Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Chapuis, G., Arend, H. & Kind, R. (1975). *Phys. Status Solidi A*, **31**, 449–454.

Cruickshank, D. W. J. (1969). *Crystallographic Computing*, edited by F. R. Ahmed, p. 226. Copenhagen: Munksgaard.

Depmeier, W. (1976). *Acta Cryst.* B**32**, 303–305.

Depmeier, W. (1977). *Acta Cryst.* B**33**, 3713–3718.

Ferguson, G. L. & Zaslow, B. (1971). *Acta Cryst.* B**27**, 849–852.

Heger, G., Mullen, D. & Knorr, K. (1976). *Phys. Status Solidi A*, **35**, 627–637.

Johnson, C. K. (1969). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 220–226. Copenhagen: Munksgaard.

Johnson, C. K. (1971). *ORTEP* II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Kammer, H. (1976a). *Helv. Phys. Acta*, **49**, 726–727.

Kammer, H. (1976b). Proc. 19th Congr. Ampère, Heidelberg, pp. 487–490.

Koetzle, T. F., Lehmann, M. S., Verbist, J. J. & Hamilton, W. C. (1972). *Acta Cryst.* B**28**, 3207–3214.

Larsen, K. P. (1974). *Acta Chem. Scand. Ser. A*, **28**, 194–200.

Peterson, E. R. & Willett, R. D. (1972). *J. Chem. Phys.* **56**, 1879–1882.

Steadman, J. P. & Willett, R. D. (1970). *Inorg. Chim. Acta*, **4**, 367–371.

Tichý, K. Beneš, J. (1975). *Acta Cryst.* A**31**, S84.

Tichý, K. & Beneš, J. (1977). *Helv. Phys. Acta*, **50**, 459–466.

Walpen, P. (1976). Diploma work, Institute for Crystallography, ETH, Zürich.

Willett, R. D. & Riedel, E. F. (1975). *Chem. Phys.* **8**, 112–122.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Comparison of Two Independent Determinations of the Structure of Calcium L-Ascorbate Dihydrate

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Two independent determinations of the crystal structure of calcium L-ascorbate dihydrate, $Ca^{2+}(C_6H_7O_6^-)_2 \cdot 2H_2O$ [Hearn & Bugg (1974). *Acta Cryst.* B**30**, 2705–2711 and Hvoslef & Kjellevold (1974). *Acta Cryst.* B**30**, 2711–2716], are compared by use of normal probability plots. The two sets of measured structure factors give a normal probability plot that is largely linear, with a slope of 2·7 and nearly zero intercept. Both sets are hence drawn from essentially similar populations that differ only slightly in systematic error distribution, with pooled standard deviations underestimated by a factor of nearly three. Difficulties in comparing the original atomic position and thermal parameters and standard deviations were obviated by additional least-squares refinement of both sets under identical conditions. A half-normal probability plot based on the refined parameters is nearly linear with a slope of 1·7 and zero intercept. The ascorbate ion is shown, from the anomalous scattering contribution to both sets of data, to be the L-enantiomer. The crystal structure of calcium L-ascorbate is best represented by the weighted mean of the two independent parameter sets.

Introduction

The chances that two or more independent determinations of a given crystal structure may be undertaken nearly simultaneously have greatly increased since automatic diffractometers and a more powerful methodology have become rather widely available. It is highly desirable in such cases to present a detailed comparison of the replicate structural information. Such information is valuable for several reasons. Should the differences between determinations be identified as primarily random, confidence in the meas-

urements and results becomes substantially enhanced. On the other hand, demonstration of systematic or, more seriously, gross differences should lead to scrutiny of these differences and, if necessary, to repetition of one or both experiments under improved conditions.

Comparison is readily made by analysis of the normal probability plots (Abrahams & Keve, 1971), and this technique has been used in several recent duplicate determinations [see, for example, Bernstein (1975), Escande & Galigné (1974), Ladd & Povey (1973), Power, Turner & Moore (1976)]. Two simultaneous and independent determinations of the structure of calcium ascorbate dihydrate [Hearn & Bugg (1974), Hvoslef & Kjellevold (1974), hereafter HB and HK respectively] were published without detailed comparison. The monoclinic unit-cell orientations chosen by HK and HB differ, making casual comparison harder than usual and emphasizing the need for more formal treatment, such as is made in the present communciation. Further, the error introduced in one set of atomic coordinates by neglecting anomalous dispersion in this polar crystal is eliminated, and the standard deviations in all parameters determined, by new refinements undertaken with the two sets of data as reported herein.

