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Accuracy of Crystal Structure Error Estimates

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Abstract

A statistical analysis of 100 crystal structures retrieved from the Cambridge Structural Database is reported. Each structure has been determined independently by two different research groups. Comparison of the independent results leads to the following conclusions: (*a*) The e.s.d.'s of non-hydrogen-atom positional parameters are almost invariably too small. Typically, they are underestimated by a factor of 1·4–1·45. (*b*) The extent to which e.s.d.'s are underestimated varies significantly from structure to structure and from atom to atom within a structure. (*c*) Errors in the positional parameters of atoms belonging to the same chemical residue tend to be positively correlated. (*d*) The e.s.d.'s of heavy-atom positions are less reliable than those of light-atom positions. (*e*) Experimental errors in atomic positional parameters are normally, or approximately normally, distributed. (*f*) The e.s.d.'s of cell parameters are grossly underestimated, by an average factor of about 5 for cell lengths and 2·5 for cell angles. There is marginal evidence that the accuracy of atomic-coordinate e.s.d.'s also depends on diffractometer geometry, refinement procedure, whether or not the structure has a centre of symmetry, and the degree of precision attained in the structure determination.

Introduction

Error estimates are ubiquitous in crystallography; almost all published atomic coordinates and temperature factors are accompanied by estimated standard deviations (e.s.d.'s), which purport to represent the precision of the crystallographic parameters. Indeed, journals such as *Acta Crystallographica insist* on the publication of e.s.d.'s [*Notes for Authors* (International Union of Crystallography, 1983)], since it is generally recognized that no physical measurement is complete without a reliable indication of its precision.

Unfortunately, crystallographic e.s.d.'s are invariably derived from least-squares covariance matrices and it is questionable whether they can be described as 'reliable'. Some years ago, the IUCr carried out a project on tartaric acid, in which seventeen independent data sets were collected and compared (Abrahams, Hamilton & Mathieson, 1970; Hamilton & Abrahams, 1970; Mackenzie, 1974). The study suggested that atomic-coordinate e.s.d.'s are typically too small by a factor of about $\sqrt{2}$, whilst temperature-factor e.s.d.'s may be underestimated by a factor of 2 or more.

In the years since the IUCr project, many thousands of crystal structures have been determined. Inevitably, some structures have been studied by two different research groups, working independently of each other. The possibility therefore exists of updating the IUCr study by comparing these accidentally duplicated structure determinations. Such a comparison has a number of advantages. Firstly, there is a large amount of data available [there are well over a hundred duplicated structures in the Cambridge Structural Database (Allen *et al.*, 1979)]. Secondly, the data pertain to a cross section of space groups, molecular compositions, *etc.*, and therefore give information about the accuracy of crystallographic e.s.d.'s under a wide variety of conditions. Thirdly, the determinations were *accidentally* duplicated, so it is safe to assume that no particular effort was made to achieve results of exceptional accuracy. We cannot be sure that this was the case in the somewhat artificial context of the IUCr study.

In this paper, we report a statistical analysis of one hundred crystal structures, each of which has been determined by two independent research groups. The object of the analysis is to investigate the accuracy of the e.s.d.'s of non-hydrogen-atom positional parameters. Cell-parameter e.s.d.'s are also considered. The e.s.d.'s of thermal parameters and H-atom coordinates are not discussed because their inclusion would have greatly increased the labour involved in the analysis.

Random and systematic error

The value of a particular atomic parameter (p) determined in a particular diffraction experiment may be expressed as:

$$p = \mu + \varepsilon_r + \varepsilon_s. \qquad (1)$$

Here, μ is the true (unknown) value of the parameter. ε_r is the 'random error' in the measurement, reflected in the inability of the refined model to fit, exactly, the observed data. This quantity may be regarded as a random variable from an unknown (perhaps nor-

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mal) distribution with standard deviation $\sigma(\varepsilon_r)$. ε_s is the 'systematic error' which arises if the atomic parameter refines to a biased value in order to accommodate certain types of errors in the observations (*e.g.* absorption). If it were possible to measure the atomic parameter many times under *identical* experimental conditions, the values of the parameter thus obtained would be distributed about a mean of $\mu+\varepsilon_s$. Only by changing the experimental conditions would the presence of systematic error be revealed, since the atomic parameter would then be distributed about a mean of $\mu+\varepsilon'_s$, where $\varepsilon'_s \neq \varepsilon_s$.

In a single diffraction experiment, it is impossible to measure precisely the standard deviation of p. However, an *estimate* of this quantity $[=\sigma(p)]$ is conventionally obtained from the least-squares covariance matrix (Rollett, 1970). E.s.d.'s obtained in this way are effectively measures of the extent to which the refined model fits the observed data (Hamilton, 1964, 1969). Consequently, $\sigma(p)$ is actually an estimate of $\sigma(\varepsilon_r)$ rather than the true standard deviation of p, σ_{true}. The object of the present study is to determine the extent to which $\sigma(p)$ is likely to be an underestimate of σ_{true}. We may anticipate that the answer will vary from structure to structure and, possibly, from parameter to parameter within a structure.

Experimental procedure

Selection of structures

The Cambridge Structural Database (Allen *et al.*, 1979) was searched for all structures which have been determined by two different research groups. Since atomic-coordinate e.s.d.'s are not stored in the database, and therefore had to be typed in by hand, our analysis was restricted to one hundred of these structures. Each one satisfied the following conditions:

(*a*) The two determinations of the structure were independent of each other (*i.e.* as far as we could tell from the structure reports, each group was unaware of the other's activities at the time of collecting data).

(*b*) Both determinations were by X-ray (rather than by neutron) diffraction.

(*c*) Both determinations were performed at about the same temperature.

(*d*) Both sets of data were collected on diffractometers.

(*e*) Neither structure determination was classified as an 'error set' in the Cambridge Database (Cambridge Crystallographic Data Centre, 1978).

(*f*) Both research groups agreed on the space group of the structure.

