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Distribution of Organic Homomolecular Crystals by Chiral Types and Structural Classes

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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

with different X-ray diffraction patterns, only 89 occur in the molecular crystals studied and more than one third of all structures belong to the space group $P2_1/c$. The six most common space groups (Table 2) cover 83.2% of all crystals investigated.

The distribution of structures by chiral types is: *A* 28.4%, *B* 55.6%, *C* 15.7% and *D* 0.3%.

The most common SC are given in Table 3, which includes only those accounting for more than 3% of all known structures of a given chiral type. Type *A* is mainly represented by SC $P2_12_12_1$, $Z=4$ (1) and $P2_1$, $Z=2$ (1). For type *B* (racemates), SC $P2_1/c$, $Z=4$ (1) is the most common, and for type *C*, $P2_1/c$, $Z=2$ ($\bar{1}$).

The conclusion about the widely varying incidence of molecular crystals' SC (Belsky & Zorkii, 1970) is fully confirmed by the present data. So far 190 SC of homomolecular organic crystals are known; 114 (60%) of them have only one or two members, i.e. are anomalous, and only 44 SC (23%) have more than five mem-

Table 2. Most common space groups of molecular crystals

Only space groups accounting for more than 1% are given.

<i>N</i>	Space group	Number of structures	%
1	$P2_1/c$	1897	37.9
2	$P2_12_12_1$	839	16.8
3	$P\bar{1}$	449	9.0
4	$P2_1$	418	8.4
5	$C2/c$	310	6.2
6	$Pbca$	247	4.9
7	$Pna2_1$	120	2.4
8	$Pnma$	94	1.9
9	$Pbcb$	58	1.2
Total		4432	88.6

Table 3. Most common SC of homomolecular crystals

Structural class	Number of structures	%*	%†
Type <i>A</i>			
$P2_12_12_1$, $Z=4$ (1)	798	56.1	16.0
$P2_1$, $Z=2$ (1)	352	24.8	7.0
$P2_1$, $Z=4$ (1, 1)	63	4.4	1.3
Type <i>B</i>			
$P2_1/c$, $Z=4$ (1)	1429	51.4	28.6
$P\bar{1}$, $Z=2$ (1)	289	10.4	5.8
$Pbca$, $Z=8$ (1)	203	7.3	4.1
$C2/c$, $Z=8$ (1)	136	4.9	2.7
$C2/c$, $Z=4$ (2)	132	4.8	2.6
$P2_1/c$, $Z=8$ (1, 1)	124	4.5	2.5
$Pna2_1$, $Z=4$ (1)	107	3.8	2.1
Type <i>C</i>			
$P2_1/c$, $Z=2$ ($\bar{1}$)	311	39.5	6.2
$P\bar{1}$, $Z=1$ ($\bar{1}$)	95	12.1	1.9
$Pnma$, $Z=4$ (<i>m</i>)	93	11.8	1.9
$P2_1/m$, $Z=2$ (<i>m</i>)	37	4.7	0.7
$Pbca$, $Z=4$ ($\bar{1}$)	34	4.3	0.7
$C2/c$, $Z=4$ ($\bar{1}$)	32	4.1	0.6

* Of structures belonging to the given chiral type.

† Of all structures studied.

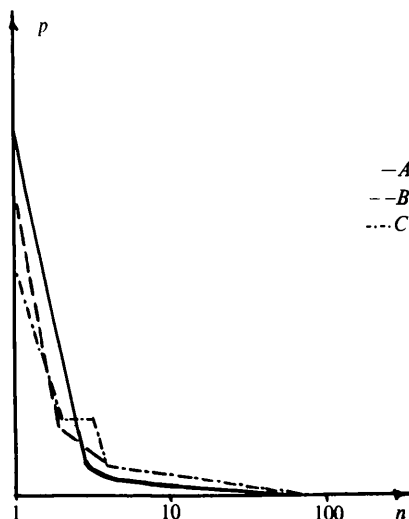


Fig. 1. Relative incidence of SC for the different chiral types.

bers. The six most common SC cover 67.7% of all structures studied.

