the I.B.M. calculations, and Prof. A. von Hippel for his interest in this work.

References

Abrahams, S. C., Collin, R. L. & Lipscomb, W. N. (1951). *Acta Cryst.* **4**, 15.

Abrahams, S. C. & Kalnajs, J. (1954). *J. Chem. Phys.* **22**, 434.

Babcock, H. D. & Herzberg, L. (1948). *Astrophys. J.* **108**, 167.

Becker, W. (1909). Thesis, Karlsruhe Technische Hochschule.

Bernal, J. D., Djatlowa, E., Kazarnovskii, I., Raikhshtein, S. I. & Ward, A. G. (1935). *Z. Kristallogr.* A, **92**, 344.

Burbank, R. D. (1953). *Acta Cryst.* **6**, 55.

Butuzov, V. P. (1947). *Dokl. Akad. Nauk. SSSR.* **58**, 1411.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Dulmage, W. J. & Lipscomb, W. N. (1951). *Acta Cryst.* **4**, 330.

Evans, H. T. (1953). Tech. Rep. 58, ONR Contract N5ori-07801, Laboratory for Insulation Research, Massachusetts Institute of Technology.

Hanawalt, J. D., Rinn, H. W. & Frevel, L. K. (1938). *Industr. Engng. Chem. Anal. Ed.* **10**, 457.

Harr, T. E. (1952). Thesis, Syracuse University.

Helms, A. & Klemm, W. (1939). *Z. anorg. Chem.* **241**, 97.

James, R. W. & Brindley, G. W. (1931). *Z. Kristallogr.* **78**, 470.

Kasatochkin, W. & Kotov, V. (1936). *J. Chem. Phys.* **4**, 458.

Kasatochkin, W. & Kotov, V. (1937). *Zh. tekh. Fiz.* **7**, 1468.

Kazarnovskii, I. A. (1930). *Zh. fiz. Khim.* **1**, 93.

Kazarnovskii, I. A. (1940). *Zh. fiz. Khim.* **14**, 320.

Kotov, V. & Raikhshtein, S. I. (1941). *Zh. fiz. Khim.* **15**, 1057.

Lu, C. S., Hughes, E. W. & Giguère, P. A. (1941). *J. Amer. Chem. Soc.* **63**, 1507.

Mattner, J. (1952). *Z. anal. Chem.* **135**, 415.

Miller, W. S. (1936). Thesis, Syracuse University.

Raikhshtein, S. I. & Kazarnovskii, I. (1932). *Zh. fiz. Khim.* **3**, 83.

Templeton, D. H. & Dauben, C. H. (1950). *J. Amer. Chem. Soc.* **72**, 2251.

Trambarulo, R., Ghosh, S. W., Burrus, C. A. & Gordy, W. (1953). *J. Chem. Phys.* **21**, 851.

Zhdanov, G. S. & Zvonkova, Z. V. (1952). *Dokl. Akad. Nauk. SSSR*, **82**, 743.

Acta Cryst. (1954). **7**, 842

The Geometrical Basis of Crystal Chemistry. Part 3

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(*Received* 7 *May* 1954)

Examples are given of some of the 3- and 4-connected three-dimensional nets derived in Parts 1 and 2, with special reference to certain groups of hydrogen-bonded structures. The general types of crystal structure are indicated for long molecules such as those of dihydroxy compounds and those containing terminal –CO.NH– groups. The crystal chemistry of P, P_2O_5, and the trioxides and trisulphides of Group 5*B* elements is discussed.

Introduction

In this Part we show how 3- and 4-connected nets form the basis of the structures of crystals of very diverse types. Some examples, such as the structures of elements, are obvious and well known, but other relationships have not been pointed out. They emphasize the elegant simplicity of the principles underlying the structures of many crystals, a simplicity which is not always evident from the usual descriptions of structures. Moreover, these systematic studies of the topological structure types which are possible for a given compound are necessary if we hope eventually to understand why a particular structure is adopted.

In order to divide a plane surface into convex polygons at least three lines must meet at each point. The plane hexagonal net is the unique way of partitioning the plane with this minimum number of lines into polygons all having the same number of sides. The importance of the hexagonal net in crystals is well known. In three dimensions continuous frameworks can be formed with the same minimum number of links meeting at each point, and some of the simpler ones have been derived and illustrated in Part 1 (Wells, 1954*a*). It might be expected that these nets also would be important in crystal chemistry, in particular the 3-dimensional analogues of the plane hexagonal net. These are the 'uniform' 3-connected nets, which have the property that the shortest circuit from any point back to itself always passes through the same total number (N) of points, N being 8, 9, 10, or 12.