(*g*) The positions of all non-hydrogen atoms were successfully located and refined in both determinations.

(*h*) The structure was not disordered.

(*i*) No positional constraints were used during the final cycles of least-squares refinement, except, possibly, for H atoms.

Subject to the above conditions, the structures were chosen on a pragmatic basis: for example, we tried to avoid structures reported in languages with which we are not familiar. The resulting set of structures (Table 1)* is therefore not random from a statistical point of view. A breakdown of the data set suggests that it is biased towards small organic structures in the common monoclinic and orthorhombic space groups. However, we believe that the structures are a good enough cross section to ensure that the results of our analysis have fairly general applicability.

Construction of data file

A data file was set up containing the following information for each pair of structure determinations:

(*a*) Space group number.

(*b*) Cell parameters and cell-parameter e.s.d.'s from both determinations.

(*c*) Atomic coordinates and atomic-coordinate e.s.d.'s (excluding H atoms) from both determinations.

(*d*) Miscellaneous information about molecular composition, data collection (*e.g.* diffractometer geometry) and refinement procedures.

For each structure, the atomic coordinates and cell dimensions from the second determination were transformed to the origin and axial setting used in the first determination (here, and throughout the analysis, the 'first' determination is defined as the one which occurs first in the Cambridge Structural Database when the entries in the database are sorted alphanumerically by reference code; see Table 1). Additionally, each set of atomic coordinates was checked to ensure that it corresponded to a chemically connected entity rather than an arbitrary crystallographic asymmetric unit.

Definition of symbols

Let: n_i = number of independently refined non-hydrogen-atom positional parameters in the ith structure. p_{ijk} = value of the jth positional parameter in the kth determination of the ith structure. $\sigma(p_{ijk})$ = e.s.d. of p_{ijk}, as derived from the least-squares analysis. Note that:

$$i=1,2,\ldots,100;\ j=1,2,\ldots,n_i;\ k=1,2.$$

Our analysis of atomic-coordinate e.s.d.'s was based

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* A full bibliography and breakdown of the data set by space group, chemical class, *etc.*, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42469 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Structures used in survey*

Given for each structure: Cambridge Structural Database reference codes for each independent determination. (Full bibliographic details have been deposited.)

1	ACCLTI	ACCLTI01	51	GRISOV01	GRISOV10
2	ACYCPV	ACYCPV01	52	HISAPH01	HISAPH10
3	ADGALA01	ADGALA10	53	HMAHPN	HMAHPN01
4	ADTALO01	ADTALO10	54	HPMSAH	HPMSAH01
5	AGALAM01	AGALAM10	55	HPZDFE	HPZDFE01
6	AHGLPY01	AHGLPY10	56	HXQUIO	HXQUIO01
7	ALITOL	ALITOL01	57	IPRNCU	IPRNCU01
8	AMBACO03	AMBACO05	58	KECYBU03	KECYBU11
9	AMGXCO	AMGXCO01	59	KHTACN	KHTACN11
10	ANISIC	ANISIC01	60	KMYRMH01	KMYRMH10
11	ARCMPH	ARCMPH01	61	LDOPAC	LDOPAC01
12	AZURAC01	AZURAC10	62	LDOPAS10	LDOPAS11
13	BARZOJ	BARZOJ01	63	LHOXAL	LHOXAL01
14	BAWREW	BAWREW01	64	LSERIN01	LSERIN10
15	BDGLOS01	BDGLOS10	65	LYCORN	LYCORN01
16	BEFTOV	BEFTOV01	66	MATOMO	MATOMO01
17	BEJZEV	BEJZEV11	67	MBDGAL	MBDGAL01
18	BEKVOC	BEKVOC01	68	MBLARA01	MBLARA10
19	BEMVOE	BEMVOE01	69	MCPROP02	MCPROP10
20	BENTAC	BENTAC01	70	MDRIBP01	MDRIBP10
21	BINAPH01	BINAPH10	71	MDTHCF10	MDTHCF11
22	BIOTIN01	BIOTIN10	72	MERPUM	MERPUM01
23	BIRKIW	BIRKIW01	73	MEYDPA	MEYDPA11
24	BNPHTA	BNPHTA01	74	MNPHCY	MNPHCY02
25	BOCLAG	BOCLAG01	75	MTHOIN	MTHOIN01
26	BPROSA	BPROSA01	76	NACTMO01	NACTMO10
27	BZDMAZ	BZDMAZ01	77	NALOXC	NALOXC01
28	CBCNIB	CBCNIB01	78	NBENDC	NBENDC01
29	CDCPPT01	CDCPPT10	79	NHOXAL01	NHOXAL10
30	CEAOXP	CEAOXP01	80	OVATAC	OVATAC01
31	CHEXDC	CHEXDC01	81	OVATOL	OVATOL01
32	CLBZAP01	CLBZAP02	82	PDOFED	PDOFED01
33	CLMPCL01	CLMPCL02	83	PHOGLY	PHOGLY01
34	CLONDC01	CLONDC10	84	PHTHAC01	PHTHAC02
35	CLPHAC	CLPHAC01	85	PYOCUC	PYOCUC01
36	COUMAR02	COUMAR10	86	SCYSCR	SCYSCR01
37	CPALMO01	CPALMO10	87	TACRIB	TACRIB01
38	CYANOF	CYANOF01	88	TARTAC	TARTAC23
39	DITCSN	DITCSN01	89	TEAMBO01	TEAMBO02
40	DLABAC	DLABAC01	90	TECLPH01	TECLPH20
41	DMBZAN01	DMBZAN10	91	TELLXD	TELLXD01
42	DPHACT02	DPHACT03	92	TEPHME03	TEPHME11
43	DPTHOA	DPTHOA01	93	TMTURS	TMTURS01
44	DTURID	DTURID01	94	TPCUCL01	TPCUCL10
45	EACXHP10	EACXHP11	95	TPENGE01	TPENGE02
46	EBGUNI	EBGUNI12	96	TPHDSB	TPHDSB01
47	EDATAR02	EDATAR10	97	TSNBNB	TSNBNB01
48	EDTMNK	EDTMNK01	98	TYRAMC	TYRAMC11
49	ENCOCT	ENCOCT01	99	URARAF01	URARAF10
50	GRISFL	GRISFL02	100	XANTOX	XANTOX01

on a study of the distributions of:

$$\delta_{ij} = (p_{ij1} - p_{ij2})/[\sigma^2(p_{ij1}) + \sigma^2(p_{ij2})]^{1/2} \qquad (2)$$

and:

$$\sigma_i = \left[\sum_{j=1}^{n_i} \delta_{ij}^2 / n_i \right]^{1/2}. \qquad (3)$$

