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The Determination of Absolute Structure. I. Some Experiences with the Rogers η Refinement

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Abstract

The η refinement of Rogers [*Acta Cryst.* (1981), A37, 734–741] has been applied to a wide range of non-centrosymmetric structures containing medium to strong anomalous scatterers; it has been shown to be an effective and robust method. The use of the general term 'absolute structure' (to signify a structure successfully distinguished from its inverse by, for example, analysis of anomalous scattering effects) is recommended.

Introduction

The absolute configuration/polar-axis direction (sometimes referred to as chirality/polarity) of a non-centrosymmetric crystal structure is often determined by least-squares refinement of both alternative models followed by a statistical comparison of R values using Hamilton's (1965) test. An attempt to provide a more reliable method was made by Rogers (1981), who suggested refining a parameter η as a factor multiplying all imaginary components f_i'' of the anomalous dispersion terms of the atomic scattering factors; η should then adopt values of +1 or −1, corresponding to the correct or incorrect model, respectively. The least-squares estimate of the standard deviation of η may then be used as a measure of confidence, being assessed against the value 2 (the range of possible η values). Some criticisms of the method have been made by Flack (1983), who suggested the use of an alternative parameter x, derived from considerations of enantiomorphic twinning, to avoid certain technical problems of η refinement in cases where the structure is almost centrosymmetric. The purpose of this article is to present the results of some η refinements based on the experience of the author and colleagues in this institute.

All structures (see Table 1), except where otherwise stated, were measured with Mo $K\alpha$ radiation on a Stoe–Siemens four-circle diffractometer in profile-fitting mode (Clegg, 1981). The η refinement is part of the standard *SHELXTL* program system (Sheldrick, 1978).

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Table 1. *Details of some non-centrosymmetric structure refinements*

Compound	Space group	R values		η	$2\theta_{\max}$	Notes
		correct	incorrect			
(1) $C_{22}H_{28}O_2Se$	$P2_1$	0·050	0·071	1·06 (4)	50	*a, b*
(2) $C_{12}H_{17}BrO_6$	$P2_12_12_1$	0·042	0·072	1·02 (2)	60	
(3) $C_{20}H_{18}AuO_2P$	$P2_12_12_1$	0·028	0·039	1·04 (2)	50	
(4) $C_{22}H_{20}FN_3OS$	$P2_12_12_1$	0·046		1·0 (3)	50	*c*
(5) $C_{22}H_{20}FN_3OS.H_2O$	$P2_1$	0·052		1·1 (2)	55	*c*
(6) $C_9H_{10}NO_6P$	$P2_12_12_1$	0·036		1·1 (2)	55	*c, d*
(7) $C_9H_{11}O_7P$	$Pna2_1$	0·045		1·1 (2)	55	*c, d*
(8) $AlCuCl_4$	$P\bar{4}2c$	0·039	0·048	1·0 (2)	55	*a*
(9) $Au_2Sr(OH)_8$	$I422$	0·031	0·039	1·09 (15)	65	
(10) $C_{84}H_{60}Au_2F_{10}Sb_4$	$P3c1$	0·084		0·65 (5)	45	*b, c, e, f*
(11) $C_{16}H_{32}AgAsF_6O_8$	$C2$	0·072		0·2 (2)	50	*c*
(12) $C_{12}H_{16}Cl_2Cu_2N_8$	$P3_221$	0·054	0·064	0·95 (5)	60	
(13) $C_{16}H_{24}ClCuN_8O_4$	$I\bar{4}$	0·044		1·00 (3)	60	*g*

References: (1) Clegg, Harms, Sheldrick, von Kiedrowski & Tietze (1980); (2) Egert (1984); (3) Jones (1984*a*); (4), (5) Jones (1984*b*); (6), (7) Jones, Sheldrick, Kirby & Briggs (1984); (8) Hildebrandt, Jones, Schwarzmann & Sheldrick (1982); (9) Jones & Sheldrick (1984); (10) Jones (1982); (11) Jones, Gries, Grützmacher, Roesky, Schimkowiak & Sheldrick (1984); (12) Clegg, Acott & Garner (1984*a*); (13) Clegg, Acott & Garner (1984*b*).

Notes

(*a*) Absolute structure by inspection of R values.
(*b*) η refinement performed after publication.
(*c*) Difference between R values $\leq 0{\cdot}001$.
(*d*) Stoe two-circle diffractometer.
(*e*) No Friedel opposites.
(*f*) Absolute structure by inspection of Au–Sb bond lengths.
(*g*) Alternative structure not refined.

Results

It is useful at the outset to classify structures into three groups, depending on the ease with which the correct model can be identified. [It should be stressed that we are confining ourselves to cases where *primary datasets* are used; techniques based on extremely careful remeasurement of selected Bijvoet pairs (Rabinovich & Hope, 1980; Ealick, van der Helm & Weinheimer, 1975) are not considered.]

