

PENTAMOND: A NEW CRYSTALLINE MODIFICATION OF CARBON

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Abstract: *Slight modifications of a crystal structure at different organizational levels result in new structures related to each other. This possibility seems not to be exhausted entirely by Nature. In this contribution a hypothetical carbon polymorph is described which consists of five-membered (C_5) rings in contrast to the known existing polymorphs. Some simple calculations make the model more plausible.*

1. INTRODUCTION

According to the well-known point of view, a crystal is a (theoretically infinite) triply periodic material pattern in which the repetitive motifs are atoms (or sets of atoms) (Feynman, Leighton and Sands, 1964; Kittel, 1961; Buerger, 1965). The nature of the transition from the atomic (or molecular) organizational level to the solid state level is an intricate problem and is far from being well understood; recall for example the high temperature superconductivity.

Prior to going into the physical details, one may scrutinize the purely structural aspects of this spatial order. This is, admittedly, the typical standpoint of the 'classical crystallographer' (Buerger, 1965). In this approach, the emphasis is on the concept of symmetry, in fact, that of the *global* symmetry (the mathematical output of this is the group theoretical formulation of geometrical crystallography). However, one may not and must not ignore that there is an underlying *topology* that

precedes the global symmetry. Indeed, the traditional classification of the polyhedral-frame structures of minerals (especially those of the silicates) is an implicit application of this topological aspect (Bragg, Claringball and Taylor, 1965; Zoltai and Stout, 1984).

By way of illustration, take some representative of covalent crystals. In an abstract sense, the crystal structure of diamond can be interpreted as an (infinite) regular graph of degree four (the C-C covalent bonds being the graph edges and the C atoms being the vertices). Of course, this particular topology of the network of carbon atoms is made possible by the nature of the vertices. Here the *valence of the vertices* is four, due to the sp^3 hybrid state of the carbon. Although this valence admits an infinite variety of linkages, the number of possible cases is strongly limited by the *local symmetry* of the vertices. This local symmetry results from the highly directional character of the covalent bonds, and in the case of carbon sp^3 orbitals it is equal to that of the regular tetrahedron. As for the realization, the actually known cases are: diamond with its cubic (global) symmetry and a rare hexagonal polymorph called a lonsdaleite (Zoltai and Stout, 1984). (They exemplify the fact that the valence *and* the local symmetry of the vertices together do not determine the actual crystal structure uniquely even on the level of topology.)

The relation of these hierarchy levels can be summarized in the following diagram (Fig. 1).

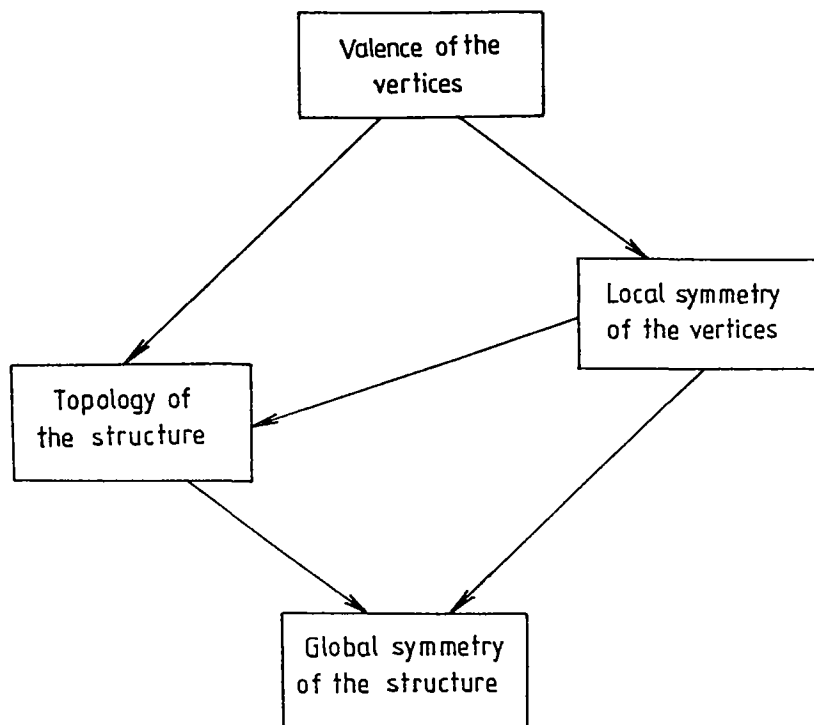


Figure 1: Hierarchy levels in a crystal structure.