The quantity δ_{ij} is the weighted difference between the first and second determinations of the jth positional parameter in the ith structure. For a given structure, the signs of the δ_{ij} are arbitrary to the extent that they depend on which determination is defined as the 'first' and which the 'second' (see definition in preceding section). If it is assumed that the population mean of the δ_{ij} is zero, the quantity σ_i is an estimate of the standard deviation of the δ_{ij} in the ith structure.

Statistical methodology

Within the ith structure, the δ_{ij} may be regarded as random variables from a normal distribution with unit variance, provided that (*a*) the p_{ijk} are independent and normally distributed, and (*b*) the $\sigma(p_{ijk})$ are accurate estimates of the true standard deviations of the p_{ijk}. If these conditions are met, the expectation value of σ_i is unity. Conversely, the expectation value of σ_i will be greater than one if the $\sigma(p_{ijk})$ are too small, and the distribution of δ_{ij} will be non-normal if experimental errors in the p_{ijk} are not normally distributed. Statistical analysis of the observed δ_{ij} and σ_i distributions can therefore provide information about the accuracy of the $\sigma(p_{ijk})$ and the nature of the atomic-coordinate error distribution.

Unfortunately, such an analysis presents several difficulties, the most important of which are:

(*a*) Within a structure, the δ_{ij} are not statistically independent of one another (see *Results*).

(*b*) Both the δ_{ij} and the σ_i distributions may be influenced by many factors, not all of which can be predicted in advance of the analysis.

(*c*) Within a structure, the δ_{ij} distribution may not be normal; between structures, the σ_i distribution is certainly not normal. Thus, statistical techniques that are based on an assumption of normality (this includes most multivariate methods; Chatfield & Collins, 1980) cannot be used without approximations.

(*d*) A preliminary inspection of the δ_{ij} and σ_i data revealed the presence of many *outliers* - values that are very significantly different from the bulk of observations in the data set. This is likely to invalidate results obtained from many parametric statistical methods (Barnett & Lewis, 1978).

(*e*) If the $\sigma(p_{ijk})$ within a structure show *systematic* differences in accuracy (*e.g.* if the e.s.d.'s of light-atom coordinates are more accurate than those of heavy-atom coordinates; see *Results*), the δ_{ij} values are effectively random variables from *more than one* underlying statistical distribution.

In the light of these difficulties, we do not believe that a rigorous statistical analysis of our data is possible. In an attempt to minimize potential sources of error, we based our analysis on simple univariate and bivariate non-parametric techniques (Siegel, 1956; Snedecor & Cochran, 1980). These techniques make very few assumptions about the data being analysed and are relatively insensitive to the presence of outliers. However, their application still necessitates some approximations and we enjoin caution in interpreting the various statistical significance levels quoted in this paper.

Results

Preliminary observations

The observed σ_i values of the 100 structures in our data set are listed in Table 2. Fig. 1(*a*) shows the distribution of 99 of these values as a histogram. The omitted value is that of squaric acid (structure 58 of Table 1; $\sigma_i = 11{\cdot}8$). This obvious outlier is discussed in the next section. The mean and median of the σ_i values (excluding squaric acid) are 1·46 and 1·39, respectively. Thus, atomic-coordinate e.s.d.'s appear to be underestimated, on average, by a factor of about 1·4–1·45. This is in exceptionally good agreement with the conclusions of the IUCr project on tartaric acid (Hamilton & Abrahams, 1970).

Table 2. *Ordered list of σ_i values*

Structure[a]	σ_i	Structure	σ_i	Structure	σ_i	Structure	σ_i
58	11·76	57	1·64	80	1·39	94	1·13
69	3·10	37	1·63	71	1·37	32	1·11
72	2·73	53	1·61	13	1·35	96	1·10
77	2·59	21	1·59	67	1·35	2	1·09
97	2·51	85	1·58	24	1·32	16	1·08
42	2·46	84	1·58	45	1·31	73	1·05
10	2·42	65	1·57	20	1·29	5	1·05
44	2·35	89	1·56	9	1·29	95	1·05
76	2·24	56	1·55	34	1·29	99	1·03
11	2·24	68	1·54	1	1·28	30	1·03
55	2·24	39	1·54	3	1·28	90	1·02
60	2·12	28	1·52	59	1·27	63	1·02
41	2·10	33	1·52	29	1·25	27	1·02
22	2·03	49	1·51	78	1·25	98	1·00
87	2·01	81	1·51	83	1·25	62	1·00
64	1·86	61	1·48	38	1·24	6	1·00
36	1·81	7	1·46	92	1·22	82	0·94
75	1·79	31	1·46	17	1·22	35	0·93
14	1·77	19	1·45	70	1·22	25	0·92
12	1·74	88	1·44	46	1·20	86	0·92
91	1·71	66	1·44	79	1·20	18	0·89
26	1·71	4	1·43	43	1·19	74	0·87
40	1·66	47	1·42	48	1·19	54	0·78
50	1·65	15	1·40	93	1·19	52	0·69
51	1·64	8	1·39	100	1·14	23	0·66

(*a*) See Table 1.

Atomic-coordinate covariances

The δ_{ij} values for squaric acid are:

In the x direction: 11·4, 14·3, 14·4, 11·9, −9·3, 19·5, −11·0, 19·8.