The principal types of framework structure

There would appear to be the following possible structure types for crystals based on 3-dimensional nets, that is, crystals in which a 3-dimensional framework can be recognized as an essential feature of the structure:

1. *Structures consisting of a single net*

(*a*) The crystal structure of an element may be simply a net in which identical atoms are placed at all points. If atoms of more than one kind are placed, ideally in some regular way, at the points of the net, then we have possible structures for compounds A_mB_n, $A_mB_nC_p$, etc., in which the fundamental network of atoms is the same. The structures of diamond, ZnS (sphalerite), $CuFeS_2$ and Cu_2FeSnS_4 are examples of the 4-connected Net 1 of Table 2 in Part 2 (Wells, 1954*b*). Examples of the 4-connected Net 15 are the structures of PtS, PdS, PdO and PtO, and CuO, the first being the most symmetrical configuration of the net (Fig. 6, Part 2) and the others less symmetrical variants.

(*b*) If atoms A are placed at the points of a net and (2-connected) atoms B along the links, we have possible structures for compounds A_2B_3, AB_2 and AB_3 from 3-, 4- and 6-connected nets respectively. Some oxide structures are related in this way to very simple nets.

(i) The coordination number of A is equal to the degree of connectedness (n) of the net. Examples: 4-connected nets → SiO_2 structures, 6-connected net → ReO_3 structure. The structures of cristobalite, quartz and tridymite have been noted as examples of the 4-connected Nets 1, 5 and 6, and illustrated as tetrahedron packings in Part 2.

(ii) The coordination number of A is greater than n. Example: the structures of the crystalline forms of P_2O_5 (see later).

(*c*) The idealised structures of certain hydroxy compounds and compounds containing equal numbers of CO and NH groups can be represented as 3-connected nets, as will be shown later.

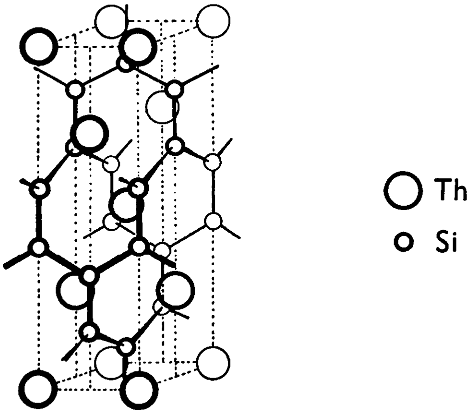


Fig. 1. The crystal structure of $ThSi_2$.

2. *Structures consisting of a single net with additional material in the interstices*

Any attempt to classify these structures would probably become a discussion of bond type rather than a geometrical classification. The following are examples.

$ThSi_2$: Si atoms form the 3-connected Net 2 with Th atoms in the interstices (Brauer & Mitius, 1942), as shown in Fig. 1 (see also Figs. 6 and 8, Part 1).

CaB_6: the B atoms from the 5-connected net of Fig. 19(*a*) of Part 1.

Framework silicates: felspars, zeolites, etc.

Hydrogen-bonded frameworks: hydrates of inert gases, SO_2, CH_3Cl, etc. (see Part 2); crystalline complexes of urea and thiourea with hydrocarbons (see, for example, Smith, 1952).

3. *Structures consisting of two or more interpenetrating frameworks*

Here we could further classify as follows, and in each case we could envisage structures with or without extraneous material.

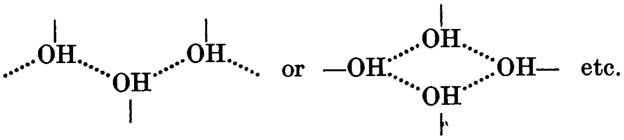
(i) All frameworks of identical constitution: Cu_2O (and the isomorphous Ag_2O); β-quinol.

(ii) Frameworks of two or more kinds: no example known.

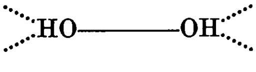
We shall now indicate briefly how these nets underlie the crystal chemistry of hydroxy compounds, carboxylic acids, keto-imino compounds, and some of the compounds of elements of Group 5 of the Periodic Table.