Normal-probability-plot analysis

Comparison of the independent HB and HK sets of structural information for calcium ascorbate dihydrate is most appropriately made following initial transformation of both sets to the reduced cell as given by HK with right-handed base vectors but retaining the molecular chirality of HB. Values of the statistic:

$$\delta p_i = |p_i(\text{HB}) - p_i(\text{HK})|/[\sigma^2 p_i(\text{HB}) + \sigma^2 p_i(\text{HK})]^{1/2}$$

[where $p_i(\text{HB})$, $\sigma p_i(\text{HB})$ are the ith position coordinate and standard deviation given by HB after transformation, and $p_i(\text{HK})$, $\sigma p_i(\text{HK})$ are corresponding values given by HK] are ordered and plotted against the expected values (X_i) of the ranked moduli of the normal deviates, as shown in Fig. 1. Values of X_i are obtained from tables of the normal probability function [for example, Tables of Normal Probability Functions (1953)] given in equation (1),

$$P(X_i) = (1/\sqrt{2\pi}) \int_{-x}^{x} e^{-\alpha^2/2} \, d\alpha. \quad (1)$$

A good approximation to $P(X_i)$ for sample size n is given by equation (2),

$$P(X_i) \simeq [3(n - i) + 2]/(3n + 1). \quad (2)$$

Table 4.3.2D in International Tables for X-ray Crystallography (1974) lists values of X_i for $n \leq 80$.

The array of 134 δp_i statistics in Fig. 1 does not depart widely from linearity, indicating that any difference in systematic error components between the two determinations is not severe. The slope of 1·51 shows that the pooled standard deviations are underestimated by about 50%. Comparison of the two sets of 180 β_{ij} is hampered by the mathematical complexities of assigning standard deviations to HB's transformed coefficients of thermal vibration. A full comparison of the two sets of structure factors $F(\text{HB})$ with transformed indices* and $F(\text{HK})$ and their assigned standard deviations $\sigma F(\text{HB})$ and $\sigma F(\text{HK})$ can, however, be immediately made using the order statistic:

$$\delta m_i = [F_i(\text{HB}) - kF_i(\text{HK})]/[\sigma^2 F_i(\text{HB})$$
$$+ k^2 \sigma^2 F_i(\text{HK})]^{1/2}$$

in a normal probability plot, as shown in Fig. 2. The value of $\sigma^2 F_i(\text{HB})$ is taken as $\sigma^2 F_i^2(\text{HB})/4F_i^2(\text{HB})$ and the scale factor k determined by a least-squares fit. The resulting common set of 1286 δm_i terms forms an array that deviates somewhat from linearity, primarily as a result of differences in anomalous scattering contribution, in intensity measurement technique, in the

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* The transformed-index HB structure factor set has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33691 (15 pp.). The HK structure factor set was previously deposited, as No. SUP 30510 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
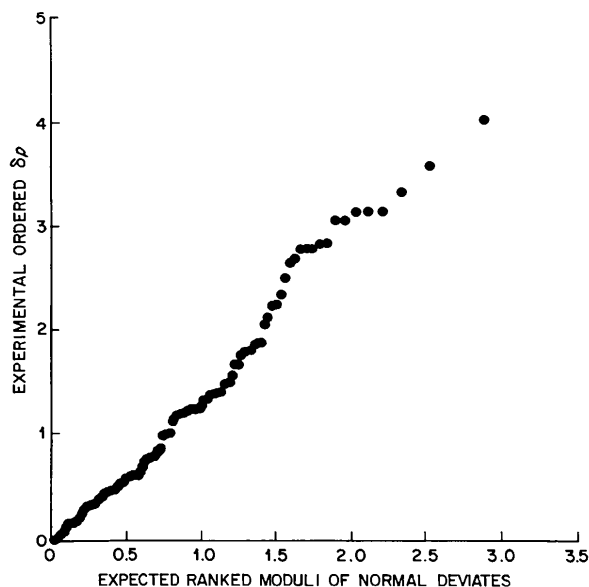

Fig. 1. Half-normal probability plot of 134 δp_i order statistics based on the transformed positional parameters given by HB and HK for calcium ascorbate dihydrate, where $\delta p_i = |p_i(\text{HB}) - p_i(\text{HK})|/[\sigma^2 p_i(\text{HB}) + \sigma^2 p_i(\text{HK})]^{1/2}$, against the expected ranked moduli of the normal deviates [see text for meaning of $p_i(\text{HB})$, $\sigma p_i(\text{HB})$, $p_i(\text{HK})$ and $\sigma p_i(\text{HK})$].

treatment of absorption and extinction, and in the estimated standard deviations. The array has a slope of 2·72 indicating an underestimation in the pooled standard deviation by a factor of nearly three. The almost zero intercept shows the scale factor k to be correctly determined.

