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TETRAHEDRAL COORDINATES AND THE DESCRIPTION OF ORGANIC MOLECULES

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The positions of atoms in the diamond and related networks can with advantage be described by a 4-coordinate system referred to axes along the tetrahedrally arranged bonds in the network. One of the four "tetrahedral coordinates" is redundant in the same way that occurs when using triangular coordinates in two dimensions to represent a ternary system, but its retention greatly facilitates the recognition and handling of symmetry. Related but different ideas have been described by Prelog[1] and Saunders.[2]

For two-dimensional space, the triangular coordinates of a point are obtained by dropping perpendiculars onto the three sides of an equilateral triangle or onto three axes mutually inclined at 120° (Fig. 1a): in the latter case $x + y + z = 0$ for all points. Similarly, in three dimensions perpendiculars are dropped onto four planes, each normal to one of the tetrahedral axes meeting at O (Fig. 1b). Again, for all points, $a + b + c + d = 0$. Two other related 4-coordinate systems have been discovered and will be described in our full paper (with Dr. D.N. Kirk).

The coordinates of all points similarly related to the origin are derived from a set $\{a\ b\ c\ d\}$ merely by permuting the coordinates with appropriate changes of sign. Such simplicity does not occur for Cartesian coordinates. Some examples are given in the Table; this should be read in conjunction with Fig. 2, which depicts a single layer of a diamond network or an array of *trans*-fused cyclo-hexane rings. (The C - C bond length is taken for convenience as 3 units; the coordinates are then integers. For brevity a negative coordinate, $-a$, is written as $\bar{a}$.) Fragments of the array (Fig.2) occur widely, e.g. in sesquiterpenes, diterpenes, steroids, D-homosteroids, and triterpenes; the system can be applied equally well to cage structures (e.g. adamantane) and to structures with cis-fused rings, and can also be extended to boat-form and bridged rings.

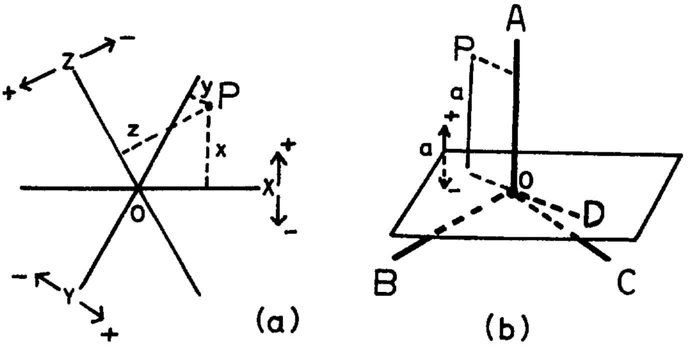

Fig. 1 (a) Triangular coordinates in two-dimensional space.

(b) Tetrahedral coordinates in three-dimensional space. (For the sake of clarity only one plane, that normal to OA, and the coordinate a are shown.)

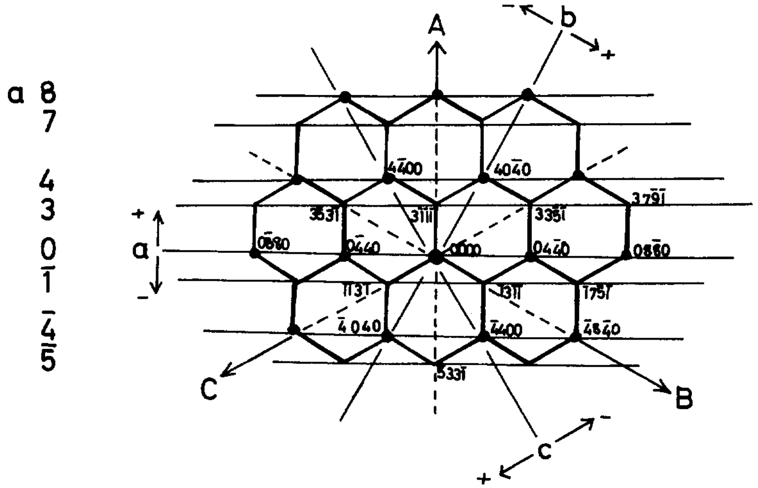

Fig. 2 A single layer of a diamond network, projected onto a plane normal to the axis OD. (Atoms marked ● have d=0; others have d=$\bar{1}$. The a coordinates are shown to the left of the figure; b and c coordinates can similarly be obtained by inspection.)

Table. Coordinates of symmetrically related sets of atoms around the origin in a diamond network (cf. Fig. 2).

Vector type	Torsion angles around successive intermediate bonds	Prelog Class (ref. 1)	Typical Coordinates
1-2	...	...	$3\bar{1}\bar{1}\bar{1}$
1-3	...	...	$4\bar{4}00$ *
1-4	±60°	±sc	$5\bar{3}\bar{3}1$
	180	ap	$7\bar{5}\bar{1}\bar{1}$
1-5	±60, ±60	II	$44\bar{4}\bar{4}$
	±60, ∓60	I	$4\bar{4}00$ *
	±60, 180	III	$8\bar{4}\bar{4}0$
	180, 180	I^v	$8\bar{8}00$

*These vectors provide alternative routes connecting the same pair of atoms.

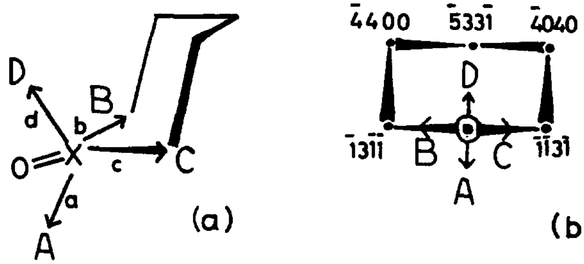

Fig. 3 A cyclohexanone ring. (a) Perspective; X is the carbonyl carbon at the origin; A and D are phantom atoms. (b) Projection onto a plane perpendicular to OX, as in diagrams for the Octant Rule.[3] Tetrahedral coordinates of ring-atoms are given.

The system is applied to cyclohexanone by assuming initially an ideally regular ring and replacing the carbonyl oxygen (Fig. 3) by two tetrahedrally disposed phantom atoms A and D. For merely descriptive purposes such idealisations are permissible and convenient in that they yield integer coordinates, but the precise positions of atoms in real molecules can be expressed as non-integral coordinates just as conveniently in a tetrahedral as in a Cartesian system. Formulae for geometrical calculations in terms of tetrahedral coordinates will be presented later.

Tetrahedral coordinates offer promise for the description of (i) the "fit" of alicyclic substrates to enzymes,[4] (ii) the positions of substituents and bonds in chiroptical studies of polycyclic ketones,[3] and (iii) the spatial relationships of atoms exhibiting long-range spin-spin coupling in n.m.r. studies,[5] especially when interpreting lanthanide shifts.[6] We foresee applications in M.O. calculations, in information retrieval, in searches for compounds containing moieties of specified geometry, and possibly in nomenclature. We also see it as a convenient method of inserting idealised molecular fragments into computer calculations - especially in digigraphics systems - as a prelude to linking them to "synthesize" molecules and optimizing the consequent strains so as to produce molecular skeleta approximating to reality, which could form the basis of molecular geometry and potential calculations. (This last application would be greatly facilitated by a comprehensive algebra described by Argyris[7] which uses a rather similar 4-coordinate system for handling the elastic deformations of sets of connected tetrahedra.)

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