Hydroxy compounds

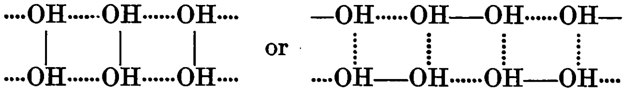
Hydrogen-bonded structures are characterized by a relatively small number of interactions between polar groups of different molecules, resulting in intermolecular distances appreciably shorter than those of normal van der Waals contacts. The crystal structures of anhydrous hydroxy compounds show that the molecules are linked together by O–H–O bonds, two from each OH group. For a mono-hydroxy compound containing no other hydrogen-bond-forming atoms in the molecule there are only two possible ways of linking up the molecules, namely, into infinite chains or closed rings:



If we join the OH groups in a dihydroxy molecule by a full line (representing the OH–OH axis of the molecule) then the structural unit is

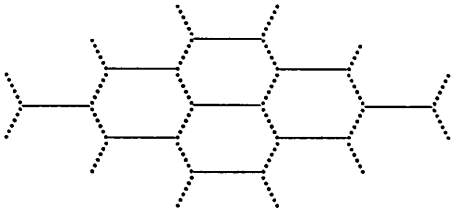


and the system of hydrogen-bonded molecules may be represented diagrammatically as a 3-connected net in which one-third of the links are full lines and two-thirds are dotted lines (O–H–O bonds). The simplest extended arrangement, the double chain:



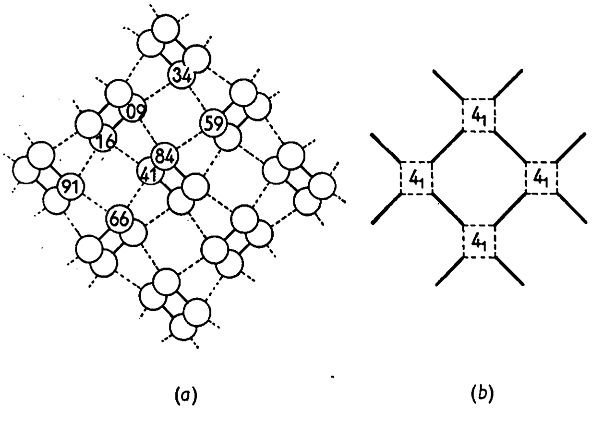
(a) (b)

is not possible in the form (*a*) for a dihydroxy compound because of the unsuitable angles between the hydrogen bonds at the OH groups (contrast keto-imino compounds, later), though arrangements like (*b*) might occur. The next simplest possibility is the plane hexagonal net:



This represents the molecular arrangement in γ-quinol and in 4:4′-dihydroxydiphenyl (Powell & Wallwork, 1951). Other possibilities for such compounds are the more complex plane 3-connected nets and the three-dimensional 3-connected nets.

The simplest dihydroxy compound is hydrogen peroxide. The projection of the structure of crystalline H_2O_2 on (001) of the tetragonal cell (Fig. 2(*a*)) is simply a distorted form of the plane 4:8 net of Fig. 2(*b*), and from the heights of the atoms it can be seen that neither the 4-gons nor the 8-gons in the projection represent closed polygons (Abrahams, Collin & Lipscomb, 1951). In fact, the idealized structure of H_2O_2 is one of the two simplest three-dimensional 3-connected nets, the enantiomorphic Net 1 described and illustrated in Part 1 (Figs. 6 and 7).

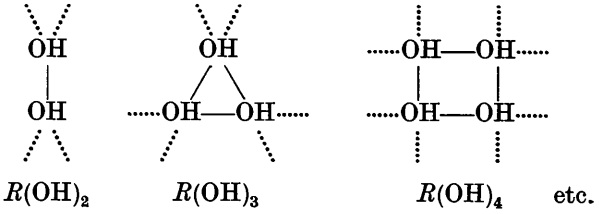


(a) (b)

Fig. 2. (*a*) Projection of the structure of H_2O_2 on (001). The figures show the heights of the atoms in terms of *c*/100. (*b*) Idealized projection, in which the full lines represent H_2O_2 molecules.

In Part 1 we showed that of the family of more complex nets related to Net 1 the next one consisting only of 10-gons is that of Fig. 15(*f*) of that paper. This is the net corresponding to the structures of both α- and β-resorcinol. The basis of the structure of β-quinol (Powell, 1947) is the 3-connected Net 9 illustrated in Figs. 6(*d*) and 11 of Part 1, in which the hexagons represent rings of six O–H–O bonds and the longer lines connecting the hexagons represent the OH–OH axes of the quinol molecules. The structure of this crystal consists of two identical nets displaced with respect to one another by one-half of the vertical distance between hexagons. The two (unconnected) nets are held apart by molecules such as CH_3OH, SO_2, etc., which are incorporated while the crystal is growing and occupy holes in the structure between adjacent hexagons of different nets.

