Acta Cryst. (1972). A28, 365

International Union of Crystallography Commission on Crystallographic Computing. Standard Tests for Crystallographic Computer Programs. I. Calculations Commonly Used in Crystal-Structure Analysis

BY F. R. AHMED

Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada K1A 0R6

D. W. J. CRUICKSHANK

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England

ALLEN C. LARSON

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, *U.S.A.*

AND J. M. STEWART

Computer Science Center, University of Maryland, College Park, Maryland 20742, *U.S.A.*

(*Received* 29 *November* 1971)

Test cases in space groups $P1$, $P\bar{1}$, $P2_1/c$, $Pmn2_1$, $P6_122$, and $I\bar{4}3d$ are presented for the types of calculation most commonly used in the analysis of crystal structures. For each test, the results include the reciprocal unit-cell parameters; $\sin\theta/\lambda$; interpolated scattering factors; calculated structure factors; interatomic distances and angles; a Fourier block; and the least-squares matrices, shifts, and estimated standard deviations. These results have been verified with different programs on different computers.

Introduction

In order to facilitate the checking of crystallographic computer programs, short standard tests have been prepared as a project of the Commission on Crystallographic Computing of the International Union of Crystallography. The calculations have been carried out at a number of different locations using different computers and programs. The results have been compared and each laboratory has been informed of the variations in results, until eventually all significant variations have been eliminated. The crystallographic program systems which have been employed for the final calculations are: the XRAY-70 system by Stewart, Kundell & Baldwin (1970), the NRC system by Ahmed, Hall, Pippy & Huber (1966), and the LASL crystal structure programs by Larson (1971). It has been quite evident, from the experience gained, that authors and users of crystallographic programs would stand to benefit considerably by trying their programs on these tests.

The present set covers the types of calculations used most commonly in the analysis of crystal structures. There are altogether six test cases in space groups $P1$, $P\bar{1}$, $P2_1/c$, $Pmn2_1$, $P6_122$, and $I\bar{4}3d$. For each of these, results are presented for the reciprocal unit-cell parameters; $\sin\theta/\lambda$; interpolated scattering factors; calculated structure factors; interatomic distances and angles; a Fourier block; and the least-squares matrices, shifts, and estimated standard deviations. The tests are of varying degrees of complexity, and are designed to examine a variety of features: isotropic or anisotropic vibrations, occupancy refinement, special positions, anomalous scattering, *etc.* The $P1$ and $P\bar{1}$ tests are about the simplest and should be tried first, and the $P6_122$ and $I\bar{4}3d$ tests are the most complex. The intermediate results given for the least-squares refinement procedure should be useful in narrowing down the sources of errors or inaccuracies in the programs. The features tested so far are, of course, not exhaustive, but they do represent a beginning.

As described by Stewart (1970), each of the test cases was initiated by taking an arbitrary cell and placing a small 'molecule' in it, either in general or special position depending on the case. Structure factors were then calculated, and a set of 'observed' data was generated from the calculated structure factors. This was done by generating a quasi-Gaussian set of random errors and applying them to the calculated structure factors. The original parameters of the structure were then displaced, and defined to be the 'trial structure'. The assumed direct cell and space group, the trial structure with assumed-standard deviations for the atomic coordinates and the generated observed structure amplitudes constituted the starting data for each test case.

Definition of the procedures

The direct and reciprocal cells

The direct unit cell is defined by the axial lengths (a,b,c) and the interaxial angles (α,β,γ). Its volume is calculated from the expression

$$V=abc(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)^{1/2}.$$

The reciprocal unit-cell parameters are derived from the relations

$$a^*=\frac{bc\sin\alpha}{V},\quad \cos\alpha^*=\frac{\cos\beta\cos\gamma-\cos\alpha}{\sin\beta\sin\gamma}$$

and similarly for b^*, c^*, β^* and γ^*. Its volume is

$$V^*=1/V.$$

The scattering factor curves

The scattering factor curves employed in the calculations, are those given for S, O and C in *International Tables for X-ray Crystallography* (1962, p. 202). For each of these atoms, the first line in the table is the one actually used. The points are at $\sin\theta/\lambda=0{\cdot}0(0{\cdot}05)0{\cdot}40$, $0{\cdot}50(0{\cdot}10)1{\cdot}30$ Å^{-1}.

In all test cases, the anomalous dispersion is excluded from the calculations. Results of space group $P6_122$ with the anomalous dispersion of the S atom included, are also given. In this case, the $\Delta f'$ and $\Delta f''$ of the S atom are taken as 0·350 and 0·869 independent of $\sin\theta/\lambda$ respectively.

Interpolation procedures

To start with, $\sin\theta/\lambda$ is evaluated from the expression $\sin\theta/\lambda=\frac{1}{2}(h^2a^{*2}+\ldots+2klb^*c^*\cos\alpha^*+\ldots)^{1/2}$. Different interpolation functions, depending on the value of $\sin\theta/\lambda$, are then employed. These functions may vary from program to program, but for the sake of reference, the scattering factor values presented herewith are calculated by the following functions, as in the NRC programs by Ahmed *et al.* (1966).

