Topological Equivalences between Organic and Inorganic Crystal Structures: 1,3,5,7-Tetrahydroxyadamantane and Caesium Chloride

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The crystal structure of 1,3,5,7-tetrahydroxyadamantane has a network of O–H···O hydrogen bonds which is topologically equivalent to the eight-coordinated net in the CsCl family of solids.

The study of organic[1,2] and inorganic[3,4] crystal chemistry has proceeded, for the most part, along independent lines. Of course, propositions such as the need to fill space most economically and the conflict between close-packing and directionality are of universal applicability. However, when these are considered along with the many differences between the molecular and ionic building blocks, characteristic respectively of organic and inorganic crystals, any possible similarity between these two vast groupings of substances seems to rapidly disappear.

However, there are certain instances when it is most profitable to seek similarities between organic and inorganic crystal structures. Naturally, such similarities must be purely topological in nature, equivalences being found between intermolecular interactions in organic solids (≈ 40 kJ mol^{-1}) and ionic and covalent bonds in inorganic solids (≈ 400 kJ mol^{-1}). For example, 1,3,5,7-tetracarboxyadamantane **1**[5] and 1,3,5,7-tetraiodoadamantane **2**[6] have crystal structures which are topologically related to diamond; the hydrogen-bonded dimer rings in **1** and I···I interactions in **2** replace the C–C bonds in diamond with the adamantyl skeleton becoming a 'super'-carbon atom. Again, the 1 : 1 complex between hexamethylenetetramine **3** and CBr_4 is analogously related to cubic ZnS with N···Br interactions instead of Zn–S covalent bonds,[7] while the 1 : 1 : 1 complex of CBr_4 **3** and 1,3,5,7-tetrabromoadamantane may be likened to LiAlSi.[8]

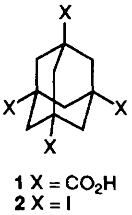
Such analogies, however, are not just formal niceties and we describe, in this communication, the crystal structure of 1,3,5,7-tetrahydroxyadamantane **4**, the packing of which is clearly understood only when it is simplified and reduced in terms of its hydrogen-bond network. Compound **4** is of interest from the crystal engineering viewpoint because of its similarity to **1** and **2**.

Compound **4** was synthesised from adamantane, using known procedures[9] and recrystallised from glacial AcOH to yield well-formed prismatic crystals, mp 317 °C. In general, the combination of high molecular symmetry with strong hydrogen-bonding compulsions can lead to complex networks and compound **4** proved to be no exception.† The crystal structure is intricate with an unusual space group, *Pbcn*, and molecules both in general and special positions. The crystal structure has several strong hydrogen bonds (O···O, O–H···O: 2.719, 170.3; 2.763, 170.4; 2.739, 177.2; 2.722, 175.3; 2.785 Å, 177.6°) and our attempts to decipher the packing by conventional methods (plots, geometrical calculations) proved uniformly unsuccessful.

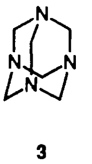
As an alternative strategy, we sought at this stage to develop a structural analogy between **4** and a simple inorganic structure. An iodo group in crystalline **2** has a supramolecular valence of one, that is each molecule is joined to four others with I···I interactions leading to a four-connected tetrahedral net.[4] A hydroxyl group, however, has a supramolecular valence of two, corresponding to a pair of hydrogen bonds, one donated and the other accepted.[10]‡ Therefore the packing of **4** should be derivable in terms of an eight-connected net. So, we simplified the crystal structure of **4** by reducing the molecules to spheres and displaying only the hydrogen bond connections. The result is shown in Fig. 1 which is easily recognisable as a quasi-BCC packing.§ If the two symmetry-independent molecules shown in red and blue are taken as distinct species, a not unwarranted assumption given that their OH group conformations are quite different, one obtains a type of CsCl structure (actually Cr_2Al)[4] where the eight-fold coordination is of the type $(B_4)R(B_4)$ for the special-position molecule and $(B_4)B(R_4)$ for the general-position molecule.

The structure diagram may now be relaxed to show the details of the hydrogen bonding (Fig. 2) and finally the complete structure (Fig. 3). All the H-atoms are ordered and the hydrogen bonds have geometrical features within the typical distance and angle ranges.

This kind of analysis has several utilitarian features: (i) complex hydrogen bond and other networks in molecular crystals can be described with a very simple, classical terminology and without recourse to new and still untested schemes for structural decoding. (ii) The method is general. For example, the crystal structure of pentaerythritol[11] which has a chemical functionality similar to **4** can also be expressed in terms of an eight-connected hydrogen-bonded net. However,



1 X = CO_2H
2 X = I
4 X = OH



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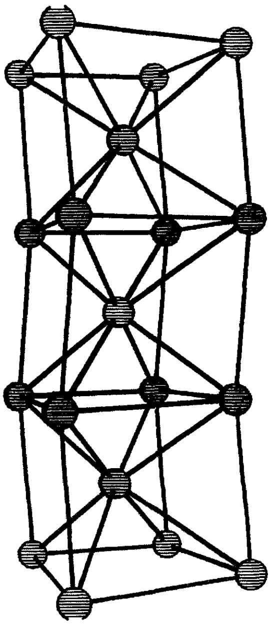

Fig. 1 The crystal structure of 1,3,5,7-tetrahydroxyadamantane **4** showing its topological relationship to the CsCl family. The molecules are represented as blue (general position) and red (special position) spheres while the hydrogen bonds are shown as lines. The pseudo-cubic unit cells are shown.