What is the heuristic significance of such considerations? Well, it may draw attention to the inexhaustible possibilities of matter. In the present contribution a hypothetical model is given which will perhaps exemplify these ideas.

The recent discovery of the 'third modification of carbon', (' C_{60} fullerene', 'footballene', etc.) (Kroto, 1989) demonstrated, among other things, that the carbon atom in sp^2 hybrid state is able to build up a structure topologically distinct from that of the graphite. Both structures form, in an abstract sense, a regular graph of degree three, but in the C_{60} structure the original local D_{3h} symmetry of the carbon atoms is somewhat violated. At the same time, among the 6-circuits of the graph 5-circuits (five-membered rings of atoms) occur as well. All this occurs at the expense of some bond angle distortions which the system obviously tolerates.

Now the question is whether the topology of the diamond can be changed so that the valence is preserved but the six-membered rings (6-circuits) are replaced by five-membered ones.

2. THE PENTAMOND STRUCTURE

Take a tiling composed of pentagonal tiles as shown in Figure 2 (solid line; plane group: $p4g$). Let a pentagonal unit correspond to the skeleton of the cyclopentane (C_5H_{10}) molecule. It turns out that such a quasi-two-dimensional net can be constructed with relatively small angle distortions (with respect to either $109^\circ 28'$ or 108°). So, our tiling is merely a plane projection of a spatial structure in which the symmetrically repeated units are not the cyclopentane skeletons but those of a larger molecule shown in Figure 3a (plane projection) and in Figure 3b (perspective view). This latter molecule is a bridged-ring system to which the systematic name tetra-cyclo-[6,2,1,1^{3,6},0^{11,12}]-dodecane may be given (for the nomenclature, see e.g., (Barton, 1979)). Figure 3b shows that it resembles a cradle. If the cradles in Figure 2 are thought to be oriented as in Figure 3a, in the same structure one finds cradles upside-down which are oriented in the other diagonal direction.

Now reflect this structure in an appropriate horizontal mirror plane and at the same time shift it in a diagonal direction by a length half of the cradle (glide reflection). Another horizontal net is obtained (dashed line in Fig. 2). Connect these two layers in an appropriate way (dotted lines in Fig. 2). Infinite repetition of this process results in a three-dimensional structure (note that repetition of the horizontal layers can be carried out by various other types of compound symmetry transformations).

It is like diamond (an infinite regular graph of degree four) and different from diamond (composed of 5-circuits instead of 6-circuits in the horizontal layers). In fact, the structure of diamond can be conceived of as an infinite repetition of cyclohexane skeletons of chair conformation, in a similar manner (for comparison, see two of such layers of diamond projected onto a (111) plane in Figure 4; note that lonsdaleite only differs in that the layers completely cover each other when viewed from above (Zoltai and Stout, 1984; Merlino, 1990), accordingly, the cyclohexane rings