Refinement and comparison of the two resulting sets of atomic coordinates

The atomic coordinates reported by HB [with published $R = 0·038$ and S (the standard deviation of an observation of unit weight) $= 2·16$], transformed to HK's reduced-cell orientation, were refined by the least-squares method using HB's structure factors with transformed indices. The transformed HK coordinates ($R = 0·036$, S not stated) were refined using the HK set of structure factors. A full matrix of 316×316 elements was used for the HB set (including the extinction parameter), 315×315 for the HK set (no extinction correction was required). In both cases, the calculations were carried out on à PDP 11/40 computer with the *Enraf–Nonius Structure Determination Package* (1977). Atomic scattering factors and anomalous dispersion corrections (f' and f'') were taken from *International Tables for X-ray Crystallography* (1974), based on Cu $K\alpha$ radiation for the HB, Mo $K\alpha$ for the HK data.

Refinement with each set of $|F|$'s, using the original weights given by HB and HK, was continued until all shifts were less than 10% of the corresponding standard deviation. Since the crystal belongs to the

polar space group $P2_1$, it is necessary to determine if structure factors calculated using the $x\bar{y}z$ set of coordinates fit the measured structure factors better than those using the corresponding xyz set. A choice may be made on the basis of the Hamilton (1965) $\mathscr{R}$-ratio, using the wR indicator values in Table 1. The HB structure factors correspond to the experimental value $\mathscr{R}(x\bar{y}z/xyz) = 1·172$, whereas the theoretical value $\mathscr{R}_{1,1005,0·005} = 1·004$. As expected, the hypothesis that the $x\bar{y}z$ set of coordinates is correct may be rejected at the 0·005 confidence level, since the xyz set corresponds to the recognized L-enantiomeric form. The HK $x\bar{y}z$ set hypothesis may similarly be rejected, since the experimental $\mathscr{R}(x\bar{y}z/xyz) = 1·031$ and the theoretical value $\mathscr{R}_{1,1977,0·005} = 1·002$. This also is expected, since HK collected their intensity measurements in a right-handed unit cell. Their original refined parameters correspond to the D-enantiomer: this inconsistency was

Table 1. *Structural refinement indicators for calcium* L-*ascorbate dihydrate*

Model	p	N	R	wR	S
HB (xyz)	316	1321	0·0374	0·0406	1·824
HB ($x\bar{y}z$)	316	1321	0·0427	0·0476	2·133
HK (xyz)	315	2292	0·0336	0·0414	2·920
HK ($x\bar{y}z$)	315	2292	0·0349	0·0427	3·015

p is the number of parameters varied, N the number of observations. R, wR and S are respectively the unweighted, the weighted agreement factor, and the standard deviation of an observation of unit weight: see, for example, Abrahams, Bernstein & Keve (1971) for definitions.

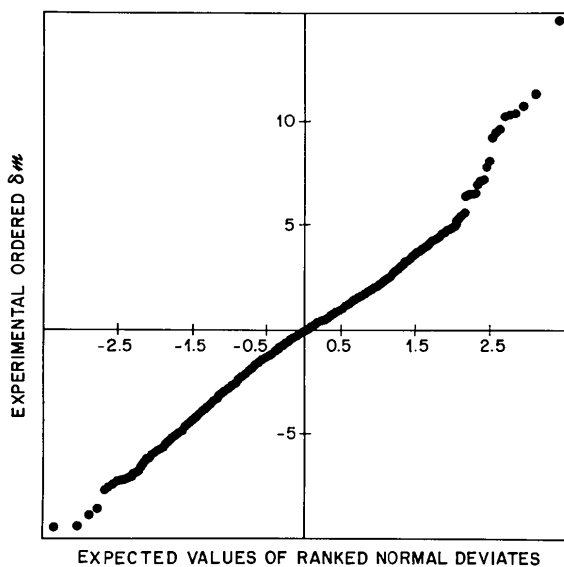EXPECTED VALUES OF RANKED NORMAL DEVIATES

