

may be 'successfully' refined by least-squares methods to an *R* value of approximately 0.35, or even lower, at about 2.0 Å resolution. We have observed, however, that correct solutions almost invariably yield to the technique documented in this paper; least-squares refinement of incorrect solutions produces no overall shifts and hence global refinement of the orientation and/or position of the molecule produces no results.

I would like to thank Mrs E. J. Dodson for introducing me to the molecular replacement method and suggesting that I go back to my early work on haemoglobin and review the results. The work referred to in this paper has had a number of contributors. I would like to acknowledge in particular the work of Robert Liddington and Deborah Harris on haemoglobin structure, and of Xiao Bing, Shirley Tolley, Colin Reynolds and Urszula Derewenda on the orthorhombic insulin crystals. I thank Professor G. G. Dodson for being a constant source of encouragement and help. Various stages of the research on human haemoglobin structure were more recently financed by the Medical Research Council and Science and Engineering Research Council. The study of orthorhombic insulin crystals is financed by Novo Research Institute, Denmark.

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On the Use of the Term 'Absolute' in Crystallography

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Abstract

The concept of 'absolute structure' as introduced by Jones [*Acta Cryst.* (1984), **A40**, 660-662] is discussed, and the term 'absolute' is extended to cases where the structure has been related to some external macroscopic physical property. The non-centrosymmetric crystal classes are divided into seven distinct categories for which specific terms are proposed: *structural chirality*, when the 'absolute structure' is determined for crystals in classes 1, 2, 3, 4, 6, 222, 422, 32, 622, 23 and 432; *absolute chirality*, when the 'absolute structure' is linked to a chiral property such as optical rotation; *absolute polarity*, when the 'absolute structure' is linked to a polar property such

as pyroelectricity; *absolute morphology*, when the 'absolute structure' is linked to the crystal habit: in this case there may be two further subdivisions - *absolute chiral morphology* (or *absolute enantiomorphism*) to describe a link to the hand of the habit, and *absolute polar morphology* to describe a link to the polar nature of the habit. It is further recommended that the term *absolute configuration* should be reserved only for molecular species and not for crystal structures.

It has been pointed out several times in recent years (e.g. Rogers, 1981; Jones, 1984*a, b*; Glazer &

Stadnicka, 1986) that the term 'absolute configuration' is often used either incorrectly or misleadingly. Jones has suggested the term 'absolute structure' to distinguish between one structure and its inverse, as determined typically by anomalous X-ray dispersion. Jones (1986) showed how ambiguities could be resolved in the non-centrosymmetric classes. However, because he was concerned mainly with chiral molecular species in crystals belonging to chiral point groups, he did not consider the possibility of chiral atomic arrangements occurring within achiral classes, but only mentioned the determination of polar axis (and absolute axis) directions. It is the purpose of the present paper to propose an unambiguous statement of what should be meant by 'absolute' when referring to structure determinations. In this connection, it is worth recalling the dictionary definition of the word *absolute*: 'self-existent and conceivable without relation to other things' - *Oxford English Dictionary*.

When anomalous-dispersion corrections are included in the X-ray structure refinement, often the structure so obtained is merely determined relative to the axes of the diffractometer and chosen description of crystal axes (e.g. Rogers, 1975). Therefore, simply refining a crystal structure in this way, and presumably choosing the best fit to different models accordingly, does not, except in the special categories I, II and III below, really provide any *absolute* knowledge about the crystal. Such a crystal structure determination is therefore incomplete and not always satisfactory. However, the use of the term 'absolute structure' seems to have become accepted and so it would be unnecessarily confusing to try to change it now.