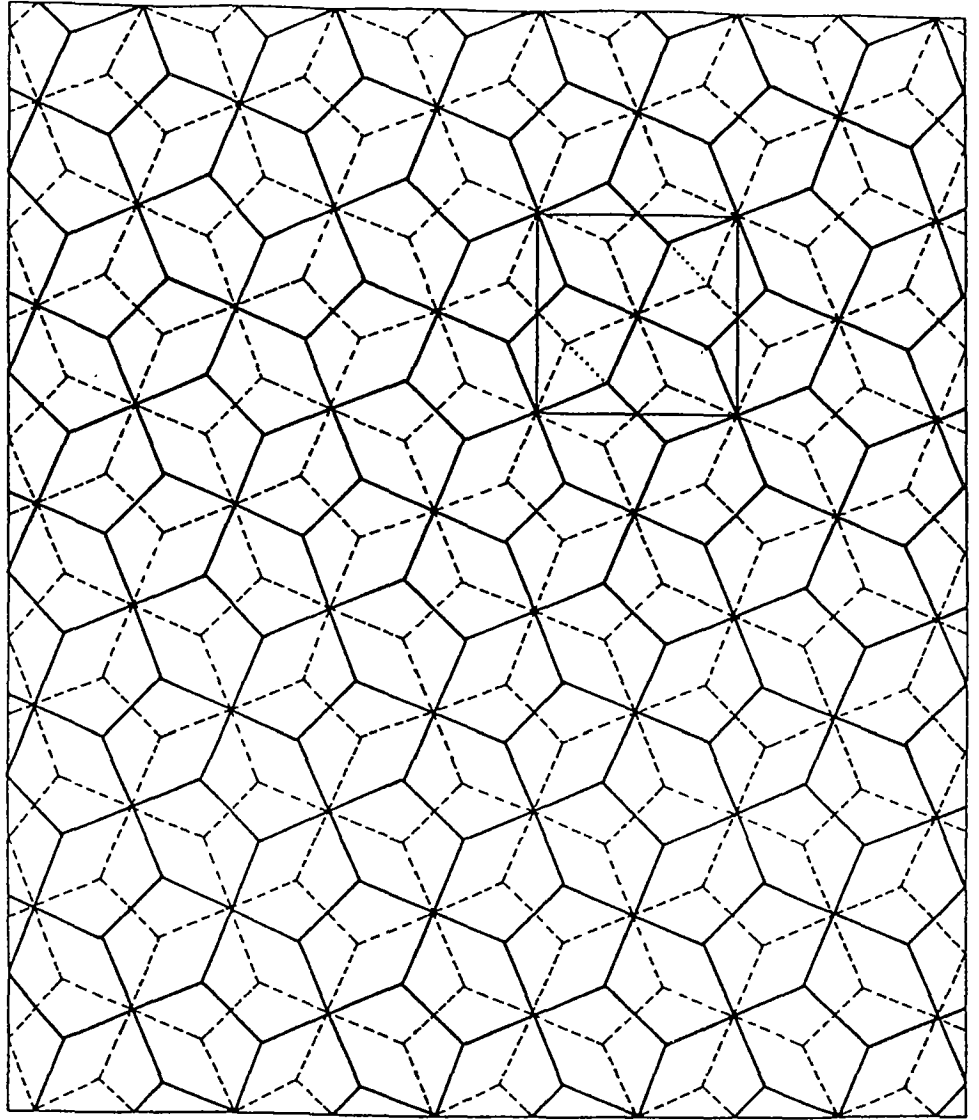


Figure 2: Projection of a layer of pentamond structure on the (001) plane (with the unit cell indicated). Dotted lines represent bonds connecting the upper pentagonal net (solid lines) to the lower pentagonal net (dashed lines); for easier visualization, they are only drawn within the marked unit cell.

providing the interlayer connection are of eclipsed conformation (Balaban, 1989)). Referring to the similarity and dissimilarity, we coined the name *pentamond* (*pentagon* + *diamond*) for this structure.

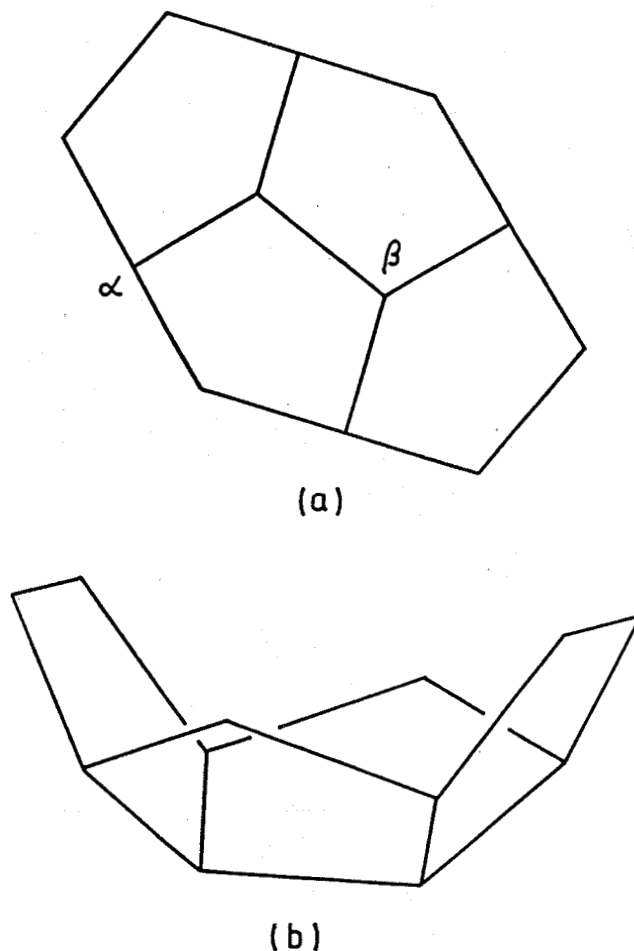


Figure 3: A repetitive unit of pentamond consisting of 12 C atoms (4 of type α , 8 of type β); (a) plane projection; (b) perspective view.

