# The Geometrical Basis of Crystal Chemistry. Part 4

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Structures based on a single net of low coordination number are unlikely to occur owing to their low densities. A study has therefore been made of systems of two or more interpenetrating three-dimensional networks. Some of the possible structure types are illustrated.

## Structures consisting of interpenetrating nets

Three-dimensional nets of low coordination number have necessarily rather open structures. If the points of a net are the centres of spheres of unit radius in contact with $p$ neighbours the volume occupied per sphere may be calculated if we assume a particular spatial arrangement of the links (lines joining centres of adjacent spheres) around each point. For close-packing ($p = 12$), for the body-centred cubic structure ($p = 8$), and for spheres at the points of a primitive cubic lattice ($p = 6$) the packing volumes are respectively 5·66, 6·16, and 8·00, as compared with 4·19, the volume of one sphere. For the simplest 4-connected Net 1 (diamond net) the value is 12·3, and for the most symmetrical configurations of the 3-connected Nets 1 and 2, 22·6 and 18·0 respectively, though the tetragonal Net 2 can be sheared parallel to (100) giving a higher density.

It is not to be expected that three-dimensional atomic nets with coordination number as low as three will be stable, and in fact no atomic 3-coordinated structure is known. Boron, for example, with packing volume 12·7 (compare diamond 12·3) forms a 5-coordinated structure (Godfrey & Warren, 1950); compare the 5-coordinated boron framework in $CaB_6$. The simplest 4-connected net occurs as the structure of diamond and isomorphous crystals. The structure of cristobalite arises by placing Si atoms at the points of the diamond net and O atoms between, but off the straight lines joining, each pair of nearest Si atoms. If the distance between the points of the net is increased still further, for example, by placing O atoms at the points and Cu atoms midway along the links, we find a new type of structure consisting of two identical interpenetrating frameworks which are not cross-linked by any primary bonds.

| | | | |
|---|---|---|---|
| Diamond: | C–C | 1·54 Å | Single 4-connected |
| Cristobalite: | Si–O–Si | 3·08 Å | Net 1 |
| Cuprite: | O–Cu–O | 3·69 Å | Two interpenetrating Nets 1 |

A similar change in structure type is observed in dihydroxy compounds the structures of which, as we have shown in Part 3,* can be represented by 3-connected nets. In crystalline hydrogen peroxide the

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* Previous parts: Wells, 1954a, b, c.

molecules are linked by O–H–O bonds into a single net. In $m$-dihydroxybenzene (resorcinol) also this is the case, but the $p$-dihydroxy compound (quinol) forms a structure consisting of two interpenetrating nets. It must, however, be noted that quinol also adopts other structures (e.g. $\gamma$-quinol has a layer structure) and that the even longer molecule of 4:4′-dihydroxydiphenyl also adopts a layer structure, showing that the nature of the structure is certainly not simply a question of the distance between the OH groups in the molecule (see later).

These considerations do, however, suggest that some of the very open frameworks may, because of their low densities, occur in crystals as systems of two or more interpenetrating nets. In general a system of two or more interpenetrating nets in which all bonds are equal in length is not a permissible arrangement because the distance between points of different nets becomes equal to or less than the distance between connected points of a net. For example, if two identical 3-connected Nets 1 (Figs. 6(a) and 7, Part 1) interpenetrate, each point is found to be equidistant from six others, though interpenetration of this enantiomorphic net with its mirror image is possible without raising the coordination number of the points.

The points of the cubic form of Net 1 are 8(a) of $I4_13$ (Fig. 1(a)); the equivalent positions 16(b) of $Ia3d$ (Fig. 1(b)) can be joined up to form two interpenetrating but independent Nets 1, one left- and the other right-handed. The equivalent positions 24(c) of $Ia3d$ are related in a similar way to 12(c) of $I4_13$ (Fig. 1(c) and (d)). The latter form an enantiomorphic 4-connected net, the former a system of two interpenetrating nets or a 'three-dimensional racemate'. Nets in which all the bonds are equal in length are, however, of rather academic interest because when we represent the structure of hydrogen peroxide or resorcinol as a 3-connected net one-third of the links in the net represent OH–OH axes of molecules and the remainder intermolecular O–H–O bonds. In $H_2O_2$ the former are shorter than the latter; in resorcinol, and generally in more complex molecules, the reverse is true.

