evidently belongs to the component which produces $h,k,3n$ reflexions with the same relative intensity and shape.

The reflexions of each component lie on a rhombohedral reciprocal lattice. The two lattices are related by the mirror plane passing through OA in Fig. 3 and the axis of rotation. In real space this plane has the indices $\{52\bar{7}0\}$ with respect to the hexagonal axes of one component. The components being twins the twin law is $\{52\bar{7}0\}$. Considering one twin component in real space, the lattice constants of the hexagonal triple primitive unit cell may be calculated: $c = 44{\cdot}2$, $a = 25{\cdot}4$ Å. The rhombohedral lattice constants are: $a = 20{\cdot}8$ Å, $\alpha = 75{\cdot}3°$. The hexagonal unit cell contains approximately 2000 atoms. The lines present on a powder diagram can be satisfactorily indexed with reference to this cell.

Symmetry considerations for one twin give hexagonal symmetry for the weighted $h,k,3n$ sections and trigonal symmetry for the weighted sections with $l \neq 3n$. Symmetry planes are absent and hence the Laue symmetry of the whole weighted reciprocal lattice for one twin is $\bar{3}$.

Discussion

As our samples are prepared from the melt and as at least one transformation takes place during cooling (Sanfourche, 1919; Smith, 1929) the conditions for growth twinning as well as transformation twinning are present. By microscopic research transformation twins could be demonstrated by Mima & Hasegawa (1960). These authors and Iokibe (1931) have described the existence of two transformations in the composition range of Cu_3Si, which could be verified by our experiments.

The presence of definite strong lines on the powder diagram makes it probable that the calculated unit cell contains a number of small units. It is conceivable that the large cell is built up from the smaller units in a number of ways, producing twins. In that case an uncommon twin law like $\{52\bar{7}0\}$ seems not unlikely. This approach may be helpful for the solution of the remaining problems, *viz.* the remarkable distribution of the reflexions and the uncommon twin law.

The author is indebted to Prof. W. G. Burgers, in whose laboratory this investigation was carried out, for his constant interest and valuable discussions. He wishes to thank Prof. P. M. de Wolff from the Department of Technical Physics for calling his attention to the paper on CuSe by Taylor & Underwood, and Dr Ir J. H. Palm for his assistance in the first stage of the X-ray experiments.

References

Iokibe, K. (1931). *Kinzoku no Kenkyu*, **8**, 433.
Mima, G. & Hasegawa, M. (1960). *Technol. Rep. Osaka Univ.* **10**, 157.
Sanfourche, M. A. (1919). *Rev. Met.* **16**, 246.
Smith, C. S. (1929). *Trans. Amer. Inst. Min. (metall) Engrs*, **83**, 414.
Taylor, C. A. & Underwood, F. A. (1960). *Acta Cryst.* **13**, 361.

Acta Cryst. (1965). **19**, 1051

A reinvestigation of the crystal structure of dialuric acid monohydrate.

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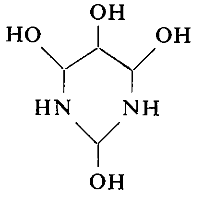
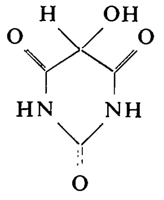
Different lines of evidence for the formula of the dialuric acid molecule seem to be at variance. Tipson & Cretcher (1951) and Davol & Laney (1956) allocated it the tetrahydroxy formula (I) on the basis of infrared spectral measurements, whereas other authors (Biltz & Paetzold, 1923; Hantzsch, 1921; and most textbooks) give it the formula (II) which follows from its chemical reactions and preparation.

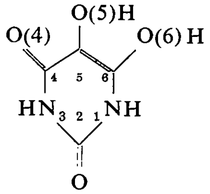
The crystal structure of dialuric acid monohydrate was deduced by Alexander & Pitman (1956) from projection data, but only 65 reflexions were collected in the two most badly resolved zones. They concluded that the formula is (III). However, there are some interesting features about this structure; for instance the bonds C(5)–O(5)H and C(6)–O(6)H [see (III) for numbering] differ by 0·10 Å from one another and the molecule is non-planar; moreover formula (III) is the one ascribed to isodialuric acid by Berend & Roosens in their classic synthesis of uric acid. Furthermore the structure has more close oxygen–oxygen hydrogen bonding approaches than it is possible to account for with the available hydrogen atoms. In particular there is an unusual hydrogen bonding interaction (of 2·68 Å) between two equivalent –OH groups related by a twofold screw axis.