In the y direction: 11·5, 10·2, 10·6, 9·1, 4·2, 6·8, 3·2, 6·4.

In the z direction: all coordinates fixed by symmetry.

If differences between the two determinations are random, the *a priori* probability that a given δ_{ij} will be positive rather than negative is 0·5. The binomial probability that all eight δ_{ij}'s in the y direction are of the same sign is then 0·008 (Siegel, 1956). The figures therefore suggest that there is a *systematic* difference between the two structure determinations of squaric acid. The sign of any δ_{ij} can be reversed by transforming the corresponding atom into a different part of the unit cell (*e.g.* by inverting the atom through a centre of symmetry, thereby reversing the signs of both p_{ij1} and p_{ij2}). Thus, the systematic difference must be related to the fact that the atomic coordinates used in calculating the δ_{ij}'s correspond to a chemically connected molecule. In other words, the δ_{ij} values indicate that the molecule, *as a whole*, is displaced in the second determination relative to its position in the first. This observation has previously been made by Semmingsen, Hollander & Koetzle (1977), who suggested that one of the determinations was unwittingly performed on a twinned crystal. Whether or not this was the case, squaric acid represents the small but finite probability that a set of atomic-coordinate e.s.d.'s will be grossly in error. Squaric acid was omitted from the remainder of our study of atomic-coordinate e.s.d.'s.

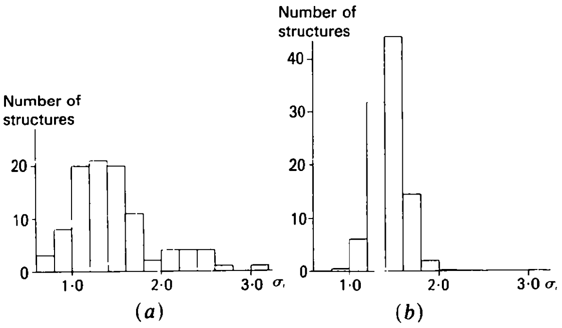

Fig. 1. (*a*) Observed distribution of σ_i values. (*b*) Expected distribution of σ_i values, obtained by computer simulation and based on the assumption that differences in the σ_i's are entirely due to sampling errors.

The 'molecular displacement' observed in squaric acid prompted us to look for similar displacements in other structure determinations. This part of the investigation was restricted to the 52 structures in our data set which contain one, and only one, discrete chemical molecule in the asymmetric unit. The procedure was analogous to that used in the study of squaric acid; *i.e.* we considered in turn each axis of each structure (excluding axes along which the origin can 'float', such as y in $P2_1$) and counted the number of positive and negative δ_{ij} values (zero δ_{ij}'s were ignored). If, along a particular axis, there are m δ_{ij} values of one sign and $M-m$ of the other ($m \leq M-m$), the binomial probability (α) of a sign distribution as extreme as this is given by:

$$\begin{aligned} \alpha &= 0{\cdot}5^{M-1} \sum_{i=0}^{m} \binom{M}{i}, && \text{if } m \neq M-m \\ \alpha &= 1, && \text{if } m = M-n \end{aligned} \qquad (4)$$

(Siegel, 1956). These expressions are based on the assumption that any given δ_{ij} is equally likely to be positive or negative. The observed distribution of binomial probabilities for the 144 axes studied is shown as a histogram in Fig. 2(*a*). The 'expected' (*i.e.* null) distribution, obtained by simulation, is shown in Fig. 2(*b*) (this distribution is not rectangular because the binomial distribution is discrete rather than continuous; Lancaster, 1949; Pearson, 1950). The simulation was performed with the aid of a pseudo-random-number generator taken from the NAG subroutine library (*NAG FORTRAN Library Manual*, 1983), and is based on the assumption that the *a priori* probability of any δ_{ij} being positive rather than negative is 0·5. Comparison of the two histograms suggests that the observed binomial probabilities tend to be smaller than expected. This was confirmed at the 99·9% confidence level by Pearson's (1950) modification of Fisher's (1936) method (see also, Birnbaum, 1954). This method is based on an analysis of the observed distribution only, so any defects in the simulation model used to obtain Fig. 2(*b*) will not affect the quoted confidence level. We conclude that the observed distribution of binomial probabilities is inconsistent with the hypothesis that the distribution of δ_{ij} signs is random for all axes studied. By the same logic as was used for squaric acid, it follows that there is a tendency for molecules *as a whole* to be displaced along one or more axial directions in some structure determinations.* Statistically, this is equivalent to saying that errors in the positions of atoms belonging to the same molecule tend to be positively correlated. Thus, the δ_{ij} values within any given structure are not strictly independent of one another.

Although Fig. 2 strongly suggests that significant 'molecular displacements' occur in some structure determinations, the effect is small in absolute terms and is only detectable because of the large amount of data analysed in this study. Fig. 3(*a*) shows the observed distribution of 'absolute molecular displacements' for the 144 axes on which Fig. 2 is based. The 'absolute molecular displacement' (d) along a given axis of the ith structure is defined here as:

$$d=\left|l\sum(p_{ij1}-p_{ij2})/N\right|, \qquad (5)$$

where l is the axial length in ångströms and the summation is over all the atomic coordinates along the axis (excluding those fixed by symmetry), there being N such coordinates. For comparison, Fig. 3(*b*) shows the 'expected' distribution of absolute molecular displacements, obtained by computer simulation. The simulation was based on the assumption that the δ_{ij} values along any axis of the ith structure are independent random variables from a normal distribution with *zero* mean and standard deviation σ_i. The observed histogram differs only slightly from the simulated one and the absolute molecular displacement is less than 0·005 Å in the majority of cases. Similar results are obtained if formula (5) is modified so that each term in the summation is weighted by atomic number.

The most significant molecular displacements found in this study (referring, now, to the complete sample except squaric acid) occur in structures 3, 11, 29, 40, 44, 55 and 64 of Table 1. We can discern no obvious common factor between these structures.