The crystal structures of hydroxy compounds containing more than two OH groups in the molecule may be represented by 4-connected nets, for example:



The simplest structure for a tetrahydroxy compound is clearly the simplest plane 4-connected net. In the molecule of pentaerythritol, $C(CH_2OH)_4$, the four OH groups are almost coplanar, and the crystal has a layer structure which can be represented diagrammatically by a 4-connected net in which one-half of the links (dotted lines) represent O–H–O bonds (Fig. 3).

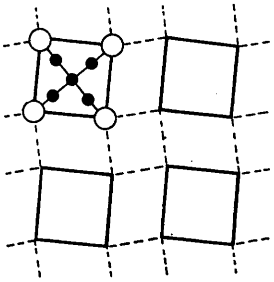


Fig. 3. Part of a layer of the crystal structure of $C(CH_2OH)_4$. Large circles represent OH groups and broken lines O–H–O bonds.

Hydrated polyhydroxy compounds

The structures of hydrated compounds $M(OH)_n.pH_2O$, where $n > 2$, can be represented by 4-connected nets if the water molecules form four hydrogen bonds. The simplest examples are hydrates such as

$C_6H_9(OH)_3 . 2H_2O$ (phloroglucitol dihydrate) and $C_6H_3(OH)_3 . 2H_2O$ (phloroglucinol dihydrate). If the OH groups form hydrogen bonds only to water molecules the simplest structures for these compounds can be derived from the very simple plane (3+4)-connected net of Fig. 4(*a*) containing the minimum of 5 points in the repeat unit. Three-dimensional nets arise by joining up layers of this type through the two 3-connected points (representing H_2O molecules), one of which is to be connected upwards (*U*) to a point of the layer above and the other downwards (*D*) to a point of the layer below. There are four kinds of layer, *A*, *A′*, *B* and *B′*, and two essentially different ways of superposing them:

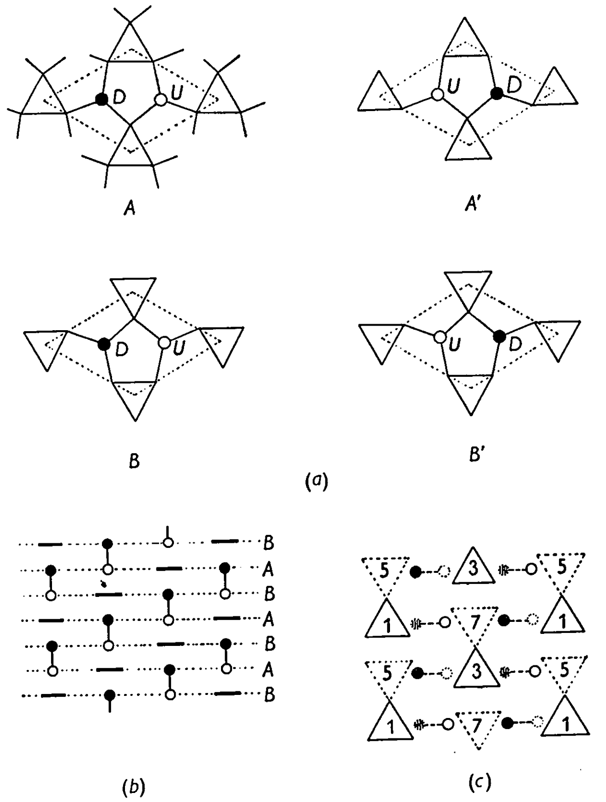


Fig. 4. Derivation of 4-connected nets representing structures of compounds $M(OH)_3 . 2H_2O$.

(*a*) Pairs of water molecules of different layers vertically above one another, giving the layer sequence *A A A A*..., in which *B* layers may be substituted for any of the *A* layers. The 6-layer sequence of Fig. 4(*b*), with rhombohedral symmetry, represents the structure of $C_6H_9(OH)_3 . 2H_2O$ and the isomorphous $C_6H_9(OH)_3 . 2NH_3$ and $C_6H_9(NH_2)_3 . 2H_2O$ (Andersen & Hassel, 1948, 1951). Sequences such as *A A A A*... and *A A′ A A′*... correspond to structures related in the same way as the diamond and wurtzite structures (Fig. 2(*c*) and (*d*) of Part 2).

(*b*) Layers are superposed as in Fig. 4(*c*), which represents the idealized structure of $C_6H_3(OH)_3 . 2H_2O$ (Bailey & Wells, 1950). In the actual structure the layers are corrugated to give rows of molecules at heights $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$ and $\frac{7}{8}$, as indicated in the figure.