We now examine the structural possibilities for 3-connected nets in which one-third of the bonds are appreciably longer than the remainder. Typical molecules would be a long dihydroxy molecule
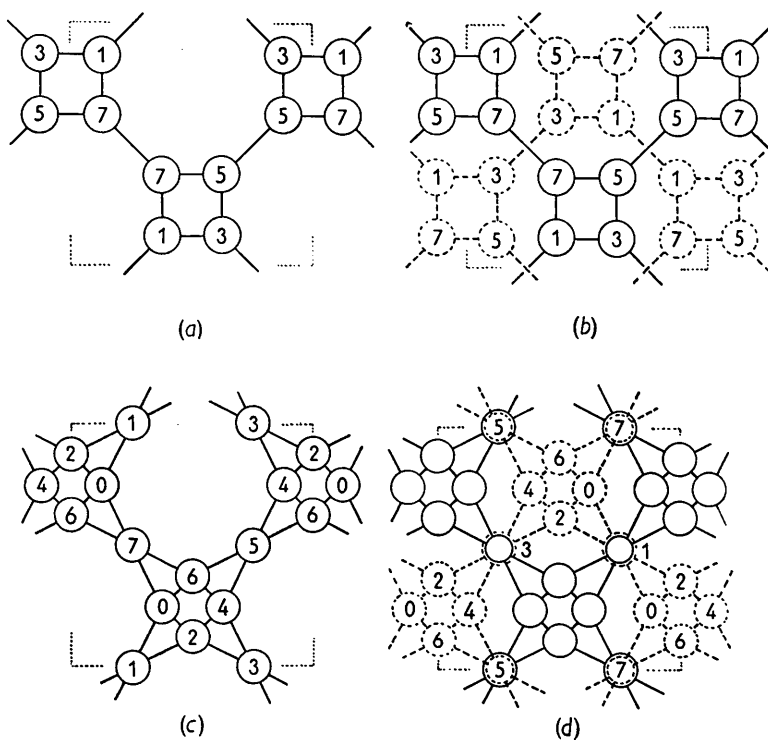
Fig. 1. Projections of cubic nets on (001). (a) 8(a) of $I4_13$. (b) 16(b) of $Ia3d$. (c) 12(c) of $I4_13$. (d) 24(c) of $Ia3d$. Figures indicate heights in terms of $c/8$.
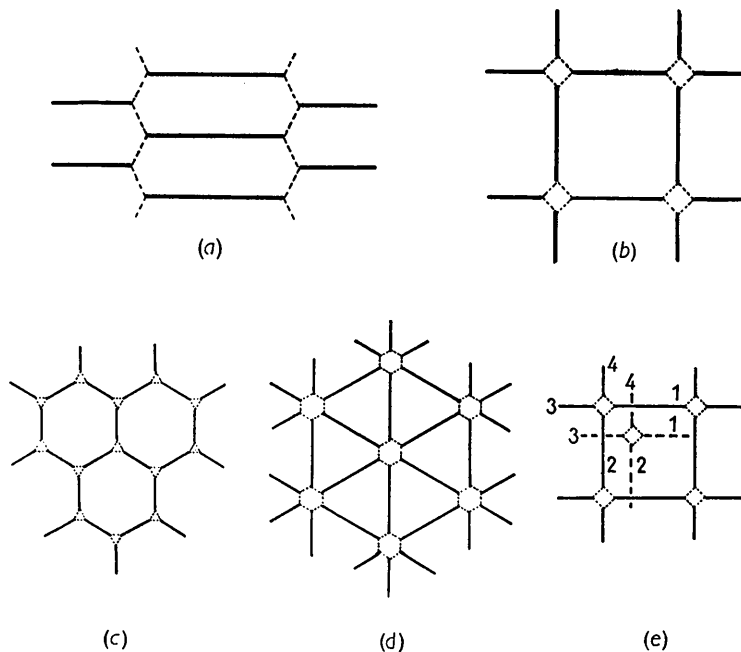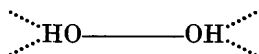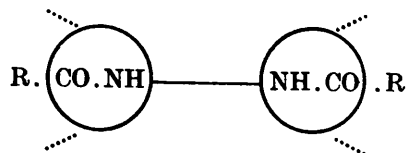


