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Acta Cryst. (1977). A**33**, 1001–1004

The Systematization of Molecular Crystal Structures

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(*Received* 4 *March* 1977; *accepted* 29 *April* 1977)

A scheme of classification of molecular crystal structures is proposed. The structures are divided into homo-, hetero and quasiheteromolecular. The next step of the classification is the division into chiral types which define the character of the systems of equivalent positions occupied by the molecules. Finally, the subdivision into chiral classes reflects the equality or inequality of symmetrically unrelated molecules. Statistical data are given about the distribution of quasiheteromolecular structures into chiral classes. The concept of an expanded (non-Fedorov) space group is proposed to describe such structures.

The rapid development of X-ray structural investigations has led to a large expansion in information about the structure of crystals. However most crystal chemists concentrate on the details of the molecular structure; the problem of the relative disposition of molecules in the crystal is often ignored or treated only superficially. Details of the architecture of molecular crystals are of interest because the solid-state reactivity and many physical and physico-chemical properties of crystalline substances depend on the molecular packing.

In this paper we propose a scheme of classification of molecular crystal structures. The Fedorov space groups are basic to this systematization but in certain cases this apparatus turns out to be insufficient. The geometrical features of some crystal structures can be described only with the aid of expanded non-Fedorov space groups.

First, we divide molecular crystals into *homomolecular* and *heteromolecular*. The former are built up of molecules having the same chemical composition and identical structural formula. The latter are composed of chemically different molecules. There is a smooth transition between these two types.

Naphthalene is a typical homomolecular crystal (Abrahams, Robertson & White, 1949; Cruickshank, 1957) where the molecules occupy the single system of equivalent positions [$P2_1/c$, $Z=2$ ($\bar{1}$)*]. Here all the molecules are symmetrically related and therefore have the same structure and environment. In crystals of tolane (Robertson & Woodward, 1938; Samarskaya, Myasnikova & Kitaigorodsky, 1968) molecules occupy two systems of positions [$P2_1/c$, $Z=4$ ($\bar{1},\bar{1}$)] and, though the symmetrically unrelated molecules are practically identical in geometry, their environments differ. In such cases, molecules of different structure can coexist in the same crystal. Thus, in crystalline isoleucine (Torii & Iitaka, 1971) half the molecules are *gauche*, the other half *trans* [$P2_1$, $Z=4$ (1,1)]. We call crystals in which chemically identical molecules occupy more than one system of equivalent positions *quasiheteromolecular*.

Crystals of tolane–diphenylmercury are heteromolecular [$P2_1/c$, $Z=2$ ($\bar{1},\bar{1}$)] (Kitaigorodsky, Myasnikova & Samarskaya, 1963). However, they do resemble tolane itself. The similarity between the molecules of diphenylmercury and diphenylacetylene (tolane) permits them to replace each other without significantly affecting the packing. A typical heteromolecular crystal with quite different molecules is the molecular complex α-D-glucose–urea (Snyder & Rosenstein,

* The symbol of the structural class to which naphthalene crystals belong is given; this concept is discussed below.

1971) [$P2_12_12_1$, $Z=4$ (1,1)]. In such crystals there is always some charge transfer from molecules of one kind to the other. Therefore the natural continuation of this series are crystals of, for example, $(NH_4)_2SO_4$.

We plan to publish a paper about the systematization of heteromolecular crystals which we interpret quite broadly as including also ionic compounds containing as one of the components univalent ions of halogens or alkali metals. Below we consider only homomolecular crystals (including quasiheteromolecular), but the principles of their systematization would hold also for crystals composed of different molecules.

The next step of classification is the division of crystals into *chiral types.*

Chirality is the property that a molecule does not coincide with its mirror image. The necessary and sufficient condition of chirality is the absence in the molecular point group of an inversion centre, mirror plane or inversion axis of higher order. Otherwise the molecule is achiral. A combination of chiral molecules may be *homochiral* if it contains only left or only right-rotatory molecules and *heterochiral* if it contains both left and right molecules.

