On Enantiomorph-Polarity Estimation

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Abstract

The behaviour of Rogers's η parameter for enantiomorph-polarity estimation is examined theoretically and experimentally on simulated intensity data for seven well-assorted compounds. An alternative parameter x, based on incoherent scattering from twin components related by a centre of symmetry, is also considered. It is found that both parameters are very well adapted to implementation in a least-squares program and converge well. The η parameter can give false and over-precise indications of chirality–polarity for structures which are nearly centrosymmetric, whereas the x parameter does not have this fault and converges more rapidly than η.

Introduction

It is common practice when determining the chirality or polarity of a non-centrosymmetric crystal to carry out least-squares refinements on the two possible sets of atomic coordinates and compare the R factors obtained by using Hamilton's R-factor test (Hamilton, 1965). Rogers (1981) has pointed to many of the theoretical and operational difficulties connected with this method. In an attempt to clarify procedures and to produce an enantiomorph-defining parameter, which may have its own error estimate, he has suggested that a parameter, η, be refined in the least squares along with the scale, coordinate, occupation and thermal parameters. η is a multiplicative factor operating on the imaginary anomalous dispersion terms f_i'' to give $\eta f_i''$ for all atom types i. Thus a value of $+1$ for η means that the correct enantiomorph or polarity is defined by the set of atomic coordinates, whereas a value of -1 implies that the crystal and the set of atomic coordinates have opposite chirality or polarity.

It will be helpful here to recall briefly one of the theoretical difficulties that Rogers (1981) has highlighted in the use of Hamilton's R-factor test. It is necessary in such a procedure to specify the number of observations used in the test. Seemingly it is common practice to take the total number of experimental intensities for this value. However, in all data sets

(apart from space group $P1$), there are reflections for which $|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})|$ and, for convenience, these will be called E reflections. E reflections may arise either accidentally or by symmetry in conjunction with special values of h, k or l, or because only one type of atom contributes to the structure factor. In any case, reflections of this type contain no information on the chirality or polarity of the crystal and hence the non-accidental E reflections should not be included in the count of the number of observations. It should be clear that, for E reflections, $|F_c(\eta = +1)| = |F_c(\eta = -1)|$ and Rogers thought that the E reflections would thus have no influence on the least-squares determination of η and its error estimate. This would very neatly avoid the problem of the count of the number of observations in using Hamilton's R-factor test.

However, it is the purpose of this paper to show theoretically and by computer simulations that E reflections do influence the least-squares determination of η and its error estimate. In certain rather drastic conditions, a double minimum (at $\eta \sim \pm 1$) can appear in the least squares. An alternative parameter x is proposed and examined. It has all of the conveniences of η but is completely uninfluenced by E reflections. It is capable of a more physical interpretation than η.

Theory

In the following structure-factor analysis, temperature factors have been omitted for the sake of simplicity. Their presence would in no way alter the conclusions of this analysis. Further, and for the same reason, the least-squares refinements are considered to be on $|F|^2$. The structure factor for the reflection $\mathbf{h}$, including the Rogers parameter η, may be written

$$F(\mathbf{h},\eta) = \sum_j (f_j^0 + f_j' + i\eta f_j'')$$

$$\times (\cos 2\pi\mathbf{h}^T.\mathbf{x}_j + i\sin 2\pi\mathbf{h}^T.\mathbf{x}_j), \qquad (1)$$

where the sum, j, is over all atoms in the unit cell, f_j^0 is the atomic scattering factor, f_j' and f_j'' are the real and imaginary parts of the anomalous dispersion and $\mathbf{x}_j$ is

the fractional atomic coordinate vector, all for the jth atom. Defining

$$C' = \sum (f_j^0 + f_j') \cos 2\pi\mathbf{h}^T.\mathbf{x}_j$$
$$S' = \sum (f_j^0 + f_j') \sin 2\pi\mathbf{h}^T.\mathbf{x}_j$$
$$C'' = \sum f_j'' \cos 2\pi\mathbf{h}^T.\mathbf{x}_j \qquad (2)$$
$$S'' = \sum f_j'' \sin 2\pi\mathbf{h}^T.\mathbf{x}_j,$$

one finds that

$$|F(\mathbf{h},\eta)|^2 = (C'^2 + S'^2) - 2\eta(C'S'' - C''S')$$
$$+ \eta^2(C''^2 + S''^2). \qquad (3)$$

Note that $|F(\mathbf{h},\eta)|^2 = |F(-\mathbf{h},-\eta)|^2$.