Fig. 2. Structure types for hydrogen-bonded crystals; screw-axes all parallel.

:HO————OH:

or a long molecule containing the grouping –CO.NH–
at each end. Since the distance C–N is short compared
with the length of the molecule we may write

R.(CO.NH)————(NH.CO).R

and regard the structure as a 3-connected net.

Two main classes of net are likely to be important in such structures.

### (1) The short (O–H–O or N–H–O) bonds are arranged around screw-axes (2-, 3-, 4-, or 6-fold)

(i) *Screw-axes are all parallel.*—These possibilities are set out in Fig. 2. (a) is simply the plane hexagonal net, which occurs in the layer structures of γ-quinol and 4:4′-dihydroxydiphenyl. The simplest nets corresponding to the projections (b), (c) and (d) are respectively the uniform 3-connected Nets 1, 5 and 6, and 21 of Part 1. Interpenetration of series of nets of this type, as shown at (e) for the net (b), will probably not occur. In (e) the molecules radiating from a helix are at heights 0, $c/4$, $c/2$, and $3c/4$ (shown as 1, 2, 3, and 4), so that the vertical clearance between molecules of different nets is $c/4$. The value of $c$ depends on the inclination to the horizontal of, for example, the O–H–O bonds around the helix; $c/4$ must therefore be less than about 2·7 Å, with a probable value of about 1½ Å (which is the average value in α-resorcinol). For molecules with only terminal OH groups we can therefore eliminate this type of interpenetrating system. However, for molecules containing terminal –CO.NH– groups, or better still –CO.(CH$_2$)$_n$.NH– groups, the pitch $c$ of the helix could be large enough to permit this type of structure, though this mode of packing does not seem very probable. In fact, for a helix of moderate pitch there may be good packing (in vertical planes) of molecules separated by $c$, as sketched diagrammatically in Fig. 7(a). As the pitch of the helix increases
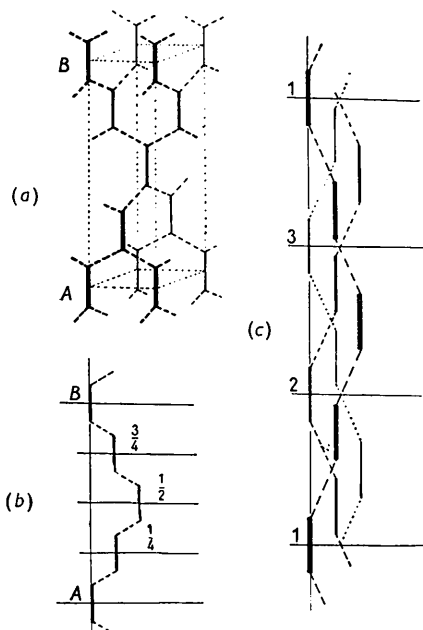
it may become possible to have two or more intertwining helices around the same axis.