Fig. 2. Normal probability plot of 1286 δm_i order statistics based on structure factors common to the two sets, where $\delta m_i = [F_i(\text{HB}) - kF_i(\text{HK})]/[\sigma^2 F_i(\text{HB}) + k^2\sigma^2 F_i(\text{HK})]^{1/2}$, against the expected normal order quantiles (see text).
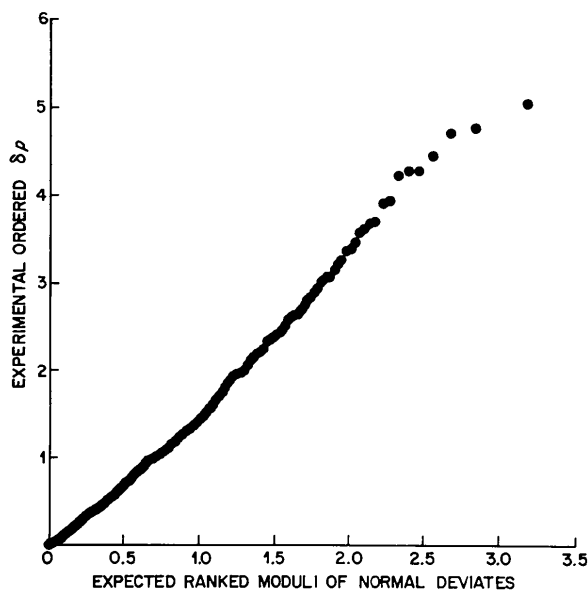

EXPECTED RANKED MODULI OF NORMAL DEVIATES

Fig. 3. Half-normal probability plot of the 315 δp_i order statistics based on the two complete xyz sets of atomic parameters refined with the transformed HB and HK structure factor sets (see text).

permissible since anomalous dispersion effects had been neglected. The present analysis shows that such neglect leads to a general displacement of the ascorbate ions by 0·011 Å (as much as seven of HK's original estimated standard deviation in the y coordinates) along b relative to the Ca^{2+} ion (cf. Ueki, Zalkin & Templeton, 1966). Both the HB and HK final sets of xyz position coordinates* correspond to the L-configuration for the ascorbate ion.

The deposited position coordinates and corresponding thermal parameters* are compared in Fig. 3 in a δp_i half-normal probability plot. The ordered δp_i array is closer to linearity than that shown in Fig. 1 but has a small change in slope for $\delta p_i > 1·5$. The average slope is 1·72, with nearly zero intercept. Examination of the 94 p_i terms with $\delta p_i > 1·5$ shows that about one third are position coordinates of O, C and H atoms: of this number, 64% are z coordinates. It is likely that the standard deviations of this group have been underestimated by a factor larger than the average 70%. The small departures of the arrays from linearity (Figs. 2 and 3) show that, to a fair approximation, the HK and HB structure factors and the deposited coordinates are drawn from the same population. The crystal structure of calcium L-ascorbate dihydrate is thus best represented by the weighted mean of the two coordinate sets, as given in Table 2.

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* The lists of fully refined position coordinates and thermal parameters (anisotropic for all atoms except hydrogen) are deposited together with the transformed HB structure factor set.

The power of the half-normal probability plot to reveal subtle but important systematic error is illustrated by the δp_i plot in Fig. 4. In constructing this plot, the deposited p_i(HB) and σp_i(HB) values are used: those of p_i(HK) and σp_i(HK), however, correspond to
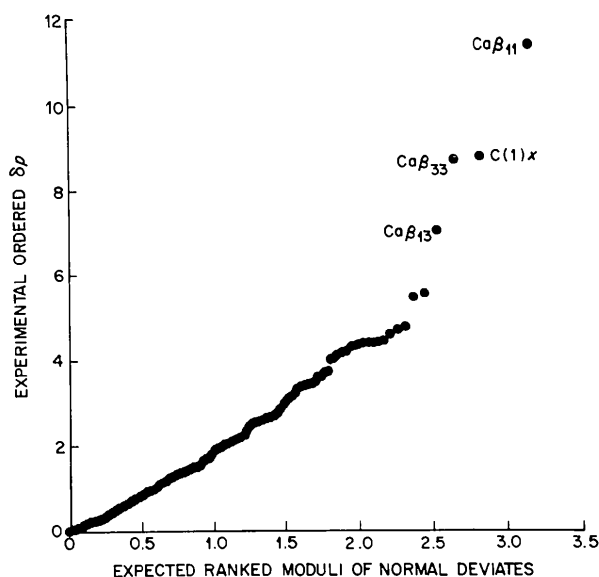

Fig. 4. Half-normal probability plot of the 315 δp_i order statistics based on the deposited HB parameters and a refined $x\bar{y}z$ HK parameter set, i.e. with the sense of the y coordinates reversed (see text).