Variation of σ_i between structures

Each of the σ_i's listed in Table 2 is an *estimate* of the standard deviation of the δ_{ij}'s in the ith structure. Any estimate is subject to random sampling errors, so it is inevitable that the σ_i's will show some variation about their mean. However, the question arises: do the σ_i show *more* variation than would be expected from sampling errors alone? Fig. 1(*b*) shows the distribution of σ_i's that would be expected if the true standard deviation of the δ_{ij}'s showed no variation from structure to structure (*i.e.* if differences between the σ_i's were entirely due to sampling errors). The distribution was obtained by computer simulation and is based on the assumption that the δ_{ij}'s in the ith structure are independent random variables from a normal distribution with zero mean and a standard deviation of 1·457 (= average of the observed σ_i values). The difference between Fig. 1(*a*) and Fig. 1(*b*) is so pronounced that, even allowing for possible deficiencies in the simulation model, there can be little doubt that the observed σ_i values show more variation than can be explained by sampling errors. Thus, the standard deviation of the δ_{ij}'s varies from structure to structure, *i.e.* atomic-coordinate e.s.d.'s are underestimated to a greater extent in some structures than in others.

We performed a number of simple tests to ascertain whether the σ_i value of a given structure can be

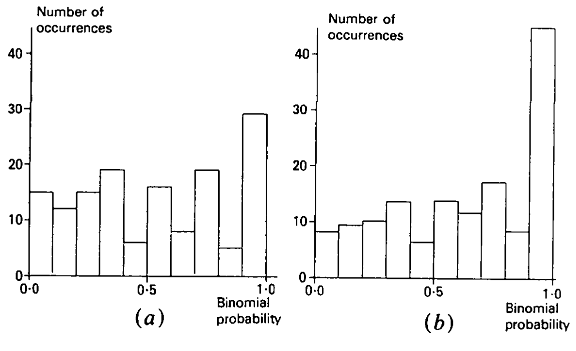

Fig. 2. (*a*) Observed distribution of binomial probabilities [see equation (4)]. (*b*) Expected (*i.e.* null) distribution of binomial probabilities, obtained by computer simulation.

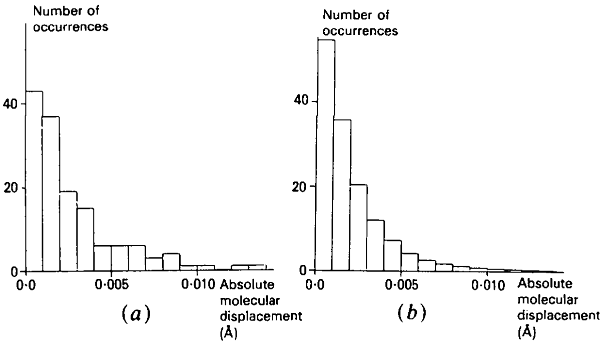

Fig. 3. (*a*) Observed distribution of absolute molecular displacements [see equation (5); one extreme observation omitted]. (*b*) Expected distribution of absolute molecular displacements, obtained by computer simulation.

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* The same conclusion is reached, at the same confidence level, if a similar analysis is performed using t-test probabilities (Snedecor & Cochran, 1980; Fisher, 1936) rather than binomial-test probabilities.

Table 3. *Breakdown of σ_i by space group and crystal system*

Space group	Number of structures	Average σ_i	Crystal system	Number of structures	Average σ_i
$P1$	2	1·26	Triclinic	8	1·31
$P\bar{1}$	6	1·32			
$P2_1$	9	1·36	Monoclinic	46	1·43
$P2/c$	1	0.92			
$P2_1/c$	23	1·42			
$C2/c$	13	1·54			
$P2_12_12_1$	25	1·65	Orthorhombic	39	1·54
$C222_1$	1	1·52			
$Pca2_1$	3	1·60			
$Pna2_1$	2	1.08			
$Iba2$	1	1·71			
$Pbcn$	3	0·97			
$Pbca$	2	1·59			
$Pnma$	2	1·24			
$P4_1$	1	1·65	Tetragonal	4	1·31
$P4_12_12$	1	1·32			
$P\bar{4}2_1c$	2	1·13			
$R\bar{3}$	1	1·58	Trigonal	2	1·25
$P3_121$	1	0·92			

correlated with any physical property of the structure, or any particular feature of the structure determinations. Table 3 shows a breakdown of σ_i with crystal system and space group. A Kruskal–Wallis analysis of variance (Siegel, 1956) suggests that there is no significant variation in σ_i between crystal systems, but the variation in σ_i between space groups is of marginal significance (90% confidence level). The mean σ_i of the 51 centrosymmetric structures is 1·41, compared with a mean of 1·51 for the 48 noncentrosymmetric structures. A Mann–Whitney test (Siegel, 1956) shows that these values are significantly different at the 91% confidence level, providing tentative evidence that e.s.d.'s in noncentrosymmetric structures tend to be less accurate than those in centrosymmetric structures.

Equation (1) suggests that σ_i will be larger (*i.e.* e.s.d.'s will be underestimated by a greater factor) in precise structure determinations than in imprecise determinations. This is because the quantity ε_s in (1) will become relatively more important as ε_r is reduced. Tentative support for this hypothesis was obtained as follows. The parameter $\bar{\sigma}(p_{ijk})$ was defined as:

$$\bar{\sigma}(p_{ijk}) = \max\left[\sum_{j=1}^{n_i} \sigma(p_{ij1})/n_i,\ \sum_{j=1}^{n_i} \sigma(p_{ij2})/n_i\right]; \quad (6)$$

i.e. for the *i*th structure, $\bar{\sigma}(p_{ijk})$ is the average of the $\sigma(p_{ijk})$ in the less precise of the two independent determinations. The Spearman rank correlation coefficient (r_s; Snedecor & Cochran, 1980) of σ_i and $\bar{\sigma}(p_{ijk})$ was found to be $-0{\cdot}148$, which is significantly different from zero at the 93% confidence level if we are prepared to accept a one-tailed probability value.