The parabolic variation of $|F(\mathbf{h},\eta)|^2$ as a function of η is shown in Fig. 1 as full lines for both an E and a non-E reflection. As the coefficient of η^2, $C''^2 + S''^2$, is non-negative, the nose of the parabola is downwards for all reflections. It can be seen that for an E reflection the slope of the curve $(\partial|F|^2/\partial\eta)$ is finite at $\eta = \pm 1$, and hence will contribute in the least-squares normal equations matrix at the ideal values of η. The derivatives $(\partial|F|^2/\partial\eta)$ for the non-E reflections are affected as well, being different at $\eta = \pm 1$.

Now consider a highly idealized weighted sum of squares as a function of η for the case of a set of E reflections. The observed 'true' values of $|F|^2$ will be taken as $|F(\mathbf{h},+1)|^2$ and the calculated values as $|F(\mathbf{h},\eta)|^2$. Thus

$$S_E = \sum_\mathbf{h} w(\mathbf{h})[|F_E(\mathbf{h},\eta)|^2 - |F_E(\mathbf{h},+1)|^2]^2, \qquad (4)$$

the subscripts E emphasizing that the sum is for a set of E reflections. Substituting (3) into (4), and using the

relation $C'S'' - C''S' = 0$, which specifies E reflections, one finds

$$S_E = (\eta^4 - 2\eta^2 + 1)\left\{\sum_\mathbf{h} w(\mathbf{h}).[C''(\mathbf{h})^2 + S''(\mathbf{h})^2]\right\}.$$

The variation of S_E as a function of η is shown in Fig. 2. There are two minima at $\eta = \pm 1$ of equal depth and separated by a maximum at $\eta = 0$ of height $\sum w(\mathbf{h})[C''(\mathbf{h})^2 + S''(\mathbf{h})^2]$ above the two minima. Thus the value of η determined in a least-squares refinement on a set of E reflections will depend on the starting value of η. It can also be seen that, depending on the value of $\partial^2 S_E/\partial\eta^2$ at the minima, the error estimate of η will be larger or smaller but necessarily finite if not all of the f'' are zero. However, E reflections contain no information on the chirality or polarity of the crystal, and one would like an ideal enantiomorph-polarity-defining parameter to have an undefined value when refined against a set of E reflections (e.g. a centrosymmetric crystal). One can also see from Fig. 2 that the double minimum (but now of different depth) can persist for non-E reflections. However, with increasing differences in $|F|^2$ between the members of Friedel pairs, the double minimum coalesces into a broader single minimum.

In summary, the functional form of Rogers's enantiomorph-polarity parameter η has two undesirable features. These are exemplified by reference to E reflections but non-E reflections can show similar although attenuated behaviour. The features are

(a) opposite chirality or polarity estimation may be obtained in a least-squares refinement depending on the starting value;
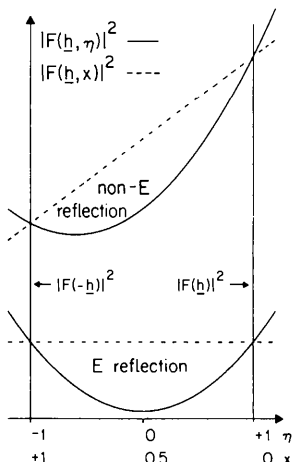