The distinguishing features of the crystal distribution by SC for chiral types *A*, *B* and *C* are illustrated in Fig. 1. This is a plot of the dependence of p on n (n values are given on a logarithmic scale), where p is the ratio of the number of members of a given SC to the total number of the members of the given chiral type, and n is the ordinal number in the sequence where the SC of the same type are presented in descending order of the number of representatives.

The chiral type *A* differs from types *B* and *C* by the relatively larger contribution from the first two SC and smaller from all other SC, the total number of which is only 38. For type *B* compared with type *C* the role of the first SC is very significant and that of the third is relatively smaller; beginning from $n=4$ the plots for types *B* and *C* practically merge. The total number of known SC is 76 for *B* and 69 for *C*.

The few type *D* representatives (only 14 structures so far studied) are distributed between seven SC of which SC $P2_1/c$, $Z=6$ ($\bar{1}$, 1) (six members) plays the leading role. All other SC are anomalous.

The analysis confirms the well-known principle that in a crystal a molecule usually loses all elements of symmetry except a centre. As can be seen from Table 3 the most common case when the molecule retains a twofold axis is SC $C2/c$, $Z=4$ (2), and a mirror plane, SC $Pnma$, $Z=4$ (*m*). A more detailed discussion of the relations between the eigensymmetry of a molecule and its space-group symmetry has been published (Belsky, 1974).

In most organic homomolecular crystals the molecules occupy a single system of equivalent positions. This means that, as a rule, all the molecules in the crystal are identical in geometry and have the same environment. At the same time structures where symmetrically unrelated molecules are present (quasi-

heteromolecular crystals) attract special interest; firstly, because non-Fedorov symmetry can often be

Table 4. Comparison of the theoretical predictions with statistical data

Structural class	Predicted incidence (%)	Statistics (%)
Asymmetric position of molecules (chiral type <i>A</i>)		
$P2_12_12_1, Z=4 (1)$	65.5	58.2
$P2_1, Z=2 (1)$	22.2	25.7
$P2_1, Z=4 (1, 1)$	1.9	4.6
$P2_12_12_1, Z=8 (1, 1)$	2.3	2.8
$C2, Z=4 (1)$	3.4	2.2
$P1, Z=1 (1)$	4.6	1.5
Centrosymmetric position of molecules (chiral type <i>C</i>)		
$P2_1/c, Z=2 (\bar{1})$	66.6	59.6
$P\bar{1}, Z=1 (\bar{1})$	14.4	18.2
$Pbca, Z=4 (\bar{1})$	7.7	6.5
$C2/c, Z=4 (\bar{1})$	5.1	6.1
$P2_1/c, Z=4 (\bar{1}, \bar{1})$	3.6	3.6
$P\bar{1}, Z=2 (\bar{1}, \bar{1})$	2.6	3.5
Twofold symmetry positions of molecules (chiral types <i>A</i> and <i>B</i>)		
$C2/c, Z=4 (2)$	54.8	49.8
$Pbcn, Z=4 (2)$	19.5	15.1
$Fdd2, Z=8 (2)$	7.7	6.8
$P2_12_12_1, Z=2 (2)$	7.3	4.2
$C2, Z=2 (2)$	5.0	3.0
$Pccn, Z=4 (2)$	3.8	3.0

Note: The predicted incidence for molecules with twofold symmetry is systematically larger than the statistical. This can be explained by not taking into account the contribution from tetragonal structures during the theoretical treatment (Belsky & Dzyabchenko, 1975).

found (Zorkii & Belsky, 1972a); secondly, because cases of coexistence of molecules with different conformation in the same crystal can be encountered. We found only 413 structures (8.3%)* where molecules occupy more than one system of positions including 22 structures with three occupied systems, 9 with four, 2 with six and 1 (selenourea) with nine.

The results obtained in this investigation are in good agreement with theoretical predictions of the probability of occurrence of different SC based on the method of potential-functions symmetry (Zorkii & Belsky, 1972b; Belsky & Dzyabchenko, 1975) (Table 4).

* We have added 61 structures published in the second half of 1975 to the data of the previous report (Zorkii, Razumaeva & Belsky, 1977).

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