Carboxylic acids

One O–H–O bond is formed by each oxygen atom of COOH groups, so that if we join up the O atoms of the carboxylic acid to form a polygon the structural scheme becomes similar to that for dihydroxy compounds. For a molecule containing *n* COOH groups we require 3-connected nets containing 2*n*-gons. For oxalic acid, represented in this way in Fig. 5(*a*), the two simplest possibilities are shown at (*b*) and (*c*), which in fact represent the structures of the *β* and *α* forms of the acid. At (*d*) and (*e*) are shown the simplest structures for tri- and tetracarboxylic acids, corresponding to (*c*) for a dicarboxylic acid. These represent layer structures or projections of three-dimensional nets.

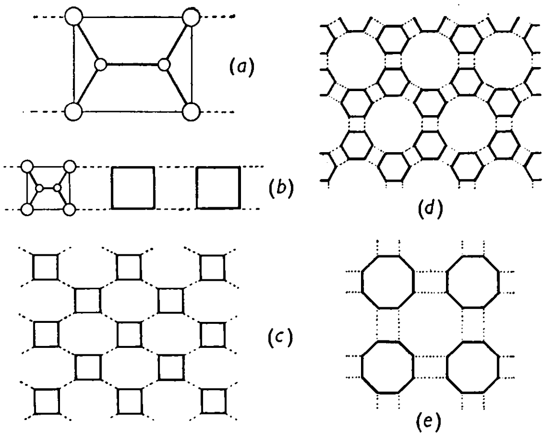


Fig. 5. The crystal structures of carboxylic acids. (*a*) Molecule of oxalic acid. (*b*) and (*c*) Crystal structures of *β* and *α* forms. (*d*) and (*e*) The corresponding structures for tri- and tetra-carboxylic acids.

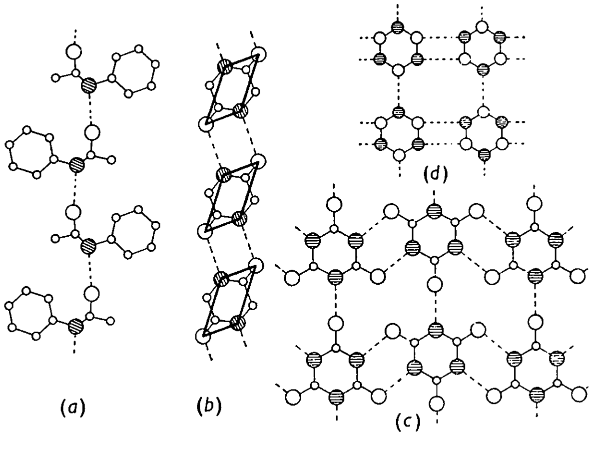


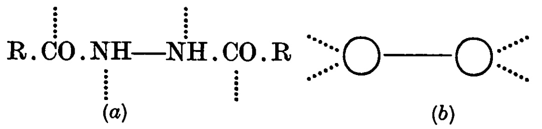
Fig. 6. Structures of crystalline compounds R(CO.NH)$_n$. (*a*) Acetanilide. (*b*) Diketopiperazine. (*c*) Cyanuric acid. (*d*) The same (diagrammatic).

Keto-imino compounds

When the numbers of CO and NH groups in the molecules are equal the structural principles are very simple. Each CO is joined to one NH by an O–H–N bond. If the hydrogen bonds are intramolecular (as, for example, in indanthrone) the structure is of the molecular (van der Waals) type. If intermolecular hydrogen bonds are formed and if there is only one CO and one NH in the molecule the only possibilities are chains or rings. Fig. 6(*a*) shows part of the crystal structure of acetanilide (Brown & Corbridge, 1948). If there are two or more CO and NH groups in the molecule the structures may be represented diagrammatically by 3-connected nets, as will be shown for three groups of compounds.

(i) *Linear molecules containing terminal* CO–NH *groups*

We may represent the molecule (*a*) diagrammatically as at (*b*):


R.CO.NH—NH.CO.R

particularly if the length of the molecule is large compared with the size of the CO–NH grouping. The structural possibilities are therefore the same as for dihydroxy compounds. Nothing has so far been published on the crystal structures of compounds of this type; we hope to give examples in a later paper.

(ii) *Ring molecules*

Here we may join up the CO and NH groups within the molecule to form a polygon (compare the carboxylic acids). For two CO and two NH the simplest structures are the chain or 4:8 plane net, as for oxalic acid. The structure of diketopiperazine is of the former type; a part of the structure is shown in Fig. 6(*b*).