(I)



(II)



(III)

Large crystals of dialuric acid monohydrate were grown by passing hydrogen sulphide through alloxan solution overnight, then allowing the solution to stand at 0 °C (Tipson &

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Cretcher, 1951). They showed the forms {101}, {100}, {001}, {010}, {111}. The space group is $P2_1/n$. The crystals slowly oxidized to alloxan in moist air but kept indefinitely under light oil.

The unit-cell dimensions, measured on a General Electric single-crystal orienter, are:

$a = 12{\cdot}714 \pm 003$ Å	$\beta = 95°24' \pm 5'$	
$b = 3{\cdot}676 \pm 003$	$D_m = 1{\cdot}812$ g.cm^{-3}	(Alexander & Pitman, 1956)
$c = 12{\cdot}949 \pm 004$	$D_x = 1{\cdot}786$ g.cm^{-3}	
	$Z = 4$	

Very small roughly spherical pieces were cut for X-ray work. The intensities were recorded photographically by the integrated Weissenberg method with Cu $K\alpha$ radiation. These were photometered and after reduction to structure amplitudes were put on the same scale by comparing common reflexions and by (hnl) double slit photographs (Stadler, 1950). Out of a possible 1270 independent reflexions, 1250 were recorded and 950 were of measurable intensity.

A three-dimensional Fourier synthesis with phases from Alexander & Pitman's (1956) structure showed that this was correct in the main and it was therefore used as a starting point for refinement. Several cycles of differential syntheses with Shiono's (1962) program for the IBM 7070 computer, and two least-squares refinements with Busing & Levy's (1959) IBM 7090 program, using anisotropic temperature factors, reduced the initial agreement index from 39 % to 10 %. The hydrogen-atom positions were found by a series of three-dimensional difference syntheses using reflexions out to $\sin\theta = 0{\cdot}85$.The first map showed up the imino hydrogen atoms quite clearly and H(6) and H(7) (see Fig. 1 for atomic numbering) less distinctly but it was only after including these atoms in a least-squares refinement of the heavier atoms, with a consequent alteration in absolute scale factor, that the other water hydrogen atoms H(8)(H_2O) and H(5) came up. The amino hydrogen atom peaks at $0{\cdot}80$ e.Å^{-3} were relatively much higher than the other peaks with H(5) = H(6) = H(8) = $0{\cdot}43$ e.Å^{-3}. Some of these [in particular H(5) and H(8)] are not greatly different from the highest background peaks and the position of these atoms must be regarded as tentative. A neutron diffraction study is in hand to locate these with more certainty.

The final R value with the hydrogen atoms included was 8·0 % for all measured reflexions and 10·1 % when the unmeasured reflexions were included at half the threshold value. A table of final F_{obs} and F_{calc} values may be obtained from the author. The final coordinate and thermal parameters are listed in Table 1. The mean e.s.d.'s from the final least-squares cycle are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}003$ Å, $\sigma(B_{ii}) = 0{\cdot}12$ Å^2, $\sigma(B_{ij}) = 0{\cdot}10$ Å^2. The closest intermolecular contacts are given in Table 2 and Fig. 2.

The structure

The bond lengths and hydrogen atom positions (Fig. 1) show the molecule to be in the 5,6-dihydroxy form (III). However, C(4)C(5) at 1·417 Å and C(5)O(5)(H) and C(6)O(6)(H) at 1·357 and 1·308 Å are significantly shorter than the single-bond values of 1·48 and 1·43 Å respectively [these are calculated by ascribing a covalent radius of 0·74 Å to the trigonally hybridized carbon after Lide (1962)]. This shows that in common with other oxypyrimidine and barbituric acid derivatives [*e.g.* violuric acid (Craven & Mascarenhas, 1964), barbituric acid (Bolton, 1963)] the conventional formula is only an approximate description of a molecule whose bonds are intermediate in character. The C(6)–O(6)(H) bond in particular must have considerable double-bond character and this can only arise from resonance involving contributions from charged forms such as $O^- = C(4)\text{–}C(5)\text{–}C(6) = O(6)^+H$ which shorten C(6)–O(6) and enhance the release of H(6). For this reason we may assume that –O(6)H(6) is the acidic group in the molecule and the anion will be:

