Tabelle 5. *Abstände der den Wassermolekülen benachbarten Chloratomen*

Cl(6)–H_2O(1)	3,28 ± 0,03 Å	Cl(6)—H_2O(2)	3,22 ± 0,02 Å
Cl(2)–H_2O(1)	3,28 ± 0,03	Cl(2)—H_2O(2)	3,26 ± 0,03
Cl(7)–H_2O(1)	3,29 ± 0,03	Cl(7)—H_2O(2)	3,28 ± 0,03
Cl(5)–H_2O(1)	3,31 ± 0,03	Cl(5)—H_2O(2)	3,34 ± 0,02
Cl(8)–H_2O(1)	3,41 ± 0,03	Cl(8)—H_2O(2)	3,61 ± 0,03
Cl(9)–H_2O(1)	3,53 ± 0,03	Cl(9)—H_2O(2)	3,65 ± 0,03
Cl(4)–H_2O(1)	3,93 ± 0,03	Cl(10)–H_2O(2)	3,75 ± 0,02

Die Berechnungen wurden im Deutschen Rechenzentrum in Darmstadt auf der IBM 7094 und im Rechenzentrum der Technischen Universität Clausthal auf der Zuse Z23 durchgeführt.

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A Method for Partial Structure Evaluation*

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A simple method is described for evaluating the correctness of a partial structure based on a discriminator function whose value depends on the absolute value of the difference between the observed and calculated Patterson functions. The method was tested on an organic compound having forty-eight light atoms, carbon and oxygen atoms, in the unit cell. The results obtained support the usefulness of the discriminator in distinguishing incorrect atom positions. This was true even with very small initial fragments where the conventional discrepancy R-index is most insensitive. The discriminator function is sensitive to correct positioning of atoms in the fragment depending on the sharpness of the peaks. Improper scaling of the observed structure factor data affected the value of the integral but not the usefulness of the discriminator.

Introduction

The crystallographer has at his disposal today a number of techniques to obtain trial structures, including such direct methods as symbolic addition and such indirect ones as Patterson superposition techniques. Using any of these techniques with reasonably complex structures, the investigator usually finds that a number of decisions must be made concerning peaks on resultant maps as to whether such peaks belong in the structure or are just spurious. The usual crystallographic discrepancy index, $R=(\sum||F^o|-|F^c||)/\sum|F^o|$ is of little help in this regard until nearly all atoms have been placed in reasonably correct positions. A much more valuable function would be one which could be used to test a structural fragment of any size – a discrepancy or discriminator function which could be used to test whether each atom as it is added in turn appears to be correct. We wish to report the development of such a function.

The discriminator function

One of the tests that can be used to evaluate the correctness of a structure is to compare the agreement between the calculated and observed Patterson functions. In a correct structure, for every peak in P^c, there should be a corresponding peak that occurs in P^o. (In fact it is easy to show that minimization of the quantity $\int (P^o-P^c)^2 dV$ is equivalent to a least-squares refinement on intensities). The same kind of approach is applicable in the case where only a fragment of the structure is known. Here also, wherever there is a peak

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in P^c_n, the calculated Patterson of a fragment of n atoms, there must be a peak in P^o if the atoms in the fragment are indeed in the correct positions. Theoretically, there would be no areas in the difference Patterson which would be negative. Thus a necessary condition that the atoms in the fragment are correctly placed is that

$$S^o_n = \int_{V_{\text{cell}}} |P^o - P^c_n| \mathrm{d}V$$

be a minimum. An absolute value rather than a square function is used since the Patterson function commonly contains multiple peaks.