Let us consider that the molecular symmetry (S_m) in a crystal is exactly equal to its position symmetry (S). Actually the eigensymmetry of the molecule, within the limits of X-ray analysis, may be somewhat higher than S. But this situation occurs only for comparatively simple molecules and, if we take into account not only nuclear configuration but also electron density and intermolecular contacts, the equality $S_m=S$ becomes exact.

The systems of equivalent positions occupied by the molecules are then divided into homochiral, heterochiral and *achiral.* This permits four chiral types of molecular crystals.

Type A. The molecules occupy homochiral systems of equivalent positions. This is possible when the space group does not have inversion centres, mirror or glide planes, or inversion axes of higher order (*i.e.* second-order symmetry elements).

Type B. The molecules occupy heterochiral systems of positions. Therefore there are second-order symmetry elements in the crystal.

Type C. The molecules occupy achiral systems of positions, *i.e.* they are situated either on inversion centres or on mirror planes or on special points of inversion axes of higher order.

Type D. Molecules occupy both achiral and heterochiral systems of positions.

Each type *A*, *B* and *C* may be divided into two subtypes (*e.g.* *A'* and *A''*). In crystals of the first subtype molecules occupy only one system of equivalent positions. In the second, two or more systems of positions are occupied. For type *D* there is only subtype *D''*.

The classification of molecular crystals by chiral types reflects the chiral correlation only between molecules related by the Fedorov space-group operations. In subtypes *A''*, *B''*, *C''* and *D''*, *i.e.* for quasi-heteromolecular crystals, the problem arises about the correlation of the geometry of molecules unrelated by the symmetry of the Fedorov group. The latter makes allowance for subdivision of the subtypes into the *chiral classes.*

To designate the different geometric relations between symmetrically unrelated molecules m_i we use the following symbols: (1) symmetrically unrelated molecules are identical (within the limits of experimental error), *i.e.* homochiral: $m_i \equiv m_j$; (2) symmetrically unrelated molecules are mirror images, *i.e.* heterochiral: $m_i \| m_j$; (3) symmetrically unrelated molecules (being achiral themselves) are equal both congruously and by mirror reflexion: $m_i = m_j$;* (4) symmetrically unrelated molecules have different structures, *i.e.* they are neither identical nor equal by mirror reflexion: $m_i \neq m_j$.

We stress that we treat the equality (or inequality) of the molecules within the limits of experimental error. For a more detailed classification it is possible to separate the cases of approximate equality when the differences in molecular structure are slightly more than experimental error but still remain small.

All possible chiral classes for crystals where one, two or three systems of equivalent positions are occupied ($k=1,2,3$) are given in Table 1. It is not difficult to write out all combinations with $k>3$.

We have studied the distribution of organic quasi-heteromolecular crystals by chiral classes (Table 2) (this part of the work was performed with the aid of Mr E. Ya. Vakhrushev). As the source data we used the reference book by Kitaigorodsky, Zorkii & Belsky

* The same symbol is used by us to designate equality of the molecules in general, when the correlation $m_i = m_j$ or $m_i \| m_j$ holds.