(ii) *Screw-axes not parallel.*—The simplest of these nets, Net 2, is illustrated in Fig. 8 of Part 1 and in Fig. 3 for the case when all links are equal in length. Let the vertical links be the long axes of molecules (as in Fig. 2(a) for the plane net). If we join the upper end of one molecule to the lower ends of the two adjacent molecules related by a translation of $a/2+c/4$ we obtain the ordinary form of Net 2, in which all the molecules belong to one connected system (compare the elevation of Fig. 3(b)). Suppose now that the molecules are much longer in relation to $c$. We may alternatively join a molecule to its two neighbours related by a translation of $a/2+3c/4$. The molecules $A$ and $B$ separated by one unit translation along the $c$ axis do
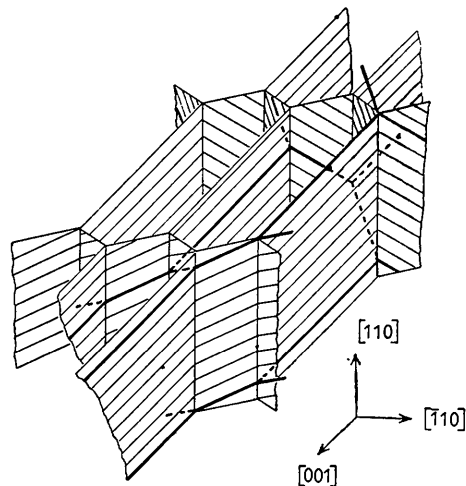


Fig. 4. System of interpenetrating 3-connected Nets 2. The axes show the relation of this diagram to the tetragonal unit cell of the single net of Fig. 3(a).

not now belong to the same net; instead, the structure consists of *three* interpenetrating networks, as shown in the diagrammatic elevation of Fig. 3(c).

Since the 3-connected Net 2 projects as the simple plane hexagonal net when viewed along a tetragonal [110] axis it follows that an indefinite number of identical nets can interpenetrate if each is related to its neighbours by a small translation along [110]. For long molecules linked together by hydrogen bonds a single net projects as in Fig. 2(a), though in the actual net the zigzag chains of hydrogen bonds are inclined to the plane of projection so that the angle between. the axes of adjacent chains in the diagram is 90°. The same projection represents the system of interpenetrating nets, a perspective view of which is shown in Fig. 4. The structure is like a honeycomb but with elongated hexagonal cells. The long walls of the tunnels are formed of molecules stacked vertically one above the other with their long axes parallel, and the short walls contain the hydrogen bonds inclined (ideally) at 45° to the horizontal.
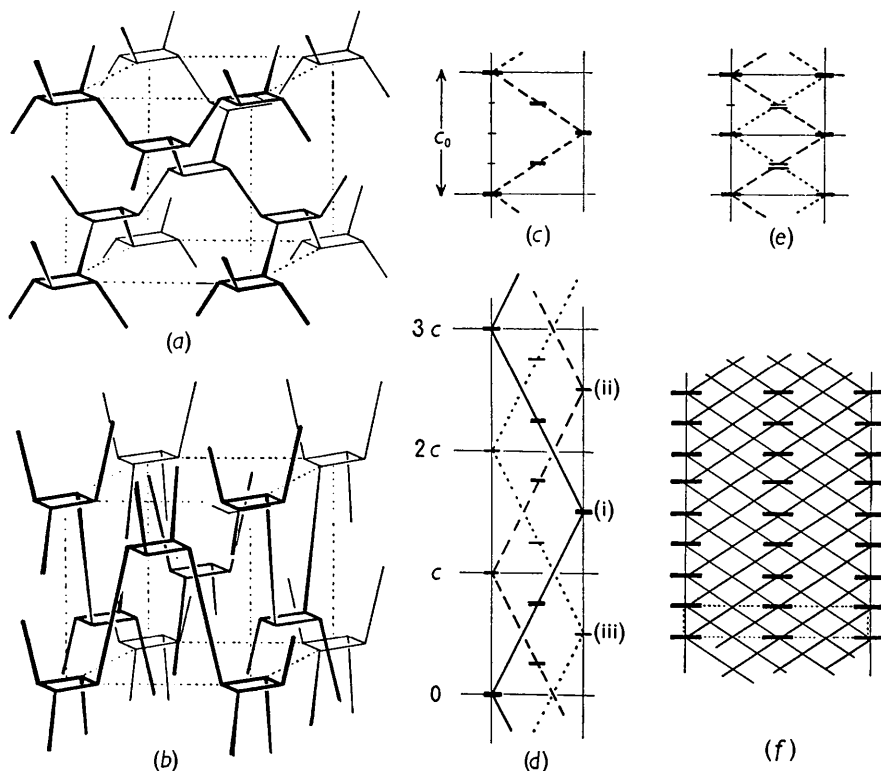


Fig. 3. Structures based on the 3-connected Net 2.