The value of S for the correct arrangement of atoms is merely the integral over the difference Patterson involving that fragment; the absolute value operation can be discarded owing to the theoretical absence of negative regions. (This does not hold for incorrect fragments where $P^o - P^c_n$ can be negative.) This expected minimum value can thus be readily calculated for any choice of a molecular fragment. If there are N atoms in the unit cell and n atoms in the selected fragment,

$$S^c_n = (\sum^N Z_i)^2 - (\sum^n Z_i)^2 = F_N(000)^2 - F_n(000)^2 \,.$$

Since the theoretical value of S can be defined and evaluated for a correct arrangement of atoms in the fragment, it is thus possible to define a discriminator index which allows an investigator to test whether a particular atom or fragment is incorrect. The discriminator index can be defined as

$$D = \frac{\Delta S^c - \Delta S^o}{\Delta S^c}$$

where ΔS^c is the theoretical change expected in S when atoms are in correct positions, and ΔS^o is the actual change in S that is observed. Thus if $n - n'$ atoms are added to a small fragment of n' atoms that have been placed correctly, the expected decrease in S is given by

$$\Delta S^c = S^c_{n'} - S^c_n = F_n(000)^2 - F_{n'}(000)^2 \,.$$

If these additional atoms are also placed in correct positions, the observed change in S,

$$\Delta S^o = S^o_{n'} - S^o_n \,,$$

will be approximately equal to ΔS^c. Thus for a correct addition to the n' atom fragment, a D value of approximately zero would be expected. If, however, the $n - n'$ atoms are placed in random positions and the Patterson peaks are reasonably sharp, it would be expected that the value of S^o_n will nearly equal that of $S^o_{n'}$, so that $\Delta S^o \simeq 0{\cdot}00$; thus $D \simeq 1{\cdot}00$. In the extreme case where there is no overlap between the new peaks in P^c_n and those present in P^o, $\Delta S^o \simeq -\Delta S^c$; $D \simeq 2{\cdot}00$.

The starting fragment may be chosen from the result of superpositions, from an electron density map computed from an initial set of phases determined from direct methods, or by any other available method. Note that no assumptions have been made regarding the size of the fragment considered; thus, it is theoretically possible to use the discriminator function to test each atom of the asymmetric unit as it is added even in the very early stages of solution. However, for unit cells containing reasonably large numbers of atoms, and thus many peaks in P^o, chances of accidental fitting of peaks would be much greater.

Experimental

To explore the applicability of the discriminator function, it was tested extensively on 1,5-gluconolactone (Hackert & Jacobson, 1969) which crystallizes in space group $P2_12_12_1$ with four molecules/unit cell. A sharpened Patterson function was used in all calculations to increase sensitivity. This resulted in an integral over the absolute value of the observed Patterson that was slightly larger than theoretically expected.

To test the method, it was decided to take advantage of existing programs which could be easily modified to do the necessary computations. A least-squares program (Busing, Martin & Levy, 1962) was modified to compute the calculated structure factors. An isotropic thermal parameter of 2·5 Å^2, the overall value obtained from a Wilson plot, was assigned to each atom in the fragment. It was, of course, necessary to use a complete set of data including unobserved values and the F_{000} reflection.

A data set containing the F^o's and F^c's was passed to a second program where sharpened coefficients (Patterson, 1935; Lipson & Cochran, 1957) were computed by

Table 1. *Discriminator values for correct fragments*

Fragment	+*n*th	ΔS^c	$S_n{}^o$	D	R
–	—	—	147042	—	—
–	O(1)	1024	145969	−0·05	0·75
O(1)	O(5)	3072	143135	0·08	0·68
O(1), O(5)	C(1)	3648	139963	0·13	0·64
O(1), O(5), C(1)	C(5)	4800	135567	0·08	0·61
O(1)–C(1), C(5)	C(4)	5952	130151	0·09	0·58
O(1)–C(5), C(4)	C(3)	7104	123236	0·03	0·54
O(1)–C(4), C(3)	C(2)	8256	115614	0·08	0·51
O(1)–C(3), C(2)	C(6)	9408	107112	0·10	0·48
O(1)–C(2), C(6)	O(2)	14336	93830	0·07	0·43
O(1)–C(6), O(2)	O(3)	16384	9058	0·10	0·37
O(1)–O(2), O(3)	O(4)	18432	63542	0·16	0·30
O(1)–O(3), O(4)	O(6)	20480	46325	0·16	0·18

$$|F^s_{hkl}|^2=[|F^o_{hkl}|^2/(k\hat{f})^2]\exp[(2B-B')\sin^2\theta/\lambda^2]$$

where $\hat{f}=\sum f_j/\sum Z_j$, B is the overall isotropic temperature factor, and B' is a variable used to minimize rippling resulting from sharpening. In the results reported below values of $2B-B'=2·0$ Å^2 and $k=1·70$ were used unless noted otherwise. The intensity of unobserved reflections was set to zero.