(i) Success impossible, improbable or extremely difficult to achieve. Light-atom structures, *i.e.* no atom heavier than F; almost-centrosymmetric structures, especially where all the heavy atoms are centrosymmetrically distributed; exactly centrosymmetric structures, by definition. One criticism by Flack (1983) of the η method, namely that the latter two subgroups may be associated with false minima in the η refinement, is valid but should be irrelevant, in that no attempt to determine absolute configuration *etc.* should be made in these cases. We have not used the η method for light-atom structures, although it might well prove successful with Cu $K\alpha$ radiation.

(ii) Failure improbable. Good quality crystals containing anomalous scatterers with large f_i''. [There is however no guarantee of success – see Iwasaki (1974).] Compounds (1)–(3) all show a large difference in conventional R value between the alternative models (thus rendering Hamilton's test a formality) and η values close to +1* with small e.s.d.'s; all starting values of η refine rapidly and robustly to +1.

(iii) All other cases, *i.e.* crystals containing anomalous scatterers with moderate f_i''. Rogers (1981) and Marsh (1981) have cast doubt on the validity of the Hamilton test in some borderline cases (when the difference in R values is so small as to be not obviously significant). It might be hoped that the η refinement would be a more reliable guide in such cases; yet Flack (1983) has in turn raised doubts as to whether indications based on η could correspond to false minima. In this context, our results for some organic compounds containing one S or P atom may be of interest. In all cases (4)–(7) Friedel opposites were measured, but otherwise no special precautions were taken. Compounds (4) and (5) both gave weak η indications [1.0(3) and 1.1(2) respectively]; η converged to these values irrespective of starting value. Both absolute configurations are in agreement with those already established by chemical and other means, which increases our confidence in the η method. Compounds (6) and (7) similarly yielded weak indications; here the absolute configuration† (or polar-axis direction) was not known, but again all starting values of η converged rapidly to *ca* +1. None of these compounds displays pseudosymmetry.

Compounds (8) and (9) are included as examples of inorganic compounds in somewhat more exotic space groups and with metal atoms on special positions.

Compound (10) is a less satisfactory case, both in terms of the quality of the data (low $2\theta_{\max}$, *ca* 60%

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* All examples have been transformed where necessary to give positive η.

† For compound (6), an achiral compound crystallizing in a chiral space group, strictly the absolute *conformation* (the sign of the torsion angles – see below).

of the data with $F<4\sigma(F)$, no Friedel opposites collected) and in the result of η refinement (η converges slowly and deviates by 7 e.s.d.'s from the ideal value +1). The polar-axis direction was originally determined not from R values (difference 0·001) but by inspection of the agreement between six chemically identical but crystallographically independent Au–Sb bond lengths; as noted by, amongst others, Cruickshank & McDonald (1967), use of the inappropriate model must lead to systematic errors in bond lengths (here >0·1 Å). [A similar recent example is the absolute configuration of $C_9H_{27}P_7Pb_3$, determined by inspection of Pb—P bond lengths: Weber, Mujica & von Schnering (1982).] The low η value may be associated with a degree of enantiomorphic twinning, the possibility of which has been neglected in examples (1)–(9).

Compound (11) is an example where it is probably hopeless to attempt a determination of absolute configuration; although the space group is $C2$, all atoms except C, H and O correspond closely to $C2/m$ (centrosymmetric). Accordingly, the η refinement is inconclusive; it does not, however, give a false minimum at +1 or −1.

Compounds (12) and (13) involve exceptional space groups where the correct analysis of anomalous scattering effects leads neither simply to an absolute configuration nor to a polar-axis direction. The space group $P3_221$ is one of an enantiomorphic pair (the other being $P3_121$) and thus here (compound 12) the space group itself is determined; this will, however, simultaneously determine the absolute configuration of the compound under investigation. Compound (13) crystallizes in space group $I\bar{4}$, a representative of a small number of non-centrosymmetric space groups that are achiral and contain no polar axes. One way of visualizing the expression of non-centrosymmetry is to regard the absolute assignment of certain axis directions (here **x** and **y**) as ambiguous until anomalous scattering is taken into account; changing **x** to −**y** and **y** to **x** transforms the set of symmetry operators to their inverse.

Absolute structure

In view of the complications introduced by compounds (12) and (13), it is often necessary to consider carefully exactly which manifestation of non-centrosymmetry is being determined by the analysis of anomalous scattering effects. It is unfortunate that there is no general expression corresponding to 'determination of absolute configuration (*or* conformation) *or* of polar-axis direction *or* resolving the ambiguity of enantiomorphic space-group pairs *or* of axis directions'. This often leads to confusion, unwieldy circumlocution (as in the earlier part of this article) or, sometimes, downright errors in the literature. To help avoid these problems, I suggest the use of 'determination of absolute structure' and use it, where appropriate, in the forthcoming articles in this series. The expression has already been used sporadically in the literature (*e.g.* Ohba, Saito, Fujinami & Shibata, 1982).

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