Fig. 5. Structures based on the 3-connected net of Fig. 11 of Part 1.

(2) *The short* (O–H–O *or* N–H–O) *bonds form closed polygons*

The net of Fig. 5(a) is derived from the diamond net by replacing each point by a square and then connecting up the corners of squares related by translations in the vertical direction of $c/4$. (This net is the tetragonal analogue of Net 9, with which we deal shortly.) Let each square represent a closed circuit of hydrogen bonds and each sloping line the long axis of a molecule. As in the case of Net 2, we could alternatively connect the corners of squares related by vertical translations of $3c/4$, giving a structure consisting of three independent interpenetrating nets. We show these two possibilities in Fig. 5(a) and (b) and as diagrammatic elevations at (c) and (d). Both structures have the same cell dimensions and the same number (8) of molecules in the unit cell. In (a) a molecule extends from $c = 0$ to $c = \frac{1}{4}$ and there are 8 complete molecules in the unit cell; in (b) a molecule extends from $c = 0$ to $c = \frac{3}{4}$, and the 8 molecules per cell are made up as follows:

Net (i):   2 whole molecules and 2 ($\frac{1}{4}$ molecules)
Net (ii):  2 whole molecules and 2 ($\frac{1}{4}$ molecules)   total 8
Net (iii): 4 ($\frac{2}{4}$ molecules)

Each of the structures of Fig. 5(a) and (b) could give rise to more complex structures because an indefinite number of nets could start off at heights between 0 and c. The number of these would be limited only by the length of the molecule and by contacts between

non-bonded atoms. The first of these compound structures derived from (a) has two interpenetrating nets, and the crystallographic repeat distance along the vertical axis has dropped to $c/2$ (Fig. 5(e)). For $n$ interpenetrating nets the repeat distance is $c/n$ and the unit cell (dotted rectangle in Fig. 5(f)) contains $n(1/n\text{th}$ parts of molecules).

Quite similar considerations apply to the 3-connected Net 9, which results from placing hexagons at the points of a primitive lattice with their planes parallel to (111), the corners of the hexagons being joined up as in Figs. 6(d) and 11 of Part 1. The hexagons may represent closed circuits of six O–H–O bonds which are linked by lines representing the long axes of molecules of a dihydroxy compound. The single net may be represented by the diagrammatic elevation of Fig.
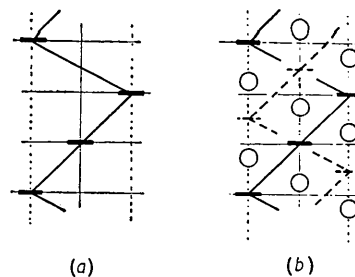


