Acta Cryst. (1979). B35, 2823

Structure du carbonate d'argent: erratum. Par R. MASSE, J. C. GUITEL et A. DURIF, *Laboratoire de Cristallographie, CNRS, 166 X, 38042 Grenoble CEDEX, France*

(*Reçu le 24 juillet 1979, accepté le 1 août 1979*)

Abstract

A computation error has been pointed out in Tableau 2 of the paper by Masse, Guitel & Durif [*Acta Cryst.* (1979). B35, 1428–1429]. The authors apologize for this, and the revised version of Tableau 2 is given. The text and other tables require no alterations.

Référence

MASSE, R., GUITEL, J. C. & DURIF, A. (1979). *Acta Cryst.* B35, 1428–1429.

Tableau 2. *Distances interatomiques* (Å) *et angles des liaisons* (°)

Ag–O(1)	2,236 (7)	O(1)–Ag–O(2)	158,7 (2)
Ag–O(2)	2,234 (7)	O(1)–Ag–O(2)	83,8 (2)
Ag–O(2)	2,440 (7)	O(1)–Ag–O(2)	119,7 (2)
Ag–O(2)	2,741 (7)	O(2)–Ag–O(2)	90,5 (2)
Ag–Ag	2,873 (2)	O(2)–Ag–O(2)	78,7 (2)
Ag–Ag	3,165 (2)	O(2)–Ag–O(2)	77,6 (2)
Ag–Ag	3,284 (2)		
Groupement CO_3^{2-}			
C–O(1)	1,302 (16)	O(2)–O(1)	2,218 (11)
C–O(2)	1,268 (9)	O(2)–O(2)	2,211 (14)
O(1)–C–O(2)	119,3 (8)	O(2)–C–O(2)	121,4 (8)

0567-7408/79/112823-01$01.00 © 1979 International Union of Crystallography

Acta Cryst. (1979). B35, 2823–2825

X-ray assignments of absolute configuration: recommended practice and an appeal. By D. ROGERS, *Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England* and F. H. ALLEN, *Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England*

(*Received 17 July; accepted 6 August* 1979)

Abstract

Some 900 assignments of absolute configuration have now been made by Bijvoet's X-ray anomalous-dispersion technique and a considerable number more by means of an internal reference standard. Such assignments often play a fundamental role in chemistry and biology. Application of the anomalous-dispersion technique requires some care and a few unfortunate errors or misleading presentations of results have occurred in the literature, but only two assignments have had to be reversed on re-investigation. Reports of such assignments tend increasingly to be hidden in the body of a paper, accompanied by minimal experimental details; this makes it difficult to abstract the assignment and to assess its validity should any suspicion arise.

X-ray assignments of the chirality or polarity of crystals now total *ca* 900, a figure which increases by about 100 *per annum*. The present authors began publishing bibliographic lists (Allen & Rogers, 1966; Allen, Neidle & Rogers, 1968, 1969; Neidle, Rogers & Allen, 1970), but discontinued them when the volumes of *Molecular Structures and Dimensions* began to be published by the Cambridge Crystallographic Data Centre (CCDC) (Kennard & Watson, 1970–79; Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1973; Kennard, Allen & Watson, 1977). 'Absolute configuration' is one of the flags incorporated in the Centre's files, though the compilers regard it as somewhat less exhaustive than the rest of their flags, mainly due to problems of abstracting that are discussed below. One can now readily identify, therefore, whether an X-ray assignment has been made of the chirality of an organic compound, organometallic compound or metal complex by reference to any of the *Molecular Structures and Dimensions* volumes, especially the *Guide to the Literature*, 1935–76 (Kennard, Allen & Watson, 1977) and bibliographic volumes 9 onwards (Kennard & Watson, 1970–79) where the absolute-configuration flag is now included as an indexing term. Exhaustive current listings can be obtained by a computer search of the corresponding CCDC magnetic tape files, copies of which are held at several centres throughout the

0567-7408/79/112823-03$01.00 © 1979 International Union of Crystallography

world (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979). Alternatively, for organic compounds only, one can consult the *Atlas of Stereochemistry*. The first edition (Klyne & Buckingham, 1974) contained 277 Bijvoet assignments and 107 more made by internal comparison up to 1970. In the second edition (Klyne & Buckingham, 1978; complete to mid-1976), the corresponding totals were 525 and 163. These two volumes contain, of course, a very much larger number of assignments made by non-X-ray methods.

Despite these aids one of us (DR) has maintained a file based on the CCDC compilation, partly to facilitate production of future editions of the *Atlas* or something like it, but mainly as a record of a continuing programme of checking. The CCDC's and DR's files do not include proteins for which separate documentation exists: absolute configurations are always used for such studies and are derived from the known chiralities of the constituent amino acids. DR's file (but not CCDC's) contains a number of assignments of chirality and polarity for inorganic crystals, but there is special difficulty in gathering these references as they are both sparse and widely scattered. The only indexes of this material that have been published were compiled by Hawkins (1973, 1977). The latter, which includes all entries in the former, contains 136 entries, of which only a few dozen relate to X-ray assignments, but the number is growing slowly and steadily.