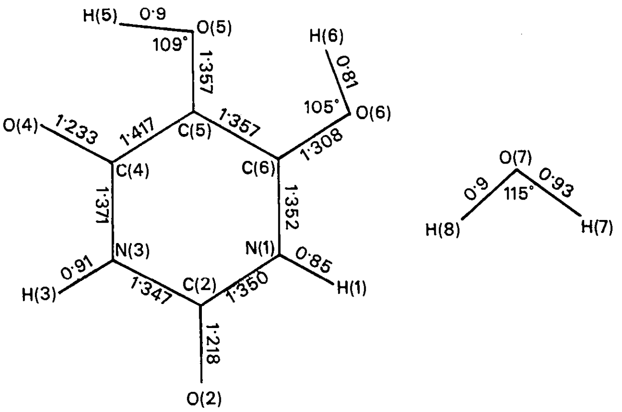
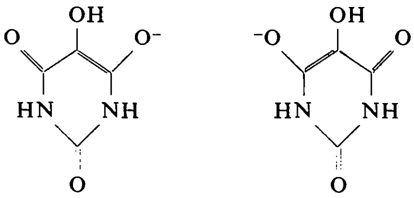
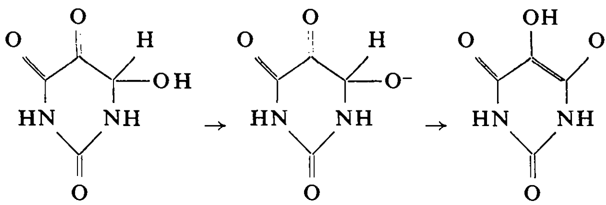


Fig. 1. Dimensions of the dialuric acid and water molecules in dialuric acid monohydrate.



As these are symmetrical there will be a gain in resonance stabilization energy on ionization which will account for the high acid strength of dialuric acid ($K_a = 1{\cdot}3 \times 10^{-3}$). Since there is no further gain in resonance energy by losing a proton from O(5) the acid should be largely monobasic and this is observed to be the case.

Formula (III) is patently not the correct one for the isomeric isodialuric acid. This is a much weaker acid than dialuric and an alternative formula for this is (IV). In strong alkaline solutions the anion (V) will form and this can be stabilised by changing to (VI) the dialuric anion.



(IV) (V) (VI)

A mechanism such as this would account for the interesting experimental fact that when alkalis are added to solutions of isodialuric acid the dialurate is obtained (Koech, 1912).

The molecule is not significantly non-planar.

Table 1. *Fractional atomic coordinates and anisotropic temperature parameters* (Å^2)

	x	y	z
C(2)	0·1389	0·2960	0·3341
C(4)	−0·0460	0·2594	0·3635
C(5)	−0·0719	0·4248	0·2656
C(6)	0·0072	0·5215	0·2077
N(1)	0·1092	0·4581	0·2424
N(3)	0·0596	0·2041	0·3910
C(2)	0·2311	0·2415	0·3645
O(4)	−0·1119	0·1663	0·4224
O(5)	−0·1738	0·5069	0·2336
O(6)	−0·0025	0·6853	0·1176
O(7)(H_2O)	−0·3159	0·5407	0·4461
H(1)	0·162	0·483	0·207
H(3)	0·078	0·069	0·449
H(5)	−0·217	0·475	0·288
H(6)	−0·077	0·723	0·093
H(7)	−0·262	0·300	0·428
H(8)	−0·300	0·580	0·500

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(2)	2·05	2·23	1·82	−0·23	0·16	−0·26
C(4)	1·84	2·16	1·89	−0·24	0·09	−0·14
C(5)	2·30	1·93	1·99	−0·08	−0·17	0·24
C(6)	2·60	2·45	1·93	−0·15	0·02	0·02
N(1)	2·12	2·94	1·93	−0·15	0·28	0·00
N(3)	2·01	2·55	1·75	0·14	−0·09	0·17
O(2)	2·05	3·93	2·26	0·17	0·08	−0·47
O(4)	2·40	3·33	2·20	0·18	0·37	0·64
O(5)	2·08	3·70	2·80	0·40	−0·13	0·68
O(6)	3·27	3·85	2·00	0·16	0·19	0·96
O(7)	3·80	7·90	4·95	1·80	−1·60	−4·35