One can distinguish two types of carbon atoms according to their role in the structure: $C(\alpha)$ and $C(\beta)$ (cf. Fig. 3a). The $C(\alpha)$ atoms belong completely to a horizontal layer, i.e., they have no interlayer bonds (check this type of vertex in Fig. 2). Accordingly, they are shared by four cyclopentane rings within one and the same layer. The function of the $C(\beta)$ atoms, on the contrary, is twofold: not only are they common vertices of (three) cyclopentane rings in a layer, but they are responsible for the interlayer linkage as well (cf. again Fig. 2).

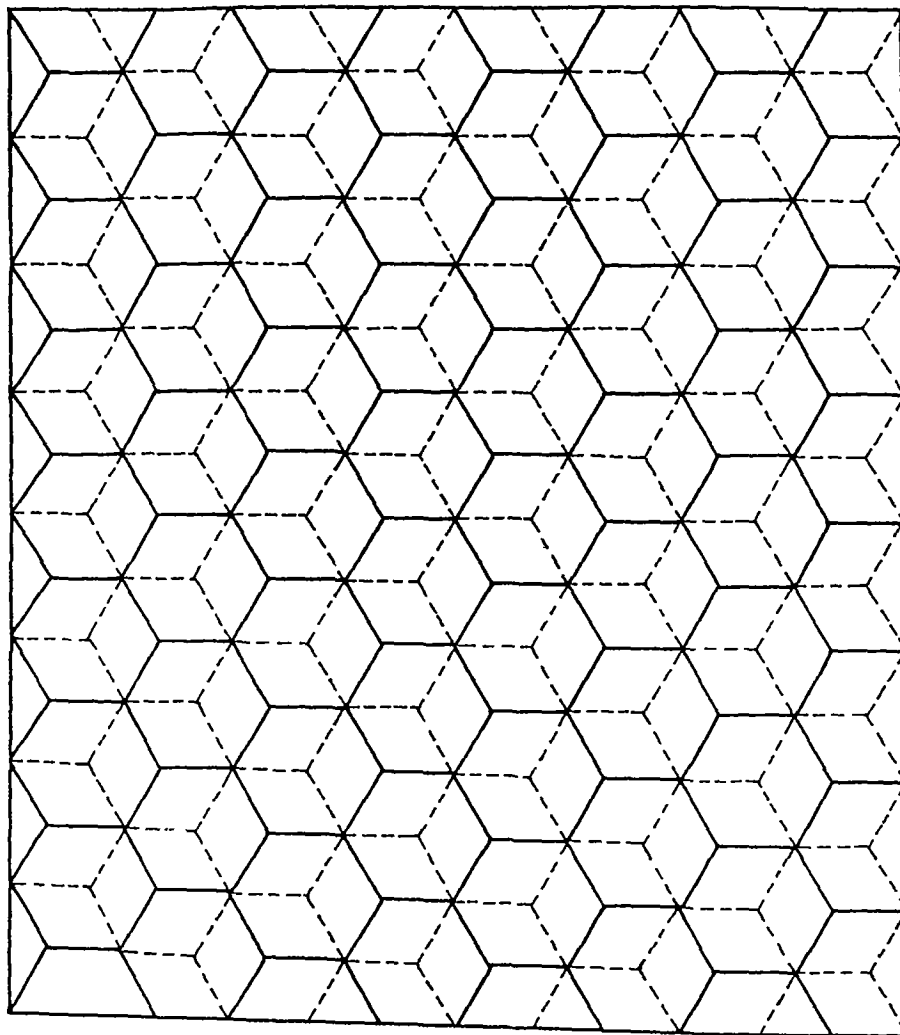


Figure 4: Projection of a layer of diamond structure on the (111) plane.

3. CRYSTALLOGRAPHIC DESCRIPTION

It is not difficult to see that we are given a tetragonal structure with a unit cell such as indicated by a square in Figure 2. The height of the unit cell is twice the inter-layer distance (the latter measured by the distance between two $C(\alpha)$ -s one over the other in adjacent layers).