1. $0<\sin\theta/\lambda\leq 0{\cdot}05$
   $f=f(0{\cdot}0)\exp(-p_1\sin^2\theta/\lambda^2)$,
where
   $p_1=400\log_e[f(0{\cdot}0)/f(0{\cdot}05)]$.
2. $0{\cdot}05<\sin\theta/\lambda\leq 0{\cdot}10$
   $f=f(0{\cdot}05)\exp[-p_2(\sin^2\theta/\lambda^2-0{\cdot}0025)]$,
where
   $p_2=(400/3)\log_e[f(0{\cdot}05)/f(0{\cdot}10)]$.
3. $0{\cdot}10<\sin\theta/\lambda\leq 0{\cdot}25$ and $0{\cdot}40<\sin\theta/\lambda\leq 1{\cdot}00$
   Interpolation is done by Newton's forward-difference formula employing the 1st, 2nd and 3rd order differences.
4. $0{\cdot}25<\sin\theta/\lambda\leq 0{\cdot}40$ and $1{\cdot}00<\sin\theta/\lambda\leq 1{\cdot}30$
   Interpolation is done as in (3) but with the backward differences.
5. $1{\cdot}30<\sin\theta/\lambda$
   Extrapolation of the curve is carried out instead of interpolation.

The thermal vibration parameters

Assuming f^0 is the atomic scattering factor at zero temperature, and q is the correction of thermal vibration, then

$$f(hkl)=f^0(hkl)\,q(hkl),$$

where

$$q(hkl)=\exp(-B\sin^2\theta/\lambda^2),$$

or

$$q(hkl)=\exp(-8\pi^2U\sin^2\theta/\lambda^2)\text{ for isotropic vibration,}$$

and

$$q(hkl)=\exp[-(\beta_{11}h^2+\ldots+2\beta_{23}kl+\ldots)],$$

or

$$q(hkl)=\exp[-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{23}b^*c^*kl+\ldots)]$$

for anisotropic vibration.

When the isotropic harmonic vibrations are expressed as if they are anisotropic, the relations between the thermal vibration parameters in the preceding expressions are as follows:

$$\beta_{11}=\tfrac{1}{4}Ba^{*2}$$
$$\beta_{23}=\tfrac{1}{4}Bb^*c^*\cos\alpha^*$$
$$U=B/8\pi^2$$
$$U_{11}=B/8\pi^2=\beta_{11}/(2\pi^2a^{*2})$$
$$U_{23}=B\cos\alpha^*/8\pi^2=\beta_{23}/(2\pi^2b^*c^*).$$

For the $P1$, $P2_1/c$ and $P6_122$ test cases with anisotropic refinement, the trial parameters correspond to isotropic vibrations. Structure factor calculations can therefore be tested isotropically or anisotropically, but the results of the least-squares refinement are given only for the anisotropic parameters.

The equivalent atomic positions

The equivalent atomic positions for the different space groups are listed in *International Tables for X-ray Crystallography* (1952). In the $P6_122$ and $I\bar{4}3d$ test cases where some of the atoms are in special positions, the multiplicity and the Wyckoff notation are listed after each atom symbol in the parameter Table. In the other test cases, all the atoms are in general positions.

Interatomic distances and angles

For the purpose of identification in these tests, the intramolecular distances and angles are defined as those between the *original* atomic positions, and the intermolecular distances as those between an original atomic position and another derived by one of the symmetry operations of the space group. The results are based on the original parameters and assumed standard deviations, before refinement.

The calculated structure factors

The A_c, B_c and $|F_c|$ are calculated with the structure factor expressions as if each space group were triclinic. The discrepancy index is defined as

$$R=\sum||F_o|-|F_c||/\sum|F_o|.$$

The number of reflexions quoted is exclusive of $F(000)$.

The electron density

The expressions for the electron density are listed in *International Tables for X-ray Crystallography* (1952). The grid intervals are 1/30th of the unit-cell edges. The Fourier results are for the original 'observed' structure amplitudes and the calculated phases for the trial structure. The $F(000)$ term is included in the calculations.

In the $P6_122$ test case, the 81 observed reflexions and those equivalent to them within one quadrant of the reciprocal space should be included in the Fourier summations. This set comprises 314 reflexions, in addition to the $F(000)$ term, related as follows:

$$|F(hkl)|=|F(ikl)|=|F(ihl)|=|F(khl)|=|F(\bar{k}\bar{l}l)|=|F(\bar{h}\bar{l}l)|\,.$$

Similarly, in the $I\bar{4}3d$ test case the 32 observed reflexions and their equivalents in the hkl octant of reciprocal space add up to 157 reflexions, plus the $F(000)$ term, to be included in the Fourier summations. The relationships involved in this case are:

$$|F(hkl)|=|F(klh)|=|F(lhk)|$$
$$=|F(khl)|=|F(hlk)|=|F(lkh)|\,.$$

It should be noted that within each set the indices should be unique without any repetition. In $P6_122$ the multiplicities assigned to the reflexions should be the same as for monoclinic space groups, and in $I\bar{4}3d$ they should be the same as for orthorhombic space groups.

