of guest inclusion in (1) and related compounds is under way.

The hydrogen-bonded host structure is not dependent on the presence of the guest, and occurs without included solvent when the diol is crystallised from acetonitrile. We note that variation of the pitch of the hydrogen bonded canal would incur minor change in the hydrogen bond dimensions, but could affect the diameter of the guest canal.

[1] S. Landa and J. Kiefmann, Coll. Czech. Chem. Comm., 1970, 35, 1005; R. Bishop and A. E. Landers, Austral. J. Chem., submitted for publication.
[2] H. C. Brown and P. Geohegan, J. Amer. Chem. Soc., 1967, 89, 1522; H. C. Brown and W. J. Hammar, ibid., 1524.
[3] For other canal complexes see: J. F. Brown, Scientific American, 1962, 207, 82; L. C. Fetterly, in 'Non-Stoichiometric Compounds,' ed. L. Mandelcorn, Academic Press, New York, 1964, p. 491.