Theoretical considerations suggest that e.s.d.'s obtained from block-matrix refinements are likely to be less accurate than those obtained from full-matrix refinements (Rollett, 1970). We found that the mean σ_i value of 34 'full-matrix' structures was 1·33, compared with a mean of 1·53 for 22 'block-matrix' structures (a structure was defined as 'full-matrix' if both determinations were refined by full-matrix least squares; a 'block-matrix' structure was one in which the less precise of the two determinations was refined by block-matrix least squares). These mean values are significantly different at the 90% confidence level (Mann–Whitney test).

The effects of diffractometer geometry were considered briefly. The mean σ_i value of 85 'four-circle' structures was 1·44, compared with a mean of 1·61 for 12 'two-circle' structures (a 'two-circle' structure was one in which the less precise of the two determinations was based on equi-inclination data; a 'four-circle' structure was one in which neither determination was based on equi-inclination data). These mean values are significantly different at the 70% confidence level (Mann–Whitney test). The low confidence level may be partly due to the small size of the 'two-circle' sample.

We were unable to correlate σ_i with absorption phenomena. Fig. 4 shows a scatterplot of σ_i against linear absorption coefficient, μ_i, for 58 structures (structures were only included in this plot if the two independent determinations were performed with radiation of the same wavelength). The evident lack of correlation is confirmed by calculation of the Spearman rank correlation coefficient ($r_s = 0{\cdot}007$; not significant). Of course, this simple analysis ignores many factors (*e.g.* crystal size, details of any absorption correction applied) and does not *prove* that σ_i is uncorrelated with absorption effects [see Srivastava & Lingafelter (1966) for some interesting comments on the effects of uncorrected absorption on least-squares results].

Variation of $|\delta_{ij}|$ within structures

In the above section, we looked at overall trends from structure to structure assuming that the δ_{ij}'s

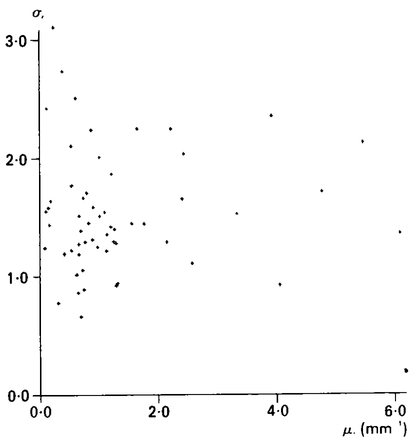


Fig. 4. Scatterplot of σ_i against linear absorption coefficient, μ_i. One extreme observation ($\sigma_i = 1{\cdot}25$, $\mu_i = 123{\cdot}8$ cm^{-1}) is omitted.

Table 4. *List of largest* $|\delta_{ij}|$ *values*

Structure[a]	Atom[b]	Coordinate[c]	$\lvert\delta_{ij}\rvert$
55	Fe(1)	z	12·35
76	Mo(1)	x	10·86
76	Mo(2)	x	9·75
97	S(1)	x	8·00
69	S(1)	z	7·78
69	O(1)	y	7·16
41	C(5)	x	7·06
42	C(1)	y	7·04
11	P(1)	z	6·96
13	Pt(1)	x	6·93
69	C(12)	x	6·93
55	O(3)	y	6·36

(*a*) See Table 1. (*b*) Atom label in first determination. (*c*) In axial setting of first determination.

within the *i*th structure are taken from a single statistical distribution with standard deviation σ_i. This was an approximation, since it is possible that the accuracy of e.s.d.'s varies systematically from atom to atom *within* a structure. Table 4 lists the twelve largest $|\delta_{ij}|$ values found in our study. Seven of them, including the five largest, involve heavy atoms ($\geq$2nd row of Periodic Table). Since the vast majority of atoms in our data set are first-row elements (C, N, O), this is most unlikely to be a chance occurrence. The data therefore suggest that $|\delta_{ij}|$ tends to be larger for heavy atoms than for light atoms.

In order to confirm this, we performed a Spearman test on each of 93 structures in our data set, testing the correlation between $|\delta_{ij}|$ and atomic number (the six excluded structures were hydrocarbons). The one-tailed Spearman probabilities (Siegel, 1956) were distributed as shown in Fig. 5. If there was no underlying correlation between $|\delta_{ij}|$ and atomic number, we would expect the probabilities to be approximately uniformly distributed in the range 0–1 (Pearson, 1950). This is evidently not the case, as was confirmed at the 99% confidence level by the method of Fisher (1936). Thus, the data suggest very strongly that heavy-atom e.s.d.'s tend to be underestimated to a greater extent than light-atom e.s.d.'s.

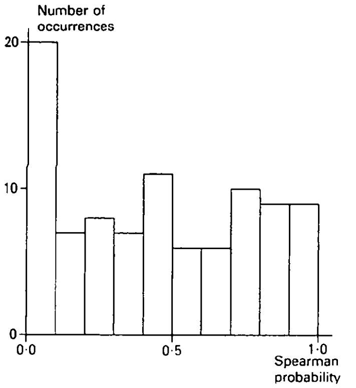


Fig. 5. Distribution of Spearman probabilities obtained when the correlation between $|\delta_{ij}|$ and atomic number is tested in each of 93 structures. Expected (*i.e.* null) distribution is rectangular in the range 0–1.