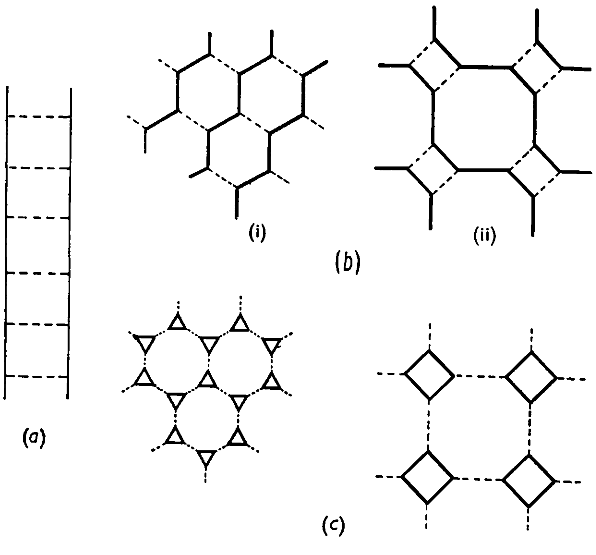


Fig. 7. Structure types for infinite chain molecules.

Cyanuric acid is an example of a molecule containing three CO and three NH groups; part of the (layer) structure is shown in Fig. 6(*c*) and in idealized form at (*d*).

(iii) *Infinite chain molecules*

The intermolecular N–H–O bonds could link the individual chains into nets extending indefinitely in one, two, or three dimensions. The simplest possibilities are those of Fig. 7. The (layer) structures of the synthetic polyamides nylon 6:6 and 6:10 are of type (*b*) (i) (Bunn & Garner, 1947). Portions of two chains of nylon 6:6, $[NH(CH_2)_6NH.CO(CH_2)_4CO]_n$, are shown in Fig. 8(*a*). The type of net, whether (i) or (ii) of Fig. 7(*b*), depends on the sequence of CO and NH groups along the chain and on the number (odd or even) of CH_2 groups between successive –CO.NH– groups. For caprolactam, $[NH(CH_2)_5CO]_n$, the arrangement is necessarily that shown in Fig. 8(*b*), i.e. the 4:8 net of Fig. 7(*b*) (ii). In Fig. 7(*c*) are shown projections of three-dimensional nets in which the triangles and squares represent helically coiled single molecules, with their axes parallel, perpendicular to the plane of the paper. The chains are cross-linked by hydrogen bonds (dotted lines). No examples of structures of this type are known.

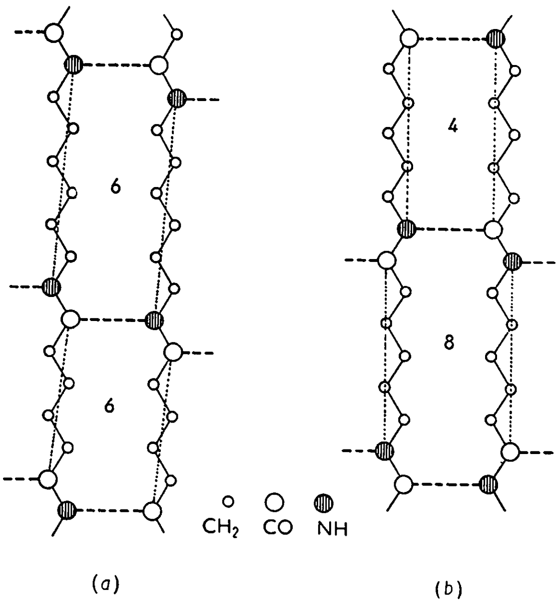


Fig. 8. Hydrogen-bonding in layers of (*a*) nylon 6 : 6 and (*b*) caprolactam.

There is, however, another very interesting possibility, the rolling-up of plane nets into open-ended cylinders or prisms. We shall illustrate this point with the hexagonal net only. This net may be drawn as in Fig. 9(*a*), and sections, of various widths, may be cut in different directions and rolled up to give arrangements such as those of Fig. 9(*b*), (*c*) and (*d*). The upper diagram of each pair shows the net when unrolled,