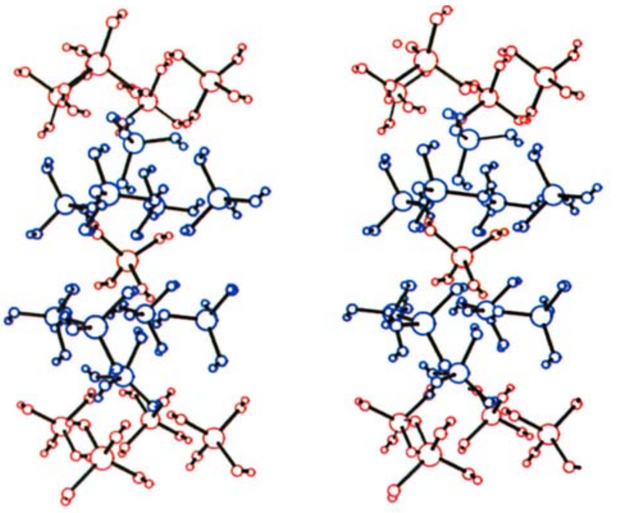

Fig. 2 Crystal structure of **4** with the hydrogen bonds explicitly shown. Notice the eight-coordination of the molecules. Blue and red molecules denote symmetry designations as in Fig. 1.

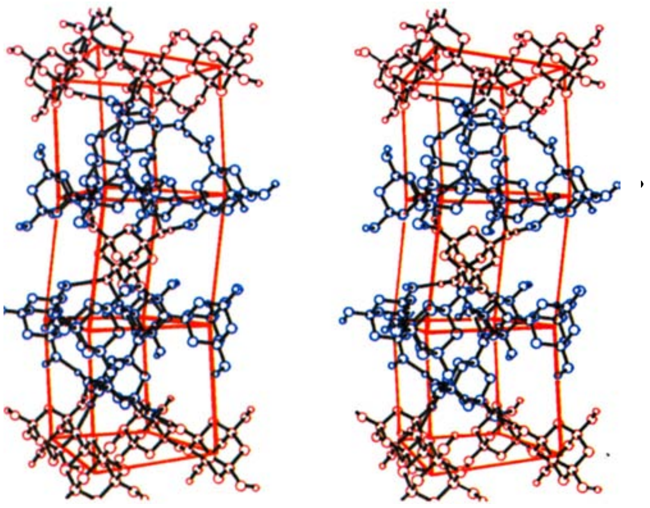

Fig. 3 Crystal structure of **4** showing the molecules in full. Notice that the red (special position) molecules lie on a two-fold axis. The pseudo-cubic unit cells are shown.

this net (Fig. 4) is different in that any given pair of adjacent nodes (molecules) is connected by two hydrogen bonds rather than by just one as in the CsCl network found in **4**. (iii) Structures can be examined in a new perspective. For instance the series, adamantane (twelve-coordinated), **3** and **4** (eight-coordinated), **1** and **2** (four-coordinated) reveals the changing balance between close-packing and directionality in a series of spherical molecules.

In conclusion it may be stated that the always present and yet almost always hidden similarity between organic and inorganic crystal structures is more easily revealed for some symmetrical organic molecules and may provide a new handle in the study of complex crystal packing arrangements.

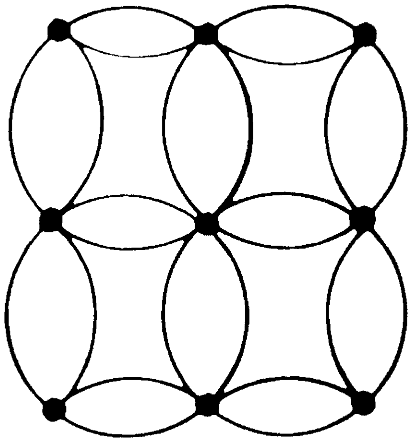

Fig. 4 Eight-connected net in the layered crystal structure of pentaerythritol. The black spheres represent molecules and the curved lines hydrogen bonds.

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Footnotes

† *Crystal data for compound* **4**, $C_{10}H_{16}O_4$, M = 200.2, orthorhombic, space group *Pbcn*, a = 24.4809(6), b = 10.9912(2), c = 11.2429(2) Å, V = 3025.2(1) Å^3, D_c = 1.32 g cm^{-3}, Z = 12, μ_{Cu} = 8.03 cm^{-1}, crystal size 0.28 × 0.36 × 0.50 mm, $2\theta_{max}$ = 140°, min and max transmission factors 0.73 and 0.85. The number of reflections considered observed was 2561 out of 2871 unique data. Final residuals R, R_w were 0.036, 0.068 for the observed data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ In **4**, the two hydrogen bonds associated with an –OH group originate from –OH groups on different neighbouring molecules.

§ Unit-cell constants for the pseudo-cubic unit cells in Fig. 1: 8.81, 8.68, 8.13 Å, 78.5, 80.7, 88.7° (top and bottom) 8.68, 8.68, 8.30 Å, 94.0, 80.0, 80.7° (centre).

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