Fig. 6. Diagrammatic elevations of (a) single Net 9 of Fig. 16 of Part 1, (b) two interpenetrating nets separated by foreign molecules (shown as circles).
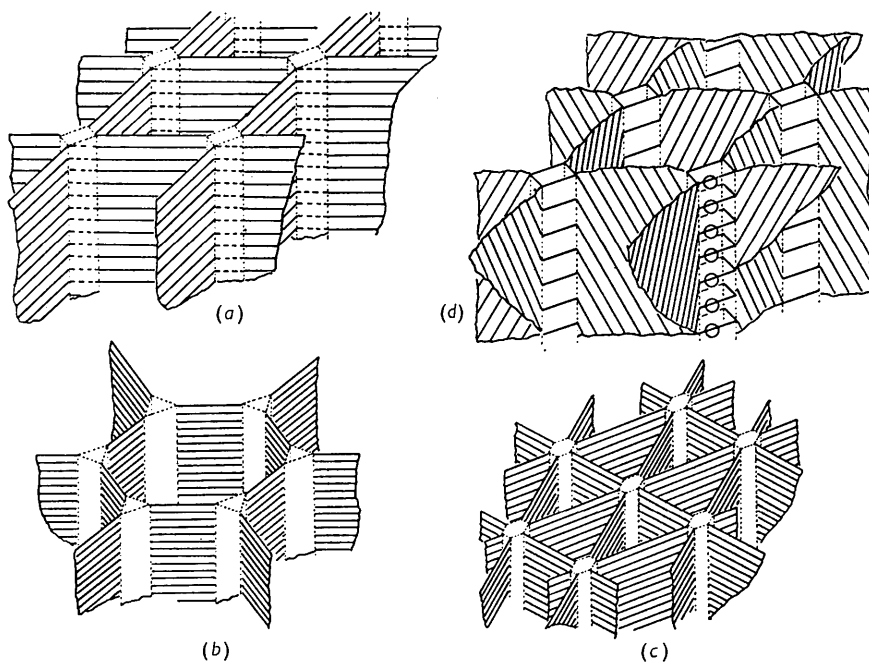
Fig. 7. Four general structure types for long molecules linked by hydrogen bonds into three-dimensional framework structures.

6(a). Fig. 6(b) shows two independent interpenetrating nets, the short horizontal lines representing hexagons viewed end-on. This is the idealized structure of β-quinol, consisting of identical interpenetrating Nets 9; it is at present the only known example among organic compounds of a crystal structure consisting of more than one net. It is possible that compounds such as 4:4'-dihydroxydiphenyl might form such structures if crystallized in the presence of suitable molecules. Normally hydroquinone forms the structure of Fig. 6(b) only in the presence of molecules which act as 'spacers' between the hexagons of the two nets, and it seems likely that foreign molecules of various sizes may be necessary to the stability of these compound framework structures.

## Some new structure types

For rather long molecules the structures arising from helical arrays of hydrogen bonds and from closed circuits of hydrogen bonds become very similar as regards their general nature, as is shown in Fig. 7. (a), (b) and (c) show the structures projecting as (b), (c) and (d) of Fig. 2, while (d) represents a series of interpenetrating nets of the type of Fig. 5(f) containing closed polygons (squares) of hydrogen bonds. If successive polygons of hydrogen bonds along a vertical axis are separated by foreign molecules (shown as circles in Fig. 7(d)) this is a limiting case of a 'clathrate' compound of the β-quinol type.

The structures of Fig. 7 contain prismatic tunnels running through the crystal, the walls consisting of layers of molecules. Of these structures only (a) and (d) can shear to become more compact, the section of a tunnel becoming a rhombus. In spite of the apparent low density of these structures they might occur if suitable groups are placed along the length of the molecule, for example, $-SO_3^-$, $-COO^-$, etc. These could project into the tunnels, the filling of which would be completed by metal or other cations and solvent molecules.

In the discussion of the interpenetration of nets containing small polygons we have considered in detail only two 3-connected nets, which have been illustrated in Figs. 11 and 16 of Part 1. In these the planes of all the polygons are parallel, so that the nets are essentially uniaxial in character. (This is therefore true also of the systems of interpenetrating nets illustrated in Fig. 7, in which the tunnels through the structures are all parallel to one direction only.) These nets are derived by placing squares and hexagons respectively at the points of the diamond net and the primitive lattice. It is also of interest to consider the nets which arise if small polygons (equilateral triangles, squares and regular hexagons) are placed at the points of appropriate cubic nets in orientations consistent with cubic symmetry (tetrahedral or octahedral). The simplest nets of this type will be illustrated in Part 5, where we shall discuss diffraction effects from an organic crystal which apparently has a new type of structure.

## References

GODFREY, T. N. & WARREN, B. E. (1950). J. Chem. Phys. 18, 1121.
WELLS, A. F. (1954a). Acta Cryst. 7, 535.
WELLS, A. F. (1954b). Acta Cryst. 7, 545.
WELLS, A. F. (1954c). Acta Cryst. 7, 842.