Reinterpretation of Pseudo-Orthorhombic Diffraction Patterns

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The pseudo-orthorhombic diffraction patterns of four of the five substances discussed by Dunitz (1964) are reinterpreted as being due to the OD character of the structures. In one instance [nonactin, $(C_{10}H_{16}O_3)_4$] the symmetry obtained is the same as that proposed by Dunitz and twinning as well as disorder observed in one specimen are explained as due to the OD character. In another instance (aza-cyclodecane hydrobromide, $C_9H_{22}N^+Br^-$) the arrangement suggested by Dunitz turns out to have OD character; there is, however, another OD arrangement which would account for the reported systematic absences and symmetry of the diffraction pattern equally well. In the two remaining instances (α-cobalt dipyridine dichloride, $Co(C_5H_5N)_2Cl_2$ and cycloundecylamine hydrobromide, $C_{11}H_{21}NH_3^+Br^-$) the arrangements suggested by Dunitz have no OD character and other arrangements with OD character which would account for the systematic absences and symmetry of the diffraction pattern are given. Equipoints and structure factor formulae are given for some of the examples and conclusions drawn for Patterson functions calculated with intensities from twinned or slightly disordered specimens. Thus it is shown how mistaken conclusions may be avoided and interpretable partial Patterson functions obtained.

Introduction

In a recent paper Dunitz (1964) has given an interpretation of the diffraction patterns of crystals of five substances obtained in his laboratory. While at least some crystals of each of these substances possess the diffraction symmetry *mmm* (at least for reflexions with *h*, *k* even), they all show pseudo-selection rules, *i.e.* systematic absences not demanded by any of the orthorhombic space groups; for examples II, III, IV and V in Dunitz's article, crystals giving diffraction patterns of monoclinic symmetry were also found. These features of the diffraction patterns were discussed in terms of twinning. In a short note (Dornberger-Schiff & Dunitz, 1965) we indicated that an alternative interpretation in terms of OD arrangements is just as compatible with the diffraction data, besides being more convincing from a structural point of view.

In the following, the interpretation in terms of OD arrangements is discussed in greater detail. The examples are treated in a sequence different from that in Dunitz's paper. Those treated first are discussed in greatest detail, whence the reader should be able to apply similar considerations to the later examples and so arrive at the conclusions outlined in the paper.

Nonactin (example IV)

In Table 1(*a*) the systematic absences are presented in a way differing from that of Dunitz (1964), but facilitating their interpretation. The conditions '*h0l* present only for $h = 4n$' and '*0kl* present only for $k = 4n$', which do not correspond to any condition demanded by an orthorhombic space group (or one of lower symmetry), are contained in Table 1(*a*) as special cases of condition (1) together with conditions (3) and (4), respectively.

Table 1(*a*). *Summary of systematic absences and symmetry of nonactin*

No.	Type of reflexion	Conditions limiting possible reflexions	Symmetry of reflections	arrangements	Character of symmetry operation (referred to whole structure)
(1)	*hkl*	$h+k=2n$	$I(hkl)\overset{?}{=}I(\bar{h}kl)$ $I(hkl)=I(h\bar{k}l)$	C	Total
(2)	*hk*0	$h=2n \quad (k=2n)$		$11a$ $11b$	Total? Total?
	For $h=2H$	$(k=2K)$		Fictitious structure with $A=a/2, \ B=b/2$	
	HKl		$\begin{cases} I(HKl)=I(\bar{H}Kl) \\ I(HKl)=I(H\bar{K}l) \end{cases}$		
(3)	*H0l*	$H=2n$		$1a1$	Partial
(4)	*0Kl*	$K=2n$		$b11$	Partial

$\overset{?}{=}$ = Inequality observed for certain samples
Total? = Possibly total

It is convenient to discuss these conditions in terms of the total symmetry elements of a fictitious structure corresponding to a selection of the structure factors of the real structure, namely those with h (and thus k) even. This fictitious structure has translational periods $a/2$, $b/2$, c and its electron density $\varrho_{fict}(x,y,z)$ is related to the electron density $\varrho(x,y,z)$ of the real structure by

$$\varrho_{fict}(x,y,z) = \tfrac{1}{2} \cdot [\varrho(x,y,z) + \varrho(x,y+\tfrac{1}{2},z)] \qquad (1)$$
$$= \tfrac{1}{2} \cdot [\varrho(x,y,z) + \varrho(x+\tfrac{1}{2},y,z)] .$$

The symmetry of the reflexions with even indices h and k and the conditions (3) and (4) shows that the fictitious structure has one of the orthorhombic space groups, *Pba2* or *Pbam*.

The b- and a-glide planes of these space groups cannot, however, correspond to total symmetry operations of the real structure, because the glide components $B/2 = b/4$ and $A/2 = a/4$ would lead to lattice translations $b/2$ and $a/2$ respectively, in contradiction to the observed lattice constants. The partial character of these symmetry operations is in keeping with the observation that $I(hkl) \neq I(\bar{h}kl)$ for odd values of h (and k), in contrast to the orthorhombic character of the intensities for the even reflexions. The a- and b-glide planes corresponding to condition (2) result in a mirror plane perpendicular to c of the fictitious structure, which accordingly has the space group *Pbam* [see Fig. 1(b)]. Conditions (1) and (2) together with the partial operations deduced from the fictitious structure lead unequivocally to the symmetry given by Dunitz (1964).
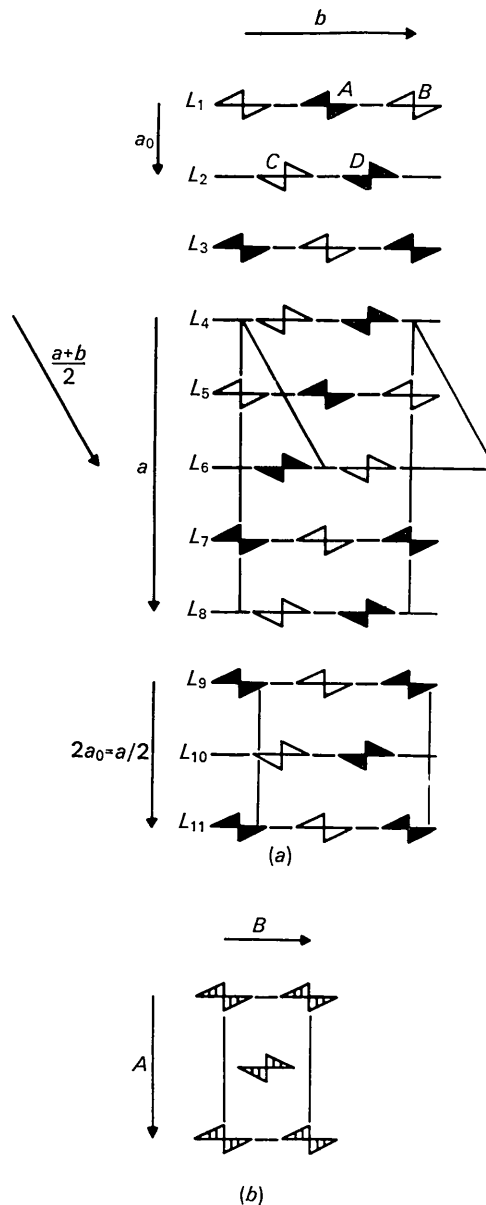
This symmetry is characterized by the total symmetry operations, and the truly partial operations corresponding* to part of the schematic† arrangement of geometrically equivalent layers shown in Fig. 1(a), namely layers L_3 to L_8. The tendency to form twins, which Dunitz suggested to be a property of para-orthorhombic structures, arises naturally from certain features of this arrangement, for although all pairs of consecutive layers are geometrically equivalent,‡ this equivalence does not suffice to determine uniquely the position of one layer (L_{p+1}, say) from the position of the preceding layer (L_p). This property characterizes it as an OD structure.