The atomic positions are as follows:

4 $C(\alpha)$: 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, 0$; 0, 0, $\frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;

8 $C(\beta)$: x, y, z ; $\bar{x}, \bar{y}, z$; $y, x, \frac{1}{2}-z$; $\bar{y}, \bar{x}, \frac{1}{2}-z$;

$\bar{x}, y, \frac{1}{2}+z$; $x, \bar{y}, \frac{1}{2}+z$; $\bar{y}, x, \bar{z}$; $y, \bar{x}, \bar{z}$

Thus the unit cell contains 12 C atoms.

By inspection, one can find the following symmetry elements in the unit cell.

- 1) $\bar{4}$ vertical rotoinversion axes: with fixed point at $C(\alpha)$ atoms;
- 2) 4_2 vertical screw axes: through the midpoints of horizontal edges;
- 3) 2_1 horizontal screw axes: parallel to edges, at the one fourth and three-fourths of the horizontal edges, at elevation 0 and $\frac{1}{2}$;
- 4) 2 horizontal rotation axes: parallel to horizontal face diagonals and between them at elevation $\frac{1}{4}$ and $\frac{3}{4}$;
- 5) n horizontal glide planes: at elevation $\frac{1}{4}$ and $\frac{3}{4}$;
- 6) c vertical glide planes: coinciding with vertical cell walls as well as halfway between them;
- 7) m vertical mirror planes: perpendicular to horizontal face diagonals at one fourth and three-fourths of them;
- 8) 2_1 horizontal screw axes: parallel to face diagonals, over midpoints of horizontal edges, at elevation $\frac{1}{4}$ and $\frac{3}{4}$;
- 9) n vertical glide planes: through horizontal face diagonals;
- 10) $\bar{1}$ inversion centres: in the centre of $\frac{1}{8}$ cells.

Thus the space group is:

D_{4h}^{16} (Schoenflies symbol) or

$P4/n\bar{c}m$ (international symbol) or

$P_{\frac{4}{n}}^{\frac{4}{2}} \frac{2}{c} \frac{2}{m}$ (complete Mauguin symbol).

The corresponding space group diagram is given in Figure 5. (We note that the list of symmetry elements, the diagram in Figure 5 and the space group pairwise determine each other taking into account the standard interpretation of the symbols especially that given in the International Tables (Buerger, 1971). Although these are well known for crystallographers, here we risked the redundancy in order to make our contribution self-contained.)

Accordingly, the point group of pentamond is $D_{4h} - 4/m\bar{m}m$ (the crystal class is a tetragonal holohedry).

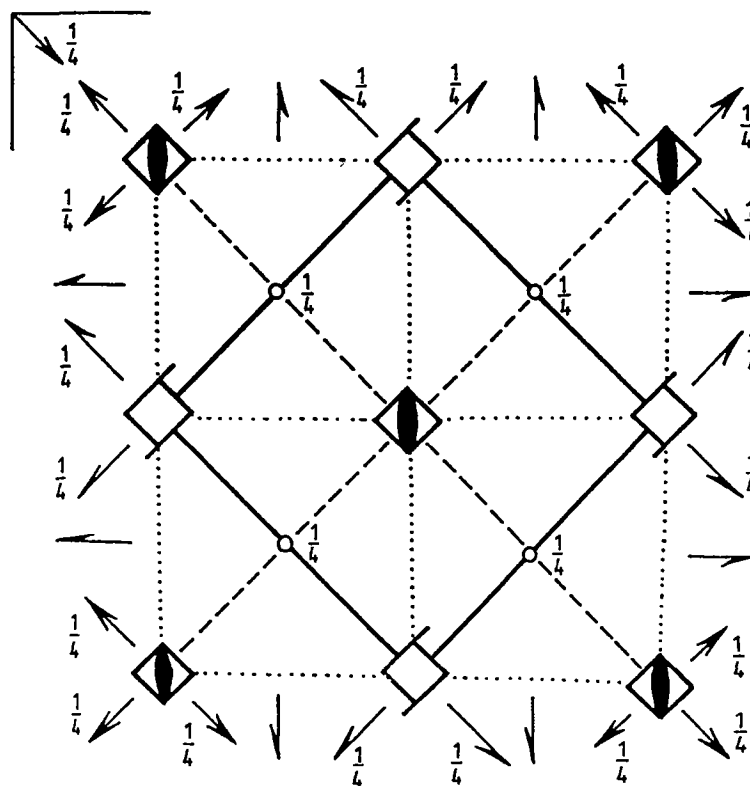


Figure 5: Space group diagram of pentamond.