Fig. 1. Variation of $|F(\mathbf{h},\eta)|^2$ as a function of η, shown as full lines, and $|F(\mathbf{h},x)|^2$ as a function of x, shown as dotted lines, for an E reflection and a non-E reflection in the lower and upper parts of the figure, respectively.
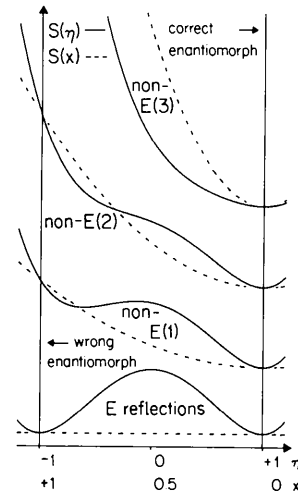

Fig. 2. Variation of S, the idealized sum of squares, as a function of η (full lines) or x (dotted lines). The lower curves are for a set of E reflections whilst the upper three sets of curves, non-E(1), non-E(2), non-E(3), are different possibilities for a set of non-E reflections.

(b) η will have a finite error estimate where an infinite estimate is desired.

The clue to removing the disadvantages in the η parameter may be seen by studying Fig. 1. The variation of $|F_c(\mathbf{h})|^2$ as a function of the enantio-morph-polarity parameter should be linear and the straight line should pass through the calculated $|F|^2$ values for the members of the Friedel pair. For an E reflection this will lead to the $|F(\mathbf{h},x)|^2$ having a constant value of $|F(\pm\mathbf{h})|^2$, shown as the dotted line in Fig. 1, where x is the new 'improved' enantiomorph-polarity-defining parameter. Further, E reflections will not contribute to the error estimate of x as $\partial|F|^2/\partial x$ is zero everywhere. The variation of a non-E reflection is also shown in Fig. 1 and the sums of squares are shown in Fig. 2.

Formally the x parameter may be defined by

$$|F(\mathbf{h},x)|^2 = (1-x)|F(\mathbf{h})|^2 + x|F(-\mathbf{h})|^2. \quad (5)$$

When the atomic coordinate set and the crystal have the same chirality or polarity, x takes the value of 0, whereas when they are opposed x becomes 1. (5) is in fact the equation for the intensity from a twinned crystal containing $100(1-x)\%$ of a component represented by the atomic coordinate set and $100x\%$ of a component related by a centre of symmetry to this set. Clearly, for a centrosymmetric crystal x is undefined. The interpretation of (5) based on twinning is of more than theoretical interest. Indeed, it is possible to obtain crystals where the two enantiomorphs or polarities are intergrown in a sample. This would be expected to occur more frequently with synthetic than with natural products. Hence, it is at least in principle possible to produce samples over the whole range of x from 0 to 1. This is certainly not the case for the η parameter as imaginary anomalous dispersion values of an arbitrary set of atoms cannot be varied simultaneously as expressed by η. It is due to the twinning interpretation that the x parameter has been defined with 'correct' and 'incorrect' endpoints of 0 and 1 rather than 1 and −1, respectively, of η.

Experimental

Least-squares refinements of η and x have been carried out on seven compounds using computer-generated data. Information specific to each compound will be found in Table 1. In all cases atomic positional coordinates, space group and cell dimensions were taken from the quoted source. Isotropic temperature factors were assigned as follows: $(100U \text{ Å}^2)$ O, N, 3·17; C, 3·80; K, Cs, Th, 0·76; Zr, Si, Ni, Sb, 0·38. No hydrogen atoms were included. X-ray scattering factors were taken from Cromer & Mann (1968), and anomalous dispersion values from International Tables for X-ray Crystallography (1974). Cu $K\alpha$ radiation was used for all compounds except for $Th(NO_3)_4.5H_2O$ where Mo $K\alpha$ was employed.