As has been pointed out before (Dornberger-Schiff, 1964), OD structures may occur as periodic structures but they are frequently disordered or twinned. This is easily understandable from energy considerations.

If the arrangement of atoms within a certain layer is energetically favourable, it will be formed again and

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* An operation is called *truly partial*, if the transformation of space characterizing it does not transform the whole structure into itself, but only part of the structure into part of the structure. If an operation transforms a layer (in the sense of OD theory) into a layer, it is called a PO.

† Following the example of Shubnikov and his school, asymmetric units are indicated in this and the following Figs. as triangles.

‡ This condition forms an essential part of the so called vicinity condition.

Fig. 1. Schematic representations related to the OD groupoid family

$$P \quad (1) \quad 1 \quad \frac{2}{b}$$

$$\left\{ \left(\frac{2_2}{b_{1/2}} \right) \; \frac{2_{\overline{1}/2}}{a_2} \; 1 \right\}$$

the probable OD groupoid family of nonactin. (a) Schematic representation of asymmetric units of a part of a disordered structure. Each triangle represents an asymmetric unit. Full triangle, $z = z_0$; empty triangle, $z = \bar{z}_0$. Parts of this arrangement correspond to arrangements of maximum degree of order:

L_1 to L_3 MDO_1
L_3 to L_8 MDO_1' (Geometrically equivalent to MDO_1)
L_7 to L_{11} MDO_2

(b) Arrangement of asymmetric units in the superposition structure. Shaded triangles, $z = z_0$ and $\bar{z}_0$.

again in the structure and, if the composition of such a layer corresponds to the composition of the sample, the whole structure will consist of such layers and nothing else. If a certain arrangement of a pair of neighbouring layers is particularly favourable, it will occur again and again throughout the structure, and if the arrangement is such that it is possible to build a structure solely with pairs of that kind, no other pairs will occur in the structure.

The nature of the most favourable layer-pair may, however, be such that no structure can be built solely with pairs of that kind. The same may be true for another, relatively favourable layer-pair. If a structure is possible in which all layer-pairs are equivalent to one or the other favoured arrangements, that structure is likely to occur. A similar statement would hold for triples but, because of the decrease of the interatomic forces with distance, the difference in interaction energy between layers one removed will, in some cases, not exclude the formation of less favourable triples, at least at intervals.

Fig. 1(a) gives a schematic representation of an arrangement composed of geometrically equivalent layers and geometrically equivalent pairs of layers, of the kind suggested by Dunitz. (His description actually corresponds to the ordered region comprising layers L_3 to L_8.) Three geometrically non-equivalent triples may be formed from such pairs of layers. They are instanced by (L_3, L_4, L_5), (L_4, L_5, L_6) and (L_2, L_3, L_4). No structure containing only triples of the first kind or triples of the second kind is possible.

If, therefore, triples of the third kind are less favourable than those of the first and second, the formation of an arrangement equivalent to part L_3 to L_8 of Fig. 1(a) is to be expected. It is described as being 'of maximum degree of order' (MDO$_1$). If on the other hand, the third kind of triple is more favourable, a periodic arrangement equivalent to part L_7 to L_{11} [Fig. 1(a)] will be formed. This is also of maximum degree of order (MDO$_2$). If, however, the difference in the energy of interaction between the various triples is not too great, ordered regions corresponding to one or the other MDO arrangement are expected to occur with occasional mistakes. Part L_1 to L_8 [Fig. 1(a)] shows how such a mistake would lead to the formation of a twin, with layer L_3 common to the two twin individuals.

The symmetry of the family of structures consisting of the same kind of layers as well as pairs of layers as in nonactin is thus given by the following symbol of the OD groupoid family (giving the plane space group of the single layer in the first and the σ-PO's* in the second line):

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* σ-PO's are defined as partial operations that transform one layer into an adjacent layer. λ-PO's are defined as partial operations that transform one layer into itself. There exist a multitude of PO's that are neither λ- nor σ-PO's, but transform a layer into a non-adjacent layer. Since any PO may be obtained as a product of σ-PO's, the set of σ-PO's suffices to characterize the groupoid of PO's.

$$P \quad (1) \quad 1 \; \frac{2}{b}$$
$$\left\{ \left(\frac{2_2}{b_{\frac{1}{4}}} \right) \; \frac{2_{\frac{1}{2}}}{a_2} \; 1 \right\}. \tag{2}$$

This expression characterizes a whole family of arrangements, some of which are periodic, others twinned (see above) and others more thoroughly disordered. The whole arrangement of Fig. 1(a) may be taken as an example of a disordered member of this family.

Some data referring to this OD groupoid family are collected in Table 1(b). Only the b-glide plane remains as a total symmetry operation for the whole disordered arrangement, whereas all other PO's are truly partial, even those corresponding to a total operation of one or other of the MDO arrangements.

Table 1(b). *Space groups of* MDO *arrangements and superposition structure for* OD *groupoid family* (2) *and systematic absences*

	Space group	Basic vectors*
MDO$_1$	$P11\,\dfrac{2}{b}$	$\frac{1}{2}(\mathbf{a}+\mathbf{b})$, $\mathbf{b}$, $\mathbf{c}$
MDO$_2$	$P2_1ab$	$\frac{1}{2}\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$
Superposition structure	$Pbam$	$\frac{1}{2}\mathbf{a}$, $\frac{1}{2}\mathbf{b}$, $\mathbf{c}$

	Possible reflexions
$\xi'kl$	All
$\xi'k0$	$k=2n$

For $k=2K$

$\xi'kl$	$\xi'=h=2H$
	Conditions of $Pbam$
	(superposition structure)

* Referred to basic vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ of rectangular cell.

The total character of the b-glide plane results from the special value $s=0$ of one of the parameters of the OD groupoid family

$$P \quad (1) \quad 1 \; \frac{2}{b}$$
$$\left\{ \left(\frac{2_2}{n_{r-1,s}} \right) \; \frac{2_r}{n_{s,2}} \; 1 \right\} \tag{3}$$

obtained from the family

$$P \; 1 \; \frac{2}{a} \quad (1)$$
$$\left\{ \frac{2_r}{n_{s,2}} \; 1 \; \left(\frac{2_2}{n_{r-1,s}} \right) \right\} \tag{4}$$

given in the table of OD groupoid families (Dornberger-Schiff, 1964, p. 88) by cyclic change of axes. This special value leads to a reduction from 4 to 2 for the number of positions of a layer compatible with the vicinity condition.