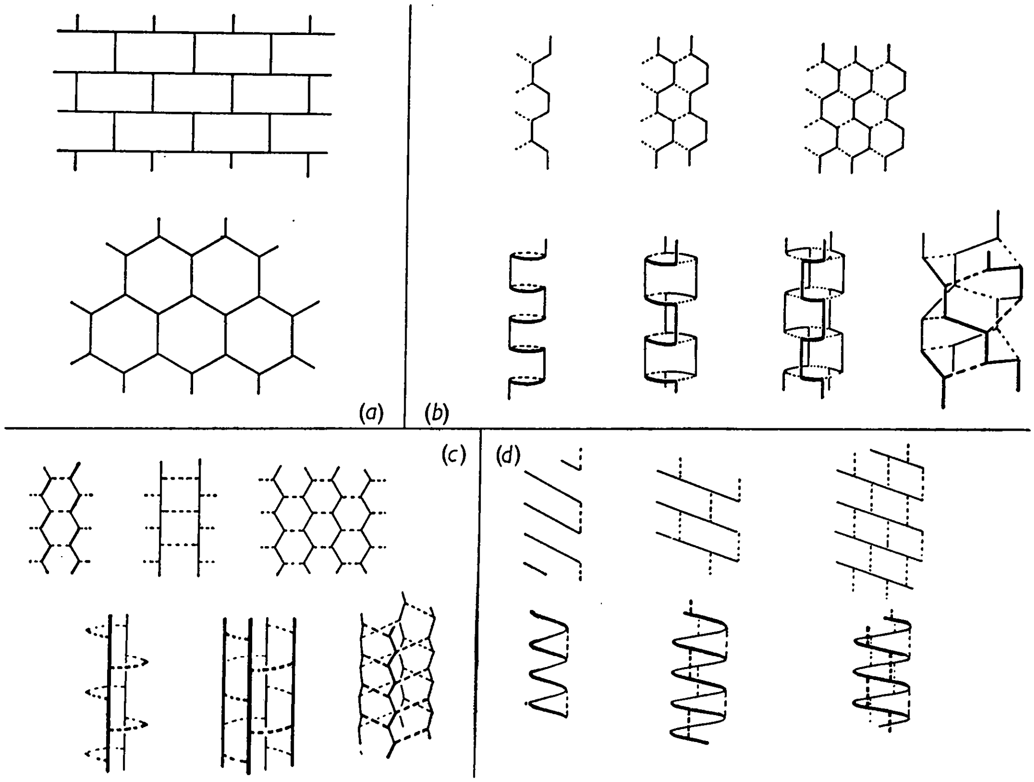


Fig. 9. Cylindrical and helical structures derived from the plane hexagonal net.

and angular forms are shown in two cases. The structures proposed by Pauling, Corey & Branson (1951) for proteins belong to one of the families of helical structures of which three examples are shown at (*d*).

The crystal chemistry of phosphorus and Group 5*B* elements

In a crystalline element in which each atom *M* is forming three bonds the atoms may be connected to form finite groups or systems of atoms extending indefinitely in one, two, or three dimensions. The simplest of these are set out in Table 1.

Table 1

		Smallest polygon or shortest circuit
(*a*)	Finite: tetrahedron	3
	cube	4
	dodecahedron	5
(*b*)	Infinite 1-dimensional	4, 5, 6
(*c*)	Infinite 2-dimensional	6
(*d*)	Infinite 3-dimensional (uniform nets)	8, 9, 10, or 12

Examples of (*a*), (*b*) and (*c*) are shown in Fig. 10, except examples of (*b*) containing 6-gons, which are the cylindrical nets of Fig. 9.

Elements

The molecules P_4 and As_4 in the vapours of the elements have a tetrahedral configuration, and similar molecules presumably occur in crystalline white phosphorus (and yellow arsenic?). Black phosphorus has a layer structure in which the layers are so puckered

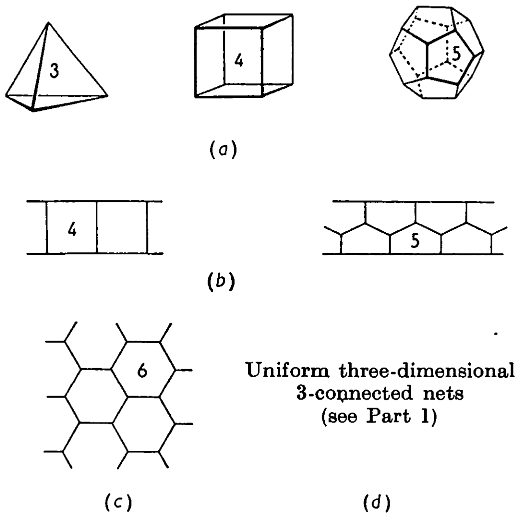
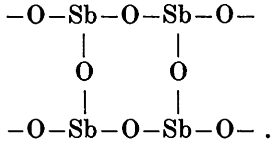


Fig. 10. The most symmetrical structures for P, P_2O_3, and P_2O_5. The closed (ring) forms of (*b*) and the cylindrical or prismatic forms of (*c*) are omitted.

as to give the appearance of double layers, but if a layer is flattened out it is seen to be simply a distorted version of the plane hexagonal net.