Data were generated for each substance by producing F_{obs} from $|F_{calc}|$ by setting $|F_{obs}| = |F_{calc}| + \Delta$, $\sigma^2(|F_{obs}|) = (0.03 |F_{calc}|)^2$, where Δ is a simulated statistical fluctuation produced by a pseudorandom number generator. The fluctuation follows a Gaussian distribution of zero mean and variance $\sigma^2(|F_{obs}|)$. Reflections were classified as observed if $I_{obs}(= Lp|F_{obs}|^2) \geq t$ and unobserved if $I_{obs} < t$ (Lp is the Lorentz–polarization factor and I_{obs} is the simulated observed intensity). Values of t are given in Tables 2 to 6. Data sets were complete, indicated by w (whole), if all reflections in the asymmetric unit of reciprocal space of the *crystal class* were used (*i.e.* Bijvoet pairs are included) or incomplete, marked by h (half), if the corresponding Laue symmetry was invoked (*i.e.* only one member of a Bijvoet pair included).

In the least-squares refinements, a scale factor, the non-symmetry-restricted fractional positional coordinates and an isotropic temperature factor for each atom were considered as variables, as well as either the η or x enantiomorph-polarity-defining parameter. The function minimized was $S = \sum w_i(|F_{o_i}|^2 - |F_{c_i}|^2)^2$, where $w_i = 1/\sigma^2(|F_{o_i}|^2)$. Only observed reflections were used in the least squares. The starting values of the atomic parameters for the refinements were the same as those used to create the data, except in some tests on thorium

Table 1. *Details of compounds used for simulations*

SR means *Structure Reports*. Type codes are: c centrosymmetric; e enantiomorphous; p polar. The coordinates for compounds 2, 3 and 4 are those for ammonium hydrogen tartrate but with the cation substituted by potassium, potassium and caesium respectively.

	Compound	Formula	Source	Space group	Type	a (Å)	b (Å)	c (Å)	Z
1	Potassium hydrogen maleate	$KC_4H_3O_4$	SR (1961)	$Pbcm$	c	4·578	7·791	15·95	4
2	Potassium hydrogen D-tartrate	$KC_4H_5O_6$	SR (1958)	$P2_12_12_1$	e	7·648	11·07	7·843	4
3	Potassium hydrogen L-tartrate	$KC_4H_5O_6$	SR (1958)	$P2_12_12_1$	e	7·648	11·07	7·843	4
4	Caesium hydrogen D-tartrate	$CsC_4H_5O_6$	SR (1958)	$P2_12_12_1$	e	7·648	11·07	7·843	4
5	Silicon zirconium	Zr_5Si_4	SR (1968)	$P4_12_12$	e	7·123	–	13·00	4
6	Thorium nitrate pentahydrate	$Th(NO_3)_4.5H_2O$	Ueki *et al.* (1966)	$Fdd2$	p	11·18	22·87	10·57	8
7	Nickel antimonide	$NiSb$	Wyckoff (1965)	$P6_3mc$	p	3·94	–	5·14	2

nitrate pentahydrate and all tests on potassium hydrogen L-tartrate.

All calculations were performed with the XRAY76 system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The changes necessary to the least-squares program *CRYLSQ* in order to refine the parameter x are based entirely on a patch modification by Schwarzenbach, see Thong & Schwarzenbach (1979), for treating twinned crystals. The refinement of η is achieved by using the f'' of a dummy atom of zero population as the variable η and constraining the other f''s to vary with the dummy. The only facility lacking in XRAY76 for η refinement was the possibility to constrain anomalous dispersion terms. All calculations were performed on a Univac 1100/61 with a representation of real values on 36 binary bits of which 27 are used for the mantissa.

In Tables 2 to 6, some results of the simulations are to be found. In order to make the comparison of the x and η refinements easier, the values of η and $\sigma(\eta)$ have been transformed by

$$\eta' = -(\eta - 1)/2, \qquad \sigma(\eta') = \sigma(\eta)/2,$$

which gives η' in the same range and interpretation as x (*i.e.* $\eta' = 0$, correct; $\eta' = 1$, incorrect, chirality or polarity).

R and G are defined as

$$R = \frac{\sum (|F_{obs}| - |F_{calc}|)}{\sum |F_{obs}|}$$

$$G = \left\{ \left[\sum_i w_i (|F_{obs_i}|^2 - |F_{calc_i}|^2)^2 \right] / (N - m) \right\}^{1/2},$$

where N is the number of observations and m the number of variables.