The fictitious arrangement described above and shown in Fig. 1(b) turns out to be the superposition structure corresponding to the OD arrangement of Fig. 1(a). The superposition structure of an OD ar-

rangement is defined (Dornberger-Schiff, 1964, p. 54) as the periodic arrangement arrived at after a certain number of steps in the following way: Starting off from a given layer L_1 all the Z different positions of the next layer L_2 leading to the given kind of pair are considered as being realized with weights $1/Z$ each; starting from these positions of L_2 the Z^2 positions (of which some may coincide) of the next layer L_3 are considered as being realized with weights $1/Z^2$ each, and so on. Hence different members of the same family of OD arrangements have the same superposition structure. In our case, $Z=2$ and pairs of the 2^2 positions of L_3 coincide.

As we shall see later, the notion of the superposition structure is very helpful for the interpretation of diffraction patterns obtained from OD structures.

Because in our case the fictitious structure is identical with the superposition structure, the intensities of the reflexions with $k=2K$ do not depend on the disorder or twinning of the particular sample but are the same for all members of the family. They correspond to the superposition structure, and, because this is periodic, reflexions with $k=2K$ occur only for integral values of $\xi'=h=2H$ [sharp reflexions; see Table 1(b)].

The orthorhombic space group of the superposition structure given in this table leads to the orthorhombic symmetry of the corresponding reflexions (with h, k even) and to the corresponding systematic absences.

For many purposes it is convenient to deduce properties – e.g. of the Fourier transform – common to all members of the family and specialize for the member of interest afterwards.

Naturally there will be certain parameters (called α_n in the following) which will have different values for different members of the OD groupoid family. The Fourier transform is obtained from the equipoints given in Table 1(c):

$$F(\xi kl)=$$
$$= \frac{1}{2Ma_0} \sum_{m=0}^{M-1} \exp(2\pi i 2m\xi) \cdot [(-1)^{\alpha_{2m}k} F_0(\xi kl)+$$
$$i^k \exp(2\pi i \xi)(-1)^{\alpha_{2m+1}k} F_0(\xi \bar{k}l)] \quad (5)$$

where $\xi = \xi'/4$ and

$$F_0(\xi kl)=(-1)^k F_0(\xi k\bar{l}) = F_0(\bar{\xi}\bar{k}l) \quad (6)$$

Table 1(c). *Equipoints of a structure belonging to the OD groupoid family (2)*

$$\left(2m, \frac{\alpha_{2m}}{2}, 0\right)+$$

$x, y, z;$ $\quad$ $x, \frac{1}{2}+y, \bar{z};$
$\bar{x}, \bar{y}, \bar{z};$ $\quad$ $\bar{x}, \frac{1}{2}-y, z;$

$$\left(2m+1, \frac{\alpha_{2m+1}}{2} + \frac{1}{4}, 0\right)+$$

$x, \bar{y}, z;$ $\quad$ $x, \frac{1}{2}-y, \bar{z};$
$\bar{x}, y, \bar{z};$ $\quad$ $\bar{x}, \frac{1}{2}+y, z.$

The x coordinates are referred to a unit vector
$a_0 = A/2 = a/4$.
$\alpha_n = 0$ or 1.

is the Fourier transform of layer L_0, whereas $\alpha_n = 0$ or 1, and $2M$ denotes the number of layers in the structure. For $k=2K$ the Fourier transform $F(\xi kl)$ becomes zero unless $2\xi = H$ where H is an integral number, and for $F(H, K, l)$ systematic absences characteristic for the space group *Pbam* of the superposition structure hold.

For $k=2n+1$ we obtain the expression

$$F(\xi kl) = \frac{1}{a_0} [S_0(\xi)F_0(\xi kl) + \exp(2\pi i\xi)i^k S_1(\xi) F_0(\xi \bar{k}l)] \quad (7)$$

with

$$S_\mu(\xi) = \frac{1}{2M} \sum_{m=0}^{M-1} (-1)^{\alpha_{2m+\mu}} \exp(2\pi i 2m\xi);$$
$$\mu = 0 \text{ or } 1. \quad (8)$$

Thus the coefficients S_μ do not depend on l.

From the values of $\alpha_{2m+\mu}$ listed in Table 1(d) for the MDO arrangements the corresponding formulae for such single crystals can easily be obtained. More important still, values for the Fourier transform at those places in reciprocal space where intensities different from zero have actually been observed may be obtained without making any assumption concerning the disordered, twinned or untwinned nature of the structure. Thus for $4\xi = \xi' = h$ with $h+k = 2n$ and $k=2n+1$ $(h=2n+1)$

$$F(hkl) = S_0 F_0(hkl) + (-1)^{(h+k)/2} S_1 F_0(h\bar{k}l) \quad (9)$$

where S_μ are constant real numbers and

$$F_0(hkl) = \frac{1}{a_0} F_0(\xi kl) \text{ for } 4\xi = h. \quad (10)$$

Table 1(d). *Values of α_n for the various arrangements of maximum degree of order*

	α_{2m}	α_{2m+1}	a	Space group
MDO$_1$	$\alpha_0 + m$	$\alpha_0 + m$	$4a_0$	$C112/b$
MDO$_1'$	$\alpha_0 + m$	$\alpha_0 + m + 1$	$4a_0$	$C112/b$
MDO$_2$	α_0	$\alpha_0 + 1$	$2a_0$	$P2_1ab$
MDO$_2'$	α_0	α_0	$2a_0$	$P2_1ab$

Only for single crystals can $S_0 = S_1 = \frac{1}{2}$ be assumed, whereas in general $S_\mu \leq \frac{1}{2}$ and $S_0 \neq S_1$. Thus structure factors calculated for the single crystal will, naturally, not agree with those observed for the twinned crystal, even if atomic coordinates are correct. Relation (9) is important because it enables us to take account of the different weights by splitting the Fourier- and Patterson series accordingly: a Patterson function calculated with the intensities observed from such a twinned crystal will contain peaks with three different weights corresponding to the relations (11) and (12):

$$|F(hkl)|^2 = S_0^2 F_0(hkl)^2$$
$$+ S_1^2 F_0(h\bar{k}l)^2 + 2(-1)^{(h+k)/2} S_0 S_1 F_0(hkl) F_0(h\bar{k}l)$$
$$\text{for } k=2n+1; \quad (11)$$

$$|F(HKl)|^2 = \tfrac{1}{4}F_0(HKl)^2$$
$$+ \tfrac{1}{4}F_0(H\bar{K}l)^2 + \tfrac{1}{2}(-1)^{H+K}F_0(HKl)F_0(H\bar{K}l)$$
$$\text{for } k=2K \text{ and } h=2H. \quad (12)$$

Patterson peaks corresponding to interatomic vectors within layer L_0 occur with weight $\tfrac{1}{4}+S_0^2$, those corresponding to interatomic vectors within L_1 occur with weight $\tfrac{1}{4}+S_1^2$ and those connecting an atom of layer L_0 to one of layer L_1 (or the other way round) occur with weights $\tfrac{1}{4}+S_0S_1$ each. As in the procedure adopted in the case of strontium metavanadate (Sedlacek & Dornberger-Schiff, 1965), the intensities of reflexions with $k=2K$ could be used separately from those with $k=2n+1$ and three partial Patterson functions would be obtained.

Function (i) with coefficients $|F(HKl)|^2$ corresponds to the fictitious structure.

