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Molecular versus structural chirality

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The rigorous proof that a structure crystallizing in any of the 65 Sohncke types of space groups is necessarily chiral is presented.

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1. Introduction

Nespolo & Benahsene (2021) have presented a detailed analysis of the relation between symmetry and chirality in crystals. Rekiş (2023) has subsequently discussed counter-examples showing that the restriction of chiral structures to a subset of Sohncke types of space groups is not justified, but did not provide a rigorous proof that a structure crystallizing in any of the 65 Sohncke types of space groups is necessarily chiral. This stimulated a more detailed investigation of the relation between molecular and structural chirality. Presented here is the rigorous proof that was missing from Rekiş's (2023) article.

2. Molecular versus structural chirality

A crystal structure S is an infinite set of atoms (under the usual assumption of treating the surface of the crystal as a defect) that is usefully partitioned into a finite number of infinite sets $O : S = \cup_i O_i$. Each set O_i is obtained by applying the infinitely many operations of the space group \mathcal{G} to a given atom X_i in the asymmetric unit. The sets O_i are called crystallographic orbits. In symbols, $O_i = \{X_j \in S \mid X_j = \mathcal{G}X_i\}$, where X_i is the i th atom in the asymmetric unit, \mathcal{G} is the space group and O_i is the orbit. In matrix formalism, this becomes $X_i = (x_i \ y_i \ z_i)^T$ and $O_i = \{X_j\} = \{(x_j \ y_j \ z_j)^T\}$, where $(x_i \ y_i \ z_i)^T$ is the column matrix of the fractional atomic coordinates of the i th atom and \mathcal{G} is the infinite group of matrix–vector pairs representing the operations of the space group.¹ In a molecular crystal, a coarser partition of the crystal structure S can be applied, by considering S as an infinite set of molecules, without explicitly considering the further partition into the atoms that build up each molecule. That comes from the fundamental difference between intra- and intermolecular bonds, which allows us to consider the molecule as the building block of the crystal.

The symmetry group \mathcal{G} of a crystal structure S composed of more than one crystallographic orbit O_i is the intersection group of the symmetry groups of those orbits. In symbols,

$$S = \cup_i O_i; \quad \mathcal{G} = \cap_i \mathcal{E}_i; \quad \mathcal{E}_i O_i = O_i. \quad (1)$$

The symmetry group \mathcal{E}_i of each crystallographic orbit O_i is called its eigensymmetry group. In the intersection, only the operations common to the eigensymmetry groups of each and

¹T indicates that the matrix has been transposed: $(x \ y \ z)$ is a row matrix, whereas $(x \ y \ z)^T$ is a column matrix.

every orbit are retained. Depending on whether \mathcal{E}_i coincides with \mathcal{G} or is a supergroup of it, O_i is called a characteristic or a non-characteristic orbit, respectively. A molecular crystal structure can be partitioned on two levels of subsystems: the molecules M_i and the atoms building the molecules. $M_i = \cup_j X_{ij}$, where the double index ij points to all the atoms j that belong to the i th molecule. The orbits are then defined as $O_i = \cup_j O_{ij} = \{M_j \in S \mid M_j = \mathcal{G}M_i\}$, and equation (1) becomes

$$S = \cup_i O_i = \cup_{ij} O_{ij}; \quad \mathcal{G} = \cap_i \mathcal{E}_i; \quad \mathcal{E}_i = \cap_j \mathcal{E}_{ij}. \quad (2)$$

In the following, when overlapping two equivalent configurations of a physical object (a molecule, a crystal structure) I use the symbol $=$ if the coincidence is pointwise and the symbol \approx for a coincidence as a set. For example, for a molecule which possesses an n -fold rotational symmetry, a rotation \mathbf{R} by $2m\pi/n$, $m \in \mathbb{Z}$, leads to $\mathbf{R}M \approx M$, which becomes $\mathbf{R}M = M$ for the special case that m is a multiple of n . I remind the reader of the usual notation Z for the number of formula units in the unit cell and Z' for the number of formula units in the asymmetric unit. For a molecular crystal, the number of formula units coincides with the number of molecules. Isometries are mappings (operations) that preserve distances and angles; their representation matrices have determinant ± 1 . They are divided into handedness-preserving (first kind) and handedness-reversing (second kind) operations, whose representation matrices have determinant $+1$ and -1 , respectively.