Table 2 shows the results on simulations with compound 1, centrosymmetric. The x refinements converge rapidly (two to three cycles), regardless of starting value, to give a very large error estimate (136) on x. This error estimate, like the actual value of x

obtained, is entirely due to rounding errors. On the other hand, refinements of η starting with $\eta' < 0.5 (\eta > 0)$ or $\eta' > 0.5 (\eta < 0)$ converge (more slowly than x) to a very precise indication of $\eta' = 0$ ($\eta = 1$) or $\eta' = 1$ ($\eta = -1$), respectively. With $\eta' = 0.5$ ($\eta = 0$) as starting value, the diagonal term corresponding to η of the least-squares normal-equations matrix calculated exactly as 0 and refinement of this parameter could not proceed.

For compounds 2 and 3, potassium hydrogen D- and L-tartrate, the refined values of x and η were independent of the starting values (the same as used for compound 1 in Table 2). All refinements gave approximately the same values of R (0.023) and G (0.95), and again the convergence of x was more rapid than η. For the L compound, the coordinates of the D enantiomorph were used in the refinements. Compound 2 gave refined values of $x = 0.013$ (10) and $\eta' = 0.007$ (10) and compound 3 gave $x = 1.0003$ (10) and $\eta' = 1.009$ (10) for the following characteristics, data set $w,(\sin \theta/\lambda)_{max} = 0.6$ Å^{-1}, threshold $t = 10.0$, 1173 observations and 46 variables.

Table 3 contains the results on simulations with compound 4, caesium hydrogen D tartrate. Again, refined values were independent of the starting values of x or η, and x converges faster than η. In this case the effect of changing the maximum value of $\sin \theta/\lambda$ has been examined. The same remarks apply for the results on compound 5, Zr$_5$Si$_4$, shown in Tables 4(a) and (b),

Table 3. *Simulations on compound 4, caesium hydrogen D-tartrate*

Data set: w; Cu $K\alpha$; threshold, t, 30·0; 46 variables.

sin θ/λ_{max} (Å^{-1})	Refined values				
	x	η'	G	R	N_{obs}
0·3	−0·002 (32)	0·017 (26)	0·989	0·021	150
0·4	−0·002 (19)	−0·010 (12)	0·946	0·023	356
0·5	−0·013 (13)	−0·011 (10)	0·937	0·023	680
0·6	−0·002 (11)	−0·002 (9)	0·946	0·023	1167

Table 2. *Simulations on compound 1, centrosymmetric*

Data set: w; $(\sin \theta/\lambda)_{max}$, 0·6 Å^{-1}; Cu $K\alpha$; threshold, t, 12·0; 432 observed reflections and 20 variables. E.s.d.'s are given in parentheses. R and G are defined in the text.

Variable	Starting value of x or η'	Refined value of x or η'	R	G
x	0·0	−106· (136)	0·022	0·894
x	0·5	−106· (136)	0·022	0·894
x	0·625	−106· (136)	0·022	0·894
x	1·0	−106· (136)	0·022	0·894
η	0·0	−0·007 (22)	0·022	0·895
η	0·375	−0·007 (22)	0·022	0·895
η	0·5	0·5	0·023	1·035
η	1·0	1·007 (22)	0·022	0·895

Table 4. *Simulations on compound 5*, Zr$_5$Si$_4$

sin θ/λ_{max} (Å^{-1})	Refined values				
	x	η'	G	R	N_{obs}
(a) Data set: w; Cu $K\alpha$; threshold 40·0; 20 variables					
0·3	0·01 (21)	−0·02 (19)	1·015	0·025	71
0·4	0·01 (9)	−0·01 (8)	0·897	0·022	166
0·5	0·032 (44)	0·035 (42)	0·913	0·022	329
0·6	−0·018 (34)	−0·012 (32)	0·912	0·023	575
(b) Data set: h; Cu $K\alpha$; threshold 40·0; 20 variables					
0·3	0·11 (31)	0·07 (27)	0·920	0·021	55
0·4	0·04 (12)	0·01 (10)	0·901	0·024	119
0·5	−0·02 (6)	−0·02 (5)	0·881	0·023	223
0·6	0·003 (40)	0·006 (40)	0·885	0·023	375

where the effect of w and h data sets is also investigated.