Function (ii) with coefficients $|F(hkl)|^2 + |F(h\bar{k}l)|^2$, $k=2n+1$ contains only those peaks corresponding to intra-layer vectors, i.e. vectors within L_0 and within L_1, but with an anti-translation of $\mathbf{b}/2$ which produces a negative trough at $(u, v+\tfrac{1}{2}, w)$ for each positive maximum at (u, v, w).

These two partial Patterson functions will appear with a constant weight each, but these weights will, in general, be different from one another.

Function (iii) with coefficients $|F(hkl)|^2 - |F(h\bar{k}l)|^2$, $k=2n+1$ contains peaks corresponding to both intra-layer and inter-layer vectors. These two kinds of peak will appear with different weights; the intra-layer peaks referring to layer L_1 will occur with negative sign, and, moreover, the anti-translation $\mathbf{b}/2$ will produce additional peaks with negative height from the positive peaks and *vice versa*. The use of the intensities of certain subsets of reflexions and/or of linear combinations of them for the calculation of partial Patterson and electron density functions has previously been suggested by Buerger (1957), and seems particularly useful in the case of OD structures because the interpretation of such partial functions can, in this case, be deduced from the knowledge of the OD groupoid family.

For nonactin it was not possible from the published data to decide whether the layers are periodic in directions $\mathbf{b}$ and $\mathbf{c}$ (as drawn) or in directions $\mathbf{a}$ and $\mathbf{c}$ (a and b axes of Fig. 1(a) and (b) interchanged). An (hkl) Weissenberg photograph* taken in this Institute makes this decision easy: it shows diffuse streaks parallel to $\mathbf{a}$ for odd k, as expected for a disordered member of the OD groupoid family given above. Maxima on the streaks correspond in position to the reflexions observed by Dunitz, i.e. the disordered crystal contains ordered regions corresponding to the MDO_1 arrangement. The systematic absences for such an arrangement are given in Table 1(b).

A sample corresponding to the other ordered arrangement (MDO_2) would also have made the distinc-

* My thanks are due to Prof. J. D. Dunitz for sending a sample of nonactin.

tion easy: lattice constants and space group absences differ for the two orientations [see Table 1(b)]. Pseudo-selection rules corresponding to the glide planes of the superposition structure are again to be expected.

It may appear that this treatment of the structure of nonactin is not essentially different from that given by Dunitz. The equipoints are actually the same for both interpretations. These interpretations differ, however, in essential points and for other similar examples they may lead to different equipoints (see below).

The procedure used by Dunitz is as follows: Take those systematic absences which might be taken as space group absences and derive the space group from them. Additional systematic absences have to be regarded as arising from additional relations between parts of the asymmetric unit within the space group. An example of such additional relations is the equivalence in projection which he deduced for nonactin and also for α-cobalt dipyridine dichloride. This equivalence 'is not a space-group requirement' (Dunitz, 1957). This is certainly true, but it will most probably have its cause in an equivalence of parts of the arrangement in space, which – not being a space-group requirement – must be brought about by partial symmetry operations. Dunitz's method of treating this phenomenon may be misinterpreted by regarding the space group as a kind of vessel given in advance, into which the molecules are put.

According to our interpretation, symmetry operations relating adjacent molecules arise primarily from the energies of interaction between such molecules in different relative positions. Molecules that are themselves not highly symmetric will certainly be arranged in such a way that one particular molecule (Fig. 1(a), molecule A, say) has neighbouring molecules (A', B, C, D) in different directions forming geometrically non-equivalent pairs with it (molecule A' being immediately above A, and translationally equivalent to it). Some of these pairs will lead to a periodicity of the structure because the neighbouring molecule is apt to attach a further molecule in a similar way, and so on, whereas other pairs may not lead to such a periodicity. Thus e.g. the translational equivalence of molecule A and molecule A' immediately above it leads to a rod of molecules parallel to $\mathbf{c}$. The pair A, B related by a glide plane leads – by continuation of this glide plane – to rods parallel to $\mathbf{b}$, and this, together with the A, A' type of interaction, produces a layer of molecules, periodic in the $\mathbf{b}$ and $\mathbf{c}$ directions.

Let us now assume that this kind of layer is energetically so favourable that layers geometrically equivalent to it will be formed again and again in the structure. The relative positions of layers of this kind will also be governed by the energies of interaction and, because of the decline of forces with distance, the relative position of pairs of adjacent layers will be most decisive. First of all, we should expect the individual layers of such a pair to have the same translations, because any other arrangement is likely to be energetically less

favourable (part β_0 of the vicinity condition,* Dornberger-Schiff, 1964, p.30). Amongst the families with the plane space group number 13 listed in the Table of OD groupoid families (Dornberger-Schiff, 1964, p. 88) there are only two not requiring a square or hexagonal net. Their symbols (after appropriate interchange of axes) are

$$P \quad (1) \quad 1 \quad \frac{2}{b}$$

$$\left\{ (1) \quad 1 \quad \frac{2_s}{a_2} \right\} \tag{13}$$

and

$$P \quad (1) \quad 1 \quad \frac{2}{b}$$

$$\left\{ \left(\frac{2_2}{n_{r-1,s}} \right) \quad \frac{2_r}{n_{s,2}} \quad 1 \right\}. \tag{14}$$

These OD groupoid families differ in their OD systems†: For (13) it is monoclinic II, for (14) orthorhombic. If the arrangement (13) were realized with $s=0$ or 1, the structure would be fully ordered (space group $P112/b$ or $B112/b$ respectively). Similarly, if (14) were realized with $r=0$ or 1 and $s=0$ or 1, the structure would be fully ordered (space group $Pbab$, $Pmab$, $Pmnb$ or $Pcnb$ respectively).

Actually, as we have seen above, the OD groupoid family (14) is realized with $r=\frac{1}{2}$ and $s=0$. The pseudo-

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* Condition β_0 could be weakened to β_1 requiring only a subgroup of the group of translations to be common to adjacent layers. But only if this subgroup contains an appreciable part of the elements of the group (e.g. half of them) could an arrangement in agreement with β_1 compete energetically with the most favourable arrangement for which β_0 holds. The lattice constants b and c in this example do not permit a relative arrangement with a subgroup containing more than 5 % of the full translational group, unless β_0 holds.

† The OD system of an OD arrangement is defined (Dornberger-Schiff, 1964, p.47) as the system of the point group corresponding to the transformations of space of the λ- and σ-PO's.

orthorhombic and para-orthorhombic character* of the arrangement arises from the orthorhombic nature of the OD system.

The para-orthorhombic character of the examples I, III, and V of Dunitz can be discussed in a similar way. The same holds for other structures with orthorhombic OD system, e.g. decaborane, (Kasper, Lucht & Harker, 1950), strontium metavanadate (Sedlacek & Dornberger-Schiff, 1965), Kurroll's salt form A (Jost, 1961), the asbestos-like form of sulphur trioxide (Westrick & MacGillavry, 1954), petalite (Zemann-Hedlik & Zemann, 1955) and orpiment (Ito, 1950).