A three-dimensional view of the unit cell of pentamond is shown in Figure 6. It is drawn in accordance with the numerical values given to the parameters a , c , x , y and z in the next section. It is seen that the six-membered rings are not completely 'eliminated' from the structure. In fact, each C_6 ring is linked by its opposite edges to a next one, forming infinite ribbons of width $c/2$. The orientation of these ribbons is (110) and $(\bar{1}\bar{1}0)$ (cf. upper half and lower half of the unit cell, respectively). Two perpendicularly oriented ribbons are joined by a common carbon atom shared by an upper and a lower C_6 ring.

4. TENTATIVE CALCULATIONS

One can easily observe in Figure 2 that there are three distinct types of bonds between the two types of carbon atoms: α - β , β - β and β - β' (a prime denotes $C(\beta)$ type atom located in an adjacent layer). The number of combinatorially possible bond angles on an atom of valence four is six, which is reduced by the local symmetry on the atom in question.

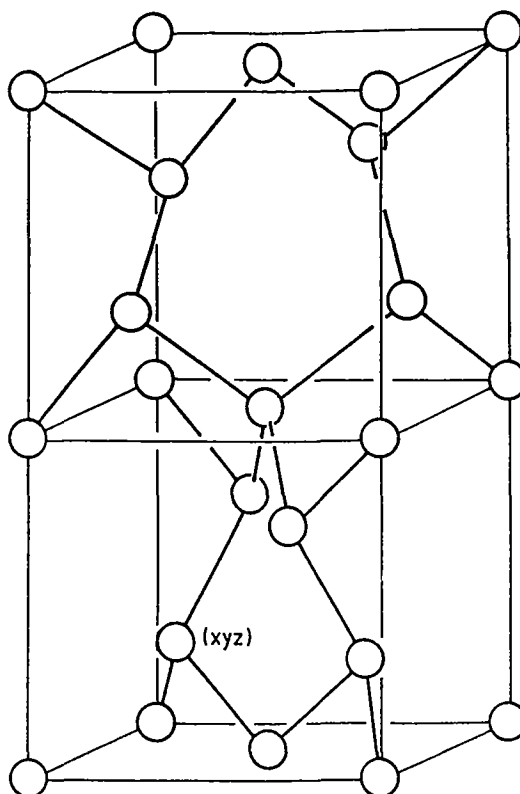


Figure 6: The tetragonal unit cell of pentamond, with coordinates of a $C(\beta)$ atom indicated.

Now observe that on the $C(\alpha)$ atoms the original local symmetry reduces according to the scheme: $43m \rightarrow 42m$ (or $T_d \rightarrow D_{2d}$ in Schoenflies notation). Hence, we have the following two types of angles here:

$\Phi(\beta\alpha\beta, \pi)$: it is projected into a straight angle on the (001) plane;

$\Phi(\beta\alpha\beta, \pi/2)$: it is projected into a right angle on the (001) plane; (cf. Fig. 2).

On the $C(\beta)$ atoms, at the outset, we can only assume the local symmetry C_s-m which is part of the global symmetry. Accordingly, we have the following angles:

$\Phi(\alpha\beta\alpha), \quad \Phi(\beta\beta\beta'), \quad \Phi(\alpha\beta\beta), \quad \Phi(\alpha\beta\beta'),$

where the last two occur twice owing to the presence of the mirror plane m .

Our approach is based on the assumption that the well-known carbon-carbon sigma bond length remains unchanged throughout the structure of pentamond. On the other hand, the bond angles listed above are allowed to deviate from the ideal tetrahedral value. It turns out that the conditions

A1) constant bond length

A2) the given local and global symmetry

only allow one free parameter for the structure calculation (global point group $D_{4h}-4/mmm$).

