Equation (10) may be considered a generalization of (5): indeed, if $\pi\mathbf{h}T_r = n\pi$, then $\alpha'^2 = \alpha^2$, $\beta'^2 = \beta^2$, $\gamma'^2 = \gamma^2$.

The distribution of $\Phi = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}}$ may be calculated by considering that $\varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}} = 2(\varphi_{\mathbf{h}} - \varphi_r)$. After a straightforward change of variable (10) becomes

$$P(\Phi \,|\, |F|) \simeq [2\pi I_0(Z)]^{-1}$$
$$\times \exp\,[Z\,\cos(\Phi + 2\varphi_r - \psi')]. \qquad (12)$$

By means of (11) it may be found that

$$\cos\,(2\varphi_r - \psi') = \Sigma_- / S \quad \text{and} \quad \sin\,(2\varphi_r - \psi') = 2\gamma / S$$

so that

$$\tan\,(2\varphi_r - \psi') = \tan\,\psi.$$

Equation (12) is therefore identical to (5): it may be concluded that $P(\Phi \,|\, |F|)$ is the same both for cs crystals and for restricted-phase reflexions in ncs crystals.

References

Cascarano, G. & Giacovazzo, C. (1984). *Acta Cryst.* A40, 305-306.
Cascarano, G. & Giacovazzo, C. (1985). *Acta Cryst.* A41, 408-413.
Giacovazzo, C. (1980). *Direct Methods in Crystallography.* New York: Academic Press.
Giacovazzo, C. (1983). *Acta Cryst.* A39, 585-592.
Hauptman, H. (1982). *Acta Cryst.* A38, 632-641.
Heinerman, I. J. L., Krabbendam, H., Kroon, J. & Spek, A. L. (1978). *Acta Cryst.* A34, 447-450.
Kroon, J., Spek, A. L. & Krabbendam, H. (1977). *Acta Cryst.* A33, 382-385.
Srinivasan, R. & Parthasarathy, S. (1976). *Some Statistical Applications in X-ray Crystallography.* Oxford: Pergamon Press.
Wilson, A. J. C. (1980). *Acta Cryst.* A36, 945-946.

Least-Squares Absolute-Structure Refinement. A Case Study of the Effect of Absorption Correction, Data Region, Stability Constant and Neglect of Light Atoms

By G. Bernardinelli and H. D. Flack

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

Abstract

X-ray diffraction intensity data measured on two four-circle diffractometers from a crystal of the compound potassium hydrogen $(2R, 3R)$-tartrate have been used to study the effect of absorption correction, data region, stability constant and neglect of light atoms in the atomic model on the least-squares estimate of the absolute-structure (inversion-twin) parameter x. It is shown that for a complete data set with Friedel pairs measured in the same plane of diffraction, an absorption correction reduced the e.s.d. of x without significantly altering its value. For data sets where only one member of each Friedel pair is allowed to contribute in the least-squares analysis, e.s.d.'s and deviations of x from its ideal value are increased compared with complete data sets containing both members of each Friedel pair. Certain aspects of combining a complete data set consisting of one asymmetric unit of reciprocal space with all-sphere measurements of absolute-structure-sensitive reflections have also been investigated. Lowering the value of the stability constant increases the e.s.d. of x, produces values of x closer to its ideal value for complete data sets and increases the variability of x for incomplete data sets. Neglect of hydrogen atoms from the atomic model produces a very small but quantifiable shift in the estimated value of x.

Introduction

In previous work (Flack, 1983; Bernardinelli & Flack, 1985) it has been shown that absolute structure may be determined very efficiently by assuming any non-centrosymmetric crystal to be an inversion twin and letting the absolute-structure (inversion-twin) parameter x be a variable in the least-squares refinement. Whereas a great deal is known about the bias that may be caused in least-squares-estimated atomic positional and displacement parameters due to systematic effects such as absorption, thermal diffuse scattering, extinction, scan-range truncation *etc.*, little at present is understood of the behaviour of the absolute-structure parameter. It is the intention of this paper to present results on four systematic effects; absorption,

data region, stability constant and neglect of light atoms from the atomic model.