α-Cobalt dipyridine dichloride (example V)

As already pointed out, the symmetry derived by Dunitz for nonactin can actually be described as an MDO arrangement of an OD groupoid family, namely family (2) (see above); this is not the case for α-cobalt dipyridine dichloride. Treated by Dunitz in a way similar to his treatment of nonactin, it does not lead to an OD arrangement. The systematic absences (Dunitz 1957, 1964) and the symmetry of intensities [Table 2(a)] would, however, be in keeping with an MDO arrangement of OD groupoid family (3) for $r=\frac{1}{2}$ and $s\neq0$. The arrangement suggested by Dunitz consists of two different kinds of layer (L_{2n} and L_{2n+1}) geometrically equivalent in projection only (see Fig.2). They consist of geometrically equivalent rods parallel to $\mathbf{b}$, arranged so that pairs of adjacent rods within a layer L_{2n} are geometrically non-equivalent to a pair within L_{2n+1}. This non-equivalence of pairs of adjacent rods is not to be expected from considerations of their energy of interaction, and because of this non-equivalence, the arrangement cannot be regarded as an OD structure built of equivalent rods.

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* According to Dunitz (1964), arrangements are called para-orthorhombic for which 'certain regularly chosen subsets of reflexions exhibit perfect mmm symmetry'. The reflexions corresponding to the fictitious structure belong, in this case, to the regularly chosen subset.

Table 2(a). *Summary of conditions limiting possible reflexions and symmetry of α-cobalt dipyridine dichloride*

No.	Type of reflection	Possible reflexions	Symmetry of reflexions	arrangements	Character of symmetry operations (referred to whole structure)
(1)	hkl	$h+k=2n$	$I(hkl)=I(\bar{h}kl)$ $I(hkl)=I(h\bar{k}l)$	C	
(2)	$hk0$	$h=2n \quad (k=2n)$		$11a$ $11b$	Total? Total?
	For $h=2H$	$(k=2K)$		Fictitious structure with $A=a/2, \quad B=b/2$	
	HKl	All	$I(HKl)=I(\bar{H}Kl)$ $I(HKl)=I(H\bar{K}l)$		
(3)	$H00$	$H=2n$		2_111	Partial
(4)	$0K0$	$K=2n$		12_11	Partial

The OD arrangement we propose consists of equivalent layers. Both arrangements – that proposed by Dunitz and that proposed here – have in common that they are of monoclinic symmetry with a rectangular C-centred unit cell. The apparent orthorhombic symmetry of the intensities of the reflexions of most crystals investigated has been explained by Dunitz as due to twinning. Such twinning is not readily explainable, however, on the basis of the arrangement suggested by Dunitz, but it is to be expected for an MDO arrangement of OD groupoid family (3): For any position of layer L_p there are four positions of L_{p+1} leading to geometrically equivalent pairs (L_p, L_{p+1}). They result from the σ-PO's given in the symbol for $r = \pm\frac{1}{2}$ and $s = \pm s_0$. Thus the equipoints of Table 2(b) are obtained. Five non-equivalent MDO's are possible. They are given in Table 2(c) with their parameters α_j, β_j, lattice constant a, space groups and – in the last column – the minimum Laue symmetry which intensities at those places of reciprocal space corresponding to these lattice constants must have, irrespective of the degree of twinning or disorder. It holds, in particular, for twinned material containing ordered regions corresponding to the particular MDO. The arrangement MDO₃ corre-
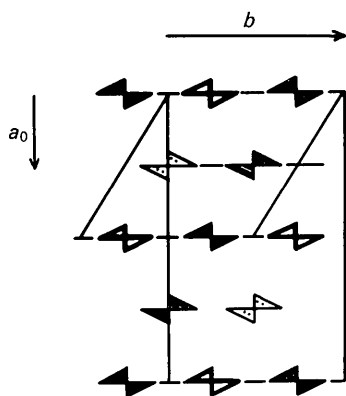
sponds to the observed lattice constants and C-centring of the unit cell. It is in accordance with the systematic absences listed in Table 2(a), although the conditions characteristic for a- and b-glide planes are observed for all $hk0$ reflexions and thus could be space group operations (as assumed by Dunitz). These observed conditions result, however, from the λ-b-glide, which, in this case, is not a total operation. Thus the conditions themselves are equally compatible with glide planes common to the whole structure or with glide planes with the same translational components, but at different levels for different parts of the structure.

If the parameter s is the ratio of integral numbers $s = R/Q$, there exists a superposition structure identical with a fictitious structure, with lattice constants $A = 2a_0$, $B = b/2$, $C = c/Q$, if R and Q are relative prime; its space group is $Pbam$ or $Pnnm$, if $R = 2n$ or $2n+1$, respectively. The corresponding subset of reflexions will show orthorhombic symmetry and the absences corresponding to the respective space group. Of this subset with $l = Q$. L only the reflexions with $l = 0$ would be observable, provided Q is fairly large. For $l = 0$ the corresponding rules are $H00$, $H = 2n$ and $0K0$, $K = 2n$, as observed.

Although there seem to be some arguments in favour of the OD interpretation of this structure, a definite proof (or otherwise) requires further experimental evidence.

Fig. 2. Schematic representation of asymmetric units in cobalt dipyridine dichloride. Black triangles, $z = z_0$; empty heavy lined triangles, $z = \bar{z}_0$; shaded triangles, $z = A + z_1$; dotted triangles, $z = A - z_1$. Assumption of Dunitz, $A = 0$; $z_1 \neq z_0$. Assumption this paper $A \neq 0$; $z_1 = z_0$.

Table 2(b). *Equipoints of a structure belonging to the family (3) with $r = \overline{1/2}$*

$$\left(2m, \frac{\alpha_{2m}}{2}, \beta_{2m}s\right) +$$

$x, y, z;$ $x, \frac{1}{2}+y, \bar{z};$
$\bar{x}, \bar{y}, \bar{z};$ $\bar{x}, \frac{1}{2}-y, z;$

$$\left(2m+1, \frac{\alpha_{2m+1}}{2} + \frac{1}{4}, \beta_{2m+1}s + \frac{s}{2}\right) +$$

$x, \bar{y}, z;$ $x, \frac{1}{2}-y, \bar{z};$
$\bar{x}, y, \bar{z};$ $\bar{x}, \frac{1}{2}+y, z.$

The x coordinates are referred to a unit vector
$a_0 = A/2 = a/4$.
α_n, β_n integral numbers,
$\beta_v - \beta_{v-1} = 0$ or $(-1)^v$.

Table 2(c). *Parameters of* MDO *arrangements, their lattice constants* **a** *and space groups for the* OD *groupoid family proposed for cobalt dipyridine dichloride*

	α_{2m+v}	β_{2m}	β_{2m+1}	**a**	Space group	Minimum Laue symmetry of intensities of twinned material	
MDO₁	α_v	β_0	β_1	$2a_0$	$P2_111$	$\begin{cases} k = 2n \\ k = 2n+1 \end{cases}$	$112/m$ $\bar{1}$
MDO₂	α_v	$\beta_0 + \varepsilon m$	$\beta_1 + \varepsilon m$	$2a_0 + r\mathbf{c}$	$P1a1$		$\bar{1}$
MDO₃	$\alpha_v + m$	β_0	β_1	$4a_0$	$C112$		$112/m$
MDO₄	$\alpha_v + m$	$\beta_0 + \varepsilon m$	$\beta_1 + \varepsilon m$	$4a_0 + 2r\mathbf{c}$	$C\bar{1}$		$\bar{1}$
MDO₅	$\alpha_v + m$	$\beta_0 + \varepsilon/2[1 - (-1)^m]$	β_1	$4a_0$	$P112/a$		$112/m$
		$\varepsilon = \pm 1$					

Lattice constants **b** and **c** equal to basic translations within the layer, inter-layer vector a_0 perpendicular to **b** and **c**.
Note added in proof: – For MDO₂ and MDO₄ the value of $\beta_1 = \beta_0 - (1 - \varepsilon)/2$.