Trioxides and trisulphides

Here each atom M is linked to three others through O or S atoms, so that the simplest structures are the nets of Fig. 10 with an O or S atom along each link. The molecules P_4O_6 and As_4O_6 in the vapour and those in the cubic forms of As_4O_6 and Sb_4O_6 have a tetrahedral configuration. The structure of crystalline P_2O_3 is not known. In the orthorhombic form of Sb_2O_3 (valentinite) there are double chains of the type



$$\begin{array}{c} -O-Sb-O-Sb-O- \\ \quad\;\; | \qquad\;\; | \\ \quad\;\; O \qquad\; O \\ \quad\;\; | \qquad\;\; | \\ -O-Sb-O-Sb-O-\,. \end{array}$$

The monoclinic form of As_2O_3, the mineral claudetite (Frueh, 1951; Becker, Plieth & Stranski, 1951), and also orpiment, As_2S_3 (Ito, 1950) have layer structures in which the As atoms are linked through O or S atoms to form the simple hexagonal net (Fig. 10(*c*)).

Phosphorus pentoxide

In this compound the structural unit is a tetrahedral PO_4 group of which three O atoms are shared with other P atoms. The fourth O atom may be neglected in this connexion since it does not form an essential part of the net. The structural possibilities for P_2O_5, which is trimorphic, are therefore the same as for P_2O_3. In the vapour (at low temperatures) and in one crystalline form there are P_4O_{10} molecules having the same tetrahedral configuration as P_4O_6 with an additional O atom attached to each P. The second form has a layer structure (MacGillavry, de Decker & Nijland, 1949) of the same kind as As_2O_3 and As_2S_3 with a fourth O attached to each P. The third modification has a three-dimensional framework (de Decker, 1941) which can be represented, in idealized form, as the 3-dimensional 3-connected Net 2, one of the two simplest nets of this type. (It might have been expected that B_2O_3 would form a 3-connected net of some sort, but apparently crystalline B_2O_3 contains both 3- and 4-coordinated B atoms (Berger, 1952).

The examples of three-dimensional 3-connected nets are summarized in Table 2.

Table 2

Net			Example
Net 1	Table 2	Part 1	H_2O_2
2			$ThSi_2$, P_2O_5 (orthorhombic I)
9			β-quinol
Fig. 15(*f*)			α-resorcinol, β-resorcinol

References

(References are given only to the more recent structural work.)

Abrahams, S. C., Collin, R. L. & Lipscomb, W. N. (1951). *Acta Cryst.* **4**, 15.

Andersen, P. & Hassel, O. (1948). *Acta Chem. Scand.* **2**, 527.

Andersen, P. & Hassel, O. (1951). *Acta Chem. Scand.* **5**, 1349.

Bailey, M. & Wells, A. F. (1950). Unpublished.

Becker, K. A., Plieth, K. & Stranski, I. N. (1951). *Z. anorg. Chem.* **266**, 293.

Berger, S. V. (1952). *Acta Cryst.* **5**, 389.

Brauer, G. & Mittius, A. (1942). *Z. anorg. Chem.* **249**, 325.

Brown, C. J. & Corbridge, D. E. C. (1948). *Nature, Lond.* **162**, 72.

Bunn, C. W. & Garner, E. V. (1947). *Proc. Roy. Soc.* A, **189**, 39.

Decker, H. C. J. de (1941). *Rec. trav. chim. Pays-Bas*, **60**, 413.

Frueh, A. J. (1951). *Amer. Min.* **36**, 833.

Ito, T. (1950). *X-ray Studies on Polymorphism.* Tokyo: Maruzen.

MacGillavry, C. H., Decker, H. C. J. de & Nijland, L. M. (1949). *Nature, Lond.* **164**, 448.

Pauling, L., Corey, R. B. & Branson, H. R. (1951). *Proc. Nat. Acad. Sci., Wash.* **37**, 205.

Powell, H. M. (1947). *J. Chem. Soc.* p. 208.

Powell, H. M. & Wallwork, S. C. (1951). *Nature, Lond.* **167**, 1072.

Smith, A. E. (1952). *Acta Cryst.* **5**, 224.

Wells, A. F. (1954*a*). *Acta Cryst.* **7**, 535.

Wells, A. F. (1954*b*). *Acta Cryst.* **7**, 545.