2.1. The proof for $Z' = 1$

Let M be an achiral molecule in the asymmetric unit of a space group \mathcal{G} . Let us assume that M alone builds up a crystal structure S under the operations of \mathcal{G} ; this means that $Z' = 1$ and $S = \mathcal{G}M$. Then, the eigensymmetry group of S necessarily coincides with \mathcal{G} , because $\mathcal{G}S = \mathcal{G}(\mathcal{G}M) \approx S$, which means that S is a characteristic orbit of M under \mathcal{G} .

Because M is achiral, the point group \mathcal{P} of M contains operations that are equally divided between first and second kind. The set of operations of the first kind builds a subgroup of \mathcal{P} of index 2. The point group of \mathcal{G} , however, is unrelated to the point group \mathcal{P} of M .

Let us suppose that the space group \mathcal{G} of S is of Sohncke type; as such, it contains only isometries g of the first kind. In symbols, $\mathcal{G} = \{g \in \mathcal{SE}(3) \mid gS \approx S\}$, where $\mathcal{SE}(3)$ is the special Euclidean group of dimension 3 consisting of isometries with linear parts having determinant $+1$. I want to explore whether S can be achiral. For that, there must be an isometry of the first kind f_1 such that f_1S can be overlapped with $\bar{1}S$. In symbols,

$$\bar{1}S \approx f_1S, \quad f_1 \in \mathcal{SE}(3). \quad (3)$$

Remembering that the inversion is an operation of order 2, equation (3) can be rewritten as follows:

$$S \approx \bar{1}f_1S, \quad f_1 \in \mathcal{SE}(3). \quad (4)$$

The product $\bar{1}f_1$ is an isometry of the second kind and the equivalence as a set expressed by equation (4) means that, although neither $\bar{1}$ nor f_1 belongs to \mathcal{G} , the product $\bar{1}f_1$ does.

The space group \mathcal{G} of S is therefore not of Sohncke type, contrary to the hypothesis. For example, if f_1 is a twofold rotation about a certain direction, equation (4) becomes $S \approx \bar{1} \cdot 2S$, which means that the space group of S must contain a mirror reflection ($\bar{1} \cdot 2 = m$) about a plane perpendicular to the direction of the twofold rotation; neither the inversion nor the twofold rotation belongs to the space group \mathcal{G} of S . One concludes that an achiral structure with $Z' = 1$ does not have a Sohncke type of space group as its symmetry group.

Sohncke types of space groups are divided into 43 achiral types and 22 chiral types, the latter subdivided into 11 pairs of enantiomorphic types. Achiral molecules crystallizing in a chiral space group (*i.e.* a space group for which also its normalizer contains only operations of the first kind) produce a chiral crystal structure because the packing of molecules is intrinsically chiral due to the chirality of the group itself, *i.e.* to the presence of screw axes with left or right handedness: n_p with $p \neq n/2$. The same holds for the 11 types of achiral space groups which contain screw axes of opposite handedness: 4_1 and 4_3 in $F4_132$, $I4_132$, $I4_122$ and $I4_1$; and 3_1 and 3_2 in $I23$, $I2_13$, $F23$, $P23$, $P2_13$, $R32$ and $R3$. The screw axis of one handedness produces a helical distribution of molecules, whereas the axis of opposite handedness maps the helices onto one another. These 33 (22 chiral plus 11 achiral) types of space groups are those in which the chirality of the molecular packing comes from the structure of the group itself. A subset was recognized by Nespolo & Benahsene (2021), who overlooked cubic groups of geometric crystal class 23.