We therefore propose an extension of the use of the word *absolute* to where the crystal structure, typically determined with the aid of X-ray anomalous dispersion, is related to some external physical property such as optical activity (in which case we talk about *absolute chirality*), electrical polarity (*absolute polarity*) or crystal morphology (*absolute morphology*). It must be stressed that structure determinations alone are not particularly useful in their own right unless they are used to explain natural phenomena of some kind. For instance, in our own case, we have for some time been interested in explaining the origin of optical rotation from a knowledge of crystal structure. We have found it frustrating to turn to a published 'absolute structure' determination, only to find that in fact it is not truly absolute. As a result, we have then had to recollect some or all of the X-ray data with a crystal in which we have observed the optical rotation ourselves and redetermine the absolute structure. Our use of 'absolute' connects the crystal structure to the outside world, so that once that connection has been made, it is no longer necessary to redo the X-ray measurement when referring to the way in which the structure correlates

Table 1. *Division into categories (I-VII) of the non-centrosymmetric classes*

		(a)	(b)	(c)
I	1 2 3 4 6	+	+	+
II	222 422 32 622 23	-	+	+
III	432	-	+	-
IV	<i>m mm2</i>	+	+	+
V	<i>4mm 3m 6mm</i>	+	-	+
VI	$\bar{4}$ $\bar{4}2m$	-	+	+
VII	$\bar{6}$ $\bar{6}2m$ $\bar{4}3m$	-	-	+

(a) 1st-rank polar; (b) 2nd-rank axial; (c) 3rd-rank polar.

with the property in question, *i.e.* the structure determination is absolute in the true sense of the word. Note that we do not insist on linking the structure to chiral and polar properties and morphology all at the same time in order to use the word 'absolute', but that just one linkage is sufficient. There are, after all, an infinite number of properties of different tensorial rank that could be chosen. What seems important to us is that the structure determination should not be left hanging in empty space!

Let us divide the 21 non-centrosymmetric classes into seven categories (Table 1). Types I, II and III, sometimes called chiral groups, contain only proper rotations, whereas the others contain improper elements other than a centre of inversion. Also in Table 1 we note whether certain properties can occur in each case. The properties are (a) 1st-rank polar,* *e.g.* pyroelectricity; (b) 2nd-rank axial, *e.g.* optical activity; (c) 3rd-rank polar, *e.g.* piezoelectricity, linear electrooptic effect. Tensor properties of other ranks could of course be considered, but the ones chosen here are sufficient to encompass all the non-centrosymmetric classes. Fig. 1 is a block diagram illustrating what can be determined from crystals in these classes.

* Crystals showing 1st-rank polar properties belong to one of the 10 polar classes. This use of 'polar' should not be confused with the concept of polar *directions*, which exist in all of the other non-centrosymmetric classes (see *International Tables for Crystallography*, 1987, p. 783).

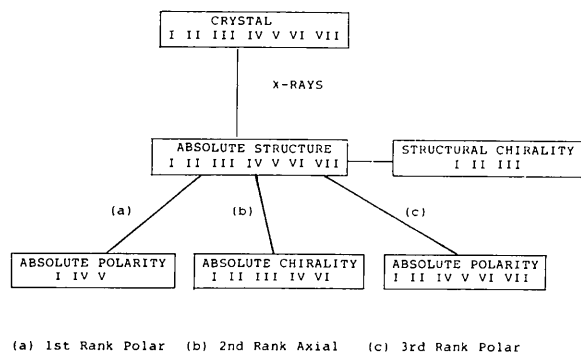


Fig. 1. Attributes of crystals in the various categories (I-VII) of non-centrosymmetric space groups.