Azacyclodecane hydrobromide (example III)

Table 3(a) contains the systematic absences and symmetry in a way corresponding to Table 1(a). Other systematic absences quoted by Dunitz (1964) are special cases of those listed.

The arrangement proposed by Dunitz and schematically shown in Fig. 3(a) would, if twinned, lead exactly to the absences and symmetry of intensities given in Table 3(a). For an untwinned crystal with such a symmetry either the reflexions hkl with $h+k+21=4n+2$ or those with $h-k+21=4n+2$ would be missing because of the translational vector $\dfrac{a+b}{4}+\dfrac{c}{2}$ or $\dfrac{a-b}{4}+\dfrac{c}{2}$. For all samples under investigation both these kinds of reflexion (h odd) were observed; thus all these samples are to be explained as twins.

The untwinned arrangement is – by arguments similar to those for the examples discussed above – an OD arrangement of maximum degree of order (MDO) with equivalent layers, pairs of layers and triples of layers. There exists, however, another arrangement consisting of equivalent layers of different symmetry, leading to the same systematic absences and symmetry of intensities, which also has to be regarded as an MDO arrangement [Fig. 4(a)]. This arrangement possesses the same total operations and the same truly partial σ-

PO's and λ-τ-PO's but different λ-ϱ-PO's, namely a c-glide plane instead of an n-glide plane. It is remarkable that an n-glide corresponding to the $p,p[n]$ of Fig. 3 exists, but this is not a λ-PO but a $p-1,p+1[n]$. Similarly a c-glide exists in the arrangement of Fig. 3 corresponding to the $p,p[c]$ of Fig. 4, but this is a $p-1,p+1[c]$. This relation between the λ-ϱ-PO's of one arrangement and $p-1,p+1[\varrho]$-PO's of the other arrangement explains why the two cases cannot be distinguished by the systematic absences. The superposition structures of the cases shown in Figs. 4 and 3 do not differ [see Fig. 3(c)]. Thus, as long as only the ordered MDO_1 arrangement is realized, there is no difference in principle between the two cases discussed. They differ only by the assignment of atoms to one particular layer. If, however, twins are formed, the boundary layer would possess the plane space group $P(n)cb$ in the first case, $P(c)cb$ in the second case. The disordered arrangements would lead to different systematic absences [Table 3(b)] and the MDO_2 arrangements would be of different symmetry [Figs. 3(b) and 4(b)].

Again, the symmetry of the reflexions and the systematic absences observed are symmetrical in h and k, so that there are two more cases to be considered, obtained from those discussed already by interchanging the a and b axes.

The three examples (nonactin, α-cobalt dipyridine dichloride and azacyclodecane hydrobromide) discussed so far have the following features in common.

Table 3(a). *Summary of systematic absences and symmetry of azacyclodecane hydrobromide*

No.	Type of reflexion	Conditions limiting possible reflexions	Symmetry of reflexions	arrangements	Character of symmetry operation (referred to whole structure)
(1)	hkl	$h+k=2n$	$I(hkl)\neq I(h\bar{k}l)$ $I(hkl)=I(hk\bar{l})$	C	Total
(2)	$hk0$	$h=2n$ $(k=2n)$		$11a$ $11b$	Total? Total?
(3)	$h0l$	$l=2n$		$1c1$	Total?
(4)	$0kl$	$l=2n$		$c11$	Total?
(5)	For $h=2H$ HKl	$H+K+l=2n$	$(k=2K)$ $I(hkl)=I(h\bar{k}l)$	Superposition structure with $A=a/2$, $B=b/2$ I	Partial

Table 3(b). OD *groupoid families and space groups of* MDO *arrangements and superposition structure compatible with the observations reported for azacyclodecane hydrobromide and possible reflexions for the corresponding disordered structures*

OD groupoid family	Lattice constants and space group of MDO_1	MDO_2	superposition structure	Possible reflexions for the disordered structures
$P\ (n)\quad c\quad b$ $\{(b_{1/2})\ a_2\quad n_{2,1/2}\}$	$\frac{1}{2}(a+b)$, b, c $P112/b$	a/2, b, c $Pnab$	a/2, b/2, c $Iccm$	(ξkl) All $(\xi 0l)\quad l=2n\quad (0kl)\quad k+l=2n$ $(\xi k0)\quad k=2n$
$P\ (c)\quad c\quad b$ $\{(b_{1/2})\ a_2\quad n_{2,1/2}\}$	$\frac{1}{2}(a+b)$, b, c $P112/b$	a/2, b, c $Pcab$	a/2, b/2, c $Iccm$	(ξkl) All $(\xi 0l)\quad l=2n\quad (0kl)\quad l=2n$ $(\xi k0)\quad k=2n$

There exist systematic absences which, referred to the cell $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, do not correspond to any space-group requirements but are seen to correspond to symmetry elements of a fictitious structure with a subcell $\mathbf{A} = \mathbf{a}/2$, $\mathbf{B} = \mathbf{b}/2$, $\mathbf{C} = \mathbf{c}$. These symmetry elements correspond to partial symmetry operations of the actual structure.

The twinning – if it occurs – is a twinning in Buerger's sense, *i.e.* the twin individuals have a layer – the boundary layer – in common. This twinning is possible because of the OD character (Holser, 1958; Dornberger-Schiff, 1959, 1961). In two of the three cases (nonactin and azacyclodecane hydrobromide) the fictitious structure referred to above is identical with the superposition structure, which possesses an orthorhombic space group. Therefore intensities of reflexions with $h = 2H$, $k = 2K$ show orthorhombic symmetry and are independent of the state of twinning or disorder of the sample – in contrast to other reflexions.
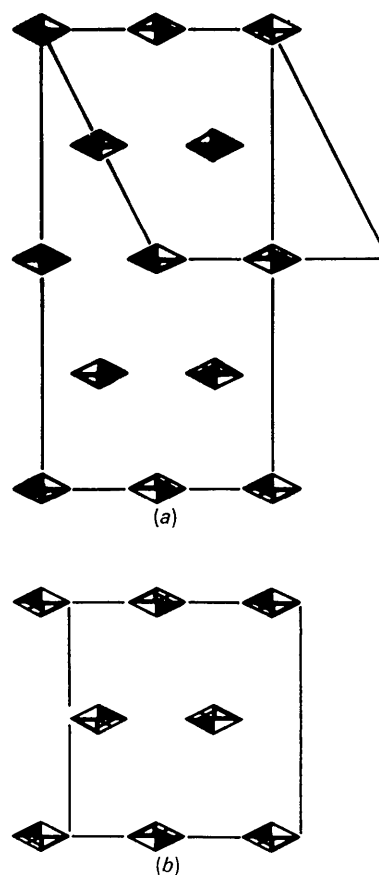

Fig. 3. Schematic representations related to the OD groupoid family

$$P \quad (n) \quad c \quad b$$
$$\{(b_{\overline{1/2}}) \quad a_2 \quad n_{2,1/2}\},$$

one of the OD groupoid families with an arrangement of maximum degree of order (MDO$_1$) compatible with the observed systematic absences and symmetry of intensities of azacyclodecane hydrobromide. (a) Schematic representations of asymmetric units of the arrangement MDO$_1$. Black triangles, $z = z_0$; empty heavy lined triangles, $z = \bar{z}_0$; shaded triangles, $z = \frac{1}{2} + z_0$; empty light lined triangles, $z = \frac{1}{2} - z_0$. (b) Schematic representation of asymmetric units of MDO$_2$. (c) Schematic representation of superposition structure. Heavily shaded triangles, $z = \pm z_0$; light shaded triangles, $z = \frac{1}{2} \pm z_0$.

