Acta Cryst. (1982). A**38**, 170

Discrimination between two enantiomorphously related space groups, without structure determination, by means of anomalous diffraction.

By J. Kroon, W. M. G. F. Pontenagel, H. Krabbendam and A. F. Peerdeman, *Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan* 8, *Utrecht, The Netherlands*

(*Received* 4 *May* 1981; *accepted* 10 *August* 1981)

Abstract

For the eleven pairs of enantiomorphous space groups there are special sums of triple-product phases (identities), the values of which depend on the space group. By means of anomalous diffraction that sum of phases can be estimated without *a priori* determination of the structure [Kroon, Spek & Krabbendam (1977). *Acta Cryst.* A**33**, 382–385]. It is shown that, as a consquence of this, *a priori* space-group determination (and enantiomorph determination) can be effected for this class of space groups.

Application of anomalous diffraction enables us to estimate triple-product phase angles Φ_i (including their signs) that differ from 0, *without* previous localization of the anomalous scatterers (Kroon, Spek & Krabbendam, 1977; Heinerman, Krabbendam, Kroon & Spek, 1978). Origin-invariant phases that differ from 0 or π are enantiomorph sensitive.

In enantiomorphously related space groups, space-group-dependent (and thus enantiomorph-dependent) relationships exist between phases φ_j of appropriate symmetry-related structure factors. For example, in $P4_1$ and $P4_3$ we note the following phase relationships of interest ($l = 4n + 1$):

$$P4_1: \varphi(hkl) = 3\pi/2 + \varphi(k\bar{h}l)$$

$$P4_3: \varphi(hkl) = \pi/2 + \varphi(k\bar{h}l).$$

For $l = 4n + 3$ the relationships are found to be interchanged.

The above implies that triple-product phases, as estimated by means of anomalous diffraction, are compatible with only one of the two space groups, *i.e.* compatible with only one of the aforementioned phase relationships. By examining whether experimentally obtained triple-product phases and assumed enantiomorph-dependent phase relationships are consistent or not it should be possible to discriminate between two enantiomorphously related space groups.

One way to carry out such a procedure is by means of special linear combinations of triple-product phases (so-called identities). We restrict ourselves to the case of quadruples

$$\Psi \equiv \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4$$

consisting of Bijvoet pairs [*i.e.* reflections related by $\bar{1}$ (Friedel pairs), $\bar{2}$, $\bar{3}$, $\bar{4}$ or $\bar{6}$ symmetry in reciprocal space]. From this condition it follows that Ψ is structure independent. However, its value depends on the reflections partaking in the quadruple, in combination with the space group, and it is restricted to 0 or to specified fractions of 2π. We observe that in the eleven pairs of enantiomorphous space groups the value of Ψ differs from 0 or π if the quadruple contains an appropriate number of Bijvoet pairs of reflections between which space-group-dependent phase relationships exist. Those quadruples are suitable to determine the enantiomorph and thus the space group.

To be more specific, the discrimination between the space groups $P4_1$ and $P4_3$, mentioned above, requires the inclusion in the identities of a number of reflections with $l = 2n + 1$, leading to an odd number of Bijvoet pairs of reflections that are related by $\bar{4}$ symmetry. For example,

$$\varphi(221) + \varphi(\bar{4}01) + \varphi(2\bar{2}\bar{2}) = \Phi_1$$

$$\varphi(\bar{2}2\bar{1}) + \varphi(103) + \varphi(1\bar{2}\bar{2}) = \Phi_2$$

$$\varphi(40\bar{1}) + \varphi(\bar{1}0\bar{3}) + \varphi(\bar{3}04) = \Phi_3$$

$$\varphi(\bar{2}\bar{2}2) + \varphi(\bar{1}22) + \varphi(30\bar{4}) = \Phi_4.$$

Taking all pertinent phase relationships into account,

$$\varphi(hkl) = -\varphi(\bar{h}\bar{k}\bar{l})$$

$$\varphi(hkl) = \pi - \varphi(\bar{k}h\bar{l}),\ l = 4n + 2,$$

$$P4_1\ (l = 4n + 1): \varphi(hkl) = 3\pi/2 - \varphi(\bar{k}h\bar{l})$$

$$P4_3\ (l = 4n + 1): \varphi(hkl) = \pi/2 - \varphi(\bar{k}h\bar{l})$$

we find

$$\Psi(P4_1) = \pi/2 \quad \text{and} \quad \Psi(P4_3) = 3\pi/2.$$

For the other ten pairs of enantiomorphous space groups, analogous space-group-dependent expressions for Ψ can readily be evaluated.

The value of Ψ calculated from the estimated values of the Φ_i's is indicative of which space group is the most probable. Since the triple-product phase determination is of a statistical nature and is also subject to experimental errors, one should involve as many identities as possible in the discrimination procedure. Finally, we stress that in the discussed case of the eleven pairs of enantiomorphous space groups the *a priori* determination of the correct space group is of vital importance for structure determination by direct methods.

References

Heinerman, J. J. L., Krabbendam, H., Kroon, J. & Spek, A. L. (1978). *Acta Cryst.* A**34**, 447–450.

Kroon, J., Spek, A. L. & Krabbendam, H. (1977). *Acta Cryst.* A**33**, 382–385.

0567-7394/82/010170-01$01.00