The experience gained in compiling and checking the entries in DR's file has led the present authors to urge the adoption of the following *desiderata* in future publications.

(1) *That the terms 'absolute chirality' or 'absolute polarity' be given prominence in the title, abstract, keywords or a section heading.* Failure to do this consistently in the past has meant that some inconspicuous references to absolute configuration have been missed by the abstractors and the corresponding flags have not been set. Some omissions have been made good, but others doubtless remain.

(2) *That brief but adequately explicit details of the Bijvoet anomalies should be published, and, if Hamilton's ratio test is used, that both R^- and R^+ should be given and clearly related to the published coordinate list.* (R^+ is based on the published coordinates with $+if''$ correction: R^- is based on either the inverse structure with $+if''$ correction, or the published coordinates with $-if''$ correction.) It is often difficult when auditing papers to decide precisely what the authors did at this stage. Some procedures seem open to objection and comments on them have been made by Rogers (1980).

(3) *That the published or deposited coordinate list when referred to right-handed axes should define the correct chirality and that the fact should be stated explicitly.* Authors must, therefore, if necessary, accept responsibility for correctly inverting their 'working list' of coordinates: long strings of typographically vulnerable negative signs are conveniently avoided by converting x into $1 - x$, *etc.* It is unfair to expect non-crystallographers who wish to use the coordinates to decide when and how to invert the lists themselves. More seriously, the publication of 'wrong enantiomer' lists in the past has, unfortunately, led to the publication of stereopairs of wrong chirality for some flagged structures in Volume A1 of *Molecular Structures and Dimensions*. The present authors are collaborating to remove such discrepancies from the CCDC structural data file.

(4) *That all diagrams and stereoformulae should depict the correct chirality and that this should be stated.* During auditing several instances were found of inconsistencies of chirality between the coordinate list and the diagrams or between different diagrams of the same molecule, and numerous instances in which no stereoformula was given. Recently, an error of this sort was revealed in the assignment of the chirality of clerodin. It arose between the completion of the Bijvoet assignment (which a recent check has shown was correct) and the preparation of the published diagrams (Paul, Sim, Hamor & Robertson, 1962; Rogers, Ünal, Williams, Ley, Sim, Joshi & Ravindranath, 1979).

(5) *That every report should contain or give reference to relevant characterizing data*; *e.g.* $[\alpha]$ at one or more stated wavelengths; other chiroptical data (CD curves, *etc.*) or morphology for chiral crystals; the polarity of pyro- or piezoelectric effects or other means of identifying the polar ends of crystals. For more detail see Abrahams (1975) and Rogers (1975, pp. 235–238). Moreover, it is no longer valid to assume that an optically active natural product occurs with only one chirality: considerable confusion existed at one stage among the iboga alkaloids and among the labdane group of diterpenes (see *Atlas of Stereochemistry*, Vol. 1, pp. 110, 111 and 152 for a summary). Another example recently came to light among the flavonoids, but only after X-ray studies of both enantiomers were complete (Karanjgoakar, Rama Rao, Venkataraman, Yemul & Palmer, 1973; Rogers, McConway, Ramachandra Rao, Ramadao Rao & Nityananda Rao, 1979).

In view of the vitally important and fundamental role of absolute chiralities in chemistry and biology it is imperative to check the published papers and to provide cross checks. Fortunately, several of the basic groupings, *e.g.* D-glucose, menthyl, L-amino acids, steroids, have occurred concordantly so often that the assignments are above suspicion, and in many other instances chemical and optical cross checks exist. If, however, an assignment does excite suspicion, there are four points to verify.

(1) That the reciprocal lattice has been referred to right-handed axes. This is aimed principally at the earlier determinations, especially those from Weissenberg photographs in view of the different makes of camera and the non-uniformity of the linkage between the oscillatory and translatory motions.

(2) That the F_c programs used correctly allow for the imaginary component, f''. Some well known programs did not (Rogers, Quick & Mazhar-Ul-Haque, 1974).

(3) That the Bijvoet anomalies are sufficiently strong and are unambiguously related to the published coordinate list.

(4) That all diagrams and stereoformulae correctly depict the true chirality when referred to right-handed axes.

Unfortunately, it is hardly ever possible to check the first two points from a publication, and the extent to which checks (3) and (4) can be made varies. So the onus of responsibility must always rest with the authors, but even they find it difficult to resurrect data and calculations after more than a couple of years. The recent reversal of the chirality of centaurepensin (the only other example of a reversal among the 900 or so assignments) is a case in point (Hewson, Pettersen & Kennard, 1972; López de Lerma, Fayos, Garcia-Blanco & Martinez-Ripoll, 1978). Despite

only a six-year interval it was impossible to find the relevant details, so the cause of the original error has not been identified. It would be a great help, therefore, if in future authors would ensure that their assignment complies with this check list. Fortunately, there is now so much automation at every stage from data collection through to the production of diagrams and stereopairs that errors are becoming increasingly rare. But even well established and proven procedures broke down somewhere with centaurepensin.