Fig. 4. Schematic representations related to the OD groupoid family

$$P \quad (c) \quad c \quad b$$
$$\{(b_{\overline{1/2}}) \quad a_2 \quad n_{2,1/2}\}$$

one of the OD groupoid families with an arrangement of maximum degree of order (MDO$_1$) compatible with the observed systematic absences and symmetry of intensities of azacyclodecane hydrobromide. (a) and (b) correspond to (a) and (b) in Fig. 3.

1-Anilino-4-chloropyromellitic acid diphenylimide (example I)

As Dunitz has shown, no orthorhombic arrangement of 8 identical molecules will account for the apparent orthorhombic symmetry of the intensities and the systematic absences listed in Table 4(a). He therefore suggested the monoclinic arrangement shown in Fig. 5(a), which indeed would account for the observed conditions, if twinned with [001] or [010] as twin axis or (010) or (100) as twin plane.

In contrast to the three examples discussed above, the arrangement shown in Fig. 5(a) has no OD character and, accordingly, no twinning with a common boundary layer is possible [see Fig. 5(b)], unless the untwinned arrangement possesses additional, non-space-group, partial operations. Without such additional partial operations it would still be possible to envisage a structure consisting of two periodic parts having a boundary layer in common, both with space group $B11b$ and with unit cells in twinning position [Fig. 5(c)]. These two parts would, however, not be geometrically equivalent. A structure built of such parts in 'pseudo twinning' positions – if it occurred at all – would not even show statistical orthorhombic symmetry of the intensities, and the reflexions with k even, whose intensities are independent of twinning, would also have only monoclinic symmetry [Fig. 5(d)].

This arrangement is therefore not in agreement with observed facts and has to be rejected. If extended regions MDO_1 [shown schematically in Figs. 6(a) and 7(a)] of one of the OD groupoid families listed in Table 4(b) were present, the observed systematic absences and symmetry of the intensities corresponding to the superposition structure would result. The orthorhombic symmetry of the other reflexions could be due to statistical distribution of the twin individuals. Apart from those obtained from these families by an interchange of the a- and b-axes, they are the only OD groupoid families (assuming equivalent layers) in agreement with the obseved facts.

Cycloundecylamine hydrobromide (Example II)

The systematic absences are similar to those of the examples discussed so far. One crystal was found, however, 'that displayed a clear breakdown of orthorhombic symmetry'. Reflexions hkl and $h\bar{k}l$ with even h and k are of almost equal intensity. According to Dunitz (1965) it is not established whether the slight differences between them are due to absorption (or similar causes) or to monoclinic symmetry of the light atom positions.

It is therefore not possible, on the basis of facts known at present, to decide whether the structure is likely to be an OD structure of equivalent layers or one of two different kinds of layer. Further discussion of this example is therefore postponed.

Table 4(a). *Summary of systematic absences and symmetry of* 1-*anilino*-4-*chloropyromellitic acid diphenylimide*

No.	Type of reflexion	Conditions limiting possible reflexions	Symmetry of arrangement	Character of symmetry operation (referred to whole structure)
(1)	hkl	$h+k=2n$	C	Total?
(2)	$hk0$	$h=2n$ $(k=2n)$	$11a$ $11b$	Total? Total?
	For $h=2H$	$(k=2K)$		Superposition structure with $A=a/2$, $B=b/2$
(3)	HKl	$H+K+l=2n$	I	Partial

No deviations of observed intensities from orthorhombid symmetry reported.

Table 4(b). OD *groupoid families and space groups of* MDO *arrangements and superposition structures compatible with the observations reported for* 1-*anilino*-4-*chloropyromellitic acid diphenylimide and possible reflexions for the disordered structures*

OD groupoid family	Lattice constants and space groups of		superposition structure	Possible reflexions for the disordered structures
	MDO_1	MDO_2		
	$\frac{1}{2}(a+b)$, b, c	a/2, b, c	a/2, b/2, c	
P (2) m b $\{(2_2)$ $n_{1,2}$ $n_{2,1/2}\}$	$B11b$	$P2_1nb$	$I2mm$	(ξkl) All $(\xi K0)$ $k=2n$
				$(0kl)$ All
P (m) 2_1 b $\{(n_{1/2,1})$ $2_{\overline{1/2}}$ $n_{2,\overline{1/2}}\}$	$B11b$	$Pm2_1b$	$Im2m$	for $k=2K$ $\xi=h=2H$ (HKl) $H+K+l=2n$ $(H0l)$ $(H+l=2n)$

Conclusions

In the interpretation of pseudo-orthorhombic structures as OD structures the pseudo-orthorhombic character is seen to be no chance product but rather a consequence of partial operations essential for the stability of the structure. The OD interpretation therefore provides a better understanding of the physical basis of the occurrence of this phenomenon. It also explains how para-orthorhombic character is brought about in the case of OD arrangements of equivalent layers. The tendency to form twins or more thoroughly disordered arrangements also follows from their OD character.

(a)

(b)

(c)   (d)
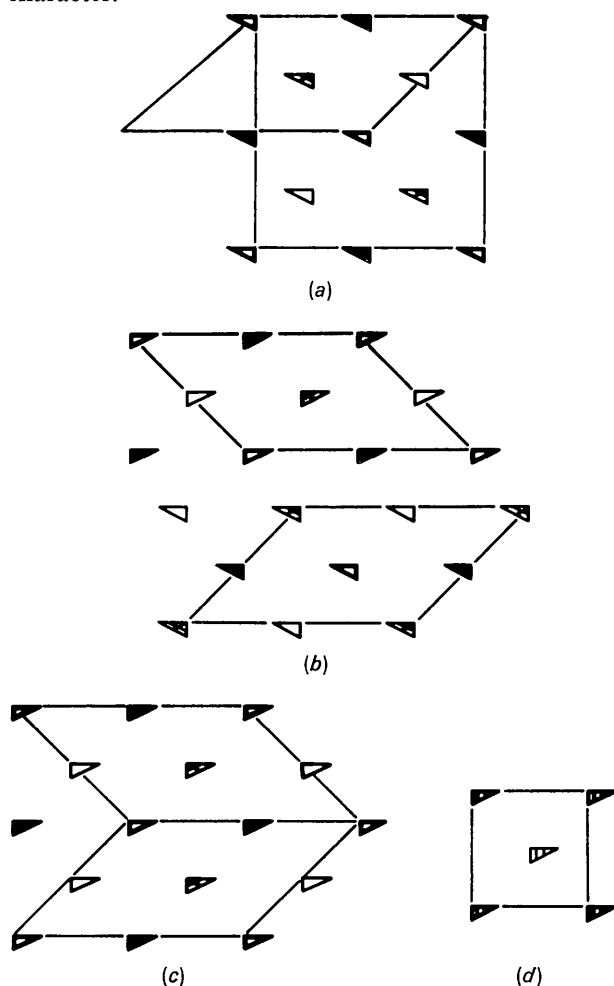
Fig. 5. Schematic representation of asymmetric units giving the observed systematic absences, as suggested by Dunitz (1964), for 1-anilino-4-chloropyromellitic acid diphenylimide. (a) Rectangular double-centred unit cell of the ordered, untwinned arrangement. The B-centred monoclinic cell corresponding to the space group B11b is also indicated. (b) Part of a twin of such an arrangement without a common boundary layer. (c) Part of an arrangement, top part corresponding to (a), bottom part consisting of layers equivalent to those of top part, unit cells in twinning position. The two parts have a boundary layer in common but are not geometrically equivalent. (d) Fictitious structure corresponding to (a) and (c).