Table 5. *Results of Friedman analyses of variance*

Structure[a]	χ^2 [b]	Structure	χ^2	Structure	χ^2	Structure	χ^2
51	19·87	94	3·57	54	1·53	8	0·60
11	9·15	97	3·46	82	1·52	89	0·60
81	9·15	41	3·26	13	1·47	42	0·57
48	8·08	5	3·23	32	1·40	49	0·55
77	8·00	36	3·20	80	1·40	16	0·46
3	7·17	57	3·20	46	1·30	45	0·44
87	6·91	69	3·18	70	1·27	26	0·40
55	6·20	35	3·11	72	1·27	19	0·31
33	6·10	37	2·92	4	1·17	65	0·29
47	5·69	74	2·80	50	1·13	98	0·20
10	5·64	34	2·63	62	1·08	93	0·18
96	5·54	21	2·60	78	1·08	22	0·13
15	4·67	75	2·28	68	0·96	39	0·12
59	4·67	20	2·24	17	0·91	99	0·12
18	4·50	56	2·18	24	0·80	66	0·11
61	4.43	2	2·00	40	0·74	60	0·08
83	3·80	30	1·97	52	0·74	28	0·06
100	3·73	29	1·95	53	0·64	6	0·00
76	3·63	44	1·78	67	0·62	90	0·00

(*a*) See Table 1. (*b*) With two degrees of freedom. The larger the χ^2 value, the greater the confidence with which we can reject the null hypothesis: the median $|\delta_{ij}|$ values in the *x*, *y* and *z* directions are not significantly different.

We also considered the possibility that, within a given structure, e.s.d.'s tend to be more accurate in some directions than in others. This was investigated as follows. A Friedman two-way analysis of variance (Siegel, 1956) was performed on each of 76 structures in our data set, testing the null hypothesis:

H_0: the median $|\delta_{ij}|$ values in the x, y and z directions *are not* significantly different,

against the alternative hypothesis:

H_1: the median $|\delta_{ij}|$ values in the x, y and z directions *are* significantly different.

The remaining 23 structures were omitted because they contained insufficient atoms for the Friedman test to be applicable (Siegel, 1956). The results of the analyses of variance are summarized in Table 5. Each individual test gives a χ^2 statistic with two degrees of freedom, and some of these appear to be significant. However, it is possible that this might occur by chance, since we are performing several tests. An approximate *overall* significance level can be obtained by summing the χ^2 values (Hamilton, 1964; Lancaster, 1949). If the null hypothesis is true in *all* structures examined, the resulting sum ($=204.7$) should also be a χ^2 variable, with 152 degrees of freedom [$=2\times$ (number of tests performed)]. The overall χ^2 value is significant at the 99% confidence level, which lends support to the alternative rather than the null hypothesis. We therefore conclude that, in at least one of the structures studied, the e.s.d.'s tend to be less accurate in some direction(s) than in others. However, the significance of the overall χ^2 value is almost entirely due to the χ^2 contributions from a handful of structures (see Table 5). The most sensible interpretation may therefore be as follows: the accuracy of atomic-coordinate e.s.d.'s does not usually vary much with direction (*i.e.* is approximately isotropic with respect to the crystal axes), but may do so in a minority of structure determinations.

Nature of atomic-coordinate error distribution

A χ^2 goodness-of-fit test (Snedecor & Cochran, 1980) was performed on each of 48 structures in our data set, testing the null hypothesis that the δ_{ij} values are normally distributed. The remaining 51 structures were not considered, either because they contained insufficient atoms for the χ^2 test to be applicable (Siegel, 1956), or because the possible effects of round-off error were deemed to be serious. It has been shown previously that rounding of the p_{ijk} and $\sigma(p_{ijk})$ may invalidate the results of goodness-of-fit tests (Taylor & Kennard, 1985). The results of the χ^2 tests are given in Table 6. An approximate overall significance level can be obtained by summing the individual χ^2 values. The resulting overall χ^2 statistic is 157·5 with 144 degrees of freedom. This is not statistically significant. Thus, although some of the *individual* χ^2 values appear to be significant, we cannot exclude the possibility that the δ_{ij}'s are normally distributed in all of the structures examined.

We next calculated the coefficients of kurtosis of all 99 structures in our data set. The coefficient of kurtosis of the *i*th structure, g_i, was computed from

$$g_i=\left[\left(\frac{1}{n_i}\sum_{j=1}^{n_i}\delta_{ij}^4\right)\Big/\sigma_i^4\right]-3 \qquad (7)$$

(Snedecor & Cochran, 1980). The mean value of the observed g_i was found to be 0·57, somewhat larger than the value of zero expected for a normal distribution. The distribution of the g_i is shown in Fig. 6; four structures (13, 18, 55 and 76 of Table 1) are omitted from this histogram because they have very large coefficients of kurtosis (7·3, 5·8, 9·6 and 8·8, respectively). The mean value of the g_i distribution drops to only 0·26 if these four structures are excluded from the calculation.

Overall, the results in this section are consistent with the hypothesis that experimental errors in atomic positional parameters are normally distributed. This is probably true even for the structures with large coefficients of kurtosis. It is notable that three of these structures (13, 55 and 76) appear in Table 4, *i.e.* contain heavy atoms with very large $|\delta_{ij}|$ values. The δ_{ij} distribution in each of these structures can be viewed as a mixture of *two* underlying distributions, one for light atoms with a standard deviation σ_{light}, and one for heavy atoms with a larger standard deviation, σ_{heavy}. The apparent non-normality of the δ_{ij}'s in these structures may therefore be due to this factor and does not necessarily imply that the p_{ijk}'s are non-normally distributed.

Table 6. *Results of* χ^2 *goodness-of-fit tests*

Structure[a]	χ^2 [b]	Structure	χ^2	Structure	χ^2	Structure	χ^2
11	10·48	5	3·76	89	2·67	26	1·80
51	8·59	2	3·65	33	2·63	60	1·78
13	7·55	96	3·65	81	2·62	76	1·73
10	7·45	77	3·58	35	2·29	70	1·64
75	6·67	47	3·51	62	2·29	72	1·44
55	6·61	88	3·24	48	2·23	65	1·37
74	6·50	18	3·06	87	2·06	99	1·14
57	6·09	80	3·01	40	2·00	30	0·59
41	5·83	37	3·01	44	2·00	82	0·53
56	5·81	53	2·79	19	1·83	50	0·45
39	4·00	54	2·75	100	1·83	3	0·39
66	3·88	61	2·70	94	1·81	34	0·22

(*a*) See Table 1. (*b*) With three degrees of freedom. The larger the χ^2 value, the greater the confidence with which we can reject the null hypothesis that the δ_{ij} are normally distributed.