Starting at the top of the figure we see that with X-ray diffraction, because of the effect of anomalous dispersion, we determine the 'absolute structure', in the sense employed by Jones, for any of the categories. Types I, II and III are special in that the chirality of a crystal in one of these categories does not depend on whether the crystal is kept in any fixed orientation with respect to the diffractometer used in determining the structure. Thus, if we determine that a particular crystal belongs to an enantiomorphic space group, say $P4_1$, rather than to $P4_3$, it still remains $P4_1$ even after the crystal has been removed from the diffractometer and no further account is taken of the orientation of the axes. The same is true for the non-enantiomorphic chiral space groups, such as $P4$ (in which case structure refinement must still include a test for all possible chiral models). In either case, Jones considers that this also means that the absolute configuration has been determined, whereas we propose to reserve the expression *structural chirality* of the crystal to describe this. Thus in types I, II and III, determination of the 'absolute structure' automatically gives the structural chirality. This is a kind of 'half-way house' towards absolutism, for such a structure is fixed and independent of the method used in obtaining the X-ray data, but it is not absolute in the full sense since we cannot relate the observed chirality to optical rotation without also measuring the optical sense on the same crystal. In molecular crystals, it is important to differentiate between chirality of the crystal structure and that of the molecules (which may, in fact, be opposite): in some cases a chiral crystal structure may consist of achiral molecules and it is just their arrangement in space that makes the structure chiral. Our term 'structural chirality' has been introduced to specify the particular importance of the crystal structure over that of its molecules. Determination of the structural chirality by whatever means implies that the chirality of the molecule is revealed. In such a case, it is usual to say that the 'absolute configuration' has been determined (even here it would be better to use the terms 'molecular chirality' or 'molecular polarity'). To avoid confusion, we suggest that 'absolute configuration' should not be used to describe chirality of the crystal structure as a whole, but rather to reserve it for molecules, where its use has long been established. It is also worth realizing that even within inorganic crystals there can be species of opposite chirality that nevertheless leave the structure chiral overall. For instance, in the quartz structure viewed along $[0001]$ there are two types of oxygen helices of opposite hand, one containing twice as many oxygens in a repeat as the other. Thus the two helices are not directly related to each other and so the quartz structure as a whole still has a 'hand'.

To go further, it is necessary to consider physical properties. Once the structure has been determined

and a chiral model has been selected, the observation of optical rotation fixes that particular structure with respect to the sign of rotation for ever. This is also true when a crystal containing a preponderance of one type of chiral molecules is dissolved to produce an optically active solution.

In the other categories, IV and VI, in which chirality can be determined, *i.e.* those in which optical activity is not symmetry forbidden, the chiral sense is lost once the crystal is removed from the diffractometer and no further account is taken of the assignment of the absolute directions of the crystal axes. Thus NaNO_2 crystals (Chern & Phillips, 1970), which belong to the optically biaxial class $mm2$, show optical activity when viewed along each of the two optic axes, because here the optic axial plane is perpendicular to the twofold axis (the mirror planes ensure that the optical sense is opposite for the two directions of view). Such a crystal, therefore, can be considered to contain opposite chiralities* at the same time, in which case, on removing the crystal from the diffractometer, one loses all track of how the positive and negative axial directions were assigned. At the same time, one no longer knows which direction should be used to view the crystal structure when trying to correlate with a particular optical chirality. Similarly the compound AgGaS_2 (Hobden, 1968) crystallizes in class $\bar{4}2m$, a point group that leads to opposite optical rotations when viewed on (100) and (010): normally this would be masked by the much bigger effect of optical linear birefringence, but it so happens that, in this crystal, Hobden found that the birefringence changes sign, passing through zero at a particular wavelength, and so the optical rotation can then be clearly seen. In these cases, X-ray diffraction alone can only determine the structure relative to the diffractometer axes (or 'absolute structure' in the sense used by Jones). To get a true 'absolute' knowledge (*i.e.* absolute chirality) of such a structure it is necessary to link the optical rotation to the structure determination. In order to do this, it is best first to observe the optical rotation in a particular direction using a large crystal and then to cut a smaller specimen from this for subsequent X-ray measurement, but throughout to maintain its alignment with the larger crystal. As far as we know, this difficult experiment has never been performed.

In the polar classes, belonging to types I, IV and V, X-ray anomalous dispersion can be used to determine the absolute direction of the polar axis with

* The existence of chiral arrangements within classes that are normally called 'achiral' is strictly analogous to the existence of polar directions in non-polar classes [as in *International Tables for Crystallography* (1987), pp. 788-789]. In both cases, more than one chirality or polarity exists within the same crystal and occurs in all of the non-centrosymmetric classes. We have not seen this analogy pointed out before (we give the equivalent table in the Appendix).

respect to the diffractometer frame of reference. However, once again, this determination is lost once this frame of reference is abandoned. If, on the other hand, the orientation is maintained and in addition the sign of a polar property such as pyroelectricity is determined, we can then relate this sign in an absolute way to the observed structure to give the *absolute polarity* (path *a*).* It is helpful also to indicate the method by which the absolute sense has been assigned by an expression such as 'absolute polarity determined by pyroelectricity'.