We are often surprised, however, to see papers submitted in which no attempt had been made to round off the work by determining the chirality in circumstances where this could have been done and would have provided valuable new or confirmatory data: the effort is trivial compared with that already put in, and we can do with all the cross checks we can get. We urge, therefore, that the assignment of chirality should be regarded as a normal outcome of structure analysis wherever the problem allows.

We are indebted to John R. Rodgers of CCDC for help in producing the present, very convenient, format of the search output.

References

ABRAHAMS, S. C. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 199–221. Copenhagen: Munksgaard.

ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* B**35**, 2331–2339.

ALLEN, F. H., NEIDLE, S. & ROGERS, D. (1968). *Chem. Commun.* pp. 308–310.

ALLEN, F. H., NEIDLE, S. & ROGERS, D. (1969). *Chem. Commun.* pp. 452–454.

ALLEN, F. H. & ROGERS, D. (1966). *Chem. Commun.* pp. 838–840.

HAWKINS, D. T. (1973). *Ferroelectrics*, **5**, 111–123.

HAWKINS, D. T. (1977). *Ferroelectrics*, **15**, 77–96 [includes all entries in Hawkins (1973)].

HEWSON, A. T., PETTERSEN, R. C. & KENNARD, O. (1972). *Cryst. Struct. Commun.* **1**, 383–388.

KARANJGOAKAR, C. G., RAMA RAO, A. V., VENKATARAMAN, K., YEMUL, S. S. & PALMER, K. J. (1973). *Tetrahedron Lett.* pp. 4977–4980.

KENNARD, O., ALLEN, F. H. & WATSON, D. G. (1977). Editors. *Molecular Structures and Dimensions. Guide to the Literature* 1935–76. Utrecht: Bohn, Scheltema & Holkema.

KENNARD, O. & WATSON, D. G. (1970–79). Editors. *Molecular Structures and Dimensions* (*Bibliographies*): Vols. 1, 2, 3; with W. G. TOWN: Vols. 4, 5; with F. H. ALLEN & S. M. WEEDS: Vols. 6, 7, 8, 9, 10. Utrecht: Bohn, Scheltema & Holkema.

KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, N. W., MOTHERWELL, W. D. S., PETTERSEN, R. C. & TOWN, W. G. (1973). *Molecular Structures and Dimensions*. Vol. A1. *Interatomic Distances* 1960–65. Utrecht: Bohn, Scheltema & Holkema.

KLYNE, W. & BUCKINGHAM, J. (1974). *Atlas of Stereochemistry*. Vol. 1. London: Chapman & Hall.

KLYNE, W. & BUCKINGHAM, J. (1978). *Atlas of Stereochemistry*, 2nd ed., Vol. 1 (revised) and Vol. 2. London: Chapman & Hall.

LÓPEZ DE LERMA, J., FAYOS, J., GARCÍA-BLANCO, S. & MARTÍNEZ-RIPOLL, M. (1978). *Acta Cryst.* B**34**, 2669–2670.

NEIDLE, S., ROGERS, D. & ALLEN, F. H. (1970). *J. Chem. Soc. C*, pp. 2340–2341.

PAUL, I. C., SIM, G. A., HAMOR, T. A. & ROBERTSON, J. M. (1962). *J. Chem. Soc.* pp. 4133–4145.

ROGERS, D. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 231–250. Copenhagen: Munksgaard.

ROGERS, D. (1980). *Acta Cryst.* To be submitted.

ROGERS, D., MCCONWAY, J. C., RAMACHANDRA RAO, B., RAMADAO RAO, U. & NITYANANDA RAO, N. (1979). *Tetrahedron Lett.* In the press.

ROGERS, D., QUICK, A. & MAZHAR-UL-HAQUE (1974). *Acta Cryst.* B**30**, 532–533.

ROGERS, D., ÜNAL, G. G., WILLIAMS, D. J., LEY, S. V., SIM, G. A., JOSHI, B. S. & RAVINDRANATH, K. R. (1979). *Chem. Commun.* pp. 97–99.

International Union of Crystallography

Acta Cryst. (1979). B**35**, 2825–2827

Prices of *Acta Crystallographica* and *Journal of Applied Crystallography*

The Executive Committee of the International Union of Crystallography has found it necessary to increase the yearly subscription rates and also the prices of back numbers for *Acta Crystallographica* and *Journal of Applied Crystallography* as from 1 January 1980. Every endeavour has been made to keep these increases to a minimum.

Acta Crystallographica

The following rates will apply for Volumes A36 and B36 (1980). All subscription rates are fixed in Danish kroner, and the US dollar equivalents given below are subject to exchange-rate fluctuations and amendment without notice.

Complete volumes, regular price per volume

Sections A & B (combined subscription)	Dkr 2265	($ 436.00)
Section A only	Dkr 565	($ 109.00)
Section B only	Dkr 1910	($ 367.00)