The starting point is the angle $\Phi(\alpha\beta\alpha)$, where the deviation from the ideal $\arccos(-1/3)=109^\circ 28'$ value is measured by a δ parameter. With this starting angle, some calculations yield the following formulas.

$$\cos\Phi(\alpha\beta\alpha) = -1/3 + \delta = 1 - 2\delta^2 \quad (1)$$

$$\cos\Phi(\beta\alpha\beta, \pi) = 1/2 + 2\delta' - 4\delta^2 \quad (2)$$

$$\cos\Phi(\beta\alpha\beta, \pi/2) = -3/4 - \delta' + 2\delta^2 \quad (3)$$

$$\cos\Phi(\beta\beta\beta') = 1 - 2\delta', \quad (4)$$

where $\delta' = \{2/3 - \delta/2\}^{1/2}$.

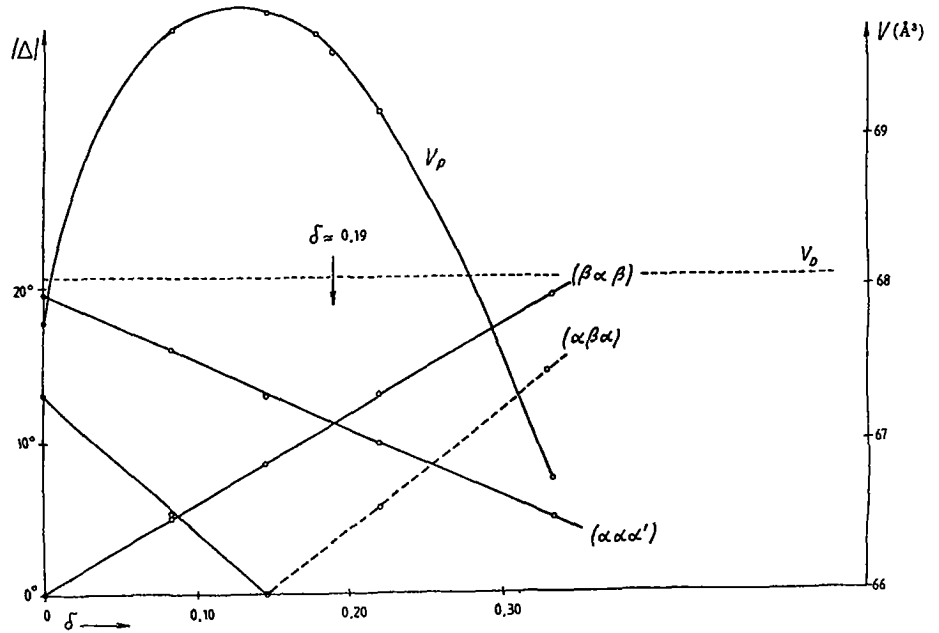


Figure 7: The dependence of angle distortions (left ordinate axis) and unit cell volume (right ordinate axis) on the δ parameter.

Using the formulas (2-4), the functions $\delta \rightarrow |\Delta|$, where $\Delta = \Phi - \arccos(-1/3)$, are plotted in Figure 7. The intersection points of curves $(\alpha\beta\alpha)$ and $(\beta\beta\beta')$ may be considered as that representing an optimum of the structure (within the limits of our approach). The corresponding value, $\delta = 0.1911$, was determined by Newton's method taking the difference of the two functions.

For this 'optimal' structure, the cell dimensions can be obtained using the following formulas:

$$a = 2 \cdot 2^{1/2} \cdot l \cdot \delta' \quad (5)$$

$$c = 2l(\{3 + 4\delta' - 8\delta'^2\}^{1/2} + 2\{\delta' - \delta'^2\}^{1/2}), \quad (6)$$

where l is the C-C sigma bond length. Its actual value, $l = 1.5445 \text{ \AA}$, is calculated from the lattice parameter of diamond ($a = 3.5668 \text{ \AA}$ (Zoltai and Stout, 1984)), assuming the carbon atoms to be hard non-overlapping spheres with radius $r = l/2$.

Hence, the cell dimensions are:

$$a = 3.3014 \text{ \AA}, \quad c = 6.3795 \text{ \AA}. \quad (7)$$

Expressing the $C(\beta)$ coordinates used in the preceding section in these units one obtains:

$$x = 0.3346, \quad y = 0.1654, \quad z = 0.1460. \quad (8)$$

(We note that these numerical values have been applied in Fig. 6.)

The bond angle values are obtained partly by formulas (1-4). Those for which no explicit formula is given are calculated from the coordinates (8). The results are summarized in Table 1.