Crystals of type VII cannot be classified by 2nd-rank axial (chiral) and 1st-rank polar properties, and so recourse must be made to at least a 3rd-rank polar property, such as piezoelectricity. When X-ray anomalous dispersion is taken into account and with the crystal orientation maintained, we can again say that the absolute polarity has been determined (path *c*), although, as above, it would be useful here to qualify this by making the statement 'absolute polarity determined by piezoelectricity' in order to distinguish this from the absolute polarity determined by a 1st-rank polar property. The use of 3rd-rank polar properties to determine polarity applies also to the other piezoelectric classes, types I, II, IV, V and VI.

Finally, the role of morphology (habit, surface features and etch pits, lustre *etc.*) should also be recognized in determining the absolute nature of the structure. For instance, the classic experiment of Coster, Knol & Prins (1930) showed that in ZnS, which crystallizes in class $\bar{4}3m$ (type VII), the dull (111) faces of the crystal were planes of Zn atoms whereas the opposite shiny faces were S planes, and so they actually determined the polarity of the structure and its relationship to the morphology. Similarly, the well known indicator faces in quartz make it possible to distinguish between two enantiomorphic crystals [Herschel (1822) was the first to note that this distinction in morphology was related to the optical rotation of quartz crystals]. Determination of the 'absolute structure' can then be linked to the morphology to obtain the *absolute polar morphology* and *absolute chiral morphology* for ZnS and quartz, respectively. The latter could also be called *absolute enantiomorphism*, since it is held by some that it is preferable not to use the term 'chiral' when describing crystals as macroscopic entities.

From the above, it can be seen that we have extended the use of the term 'absolute' to embrace any link between structural chirality or polarity and macroscopic properties. We strongly support the appeal made several years ago by Rogers (1979) that the titles of papers dealing with absolute configura-

tions should include more precise terms. We recommend that these titles should also indicate the method used to determine the relation between structure and property (this is particularly important for the various crystallographic abstracting services). Titles beginning 'The crystal structure and absolute chirality determined by optical rotation of . . .' or 'The crystal structure and absolute polarity determined by pyroelectricity of . . .' are examples that give the salient information.

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APPENDIX

As mentioned earlier in a footnote, there is an analogy between the concepts of chiral and polar directions in the 21 non-centrosymmetric classes. The following is a table of such chiral directions presented in the same way as in Table 10.5.2 of *International Tables for Crystallography* (1987). All directions normal to a mirror plane and all those contained within a mirror plane are non-chiral. All directions other than those in the column 'Non-chiral directions' are chiral.

System	Class	Chiral symmetry axes	Non-chiral directions
Triclinic	1	None	None
Monoclinic	2	[010]	None
unique axis <i>b</i>	<i>m</i>	None	[<i>u0w</i>], [010]
Monoclinic	2	[001]	None
unique axis <i>c</i>	<i>m</i>	None	[<i>uv0</i>], [001]
Orthorhombic	222	[100], [010], [001]	None
	<i>mm2</i>	None	[0 <i>vw</i>], [<i>u0w</i>]
Tetragonal	4	[001]	None
	$\bar{4}$	None	[001]
	422	[001], [100], [010], [110], $\bar{1}\bar{1}0$	None
	4 <i>mm</i>	None	[0 <i>vw</i>], [<i>u0w</i>], [<i>uw</i>], [$\bar{u}w$], [<i>uw</i>], [$\bar{u}w$], [0 <i>vw</i>], [<i>u0w</i>]
	$\bar{4}2m$	[100], [010]	[<i>uw</i>], [$\bar{u}w$]
	4 <i>m2</i>	[110], $\bar{1}\bar{1}0$	[0 <i>vw</i>], [<i>u0w</i>]
Trigonal (hexagonal axes)	3	[001]	None
	321	[001], [100], [010], $\bar{1}\bar{1}0$	None
	312	[001], [210], [120], $\bar{1}\bar{1}0$	None
	3 <i>m1</i>	None	[2 <i>uw</i>], [<i>u2uw</i>], [$\bar{u}w$], [100], [010], $\bar{1}\bar{1}0$], [<i>uw</i>], [0 <i>vw</i>], [$\bar{u}w$], [210], [120], $\bar{1}\bar{1}0$]
	31 <i>m</i>	None	[<i>uw</i>], [100], [010], $\bar{1}\bar{1}0$], [<i>uw</i>], [0 <i>vw</i>], [$\bar{u}w$], [210], [120], $\bar{1}\bar{1}0$]

* A good example of the failure to appreciate this point can be found in the paper on AgNO₂ by Ohba & Saito (1981) who made the meaningless claim that they had determined the absolute polarity using measured Bijvoet pairs (though no measurement of polarity was attempted!).