Note that the action of two screw axes of opposite handedness, n_p and n_{n-p} , on an atom equidistant from them produces pairs of equivalent atoms at $2\pi/k$, $k = [1, p]$, both translated by k/n . These pairs are related by a mirror reflection about a plane perpendicular to the line segment between the two screw axes and bisecting that line segment. This mirror reflection is, in general, a partial operation, unless the atoms building the molecule are all contained in the plane, *i.e.* the molecule is planar and aligned parallel to the screw axes. If that is the case, the molecule is itself equidistant from the two screw axes, the mirror reflection is a global operation, and the space group of S is not \mathcal{G} but a non-Sohncke supergroup of \mathcal{G} that contains that mirror reflection.

In the absence of a handedness-bearing screw axis, the operations of a Sohncke type of space group \mathcal{G} result from a combination (in a set-theoretical meaning) of rotations n or screw rotations $n_{n/2}$ (2_1 , 4_2 or 6_3) – which may also coexist, like *e.g.* in space groups of type $C2$ – with the translation vectors. Two possible results may occur:

(1) The operations of \mathcal{G} produce a chiral crystal structure. An example is provided in Fig. 1 of Rekis (2023).

(2) The operations of \mathcal{G} produce an achiral crystal structure. In that case, equation (4) holds and \mathcal{G} is not the eigensymmetry group of S ; *i.e.* S is not a characteristic orbit of \mathcal{G} . In other words, \mathcal{G} is a subgroup of the space group of S , which, because it contains isometries of the second kind, is not of Sohncke type.

Nespolo & Benahsene (2021) have assumed that the condition for the packing of achiral molecules to result in a

chiral structure is the presence of handedness-bearing screw axes. As shown above, that condition is sufficient but is not necessary and has to be lifted.

The question remains whether the packing of achiral molecules in a Sohncke type of space group is necessarily chiral. In the above derivation we have assumed that $Z' = 1$. In this case, the crystal structure S is obtained as an orbit of M under \mathcal{G} . In other words

$$S = \mathcal{G}M = \cup_i g_i M, \quad g_i \in \mathcal{G} \subset \mathcal{SE}(3). \quad (5)$$

2.2. The extension to $Z' > 1$

If instead $Z' > 1$, there exist isometries that map the different molecules in the asymmetric unit. These isometries are, however, partial operations, *i.e.* operations acting on a subspace of the structure, which do not show up in the space group \mathcal{G} (Nespolo, 2008). These partial operations may be of second kind, without raising any contradiction with respect to the Sohncke nature of the space group, because a space group contains only total operations. Let us consider the simplest case $Z' = 2$ and let us indicate as M_1 and M_2 , respectively, the two molecules in the asymmetric unit (the generalization to any Z' being straightforward). Equation (5) can be rewritten as follows:

$$S = \mathcal{G}(M_1 \cup M_2) = \cup_i g_i (M_1 \cup M_2), \quad g_i \in \mathcal{G} \subset \mathcal{SE}(3). \quad (6)$$

Let us call \hat{h}_{II} the partial isometry of the second kind mapping M_1 to M_2 ; the symbol \hat{h} is reminiscent of the graphical symbol \mapsto used to indicate a partial function, in contrast to the symbol \rightarrow for a total function. The mapping can be written as follows:

$$M_1 \mapsto M_2 : \hat{h}_{II} M_1 = M_2. \quad (7)$$

The existence of a partial operation of the second kind is compatible with the achiral nature of the molecules it maps; if the molecules were chiral, the crystal structure would correspond to a racemic crystal. Let g be an operation of the space group \mathcal{G} , which maps M_1 to M'_1 and M_2 to M'_2 , where M'_1 and M'_2 are outside the asymmetric unit:

$$M'_2 = gM_2; \quad M'_1 = gM_1. \quad (8)$$

For space groups of type $P1$, $Z = Z'$ and g is a translation. For all the other types of space groups, $Z > Z'$ and operations $g \neq 1$ with nontrivial linear part do exist.