Table 1. *The chiral classes*

	Chiral types			
k	*A*	*B*	*C*	*D*
1	$A(m)$	$B(m)$	$C(m)$	$D(m)$
2	$A(m_1 \equiv m_2)$ $A(m_1 \| m_2)$ $A(m_1 \neq m_2)$	$B(m_1 \equiv m_2)$ $B(m_1 \neq m_2)$	$C(m_1 \equiv m_2)$ $C(m_1 \neq m_2)$	$D(m_1 \equiv m_2)$ $D(m_1 \neq m_2)$
3	$A(m_1 \equiv m_2 \equiv m_3)$ $A(m_1 \equiv m_2 \| m_3)$ $A(m_1 \equiv m_2 \neq m_3)$ $A(m_1 \| m_2 \neq m_3)$ $A(m_1 \neq m_2 \neq m_3)$	$B(m_1 = m_2 = m_3)$ $B(m_1 = m_2 \neq m_3)$ $B(m_1 \neq m_2 \neq m_3)$	$C(m_1 = m_2 = m_3)$ $C(m_1 = m_2 \neq m_3)$ $C(m_1 \neq m_2 \neq m_3)$	$D(m_1 = m_2 = m_3)$ $D(m_1 = m_2 \neq m_3)$ $D(m_1 \neq m_2 \neq m_3)$

Table 2. *The distribution of organic quasiheteromolecular crystals by chiral classes*

Chiral type	Molecules occupy two systems of positions			Molecules occupy three systems of positions		
	$m_1=m_2$	$m_1 \| m_2$	$m_1 \neq m_2$	$m_1=m_2=m_3$	$m_1=m_2\neq m_3$	$k>3$
A	70	1	21	5	1	3
B	124	—	30	6	1	3
C	36	—	6	2	—	1
D	9	—	4	2	—	—
Total	239	1	61	15	2	7

(1977), *Referativny Zhurnal Khimiya* (chemical abstracts journal in Russian) and original reports. The data cover the period from 1929 to 1975. The allocation of the structures to the different chiral classes was performed on the basis of qualitative comparison of the framework of the molecules. In so doing we were guided by the estimation of molecular similarities given by the authors of structural reports and also by their figures and numerical tables of the geometrical features. We considered as different those molecules having qualitatively unequal conformations. It is clear that such an approach is somewhat subjective. Therefore, the data from Table 2 are to be considered as preliminary. In future we plan to perform a quantitative correlation of symmetrically unrelated molecules by minimization of $\sum_{i=1}^{N} \omega_i R_i$, where R_i is the distance between the same corresponding atoms of the molecules compared (at their closest approach), ω_i are weighting coefficients, and N is the number of atoms in the molecule.

During the processing we encountered 352 organic quasiheteromolecular structures, including 7 where molecules occupy more than three systems of equivalent positions (we used only data where all the atoms were located, except perhaps H atoms). For 325 structures we managed to perform a qualitative comparison of the molecules; in the other cases the information in the original papers was insufficient for allocating the structure to a class without doing special calculations.

As can be seen from Table 2 most quasiheteromolecular crystals are built of similar molecules. This creates the prerequisites for what we call supersymmetry (Zorkii & Belsky, 1972). It turns out that in many cases the molecules unrelated by Fedorov space group symmetry can nevertheless be transformed into each other by the special operation τ which includes rotation by an angle φ and a shift along the rotation axis L. φ is equal to $360°/n$, where $n=2,3,4$ (so far we have encountered only these values of n). The axis L is always situated in a special position with respect to the crystallographic axis (*e.g.* parallel to one coordinate plane or axis). τ does not belong to the Fedorov space group, but transforms symmetrically unrelated molecules. An example is the above-mentioned crystal structure of tolane. For the description of such structures we proposed the concept of expanded groups of supersymmetry (non-Fedorov space groups).

We encountered two structures of the chiral type *A* built up of heterochiral molecules. In barbital [$P2_1$, $Z=8$ (1^4)] (Craven & Vizzini, 1971) the molecules occupy four systems of positions whereas the symmetrically unrelated molecules are congruous pairwise and the molecules of different pairs are mirror images. DL-Methylsuccinic acid [$P2_1$, $Z=4$ (1,1)] (Schouwstra, 1973) is also built up of heterochiral symmetrically unrelated molecules. It is possible that among other crystals there are more of this kind, but insufficient details were given by the authors of the original papers.