Tables 5(a) and (b) present the results for the polar compound 6, thorium nitrate pentahydrate. Starting values have no effect on refined values here. The refinements on the w data set were made with the z coordinate of the thorium atom fixed, starting coordinates being those used to generate the data set. For the h data set, refinements were made with $z(Th)$ both fixed and variable and found to give identical results in all cases. Moreover, the starting coordinates were generated by carrying out a preliminary refinement with $(\sin \theta/\lambda)_{max} = 0.6$ Å^{-1} from the model coordinates but fixing $\eta = -1$ ($x = 1$). This gives the worst possible bias to the starting coordinates.

The final compound, NiSb, number 7, studied in these simulations is polar of structure type NiAs and may be used to represent a gradual transition from centrosymmetry to polarity. The point positions of atoms in a NiAs-type structure are

$$R(Ni)\ 2(a)\ \ 0,0,z\ \ 0,0,\tfrac{1}{2}+z$$

$$X(As)\ 2(c)\ \ \tfrac{1}{3},\tfrac{2}{3},z\ \ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{2}+z,$$

and taking $z(Ni)$ arbitrarily as 0, one finds $z(As) \simeq 0.25$.

Table 5. *Simulations on compound* 6, $Th(NO_3)_4.5H_2O$

$\sin \theta/\lambda_{max}$ (Å^{-1})	Refined values				
	x	η'	G	R	N_{obs}
(a) Data set: w; Mo $K\alpha$; threshold 100; 45 variables					
0.3	−0.021 (45)	−0.018 (46)	0.889	0.018	145
0.4	−0.001 (33)	−0.007 (34)	0.919	0.022	339
0.5	−0.005 (28)	−0.010 (29)	0.936	0.023	683
0.6	−0.007 (25)	−0.008 (26)	0.948	0.023	1150
(b) Data set: h; Mo $K\alpha$; threshold 100; 45 or 46 variables					
0.3	0.17 (14)	0.15 (13)	0.770	0.015	87
0.4	0.13 (11)	0.11 (11)	0.938	0.021	195
0.5	0.01 (8)	0.03 (8)	0.914	0.022	381
0.6	0.01 (6)	0.04 (7)	0.908	0.022	631

However, with $z(As) = 0.25$, the structure becomes exactly centrosymmetric. Table 6 gives the results of simulations on five different data sets generated with various values of $z(Sb)$ and $z(Ni) = 0$. $z(Sb)$ was fixed as a parameter at the model value in the refinements but $z(Ni)$ was allowed to vary. Refined values of η' are dependent on starting values in this case.

Discussion

Considering the results obtained on compounds 1 and 7 which are centrosymmetric or nearly so, it will be seen that the x and η parameters behave in the manner to be expected from theory. x estimation gives rise to a single value with a very large error indicating that polarity is either badly or completely undefined. η estimation, however, gives rise to two possible values, depending on where the refinement is started, and the associated error estimates are very small, indicating a very precisely defined polarity. In contrast, in all the other tests, both x and η refine, independent of the starting value, to a single value which is within 1.5 estimated standard deviations of the known 'correct' value. The tests which limit $(\sin \theta/\lambda)_{max}$ or which use compound 5 with space group $P4_12_12$ are intended to increase the proportion of E reflections in the data set and hence to produce the greatest effect on the η parameter. Limiting $\sin \theta/\lambda$ also reduces the relative influence of f'' on the structure factors. The same objective was followed in the tests on compound 6, by not only limiting $\sin \theta/\lambda$ but by using an incomplete data set in conjunction with biased starting parameters, as Ueki, Zalkin & Templeton (1966), Cruickshank & McDonald (1967) and Templeton, Templeton, Zalkin & Ruben (1982) have shown how incorrect polarity produces coordinate shifts in such situations. One needs to go even further than this, however, as in the tests on compound 7, to produce incorrect results on η although x remains a reliable estimate in all the tests performed here.