Trigonal (rhombohedral axes)	3	[111]	None
	32	[111], [1 $\bar{1}$ 0], [01 $\bar{1}$], [$\bar{1}$ 01]	None
	3m	None	[uuw], [uvv], [uvu], [1 $\bar{1}$ 0], [01 $\bar{1}$], [$\bar{1}$ 01]
Hexagonal	6	[001]	None
	6	None	[001], [uv0]
	622	[001], [100], [010], [1 $\bar{1}$ 0], [210], [120], [1 $\bar{1}$ 0]	None
	6mm	None	[2uuw], [u2uw], [u \bar{u} w], [u0w], [0vw], [uuw]
	6 \bar{m} 2	None	[2uuw], [u2uw], [u \bar{u} w]
	62m	None	[u0w], [0vw] [u \bar{u} w]
Cubic	23	(111), (100)	None
	43m	None	[uuw], [u \bar{u} w], [uvu], [u $\bar{v}v$], [uvv], [u $\bar{v}\bar{v}$]
	432	(111), (100), (110)	None

Note that in classes 4mm, 3m, $\bar{6}$, 6mm, $\bar{6}2m$ and $\bar{4}3m$ all second-rank axial tensors [at least the symmetric parts; see Agranovitch & Ginzburg, (1965)] are zero, whereas higher-order (4 and 6) symmetric axial tensor components do occur (Molchanov, 1966). This extension to higher-order tensor components is just

like the extension from 1st- to 3rd-rank polar tensors implied in Table 10.5.2 of *International Tables for Crystallography* (1987).

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Bragg's Law with Refraction

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Abstract

Expressions for Bragg's law have been derived for the general case of Bragg diffraction in which an incident beam strikes a crystal surface at an angle α , is then diffracted by planes inclined to the surface by φ and leaves the same surface at an angle β . The crystal is assumed to have a refractive index $n = 1 - \delta$ and λ is the X-ray wavelength in air or vacuum. Under these conditions Bragg's law can be written as

$$\lambda = 2d(1 - \delta)[\cos \varphi \sin(\alpha - \delta/\tan \alpha) + \sin \varphi \cos(\alpha - \delta/\tan \alpha) \cos \sigma]$$

and

$$\lambda = 2d(1 - \delta)[\cos \varphi \sin(\beta - \delta/\tan \beta) + \sin \varphi \cos(\beta - \delta/\tan \beta) \cos \tau].$$

σ and τ are dihedral angles defined in terms of N ,

the normal to the crystal surface; d^* , the normal to the diffracting planes; $-s_0$, a ray in air antiparallel to the incident beam and s , the diffracted ray in the air. σ is the angle between $(-s_0, N)$ and (d^*, N) and τ the angle between (s, N) and (d^*, N) . When the plane of diffraction contains N , σ and τ are either 0 or 180° and Bragg's law takes the form

$$\begin{aligned} \lambda &= 2d(1 - \delta) \sin(\alpha - \delta/\tan \alpha \pm \varphi) + \varphi \text{ for } \sigma = 0^\circ \\ &\quad - \varphi \text{ for } \sigma = 180^\circ \\ \lambda &= 2d(1 - \delta) \sin(\beta - \delta/\tan \beta \pm \varphi) + \varphi \text{ for } \tau = 0^\circ \\ &\quad - \varphi \text{ for } \tau = 180^\circ. \end{aligned}$$

The magnitude of the refraction effect varies primarily with X-ray wavelength, electron density, and beam-to-crystal angle. Because of refraction the beam-to-crystal-surface angle required to satisfy Bragg's law can change by 10^{-4} to 10^{-1} degrees.