The combination of a total operation and a partial operation is another partial operation:

$$M'_2 = gM_2 \stackrel{\text{eq(7)}}{=} g(\hat{h}_{II} M_1) \stackrel{\text{eq(8)}}{=} g[\hat{h}_{II}(g^{-1} M'_1)] = g\hat{h}_{II} g^{-1} M'_1. \quad (9)$$

Equation (9) simply expresses the well known fact that the mappings of two pairs of objects related by an isometry are conjugated under that isometry. The mapping $M'_2 \mapsto M_1$ is also easily obtained:

$$M'_1 = gM_1 = g\hat{h}_{II}^{-1} M_2. \quad (10)$$

The structure S is the union of S_1 and S_2 , where S_1 is the orbit of the molecule M_1 under \mathcal{G} and S_2 is the orbit of the molecule M_2 . S can now be written as follows:

$$S = S_1 \cup S_2 = \mathcal{G}(M_1 \cup \hat{h}_{II} M_1) = \mathcal{G}(1 \cup \hat{h}_{II}) M_1. \quad (11)$$

\mathcal{G} is assumed to be the full symmetry group of the union S of the two orbits S_1 and S_2 , but neither S_1 nor S_2 needs to be a characteristic orbit of \mathcal{G} . Indeed, if $S = S_1 \cup S_2$, then $G = \mathcal{E}(S_1) \cap \mathcal{E}(S_2)$, where \mathcal{E} is the eigensymmetry group, but each of $\mathcal{E}(S_1)$ and $\mathcal{E}(S_2)$ may be a proper supergroup of \mathcal{G} .

For the inverted structure one gets

$$\bar{1}S = \bar{1}(\mathcal{G}M_1 \cup \mathcal{G}M_2) = \bar{1}\mathcal{G}M_1 \cup \bar{1}\mathcal{G}\hat{h}_{II} M_1 = \bar{1}(\mathcal{G} \cup \mathcal{G}\hat{h}_{II}) M_1. \quad (12)$$

An isometry g is represented by a matrix–vector pair (g, t) , where the matrix g represents the linear part and the vector t the translation part. For the inversion through the origin, the representation is $(\bar{1}, 0)$. Let us compare $(\bar{1}, 0)(g, t)$ and $(g, t)(\bar{1}, 0)$:

$$(\bar{1}, 0)(g, t) = (-g, -t), \quad (13)$$

$$(g, t)(\bar{1}, 0) = (-g, t). \quad (14)$$

The two operations have the same linear part but inverted translation parts and are conjugated under the inversion through the origin. In fact, for any isometry (g, t) one gets

$$(\bar{1}, 0)(g, t)(\bar{1}, 0) = (g, -t). \quad (15)$$

The space group $\mathcal{G}_+ = \cup_i (g_i, t_i)$ and the space group $\mathcal{G}_- = \cup_i (g_i, -t_i)$, which differ by the sign of the translation part of each operation, are conjugated under the inversion through the origin and, if they are different, form an enantiomorphic pair. In other words, if different, then \mathcal{G}_+ and \mathcal{G}_- are chiral groups. If, however, the inversion belongs to the Euclidean normalizer of the space group, then $\mathcal{G}_+ = \mathcal{G}_-$ and $\bar{1}\mathcal{G} = \mathcal{G}$. \mathcal{G} is thus an achiral group. For achiral groups equation (12) can therefore be rewritten as follows:

$$\bar{1}S = \bar{1}(\mathcal{G} \cup \mathcal{G}\hat{h}_{II}) M_1 = (\bar{1}\mathcal{G} \cup \bar{1}\mathcal{G}\hat{h}_{II}) M_1 = (\mathcal{G}\bar{1} \cup \mathcal{G}\bar{1}\hat{h}_{II}) M_1. \quad (16)$$