Crystals in which molecules of qualitatively different structure (*i.e.* stereoisomers) coexist are encountered quite often (approximately 20%). Here three main situations exist: (1) coexistence of conformers such as boat and chair; (2) coexistence of molecules with axial or equatorial orientation of bonds; (3) coexistence of rotational isomers.

We plan to publish a paper concerning both the new data about supersymmetry and structures built up of molecules with different geometry. Here we touch upon this problem only so far as it concerns the systematization of the molecular crystals.

The distribution of quasiheteromolecular crystals by chiral types is: *A* 32·2%; *B* 50·4%; *C* 13·1% and *D* 4·3%. This distribution does not differ significantly from that of all homomolecular organic crystals (including those where one system of positions is occupied), except that the contribution of type *D* is about zero to the total number of homomolecular organic structures studied (more than 5000).

Certain *structural classes* (Zorkii, Belsky, Lazareva & Poray-Koshits, 1967; Zorkii, Belsky & Poray-Koshits, 1972) are characteristic for each chiral type and subtype. The structural class defines to a large extent the relative disposition of the molecules in the crystal. The distribution of molecular crystals by structural classes has been discussed (Belsky & Zorkii, 1970). In the next paper we present new data of this distribution (Belsky & Zorkii, 1977).

Finally, we note that, in the present classification, crystals with a statistical arrangement of molecules have no place. The peculiar features of such crystals require special treatment.

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Acta Cryst. (1977). A**33**, 1004–1006

Distribution of Organic Homomolecular Crystals by Chiral Types and Structural Classes

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(*Received* 4 *March* 1977; *accepted* 29 *April* 1977)

Statistical data are given for the distribution of organic and elemento-organic homomolecular crystals by chiral types and structural classes (with data published in 1929–1975). The resulting material reflects the general principles of molecular crystal construction and is in accord with the theoretically predicted incidence of different structural classes based on the potential functions symmetry method.

Zorkii, Belsky, Lazareva & Poray-Koshits (1967) proposed the concept of structural class (SC) as the main unit for the systematization of molecular crystal structures. SC unites crystals of the same space-group symmetry with the molecules occupying monotypic systems of equivalent positions and therefore defines the rules governing the relative positioning of the molecules.

Belsky & Zorkii (1970) discussed data based on 3259 reports published up to 1967 in terms of the distribution of homomolecular (*i.e.* composed of chemically identical molecules) crystals by SC.

Here we report updated data which reveal some new features. We have used only the results of complete structure investigations where all atoms were located (except perhaps the H atoms); this guarantees to a large extent the reliability of the source data. We performed our analysis not only for SC but also for chiral types; this gives a better idea about conformity with the rules of molecular crystal structure composition. Because of the rapid growth of X-ray structural information we limited ourselves to organic and elemento-organic compounds, *i.e.* those containing C, H, halogens, O, S, Se, Te, N, P, As, Si and B. Our results are based on 5002 reports of homomolecular crystals determined up to 1975. We do not think that the rules of inorganic molecular crystal composition will be very different from those of organic, and the results obtained should be typical of all homomolecular crystals.

Following Zorkii, Razumaeva & Belsky (1977) we distinguish four chiral types: *A*, molecules occupy only homochiral systems of positions, *i.e.* symmetrically related molecules are identical; *B*, molecules occupy only heterochiral systems of positions, *i.e.* the crystals are racemic; *C*, molecules occupy only achiral positions, *i.e.* there is no difference between racemic and congruous molecules; *D*, molecules occupy both achiral and heterochiral positions.

Table 1 shows that 96·7% of organic homomolecular crystals belong to systems of low symmetry, mainly monoclinic and orthorhombic. Of 219 space groups

Table 1. *Distribution of homomolecular crystals by crystal systems*

Crystal system	Number of structures	%
Monoclinic	2794	55·9
Orthorhombic	1562	31·2
Triclinic	478	9·6
Tetragonal	92	1·8
Hexagonal (including trigonal)	68	1·4
Cubic	8	0·1