Table 6. *Simulations on compound* 7, NiSb

Data set: w; Cu $K\alpha$; threshold 500; 5 variables; 33 observations. $(\sin \theta/\lambda)_{max}$ 0.6 Å^{-1}. R values in range 0.024 to 0.026. G values in range 0.965 to 1.008, $z(Sb)$ fixed.

$z(Sb)$	Starting value of x or η'	Refined values		$z(Ni)$ x variable	$z(Ni)$ η variable
		x	η'		
0.250	0.0	*	−0.29 (24)	0.0091 (66)	−0.0051 (26)
0.250	1.0	*	1.29 (24)	0.0091 (66)	0.0051 (26)
0.245	0.0	0.69 (48)	−0.30 (24)	0.0031 (57)	−0.0082 (26)
0.245	1.0	0.68 (43)	1.30 (24)	0.0031 (57)	−0.0018 (26)
0.240	0.0	0.42 (23)	0.37 (20)	0.0019 (39)	0.0029 (36)
0.240	1.0	0.42 (23)	1.32 (27)	0.0019 (39)	−0.0076 (31)
0.230	0.0	0.24 (13)	0.21 (13)	0.0014 (24)	0.0018 (23)
0.230	1.0	0.24 (13)	0.21 (13)	0.0014 (24)	0.0018 (23)
0.200	0.0	0.079 (70)	0.073 (73)	0.0021 (13)	0.0022 (13)
0.200	1.0	0.079 (70)	0.073 (73)	0.0021 (13)	0.0022 (13)

* The e.s.d. was practically too large for the machine precision as the least-squares matrix was 'almost' singular.

In general, the estimated standard deviation of x is larger than the corresponding value of η. This is particularly noticeable in data sets with a large proportion of E reflections such as those with a low sin θ/λ cut-off. When the proportion of E reflections diminishes or the Bijvoet differences become large, the error estimates of x and η are practically identical but with a slight tendency for those of η to be larger than those of x. This latter effect may be due to the sum of squares for η refinement depending on η^4 and for x only on x^2. The curve of $y = x^4$ has a flatter minimum than that of $y = x^2$ as may be seen in Fig. 2 for data set non-$E(3)$.

In all cases it has been observed that the refinement with x converges more rapidly than with η. The refinements carried out here were on $|F|^2$ and from (5) and (3) it can be seen that x is a *linear* function, and η a *quadratic* function of $|F|^2$. It is thus not surprising that x should converge faster than η. With refinements on $|F|$, $|F|$ becomes a non-linear function of either x or η and the difference in speed of convergence may be less marked.

Conclusion

Rogers's suggestion of a continuous variable for enantiomorph-polarity estimation is highly suited to automatic computation. A simple logical switch based on centrosymmetry could easily be used to key the refinement of such a variable. This would help to avoid the bias in published atomic coordinates such as has been revealed by Templeton, Templeton, Zalkin & Ruben (1982). Rogers's exceedingly valuable contribution has presumably not met with the widespread use that it deserves due to the nonavailability of suitable programs. To the present day and to the author's knowledge only two papers have been published in which η refinement has been used (Hanson, Rivett, Ley & Williams, 1982; Mara, Singh, Thomas & Williams, 1982).

It would seem, however, that Rogers has erred in his choice of enantiomorph-polarity parameter and that x as defined in (5) is to be preferred as being faster and more reliable than η.

Note added in proof: The refinement of the enantiomorph-polarity parameter x has now been added as a permanent feature in our implementation of the X-RAY76 system. The current version allows refinement on $|F|$, $|F|^2$ or I, and x is varied automatically in the final stages of refinement with a non-centrosymmetric structure. Coordinate constraint(s) for polar space groups are now automatically generated. Users of X-RAY72 or X-RAY76 are invited to write to the author for details.

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