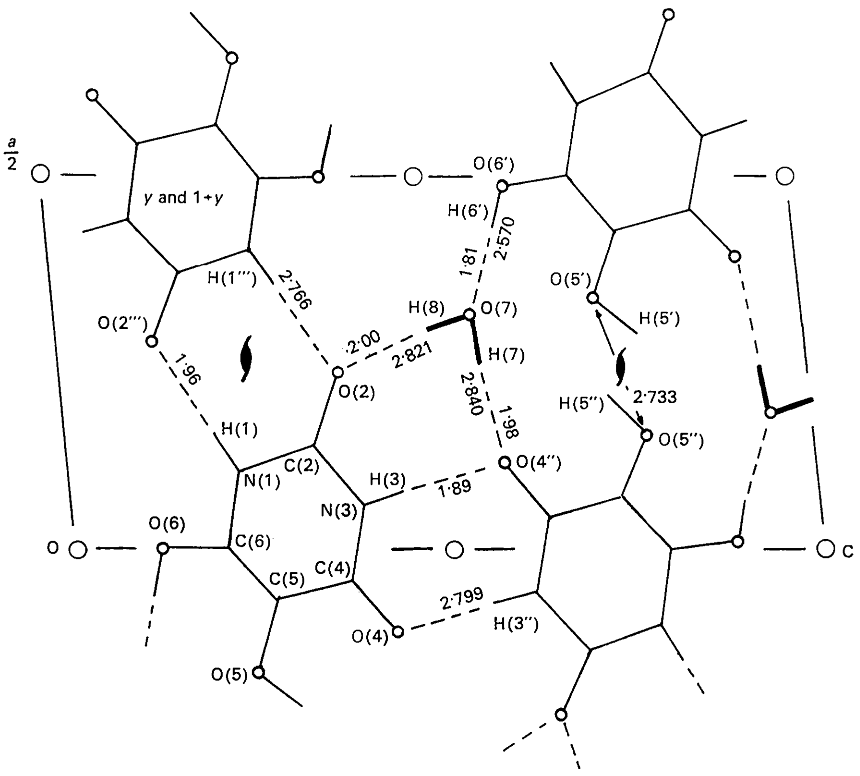


Fig. 2. The hydrogen-bonding network in dialuric acid monohydrate projected on (010). Broken lines indicate hydrogen bonds. The exact situation at O(5')---O(5'') is not yet clear as H(5) showed up poorly on the difference map.

Table 2. *The intermolecular distances less than* 3·6 Å

Atom	to atom			Distance
C(2)	(I)	N(1)	(IX)	3·310 Å
	(I)	N(3)	(VI)	3·584
	(IV)	O(2)	(V)	3·582
	(II)	O(6)	(X)	3·581
	(IV)	H(1)	(IX)	2·88
	(II)	H(8)	(X)	2·86
C(4)	(I)	C(5)	(IX)	3·324
	(I)	C(6)	(IX)	3·485
	(I)	O(4)	(VI)	3·538
	(I)	O(5)	(IX)	3·551
	(II)	H(3)	(VII)	2·776
C(5)	(I)	C(6)	(IX)	3·570
	(I)	O(4)	(VI)	3·465
	(IV)	O(5)	(XI)	3·581
	(I)	O(6)	(IX)	3·487
	(VI)	O(7)	(VIII)	3·543
	(IV)	O(7)	(XI)	3·443
C(6)	(I)	O(6)	(VI)	3·475
	(I)	O(6)	(IX)	3·286
	(IV)	O(7)	(VIII)	3·385
N(1)	(I)	N(3)	(VI)	3·442
	(I)	O(2)	(VI)	3·568
	(IV)	O(2)	(V)	2·766
	(I)	O(6)	(IX)	3·502
N(3)	(II)	O(4)	(VII)	2·799
	(II)	O(4)	(X)	3·367
	(II)	H(3)	(VII)	3·01
O(2)	(IV)	O(2)	(V)	3·560
	(II)	O(4)	(VII)	3·598
	(IV)	O(6)	(IX)	3·443
	(II)	O(7)	(X)	2·821
	(IV)	H(1)	(IX)	1·96
	(II)	H(8)	(X)	2·00
O(4)	(II)	O(4)	(VII)	3·543 Å
	(I)	O(5)	(IX)	3·480
	(IV)	O(5)	(XI)	3·288
	(I)	O(7)	(V)	2·840
	(II)	H(3)	(VII)	1·89
	(I)	H(7)	(V)	1·98
	(I)	H(8)	(V)	3·08
C(5)	(IV)	O(5)	(VIII)	2·733
	(I)	O(7)	(V)	3·437
	(IV)	O(7)	(VIII)	2·835
	(IV)	O(7)	(XI)	3·091
	(I)	H(7)	(V)	2·95
	(IV)	H(7)	(VIII)	2·43
	(IV)	H(5)	(VIII)	2·21
	(IV)	H(5)	(XI)	2·40
O(6)	(III)	O(6)	(VI)	3·342
	(IV)	O(7)	(VIII)	2·570
	(IV)	H(7)	(VIII)	3·02
	(IV)	H(8)	(VIII)	3·16
O(7)	(IV)	H(6)	(VIII)	3·24
	(IV)	H(6)	(XI)	1·81
H(3)	(II)	H(3)	(VII)	2·54
H(6)	(IV)	H(7)	(VIII)	2·22
	(IV)	H(8)	(VIII)	2·48
H(7)	(I)	H(5)	(V)	2·06