Results of bond angle calculation in pentamond at $\delta = 0.1911$

Symbol of angle	Φ	Δ
$(\alpha\beta\alpha)$	$98^\circ 11'$	$-11^\circ 17'$
$(\beta\alpha\beta, \pi)$	$105^\circ 51'$	$-3^\circ 37'$
$(\beta\alpha\beta, \pi/2)$	$111^\circ 19'$	$1^\circ 51'$
$(\beta\beta\beta')$	$120^\circ 45'$	$11^\circ 17'$
$(\alpha\beta\beta)$	$104^\circ 49'$	$-4^\circ 39'$
$(\alpha\beta\beta')$	$112^\circ 47'$	$3^\circ 19'$

Table 1

Equality of the last two numerical values $(\alpha\beta\beta)$ and $(\alpha\beta\beta')$ in this Table would mean a C_{2v} - $mm2$ local symmetry on the $C(\beta)$ atoms. Since they differ, the originally assumed symmetry does occur (viz. C_s - m).

It is seen that the angle strains are relatively small, except for the case of $\pm 11^\circ 17'$. Unfortunately these latter cannot be simultaneously reduced, as we saw just now (cf. Fig. 7). Here we have to suppose that the structure will tolerate this amount of strain. The unit cell volume has also been calculated as follows:

$$V = 16\delta^3(\{3\delta'^4 + 4\delta'^5 - 8\delta'^6\}^{1/2} + 2\{\delta'^5 - \delta'^6\}^{1/2}). \quad (9)$$

Its dependence on the δ parameter is shown in Figure 7. It has a maximum in the vicinity of our optimum point. At this optimum, its value is $V = 69.551 \text{ \AA}^3$.

We compare the *packing efficiency* in the structure of pentamond and diamond. This number is usually given as the percentage of the volume occupied by (hard spheres of) atoms in the unit cell. It is well known and is easily checked that in the diamond structure it is equal to $(\sqrt{3}\pi/16) \times 100\% = 34.01\%$. The ratio of packing efficiencies in the two structures can be obtained by the quotient

$$q(P/D) = Z_P V_D / Z_D V_P, \quad (10)$$

where V_P , V_D and Z_P , Z_D are the unit cell volume and the number of atoms in the unit cell of the two structures, respectively (note that this ratio can be considered as the reciprocal ratio of molar volumes as well). By appropriate substitution we obtain: $q(P/D) = 0.9786$. Hence, the packing efficiency in pentamond is 33.28%, that is, a bit 'worse' in comparison with diamond.

If $q(P/D)$ were greater than one, it would provide the theoretical possibility of preparing pentamond by some high-pressure technique. Our model, based on the assumptions A1 and A2, does not feed such hopes. However, as we shall see at once, the situation is not quite hopeless.

5. CONCLUSIONS

It is to be emphasized that our approximation is merely a first approximation and one of the simplest possible. Indeed, the assumptions A1 and A2 are relatively strict. They can be relaxed, both separately and jointly. Of course, this can be done at the expense of an increased number of free parameters. A simultaneous treatment of more than one degree of freedom requires finer methods which would be the object of subsequent contribution(s).

Such 'structure refinement' will possibly result in a more efficient packing of C atoms (while preserving the topology established in the present paper). A physical consequence of this would be the location of the region of existence in a high-pressure part of the $p-T$ phase diagram of carbon. At the moment, this is an interesting and quite open problem both geometrically and physically.

Of course, the problem of locating the region of existence is preceded by the problem of the possibility of existence. This refers not only to the natural occurrence of pentamond but to its technical realizability as well.

Here a disturbing factor may be the amount of angle strain (in particular that originating from $\Phi(\alpha\beta\alpha)$ and $\Phi(\beta\beta\beta')$). However, we expect that refined (hence more

realistic) structure models would exhibit a more tolerable amount of strain (on the other hand, if carbon atoms are inclined to build up such a structure at all, they would find the true optimum automatically).

Since carbon atoms obviously do not overexert themselves to organize into pentamond structure spontaneously (otherwise pentamond would be a well known mineral such as diamond and graphite), here we refer to a relatively recent level (at least in our terrestrial environment) of the evolution of matter: this is the 'controlled evolution' or technological stage. Well, here is a challenge to materials scientists, solid state chemists and/or other experts on modern synthetic methods such as of catalytic vapour deposition, laser fusion and so on.

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