In arrangements of equivalent layers that do not correspond to single crystals, certain sets of layers scatter out of phase for certain sets of reflexions and in phase for others. This may give rise to serious errors, if not properly allowed for. The considerations presented here should act as a warning against such errors and point the way to the optimal use of the experimental data in solving the crystal structure.

My special thanks are due to Prof. J. D. Dunitz for extended discussions on the subject, in the course of which he suggested that I should write this paper, and which actually continued until the last formulation of the paper. He also very kindly put crystals and X-ray diagrams at my disposal. I gratefully acknowledge many discussions with coworkers of this Institute and with Ing. S. Durovic (Bratislava), which helped to improve the presentation of the subject matter.

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(a)   (b)

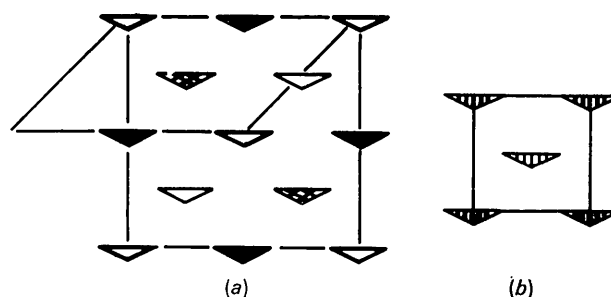Fig. 6. Schematic representation of asymmetric units corresponding to Fig. 5 but with additional partial mirror plane perpendicular to b corresponding to an OD groupoid family

$$P \quad (2) \quad m \quad b$$
$$\{(2_2) \quad n_{1,2} \quad n_{2,1/2}\} .$$

(a) Rectangular unit cell of the arrangement of maximum degree of order corresponding to Fig. 5(a). (b) Fictitious arrangement corresponding to Fig. 5(d), in this case also superposition structure.
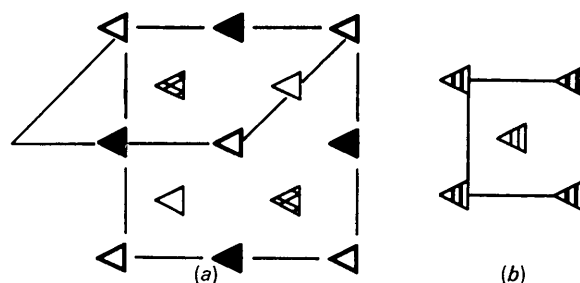

(a)   (b)

Fig. 7. Schematic representation of units corresponding to Fig. 5 but with additional mirror plane perpendicular to a, corresponding to an OD groupoid family

$$P \quad (m) \quad 2 \quad b$$
$$\{(n_{\overline{1/2}}, 1) \quad 2_{1/2} \quad n_{2,1/2}\}$$

(a) and (b) correspond to (a) and (b) in Fig. 6.

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Structure of Leurocristine Methiodide Dihydrate by Anomalous Scattering Methods; Relation to Leurocristine* (Vincristine) and Vincaleukoblastine (Vinblastine)

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The complete molecular structure including the stereochemistry and the absolute configuration of leurocristine methiodide dihydrate, $(C_{47}H_{59}O_{10}N_4^+)I^-.2H_2O$, has been determined by the combination of two crystallographic methods based on the anomalous scattering of X-rays. The structures of the antileukemia agent leurocristine (Vincristine) and the oncolytic alkaloid vincaleukoblastine (Vinblastine) are, therefore, established.

The crystals used in the study were monoclinic in space group $P2_1$ with two molecules in the unit cell of dimensions $a=10\cdot96\pm0\cdot05$, $b=21\cdot89\pm0\cdot05$, $c=12\cdot68\pm0\cdot01$ Å and $\beta=124°\ 53'\pm10'$. The final value of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ is $0\cdot12$ for 1378 reflections.

Several new crystallographic approaches to the determination of molecular structures employing anomalous scattering are proposed.

Vinca rosea Linn. of the family *Apocynaceae*, better known as Madagascar periwinkle, grows throughout the world, and has been known for centuries in the folk medicine of both civilized and uncivilized cultures as a cure or preventive for many assorted ailments (d'Sévigné, 1684;‡ Peckolt, 1910; Watt & Breyer-Brandwijk, 1962; Garcia, 1954; Johnson, Wright, Svoboda & Vlantis, 1960; Johnson, Armstrong, Gorman & Burnett, 1963; Schlittler, 1964). Its reputed activity in the treatment of diabetes prompted two groups in 1949 to begin systematic studies. However, both groups, one at the Eli Lilly Research Laboratories in Indianapolis, including Svoboda, Johnson, Neuss & Gorman, and the other at the Collip Laboratories of the University of Western Ontario, including Noble, Beer and Cutts, failed to observe any effect on the blood sugar content when laboratory animals were treated with extracts of this periwinkle. However, both groups noted the development of acute leukopenia when extracts of the leaf were administered, and finally in 1958 Beer succeeded in isolating a crystalline alkaloid, christened vincaleukoblastine, which produced severe leukopenia (Noble, Beer & Cutts, 1958). Since that time some sixty different alkaloids have been isolated from *Vinca rosea* Linn. Twenty of these have consisted of two alkaloids joined chemically, and four of these twenty exhibit antitumor activity. Clinical tests on (Svoboda, 1964) two of these four, vincaleukoblastine (VLB) and leurocristine (LCR) have proved activity against a large number of human tumors, and LCR has shown some effectiveness in the treatment of leukemia (Johnson, Wright, Svoboda & Vlantis, 1960). The effectiveness in many cases is restricted by the limit imposed on dosages by toxic side effects: chiefly acute leukopenia (Gorman, Neuss, Svoboda, Barnes & Cone, 1959; Frei, Franzino, Shnider, Costa, Colsky, Brindley, Halsey, Holland, Gold & Jonsson, 1961) when VLB is used, and neuromuscular abnormalities (but little or no leukopenia) when LCR is administered (Armstrong, Dyke, Fouts & Gahimer, 1961).

The molecular structures of these chemically joined alkaloids, especially of LCR and VLB, have been studied by several methods. Vindoline, which can be isolated

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