Table 2. *Weighted mean atomic position coordinates for calcium L-ascorbate dihydrate*

Values have been multiplied by 10^5 for Ca^{2+}, by 10^4 for O and C, and by 10^3 for H. Standard deviations are given in parentheses.

	x	y	z		x	y	z
Ca^{2+}	78695 (5)	0	52660 (6)	O(5)B	−1407 (2)	9225 (1)	2215 (2)
C(1)A	3526 (3)	8229 (2)	233 (3)	O(6)B	699 (2)	9411 (1)	6166 (3)
C(2)A	4918 (3)	7953 (1)	−428 (3)	OW(1)	5493 (2)	93 (1)	2000 (3)
C(3)A	5093 (3)	7092 (1)	−178 (3)	OW(2)	568 (2)	5391 (1)	975 (3)
C(4)A	3814 (2)	6810 (1)	937 (3)	H(C4)A	310 (3)	642 (2)	13 (3)
C(5)A	4627 (2)	6564 (1)	3356 (3)	H(C5)A	532 (3)	702 (2)	407 (4)
C(6)A	5638 (3)	5752 (2)	3696 (4)	H(1)(C6)A	643 (3)	575 (2)	279 (4)
O(1)A	2922 (2)	8940 (1)	212 (3)	H(2)(C6)A	624 (3)	576 (2)	529 (4)
O(2)A	5902 (2)	8534 (1)	−1086 (2)	H(O2)A	642 (4)	839 (2)	−202 (5)
O(3)A	6118 (2)	6582 (1)	−650 (3)	H(O5)A	276 (3)	682 (2)	408 (5)
O(4)A	2810 (2)	7561 (1)	972 (3)	H(O6)A	476 (4)	478 (2)	259 (5)
O(5)A	3347 (2)	6443 (1)	4414 (3)	H(C4)B	−205 (3)	769 (2)	248 (4)
O(6)A	4505 (2)	5053 (1)	3183 (3)	H(C5)B	18 (3)	839 (2)	168 (4)
C(1)B	62 (2)	6711 (1)	5973 (3)	H(1)(C6)B	187 (3)	930 (2)	381 (5)
C(2)B	−874 (2)	7208 (1)	7056 (3)	H(2)(C6)B	209 (4)	847 (2)	545 (5)
C(3)B	−1540 (2)	7896 (1)	5780 (3)	H(O2)B	−184 (3)	684 (2)	917 (5)
C(4)B	−1053 (2)	7816 (1)	3673 (3)	H(O5)B	−206 (3)	903 (2)	139 (4)
C(5)B	−195 (2)	8559 (1)	2910 (3)	H(O6)B	108 (5)	931 (3)	741 (7)
C(6)B	1288 (3)	8937 (2)	4638 (4)	H(1)OW(1)	472 (4)	24 (3)	146 (6)
O(1)B	821 (2)	6042 (1)	6509 (2)	H(2)OW(1)	507 (3)	992 (2)	168 (4)
O(2)B	−960 (2)	6989 (1)	9096 (2)	H(1)OW(2)	77 (4)	521 (3)	−8 (6)
O(3)B	−2516 (2)	8490 (1)	6052 (3)	H(2)OW(2)	16 (4)	587 (2)	59 (5)
O(4)B	58 (2)	7088 (1)	4020 (2)				

the refined values obtained with the HK($x\bar{y}z$) model coordinate set, *i.e.* with the sense of the best y coordinates reversed, giving the D-enantiomer with $wR = 0.0427$. It is probable that the significant error produced in several Ca anisotropic temperature factors, shown in Fig. 4, results from minimization in the least-squares refinement of the effects of Ca anomalous scattering in an incorrect enantiomeric model.

Interatomic distances

The weighted mean of the two sets of refined coordinates, given by

$$\hat{x}_i = [x_i(HB)/\sigma^2 x_i(HB) + x_i(HK)/\sigma^2 x_i(HK)]/$$

$$[1/\sigma^2 x_i(HB) + 1/\sigma^2 x_i(HK)],$$

together with the corresponding variance of the weighted mean

$$\sigma^2 \hat{x}_i = 1/\{[1/\sigma^2 x_i(HB) + 1/\sigma^2 x_i(HK)]\},$$

Table 3. *Selected interatomic distances based on weighted mean of HB and HK coordinates*

Distances are in ångströms, standard deviations in parentheses. *A, B* refer to the ascorbate anions.