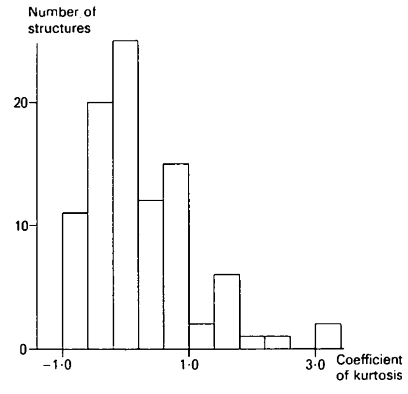


Fig. 6. Observed distribution of coefficients of kurtosis.

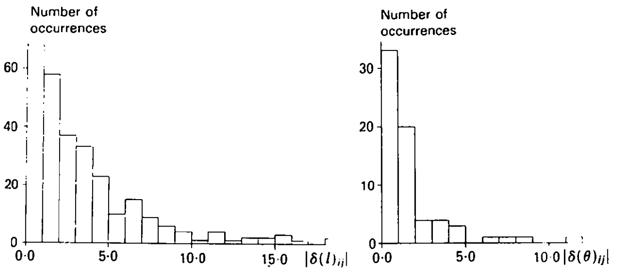
Cell-parameter e.s.d.'s

This part of the study was restricted to the 96 structures in our data set for which cell-parameter e.s.d.'s were available from both determinations. For each cell length and angle not fixed by space-group symmetry, we calculated weighted differences analogous to those used for atomic-coordinate e.s.d.'s. Thus, for the *j*th cell length ($j=1,2,3$ for triclinic, monoclinic, orthorhombic structures; $j=1,2$ for trigonal, tetragonal; $j=1$ for rhombohedral) in the *i*th structure,

$$\delta(l)_{ij}=(l_{ij1}-l_{ij2})/[\sigma^2(l_{ij1})+\sigma^2(l_{ij2})]^{1/2}, \qquad (8)$$

where l_{ijk} is the value of the cell length as determined in the *k*th determination, and $\sigma(l_{ijk})$ is its e.s.d. Similarly, for cell angles:

$$\delta(\theta)_{ij}=(\theta_{ij1}-\theta_{ij2})/[\sigma^2(\theta_{ij1})+\sigma^2(\theta_{ij2})]^{1/2} \qquad (9)$$



(*a*) (*b*)

Fig. 7. (*a*) Observed distribution of weighted cell-length deviations, $|\delta(l)_{ij}|$. The mean value of $|\delta(l)_{ij}|$ is 3·66 and the standard deviation of the $\delta(l)_{ij}$ distribution is 5·70. The latter figure drops to 4·58 if the five most extreme observations are omitted from the calculation. (*b*) Observed distribution of weighted cell-angle deviations, $|\delta(\theta)_{ij}|$. The mean value of $|\delta(\theta)_{ij}|$ is 1·70 and the standard deviation of the $\delta(\theta)_{ij}$ distribution is 2·65.

($j=1,2,3$ for triclinic structures; $j=1$ for monoclinic, rhombohedral).

In total, there were 281 independent $\delta(l)_{ij}$ values and 68 $\delta(\theta)_{ij}$'s. Histograms of the distributions of $|\delta(l)_{ij}|$ and $|\delta(\theta)_{ij}|$ are shown in Fig. 7(*a*) and (*b*), respectively; two extreme observations are omitted from Fig. 7(*a*) [$\delta(l)_{ij}=38{\cdot}54$ for the *c* axis of structure 72 of Table 1, and $\delta(l)_{ij}=29{\cdot}95$ for the *c* axis of structure 60].

The data in Fig. 7 show that cell-length e.s.d.'s are grossly underestimated, perhaps by an average factor of 5 or more. Cell-angle e.s.d.'s are more reliable but are still underestimated by an average factor of about 2·5. Most of the cell parameters on which Fig. 7 is based were measured on four-circle diffractometers but it is interesting that some of the worst discrepancies correspond to measurements made on two-circle diffractometers. Two of the largest cell-length discrepancies are due to simple calculational error (Ahmed & Neville, 1982) and one to polymerization of the crystal during irradiation (Marsh & Waser, 1970). The most interesting discrepancies are the largest: $|\delta(l)_{ij}|=38{\cdot}54$ and $|\delta(\theta)_{ij}|=11{\cdot}18$, both observed in structure 72 (6-mercaptopurine monohydrate). Detailed investigations by Brown (1969) suggest that these discrepancies reflect *genuine* differences in the 'optimum' cell parameters of two different crystals of the 'same' substance. These were ascribed to differences in the purity and/or mosaic spread of the crystals.

Olga Kennard is a member of the external staff of the Medical Research Council. We wish to thank Professor A. J. C. Wilson and Drs F. H. Allen, A. G. Orpen, P. R. Raithby and D. J. Watkin, who offered advice on some of the results described herein.

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Acta Cryst. (1986). B42, 120

Obituary

John E. Derry
30 July 1946–2 September 1985

Dr John E. Derry, Deputy Technical Editor of the International Union of Crystallography, died on 2 September 1985. He was born in Birmingham in 1946. After graduating from Birmingham University in chemistry in 1967 he continued his studies there for a PhD in crystallography under Dr T. A. Hamor. He joined the Union in 1972 as an Editorial Assistant, being promoted to Assistant Technical Editor in 1976, a position which was designated Deputy Technical Editor in 1983.

He was responsible for the editing and production of Section B and Section C of *Acta Crystallographica.* He brought to this work considerable editorial skills and an enviable capacity for handling papers rapidly and with great accuracy on a wide range of complicated structure determinations. He was the Union's expert on chemical nomenclature and recently had been developing checking procedures with various crystallographic data bases for crystal structure papers submitted for publication in the Union's journals.

His other interests included literature, particularly science fiction, films, and hill walking. His quiet efficiency, his dry sense of humour and his concern for the editorial staff working under him made him popular with his colleagues, who held him in high esteem.

He is sorely missed.