MOLECULES OCCASIONALLY CAN ATTAIN CLOSE PACKING ONLY IN TRANSITIONAL SPACE GROUPS

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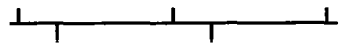
As substantiated by *ca* two hundred thousand crystal structures archived in the Cambridge Structural Database (CSD, Allen & Kennard, 1993), majority of organic molecules reaches the optimum of close packing by the use of simple crystal (triclinic and/or monoclinic) symmetries. Indeed, 62% of the known crystal structures are formed in three centric space groups $P\bar{1}$ (No. 2) $P2_1/c$ (No 14) and $C2/c$ (No. 15). In particular, the symmetry pair $2_1/c$ is overwhelmingly popular in the crystals as shown e.g. by the prevalence of $P2_1/c$ (35%) over the triclinic space group $P\bar{1}$ (19%). Present work reports on a dozen of rare structures in which this symmetry pair takes place in *oblique* (triclinic) unit cells. Since the formation of $2_1/c$ requires at least one orthogonal coordinate, in a triclinic unit cell it can be only pseudo symmetry, labeled as $*2_1/*c$. Of course, the positions of such symmetries (either twofold screw axis or glide plane, or both) should always exhibit some, even very slight distortion and/or displacements. Recently, we focused our attention (Kálmán & Argay, 1998) on crystals with space group $P\bar{1}$ and Z=8 in which such pseudo symmetries seem to improve the close packing. According to the CSD files seven entries have been reported with reference to pseudo symmetries. Four relevant entries were found among the 14 crystal structures that had not been screed for non-crystallographic symmetries. Each structure was checked for the possibility of a transformation into a unit cell of higher (*e.g.* monoclinic) symmetry (Spek, 1988). In such a way four pseudo-monoclinic structures were identified.

A unit cell with Z=8 implies that at least two pairs of $*2_1/*c$ accommodate the eight molecules with four on each *orbit*. However, to avoid collision one or more symmetries on these $*2_1/*c$ orbits must change position(s) with respect to the crystallographic center of symmetry that is the Archimedean point of these crystals. In standard array (space group $P2_1/c$) both rotors (2_1) and mirror (c or n) are separated from $\bar{1}$ by ¼-¼, respectively. A migration, say of glide plane $*c$ along the respective crystal axis from ¼ towards 0 automatically implies its mirror related motion towards ½, and this duplication is repeated around ¾, as well. Such a motion of $*c$ toward $\bar{1}$ is automatically reflected in the translation of the complementary operator $*2_1$ by an asymmetry and *vice versa*. If the migration from ¼ is $\pm\mu$, then the novel translation is $\tau = 2(¼-\mu) \rightarrow 2(¼+\mu)$, respectively. Such unusual orbits, termed as *secondary* pseudo symmetries were observed in BOKXII EXCHLN FODYEC and KUJZOE (REFCODES in CSD) with migration $\mu < 1/8$. Migrations reach their midpoint with $\mu = \pm 1/8$ when the positions of $(2n-1)1/8$ are accompanied by ¼→¾→translation(s) of the complementary operator:



Such pseudo symmetries are developed in KUGWUE and YIHHOM. Further levels of development towards an orthogonal (at least monoclinic) unit cell were shown by CIJSAP, DILFEJ, DIYMED and VARCOG.

In the centered monoclinic unit cells of CIJSAP, DILFEJ and VARCOG the eight molecules pertaining to the original triclinic lattice are located on two orbits bound now to *orthogonal* axis. They can be described by the same symmetry triplet:

$$2_q(1/8,Y,¼) \leftrightarrow n_q(X_q,1/8,Z) \equiv \bar{1}(0,0,0) \qquad (1)$$

where translation q is ¼→¾, while X,Y,Z indicate the infinite extension(s) of the commutative (↔) operators and $\bar{1}(0,0,0)$ is one of the crystallographic inversion centers in the origin. In DIYMED the unit cell transformation with the lowest *fm* =