Note that $\bar{1}\hat{h}_{II}$ is a partial operation of the first kind, because both $\bar{1}$ and \hat{h}_{II} are of second kind. If now one assumes that the structure be achiral, one has to apply again equation (3), which leads to

$$f_1 S = f_1(\mathcal{G} \cup \mathcal{G}\hat{h}_{II}) M_1 = (f_1 \mathcal{G} \cup f_1 \mathcal{G}\hat{h}_{II}) M_1 \approx \bar{1}S = (\mathcal{G}\bar{1} \cup \mathcal{G}\bar{1}\hat{h}_{II}) M_1. \quad (17)$$

For equation (17) to be satisfied one has to find for every g_i in \mathcal{G} operations g_k and g_l such that

$$f_1 g_i = g_k \bar{1} \hat{h}_{II} \quad \text{and} \quad f_1 g_i \hat{h}_{II} = g_l \bar{1}, \quad (18)$$

keeping in mind that the operations in \mathcal{G} and f_1 are operations of the first kind and \hat{h}_{II} and $\bar{1}$ are operations of the second kind.

Table 1

Revised relation between the chirality of molecules and the chirality of crystal structures they may form [modified after Nespolo & Benahsene (2021)].

	Achiral crystal structure	Chiral crystal structure
Achiral molecules	165 non-Sohncke types of space group: racemic crystals	65 Sohncke types of space group
Chiral molecules, enantiopure scalemic solution	Impossible	65 Sohncke types of space group
Chiral molecules, enantioenriched scalemic solution	230 types of space group: type I (disordered) solid solutions	65 Sohncke types of space group: scalemic crystals or scalemic conglomerates
Chiral molecules, racemate	165 non-Sohncke types of space group: racemic crystals 65 Sohncke types of space group: kryptoracemates	65 Sohncke types of space group: racemic conglomerates

Let us consider a molecule M'_j in S_j ($j = 1$ or 2). Then M'_j can be written in the form $M'_j = gM_j$ for some g in \mathcal{G} [equation (8)]. Choosing $g_i = g^{-1}$ in equation (18) gives $f_1 g^{-1} = g_k \bar{1} \bar{h}_{II}$, and multiplying both sides by $\bar{1} g_k^{-1}$ from the left and by g from the right, one obtains

$$\bar{h}_{II} g = \bar{1} g_k^{-1} f_1. \quad (19)$$

Since the assumption is that \mathcal{G} is an achiral group and thus $\bar{1}$ lies in the normalizer of \mathcal{G} , one has $\bar{1} g_k^{-1} = g_m \bar{1}$ for some g_m in \mathcal{G} . This gives [equation (8)]

$$\bar{h}_{II} M'_j = \bar{h}_{II} g M_j = \bar{1} g_k^{-1} f_1 M_j = g_m \bar{1} f_1 M_j. \quad (20)$$

Now, f_1 maps S to $\bar{1}S$ [equation (3)] and $\bar{1}$ maps it back to S , so $\bar{1} f_1 M_j$ lies in S , and since g_m belongs to \mathcal{G} , $\bar{h}_{II} M'_j = g_m \bar{1} f_1 M_j$ still lies in S . As an operation of the second kind, $g_m \bar{1} f_1$ must swap S_1 and S_2 . Hence \bar{h}_{II} maps every molecule M'_1 in S_1 to a molecule in S_2 and every molecule M'_2 in S_2 to a molecule in S_1 . This means that \bar{h}_{II} is a global operation of S , contrary to the hypothesis. Since \bar{h}_{II} is assumed to be of the second kind, this is inconsistent with \mathcal{G} being of Sohncke type. The result is therefore that a structure crystallizing in a Sohncke-type space group is necessarily chiral.

3. Discussion

I have provided the proof that a structure crystallizing with a space group of Sohncke type is necessarily chiral. This proof modifies one entry in Table 2 of Nespolo & Benahsene (2021): the revised classification of the relation between the chirality of molecules and the chirality of crystal structures in presented in Table 1.

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