(I), (V) $= x, y, z$
(II) $= -x, -y, -z$
(III) $= \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
(IV) $= \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(VI) $= x, 1+y, z$
(VII) $= x, y, z-1$
(VIII) $= x-1, y, z$
(IX) $= x, y-1, z$
(X) $= x, y-1, z-1$
(XI) $= x-1, y, z$

The hydrogen-bonding scheme deduced from the approach distances (Table 2) and hydrogen atom positions is shown in Fig. 2. The shortest hydrogen bond is O(6)–H(6)–O(7)(water) and at 2·570 Å must be of the same order of strength as the hydrogen bonds in carboxylic acids. This is keeping with the conclusion above that H(6) is the 'acid' hydrogen in the diuluric molecule.

The water molecule is only hydrogen-bonded to three other atoms, O(6) (2·570 Å), O(4) (2·840 Å) and O(2) (2·821 Å), and not tetrahedrally to four atoms as is commonly the case. The O(7) (water)---O(5) distance of 2·835 is within the limits of hydrogen bonding and normal approach distance for two oxygen atoms. It is not a hydrogen bond, [or a bifurcated hydrogen bond for H(7) is already interacting with O(4)] in the strict sense however, as O(5) ---H(7) is 2·43 Å and the O(5)(H7)O(7) angle is 107°. An OH distance of 1·8 to 2·0 Å would be expected for hydrogen bonding (with O–H–O rectilinear), or 2·6 Å in a normal contact. The coordination of hydrogen-bonded atoms around the water molecule is similar to, but not the same as, the threefold planar hydrogen-bonded coordination about water molecules found in barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961) and cytosine monohydrate (Jeffrey & Kinoshita, 1963) as O(7) (water) is 0·45 Å out of the plane defined by O(2), O(4) and O(6).

An interesting feature of the packing is the interaction between crystallographically equivalent O(5)–H(5) groups across the screw axis (Fig. 2). The O(5′)---O(5″) distance of 2·730 Å is the closest intermolecular approach in the structure apart from O(6)–H(6)---O(7). Each O(5) is close to an H(5) (at y and $1+y$) at distances of 2·2 and 2·4 Å; this is extended indefinitely throughout the crystal by the operation of the twofold screw axis parallel to **b**. However the H(5) peak on the difference map was very low and a full description of the O(5)---O(5″) hydrogen bonding must await the results of the neutron diffraction study.