The sharpened coefficients were passed to a third program which involved a modified Patterson calculation to compute a numerical approximation for S, the integral over the absolute value of the difference Patterson, and to calculate the D index.

Results

The necessary condition that S be a minimum for a correct fragment was tested by building up a fragment of the gluconolactone molecule. Since there are four equivalent positions, the size of the fragment increases by four for each new atom added. The starting point was taken as the integral over the absolute value of a sharpened Patterson. In Table 1 are shown the results obtained for increasing the size of a correct fragment one atom/molecule at a time from $n'=0$ to $n'=44$ (11 atoms/molecule, with 4 molecules/cell). In every case low D values were obtained, indicating good agreement with the observed Patterson. Note that the magnitude of ΔS^c increases rapidly as the size of the n' fragment increases.

In order for the discriminator to be useful, it is necessary that a minimum value of S be not only a necessary but also a sufficient condition that atoms in a fragment be correctly positioned. The results obtained when incorrect peak positions were tested are shown in Table 2. These positions in general were selected from peaks remaining on a map obtained from a set of four symmetry maps (Patterson maps) superpositions, and thus partial fitting of the observed Patterson would be expected. These values are all significantly higher than those in Table 1. Also note that the difference in D values for a given n' fragment is much more noticeable than the corresponding changes in the R-indices, particularly for the small fragment sizes.

Table 2. *Discriminator values for incorrect fragments*

Fragment	+*n*th	*D*	*R*
O(1)	O*	0·82	0·72
O(1), O(5)	O*	0·68	0·64
O(1), O(5), C(1)	C*	0·52	0·64
O(1), O(5), C(1)	C*	0·47	0·62
O(1), O(5), C(1)	C*	0·40	0·62
O(1), O(5), C(1)	O*	0·71	0·63
O(1), O(5), C(1)	O*	0·59	0·61
O(1)–C(1), O(5)	C*	0·42	0·59
O(1)–C(5), C(4)	C*	0·50	0·56
O(1)–C(4), C(2)	C*	0·49	0·53
O(1)–O(3), O(4)	O*	1·24	0·36

* Indicates atom position selected from different spurious peaks on resultant superposition map.

The results shown in Tables 1 and 2 were obtained using least-squares fitted positional parameters for the various atoms in the correct fragment. The sensitivities of S and the discriminator index D to exact positioning are shown in Table 3. Note that minimizing S corresponds to improving the trial position of the atom added to the fragment. Since the values obtained are dependent on the size of the peaks in the sharpened Patterson, one might well expect that the degree of sensitivity could be adjusted by modifying the thermal coefficient used in computing the sharpened coefficients. Indeed this is the case, as shown in Table 4. As expected, reducing the thermal parameter to $2B-B'=1·0$ Å^2 results in broader peaks that are more easily fitted, and increasing the thermal parameter to $2B-B'=3·0$ Å^2 results in sharper peaks with increased sensitivity. Note, however, that with correct positioning the D values are similarly low for either degree of sharpening.

Table 3. *Sensitivity to correct positioning*

[Fragment −O(1), O(5), C(1); +*n*th −O(3)]

Displacement Å	*D*	*R*
0·0	0·03	0·59
0·113	0·08	0·59
0·118	0·10	0·59
0·185	0·19	0·60
0·226	0·18	0·59
0·339	0·29	0·60
0·370	0·37	0·61

Table 4. *Dependence of sensitivity on thermal coefficient used in sharpening*

[Fragment −O(1)–O(5), C(4); +*n*th −C(3)]

Displacement (Å)	D^a	D^b	*R*
0·0	0·02	0·00	0·54
0·123	0·03	0·07	0·54
0·246	0·06	0·28	0·55
0·370	0·13	0·52	0·56

a $2B-B'=1·0$ Å^2.
b $2B-B'=3·0$ Å^2.