0.025 results in a space group $C2/c$ (No. 15). Here a simpler transitional orbit $2_1/c_q$ is generated:

$$2_1(0,Y,1/8) \leftrightarrow c_q(X,1/4,Z) \equiv \bar{1}(0,0,0) \quad (2)$$

Naturally, eqs (1) and (2) automatically suggest a third triplet:

$$2_q(0Y,1/4) \leftrightarrow c(X,1/8,Z) \equiv \bar{1}(0,0,0) \qquad (3)$$

These three triplets or *non crystallographic* space groups: $P2_q/n_q$ $P2_1/c_q$ and $P2_q/c$ can also be deduced from the topological operations on the most popular space group $P2_1/c$ (or $P2_1/n$) (No.14). Let us write two alternative triplets for $P2_1/c$

$$2_1(0,Y,1/4) \leftrightarrow \bar{1}(0,0,0) = c(X,1/4,Z) \ (\mathbf{4a}) \qquad c(X,1/4,Z) \leftrightarrow \bar{1}(0,0,0) = 2_1(0,Y,1/4) \ (\mathbf{4b})$$

Then let us shift the 1/4 parameters by $\mu=\pm 1/4$ to 0 and 1/2 on the left sides of eqs. (4):

$$2_1(0,Y,0) \leftrightarrow \bar{1}(0,0,0) = m(X,1/4,Z) \ (\mathbf{5a}) \qquad c(X,0,Z) \leftrightarrow \bar{1}(0,0,0) = 2(0,Y,1/4) \ (\mathbf{5b})$$

Both novel eqs. (5a) and (5b) define a standard space group, either $P2_1/m$ (No.11) or $P2/c$ (No.13), respectively. In the next step on their right sides the 1/4 parameters are shifted to 0 and 1/2, which give one common triplet

$$2(0,Y,0) \leftrightarrow m(X,0,Z) = \bar{1}(0,0,0) \qquad (6)$$

for space and *point* group $P2/m$ (No.10). However, if the symmetry migrations stop at the midpoints between 1/4 and 0, then *mutatis mutandis,* just the three *transitional* space groups described by eqs.(1)-(3) are generated

$$P2_1/m \leftarrow \boldsymbol{P2_1/c_q} \leftarrow P2_1/c \rightarrow \boldsymbol{P2_q/c} \rightarrow P2/c$$
$$\downarrow$$
$$\boldsymbol{P2_q/c_q}$$
$$\downarrow$$
$$P2/m$$

Duplication of the crystallographically *irregular* symmetries (in space group $P2_q/c_q$ there are four glide planes and eight screw axes) with their halved functions give greater freedom especially for small molecules to establish the optimum of

close packing when, *e.g.* slight so called *sporadic* conformational differences do not permit to form standard space group. Of course, the number of molecules on the $2_1/c_q$ $2_q/c$ and $2_q/c_q$ orbits invariably remains four.

Summing up, these centered and transitional monoclinic unit cells with their different imperfectness attest the ability of Nature to utilize *doubled* transitional symmetries whenever it is expedient. Of course, no perfect formation of such symmetries is permitted, since this would violate the absolute priority of standard space group(s) using regular (symmetric) translations. Consequently, they cannot occur independently. Even in the best case they are embedded in centered monoclinic unit cells that also retain some sort of imperfectness. However, the controlled imperfectness of these symmetries necessarily tolerate small and sporadic conformational differences retained from the liquid phase. They are favorable enough to optimize molecular close packing.

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REFERENCES

Allen, F.H. and Kennard, O.(1993) 3D Search and research using Cambridge Structural Database. *Chem. Des. Automat. News*, 8, 31-37 .

Kálmán, A. and Argay, Gy.(1998) On the birth of symmetries: Topological description of pseudo symmetries in the triclinic unit cell of *trans*-cyclohexa[*f*]-2,3,4,5,5a,9a-hexahydro-2-methyl-4-phenylaminocarbonyl-1,4-oxazepin-3-one and other structures crystallized with space group $P\bar{1}$ and *Z*=8. *Acta Cryst. Sect. B,* .

Spek, A. L.(1988) *LEPAGE* an MS-DOS program for the determination of the metrical symmetry of a translation lattice. *J. Appl. Cryst.* 21, 578-579 .