These systematic effects have been tested on X-ray diffraction intensities measured on one compound: potassium hydrogen $(2R,3R)$-tartrate. [A study of the same compound at low temperature has recently appeared in the literature (Buschmann & Luger, 1985).] This compound has a well established chirality which is clearly expressed in the diffraction data. Problems of pseudosymmetry and free origins will not be considered here.

Experimental

Single crystals of potassium hydrogen $(2R,3R)$-tartrate, $C_4H_5O_6K$, $M_r = 188 \cdot 2$, obtained commercially from Fluka, were grown from aqueous solution at 294 K. Colourless rhombic disphenoid crystal of average dimensions $0 \cdot 09 \times 0 \cdot 33 \times 0 \cdot 52$ mm with faces $\{010\}$ (well developed), $\{130\}$, $\{011\}$ and $\{\bar{1}1\bar{1}\}$, the crystal being elongated along [001] (Porter, 1928); $[\alpha]_D^{20}$ +32·0° ($c = 10$ in $1M$ NaOH); $P2_12_12_1$, $a = 7 \cdot 799$ (1), $b = 10 \cdot 669$ (2), $c = 7 \cdot 625$ (2) Å, $V = 634 \cdot 5$ (2) Å^3, $Z = 4$, $D_x = 1 \cdot 970$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 807$ mm^{-1}, $F(000) = 384$, 294 K, Philips PW1100 diffractometer, graphite monochromator, cell dimensions from 30 reflections [$2\theta = 34$–43°]; data collection: $\sin \theta / \lambda < 0 \cdot 71$ Å^{-1}, $h = 0 \rightarrow$ 10, $k = 0 \rightarrow 14$, $l = 0 \rightarrow 10$ and all antireflections of these measured in the same plane of diffraction as the reflection, $\omega / 2\theta$ scans, ω-scan angle $(1 \cdot 2 + 0 \cdot 25 \tan \theta)°$; absorption correction by Gaussian grid integration on grid of $12 \times 12 \times 12$ points, $1 \cdot 066 < A^* < 1 \cdot 288$; three standard reflections 345, $\bar{3}45$, $3\bar{4}5$ varied by a maximum of 0·9%; 1087 Friedel pairs measured; 1848 independent reflections for refinements using the 'complete' data set; 1087 independent reflections for refinements using data sets containing only one member of a Friedel pair; all reflections in a data set contribute in the least-squares refinements; R values given for reflections with $I > 2\sigma(I)$; initial coordinates taken from caesium hydrogen $(2R,3R)$-tartrate (Templeton & Templeton, 1978); refinement on $|F|^2$; hydrogen atoms located from difference electron density map and fixed with isotropic displacement parameters of $U = 0 \cdot 038$ Å^2; 101 parameters refined – one scale factor, one absolute-structure parameter and, for each non-hydrogen atom, three positional and six anisotropic displacement parameters; no extinction correction; $w(|F|^2) = [\sigma^2(|F|^2) + (p|F|^2)^2]^{-1}$ with σ^2 taken from counting statistics alone and $p = 0 \cdot 02$ or $p = 0 \cdot 0$; in the final cycles of refinement average shift/e.s.d. in the range $1 \cdot 0$ to $1 \cdot 9 \times 10^{-4}$ with a maximum shift/e.s.d. of $8 \cdot 0 \times 10^{-4}$; atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); all calculations performed with a local version of

*XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).* A summary of the values obtained from the structure refinement with this set is presented in Table 1.

A second set of intensity data were measured on an Enraf–Nonius CAD-4 diffractometer. The same crystal was used in its previous mount. The measurement conditions were very similar to those previously used on the Philips PW1100 diffractometer. The reflections measured comprised one complete data set as on the PW1100. Furthermore, those 25 reflections (and their antireflections, and all reflections symmetry equivalent to these – making 200 measurements in all) having the largest values of $(|F_c(h, k, l)|^2 - |F_c(-h, -k, -l)|^2)/\sigma$ were also measured. In using the CAD-4 data, refinements have been made on the complete data set under the same conditions as for the PW1100 data and on the selected Friedel-pair measurements where there were only three variables in the least squares – one scale factor, one attenuator factor and one absolute-structure parameter, the other parameters taking values obtained from the refinement on the complete data set.* The results are summarized in Table 2.