Ca–O(1)B	2·426 (2)		Ca–O(5)A	2·521 (2)
Ca–O(3)B	2·482 (2)		Ca–O(6)A	2·466 (2)
Ca–O(5)B	2·519 (2)		Ca–OW(2)	2·432 (2)
Ca–O(6)B	2·439 (2)		Ca–OW(1)	2·410 (2)

	A	B		A	B
C(1)–O(1)	1·231 (3)	1·229 (3)	C(3)–C(4)	1·516 (4)	1·518 (4)
C(1)–O(4)	1·365 (3)	1·374 (3)	C(4)–O(4)	1·453 (3)	1·451 (3)
C(1)–C(2)	1·417 (4)	1·421 (4)	C(4)–C(5)	1·533 (3)	1·528 (4)
C(2)–O(2)	1·375 (3)	1·366 (3)	C(5)–O(5)	1·436 (4)	1·431 (3)
C(2)–C(3)	1·371 (4)	1·370 (3)	C(5)–C(6)	1·514 (4)	1·508 (3)
C(3)–O(3)	1·275 (3)	1·288 (3)	C(6)–O(6)	1·422 (4)	1·425 (4)

	O–H	H···O	O···O
O(2)A–H···O(3)B	0·91 (5)	1·67 (5)	2·549 (3)
O(5)A–H···O(4)B	0·75 (4)	2·26 (4)	2·863 (3)
O(5)A–H···O(4)A	0·75 (4)	2·32 (4)	2·740 (3)
O(6)A–H···O(2)A	0·59 (4)	2·23 (4)	2·715 (3)
O(2)B–H···O(3)A	0·78 (4)	1·79 (4)	2·570 (3)
O(5)B–H···O(2)A	0·66 (4)	2·13 (4)	2·793 (2)
O(6)B–H···O(1)A	0·65 (5)	2·20 (4)	2·785 (2)
OW(1)–H(1)···O(5)B	0·82 (6)	2·20 (5)	2·972 (3)
OW(1)–H(2)···O(2)B	0·73 (5)	2·20 (5)	2·917 (3)
OW(2)–H(2)···O(3)A	0·67 (5)	2·04 (5)	2·710 (3)
OW(2)–H(1)···O(1)A	0·91 (5)	1·88 (5)	2·779 (3)

are given in Table 2 and result in the selected interatomic distances of Table 3, based on the weighted mean lattice constants $a = 8.3365$ (17), $b = 15.7860$ (28), $c = 6.3612$ (17) Å, $\beta = 107.479$ (9). Comparison of the interatomic distances in Table 3 with those in HK's Tables 3 and 5 and Fig. 2 shows no differences greater than two weighted mean standard deviations. Comparison with HB's Tables 5 and 6 shows four distances that differ by more than three weighted mean standard deviations, *i.e.* C(1)B–O(1)B, C(4)A–C(5)A, OW(1)···O(3)A and H(2)···O(3)A, but only the H···O distance differs by more than two of HB's estimated standard deviations.

It is concluded that the weighted mean set of coordinates is more representative of the structure of calcium L-ascorbate dihydrate than either set taken separately, both having been demonstrated as drawn from essentially the same statistical population.

References

ABRAHAMS, S. C., BERNSTEIN, J. L. & KEVE, E. T. (1971). *J. Appl. Cryst.* **4**, 284–290.

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

BERNSTEIN, J. (1975). *Acta Cryst.* B**31**, 1268–1271.

Enraf–Nonius Structure Determination Package (1977). Edited by B. FRENZ & Y. OKAYA. Molecular Structure Corporation, College Station, Texas.

ESCANDE, A. & GALIGNÉ, J. L. (1974). *Acta Cryst.* B**30**, 1647–1648.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

HEARN, R. A. & BUGG, C. E. (1974). *Acta Cryst.* B**30**, 2705–2711.

HVOSLEF, J. & KJELLEVOLD, K. E. (1974). *Acta Cryst.* B**30**, 2711–2716.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LADD, M. F. C. & POVEY, D. C. (1973). *Acta Cryst.* B**29**, 2973–2975.

POWER, L. F., TURNER, K. E. & MOORE, F. H. (1976). *Acta Cryst.* B**32**, 11–16.

Tables of Normal Probability Functions (1953). National Bureau of Standards, *Applied Mathematics Series* 23, US Government Printing Office, Washington.

UEKI, T., ZALKIN, A. & TEMPLETON, D. H. (1966). *Acta Cryst.* **20**, 836–841.