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References

ALEXANDER, L. E. & PITMAN, D. T. (1956). *Acta Cryst.* **9**, 501.
BILTZ, H. & PAETZOLD, H. (1923). *Liebigs Ann.* **433**, 70.
BOLTON, W. (1963). *Acta Cryst.* **16**, 166.
BUSING, W. & LEVY, H. A. (1959). Oak Ridge National Laboratory, Central Files, No. 59-4-37.
CRAVEN, B. M. & MASCARENHAS, Y. (1964). *Acta Cryst.* **17**, 407.
DAVOL, J. & LANEY, D. H. (1956). *J. Chem. Soc.* p. 2124.
HANTZSCH, A. (1921). *Ber. dtsch Chem. Ges.* **54**, 1271.
JEFFREY, G. A., GHOSE, S. & WARWICKER, J. O. (1961). *Acta Cryst.* **14**, 881.
JEFFREY, G. A. & KINOSHITA, Y. (1962). *Acta Cryst.* **16**, 20.
KOECH, P. (1912). *Liebigs Ann.* **315**, 248.
LIDE, D. R. (1962). *Tetrahedron*, **17**, 125.
SHIONO, R. (1962). Program No. 330, I.U.Cr. *World List of Crystallographic Computer Programs*, 1st. edn.
STADLER, H. P. (1950). *Acta Cryst.* **3**, 262.
TIPSON, R. S. & CRETCHER, L. H. (1951). *J. Org. Chem.* **16**, 1091.

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Unit cell and space group of sublimed fumaric acid.

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In the course of an investigation of the crystallization of fumaric acid, two different crystalline forms were found.

One is obtained when a water solution is allowed to crystallize. This form was studied by Reis & Schneider (1928) who claimed it to be monoclinic, whereas Yardley (1925) reported it as triclinic. Our experimental data from an identical type of crystallization agree with the Reis & Schneider work.

A second type of crystallization was obtained by sublimation of the previous form at 220–235 °C. This new crystalline form is predominantly composed of needlelike contact twins. The twins are formed by two enantiomorphic structures in which the $(10\bar{1})$ plane is the plane of composition and also the twin-plane. The new cell is triclinic and is not, so far as we know, covered by any publication. Its parameters are:

$$a=4\cdot52\pm0\cdot02,\quad b=7\cdot51\pm0\cdot02,\quad c=5\cdot40\pm0\cdot04\ \text{Å}$$
$$\alpha=136\cdot7\pm0\cdot3^\circ,\quad \beta=110\cdot6\pm0\cdot3^\circ,\quad \gamma=72\cdot8\pm0\cdot3^\circ\,.$$

The number of molecules per unit cell is one. A calculated density of 1·63 g.cm^{-3} agrees with the observed density of 1·60 g.cm^{-3}. The space group $P\bar{1}$ is suggested by the absence of pyroelectric effect.

No further work on this compound is planned.

References

REIS, A. & SCHNEIDER, E. (1928). *Z. Kristallogr.* **68**, 543.
YARDLEY, K. (1925). *J. Chem. Soc.* **127**, 2207.

Acta Cryst. (1965). **19**, 1055

Standard deviation of coordinates as a function of the residual and temperature coefficient.

By E. STANLEY, *University of Saskatchewan, Regina Campus, Regina, Saskatchewan, Canada*

(*Received* 21 *April* 1965)

Tables of R, the residual, as a function of the standard deviation of coordinates, $\sigma(r)$, and temperature coefficient, B, have been calculated in two and three dimensions (Stanley, 1964, 1965). It has been suggested that tables in which the standard deviation of coordinates as a function of the residual were tabulated might be more use. These tables have now been prepared by interpolation from those previously published and give the values of $\sigma(r)$ in Å as a function of R and B for carbon atoms of the form suggested by Vand, Eiland & Pepinski (1957) within the limit of the sphere of reflexion of Cu $K\alpha$ radiation. From these tables it is probably more obvious how the data and the symmetry control the value of the residual. For three-dimensional data for a structure in a centrosymmetric space group with zero temperature coefficient, a residual of 5 % corresponds to a standard deviation of coordinates of 0·009 Å. The same residual for two-dimensional data for a structure in a non-centrosymmetric space group and a temperature coefficient of 4 Å^2 corresponds to a standard deviation of coordinates of 0·022 Å.

A comparison with other methods of estimating the standard deviation is interesting. The method of Booth (1947), as might be expected, gives estimates which agree very well with the present work. The [001] projection of triphenyl phosphate (Davies & Stanley, 1962) has a value of $R=14\,\%$ and a value of $B=4\cdot5$ Å^2. The value of $\sigma(r)$ calculated by Booth's method is 0·04 Å. This agrees very well with the value of 0·04 Å obtained from the tables. Comparison with estimates of standard deviations made from the values of the slopes of the difference map at atomic