Results and discussion

Absorption correction

Comparison of refinements 1 and 2, carried out on the complete data set including hydrogen atoms in the structure-factor calculation, shows the effect of performing an absorption correction. One sees that the absorption correction has lowered both R and S. The estimated value of the absolute-structure parameter has not altered but its e.s.d. has diminished in the same proportion as S.

In attempting to understand this result one must recall several important details of the data collection. The data set consists of measurements of Friedel pairs (*i.e.* reflection hkl and its antireflection $\bar{h}\bar{k}\bar{l}$) and these have been measured in the same plane of diffraction (*i.e.* the plane of the incident and reflected ray directions). For this geometry the absorption corrections for reflection and antireflection are identical if the crystal is centrosymmetric in shape (see for example Clegg, 1984). This is very closely the case for the crystal used here. Using the same plane of diffraction and scanning mode also implies the equality of any thermal-diffuse-scattering or multiple-scattering correction to the integrated intensities of reflection and

Table 1. *Summary of refinements on potassium hydrogen $(2R,3R)$-tartrate from the Philips PW1100 diffractometer data*

AC indicates whether an absorption correction was applied (Y) or not (N). DS indicates whether a complete (C) data set (both reflections of a Friedel pair) or just one of the two ($H = $ half) was used. In the latter case a $+$, $-$ or $*$ indicates that reflections with all indices positive ($+$), with all indices negative ($-$) or with a pseudo-random choice of one of the Friedel opposites ($*$) were used respectively. HD indicates whether hydrogen atoms were included (Y) or not (N) in the structure-factor calculation. $R = [\sum (\|F_o| - |F_c\|)/\sum |F_o|]$, $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(N_{obs} - N_{var})]^{1/2}$. Only reflections with $|F|^2 > 2\sigma(|F|^2)$ contribute to R. All reflections contribute in the least squares and to S. x is the absolute-structure parameter with e.s.d. in parentheses obtained using stability constants $p = 0.02$ or 0.0 in the weighting scheme. Individual values of R and S for the $p = 0.0$ refinements are not given but are in the range $6.9 < R < 8.1$ and $10.53 < S < 12.06$.

Data set	AC	DS	HD	$p = 0.02$			$p = 0.0$
				$R(\%)$	S	x	x
1	N	C	Y	3.0	2.28	$-0.012\,(51)$	$-0.007\,(155)$
2	Y	C	Y	2.7	2.04	$-0.012\,(45)$	$-0.003\,(142)$
3	N	C	N	3.8	3.00	$-0.009\,(67)$	$-0.002\,(178)$
4	Y	C	N	3.5	2.86	$-0.009\,(63)$	$0.001\,(169)$
5(a)	Y	$H+$	Y	3.0	2.31	$-0.055\,(76)$	$0.20\,(20)$
5(b)	Y	$H-$	Y	3.0	2.32	$0.005\,(74)$	$-0.24\,(20)$
5(c)	Y	$H*$	Y	3.0	2.31	$-0.022\,(76)$	$0.23\,(20)$
5(d)	Y	$H*$	Y	3.0	2.30	$0.022\,(76)$	$0.29\,(20)$
5(e)	Y	$H*$	Y	3.0	2.29	$0.009\,(76)$	$0.39\,(20)$
5(f)	Y	$H*$	Y	3.0	2.30	$-0.057\,(76)$	$-0.16\,(20)$
5(g)	Y	$H*$	Y	3.0	2.31	$-0.054\,(77)$	$0.20\,(20)$

Table 2. *Summary of refinements on potassium hydrogen $(2R,3R)$-tartrate from the Enraf-Nonius CAD-4 diffractometer data*