In all the results presented thus far, a fixed least-squares scale factor, $k=1·70$, was used. To test the effect of improper scaling of the structure factor data, additional values of S and D were computed with slightly erroneous scale factors. The results in Table 5 were obtained using scale factors of 1·60 and 1·80. Comparing these results and those in Table 1, it is noticed that although the value of S varies appreciably, the D factors are very similar.

Discussion

We have shown that the discriminator index D is useful for partial structure evaluation. Admittedly these results have been obtained using only one structure (48 atoms/unit cell) for test purposes, and greater difficulty would be anticipated as the number of atoms per cell increases. Further investigations are now in

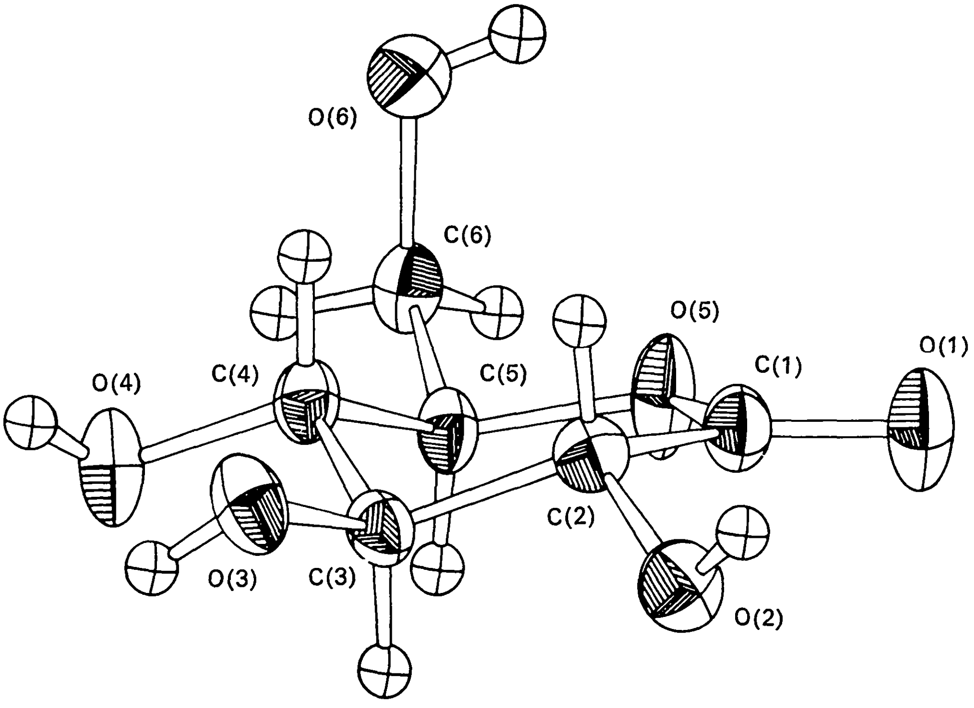

Fig. 1. 1,5-D-Gluconolactone.

Table 5. *Sensitivity to improper scaling of F^o values*

Fragment	$+n$th	S^c	D	R	S^d	D	R
–	—	151624	—	—	144412	—	—
–	O(1)	150632	0·03	0·74	143487	0·10	0·71
O(1)	O(5)	147667	0·03	0·66	140680	0·09	0·64
O(1), O(5)	C(1)	144516	0·14	0·64	137533	0·14	0·62
O(1), O(5), C(1)	C(5)	140282	0·12	0·62	133085	0·07	0·59
O(1)–C(1), C(5)	C(4)	134830	0·08	0·58	127479	0·06	0·56
O(1)–C(5), C(4)	C(3)	128093	0·05	0·55	120500	0·02	0·53
O(1), O(5), C(1)	C*	142219	0·52	0·61	134925	0·46	0·60
O(1)–C(5), C(4)	C*	132328	0·65	0·56	124567	0·59	0·55

c $k = 1{\cdot}60$
d $k = 1{\cdot}80$
* Refer to Table 2.

progress on previously unsolved structures to explore the general applicability of the method to systems of different numbers of atoms and of different crystallographic symmetry. Other investigations suggested by our results on the 1,5-gluconolactone molecule are in progress, namely, attempts to improve the atomic positions in the fragment and obtain better estimates of the scale factor. The production of an efficient computer program to allow more general application of this method is also being studied.

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