Refinements are on absorption-corrected data with hydrogen atoms included. A stability constant of $p = 0.006$ was used. DS indicates the data set used: C, complete asymmetric-unit data set (both reflections of a Friedel pair); $O+++$ 25 selected Friedel pairs taken from the $+h$, $+k$, $+l$ and $-h$, $-k$, $-l$ octants; $O-++$ selected Friedel pairs symmetry equivalent to $O+++$ but in the $-h$, $+k$, $+l$ and $+h$, $-k$, $-l$ octants; likewise for $O+-+$ and $O++-$; U is the union of $O+++$, $O-++$, $O+-+$ and $O++-$; A is the average over symmetry-equivalent reflections in U. $R = [\sum (\|F_o| - |F_c\|)/\sum |F_o|]$, $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(N_{obs} - N_{var})]^{1/2}$. Only reflections with $|F|^2 > 1.5\sigma(|F|^2)$ contribute in the least squares and to S. N_{obs} and N_{var} are respectively the number of reflections and number of variables used in the refinements. x is the absolute-structure parameter with e.s.d. in parentheses.

Data set	DS	$R(\%)$	S	N_{obs}	N_{var}	x
6	C	3.1	2.08	1838	102	$0.03\,(5)$
7(a)	$O+++$	1.7	2.95	50	3	$-0.07\,(14)$
7(b)	$O-++$	2.1	3.95	50	3	$0.10\,(18)$
7(c)	$O+-+$	1.7	2.90	50	3	$-0.02\,(13)$
7(d)	$O++-$	1.9	3.11	50	3	$-0.03\,(14)$
8	U	1.9	3.24	200	3	$-0.002\,(75)$
9	A	1.9	6.86	50	3	$-0.08\,(11)$

antireflection (Gabe, 1985). Furthermore, for small anomalous scattering effects, one obtains near equality of secondary extinction corrections even if these are anisotropic. In carrying out a least-squares refinement against a data set containing systematic errors, biased model parameters will arise which attempt to model the systematic error. In the case of absorption it is well established that scale factors and atomic-displacement parameters are the variables which are most affected. Bias in these variables results in a bias in the calculated structure-factor amplitudes of reflection and antireflection which are essentially equal. Consequently the observed and calculated differences between reflection and antireflection tend to agree and no bias in the absolute-structure parameter is produced if the systematic effects are left uncorrected. However, as a correction for absorption will produce a better overall fit to the data, the goodness of fit will be lowered and the e.s.d.'s of all parameters, including the absolute-structure parameter, will be reduced in the standard practice (used here) of multiplying all e.s.d.'s by the goodness-of-fit value.

The near equality of the systematic effects would not arise if either the antireflection had been measured in another plane of diffraction or a reflection symmetry equivalent to $\overline{hkl}$ had been chosen. In such cases bias in the absolute-structure parameter might result.

Data region

Refinements on data sets 2 and 5(a)-(g) presented in Table 1, which have been carried out on absorption-corrected data with hydrogen atoms included, show the effect of altering the choice of reflections contributing to the least-squares refinement. All values of x are within one e.s.d. of the ideal value of 0.0 and the e.s.d. obtained from the complete data set is significantly smaller than that from the half data sets. This reduction in the e.s.d. of x is not matched by the reduction in the value of S, the goodness of fit. The inclusion of all Friedel pairs has improved the estimation of the absolute-structure parameter more than the overall goodness of fit would have indicated. Although the complete data set is clearly superior in its ability to provide reliable estimates of the absolute-structure parameter, Table 1 indicates that satisfactory results may also be obtained from the half data sets.

In examining the results in Table 2 on 25 selected reflections one sees that all values of x lie within one e.s.d. of the ideal value of 0. The most satisfactory result in terms of x and its e.s.d. is obtained by using the 200 whole-sphere selected measurements without averaging. Further, the values of the goodness of fit obtained from the different refinements are very revealing. In increasing value of S, the O data sets are arranged as follows: $O+-+ < O+++ < O++- < O-++$, the difference between $O+-+$ and $O+++$ being small. This is typical of other data sets that we

have handled. The selected Friedel-pair measurements coming from the same region of reciprocal space in which the main data set was measured have one of the lowest values of the goodness of fit. This must be due to the model parameters resulting from refinement on the main data set with the same crystal compensating (at least partially) for its systematic errors. Consequently the model fits the data coming from the same region as the main data set better than those from other regions. On using the whole-sphere selected Friedel pairs one finds that the goodness of fit without averaging has a value between the largest and smallest for the O sets but with an improved e.s.d. of x, whilst, after averaging, S has increased considerably with an e.s.d. of x slightly smaller than any of the O sets. One suspects that the results of the averaged data set depend intricately on the algorithm used to obtain the mean values and their e.s.d.'s.

Stability constant

The results of the column marked x ($p = 0 \cdot 02$) in Table 1 were obtained using a weighting scheme with a stability constant p of $0 \cdot 02$ in the calculation of the total intensity variance. This is intended to be a typical value for diffractometer data. The effect on the estimation of the absolute-structure parameter of setting p equal to $0 \cdot 0$ may be seen by studying the column marked x ($p = 0 \cdot 0$) in Table 1. The values of the absolute-structure parameter for the complete data sets are now systematically closer to the ideal value of $0 \cdot 0$ although with much increased e.s.d. due to the poorer fit of the data. Even so, the e.s.d. of x has not increased to the same extent as S in going from the $p = 0 \cdot 02$ to $p = 0 \cdot 0$ refinement. For the half data sets one finds a very much greater variability in the value of x obtained and an increase in the e.s.d. approximately proportional to that found for the complete data set. The change in the weighting scheme from $p = 0 \cdot 02$ to $p = 0 \cdot 0$ corresponds to an increase in the weight of the medium and strong reflections over the weaker ones. It is amongst these medium and strong reflections that one finds those which are the most sensitive to the absolute structure of the crystal. As we have shown above, the estimation of x from a complete data set is very insensitive to the common systematic errors affecting diffraction data and hence the $p = 0 \cdot 0$ refinement produces an improved value of the estimate of x albeit with a greatly increased e.s.d. due to the poor *overall* fit for the complete data set. The half data sets will not have the same built-in independence of absolute-structure-parameter estimator to systematic effects and hence one finds much more fluctuation of x in the $p = 0 \cdot 0$ than in the $p = 0 \cdot 02$

refinements because of the increased sensitivity to absolute structure.

Neglect of light atoms

Comparison of refinements 2 and 4, carried out on the complete absorption-corrected data set, shows the effect of neglecting the hydrogen atoms in the structure-factor calculation. One can see that the estimated value of x is very little influenced.

Concluding remarks

From this study, the absolute-structure parameter appears to be very stable and insensitive to systematic errors. Clearly, attention has to be paid to the choice of stability constant and to the merging of data measured in different regions of reciprocal space. However, it might seem that absolute structure could always be determined whatever the (lack of) care used in collecting and correcting the data and in doing the least-squares refinement. To what extent are the conclusions reached here of general applicability? It is clear that potassium hydrogen $(2R, 3R)$-tartrate has a well established chirality which is clearly expressed by way of anomalous dispersion in the diffraction measurements. Further, absorption is not appreciable. For systems where these conditions do not pertain, particularly for pseudo-centrosymmetric space groups or those non-centrosymmetric ones where there is a free choice of origin, further study is under way. For these cases we consider the measurement of a complete data set as mandatory.

References

BERNARDINELLI, G. & FLACK, H. D. (1985). *Acta Cryst.* A41, 500–511.
BROWN, I. D. (1985). *Acta Cryst.* A41, 399.
BUSCHMANN, J. & LUGER, P. (1985). *Acta Cryst.* C41, 206–208.
CLEGG, W. (1984). *Methods and Applications in Crystallographic Computing*, edited by S. R. HALL & T. ASHIDA, pp. 30–40. Oxford: Clarendon Press.
FLACK, H. D. (1983). *Acta Cryst.* A39, 876–881.
GABE, E. J. (1985). *Crystallographic Computing* 3: *Data Collection, Structure Determination, Proteins, and Databases*, edited by G. SHELDRICK, C. KRUEGER & R. GODDARD, pp. 3–17. Oxford: Clarendon Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
PORTER, M. W. (1928). *Z. Kristallogr.* 68, 531–542.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
TEMPLETON, L. K. & TEMPLETON, D. H. (1978). *Acta Cryst.* A34, 368–371.