The least-squares refinement

The quantity that is being minimized in the least-squares calculations is

$$R_1=\sum w(|F_o|-|F_c|)^2$$

where $\sum$ is over all the non-equivalent observed reflexions listed with each test, and w is the weight. When w is not equal to 1·0 for all reflexions, the square root of w is listed in the structure factor tables.

The elements of the upper triangle of the symmetric least-squares original matrix and its inverse matrix, are listed for the block-diagonal approximation with one block per atom. The vector, and the resulting shifts of this procedure are also listed in the same table.

In the block-diagonal approximation, the scale shift is calculated separately from a 2×2 matrix involving the scale and (dummy) overall isotropic temperature factor as the variable parameters. This procedure is necessary because of the very high correlation of the scale with the thermal vibration parameters (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). The effect of the change of scale upon the individual vibration parameters derived from the 9×9 or 4×4 matrices can be allowed for by augmenting the individual ΔU_{ij} or ΔU by $(\Delta\bar{U}_2-\Delta\bar{U}_1)$, where $\Delta\bar{U}_2$ is the change of overall vibration from a 2×2 matrix and $\Delta\bar{U}_1$ is obtained from the 1×1 matrix (*i.e.* the diagonal element of the 2×2 matrix) for the dummy temperature factor alone.

The shifts and estimated standard deviations are also given for full-matrix calculations. The scale shifts given in the Appendices are those required to bring $|F_o|$ on a level with $|F_c|$.

Treatment of atoms in special positions

For atoms in special positions, the rows and columns corresponding to the fixed atomic parameters are eliminated from the matrices. In such cases, the site symmetry also imposes restrictions on the U_{ij} parameters. As an example, in the $P6_122$ test case, the S atom at position $(x,\bar{x},\frac{1}{12})$ should have $U_{22}=U_{11}$ and $U_{23}=U_{13}$; and the O atom at position $(\bar{x},\bar{x},\frac{2}{3})$ should be $U_{22}=U_{11}$ and $U_{23}=-U_{13}$. Thus, the only parameters that have to be refined for the S and O atoms are x, U_{11}, U_{33}, U_{12}, and U_{13}, but at the same time the derivatives of these parameters should be adjusted to take into account their relationships to the omitted parameters. Since the S atom has $y=-x$, its coordinates can be expressed in terms of one independent variable X as $(X,-X,\frac{1}{12})$. In this case, the derivative needed for the least-squares is $\partial|F_c|/\partial X$ and, as explained by Cruickshank *et al.* (1961) and Cruickshank (1970), this should have the value

$$\frac{\partial|F_c|}{\partial X}=\frac{\partial|F_c|}{\partial x}\frac{\partial x}{\partial X}+\frac{\partial|F_c|}{\partial y}\frac{\partial y}{\partial X}=\frac{\partial|F_c|}{\partial x}-\frac{\partial|F_c|}{\partial y}.$$

The other parameters should also be adjusted in a similar manner.

Estimated standard deviations

1. In the least-squares refinement, the estimated standard deviation of a given parameter p_i is derived by the expression

$$\sigma(p_i)=[(a^{-1})_{ii}(\sum w\Delta^2)/(m-n)]^{1/2}$$

where $(a^{-1})_{ii}$ is a diagonal element of the inverse matrix, m is the number of reflexions included, and n is the number of parameters being refined.

2. The standard deviations of the bond lengths and angles are based on the assumed standard deviations for the trial structure. The unit-cell edges are assumed to have zero errors, and the covariances between parameters are ignored in the present calculations. The expressions used for calculating the e. s. d.'s quoted in the Appendices are given explicitly under (*a*) and (*b*). Other procedures have produced results which in some cases are different by $\pm0{\cdot}005$ Å and $\pm0{\cdot}017°$ for the e. s. d.'s of the bond lengths and angles respectively.

(*a*) *Bond lengths*

If **T** is the matrix that transforms the atomic fractional coordinates to orthogonal coordinates in Å, such as

$$\mathbf{X}'=\mathbf{T}\,.\,\mathbf{x}\ (\text{Å}),*$$

* Text continued on p. 392

APPENDIX *A*

Test case *P* 1

Table *A*1. *Crystal data*

Direct cell		Reciprocal cell			
a	5·75 Å	a^*	0·2058 Å^{-1}	$F(000)$	30·0
b	5·90	b^*	0·1973	Scale	1·0
c	4·75	c^*	0·2184	Weights	1·0
α	94·00°	α^*	79·11°	Relaxation factor	1·0
β	101·00	β^*	75·08	Occupancy factors	1·0
γ	119·00	γ^*	59·42	Restricted parameters	$x,y,z(S)$
V	135·86 Å^3	V^*	0·00736 Å^{-3}		

Table *A*2. *Parameters of the trial structure* (U, β_{ij} *and* $U_{ij}\times 10^5$)

	x	y	z	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	U	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0·0	0·0	0·0	2·8	2964	2726	3339	1446	810	570
	0·0	0·0	0·0	3546	3546	3546	3546	1804	913	670
O	0·190	−0·090	0·210	3·1	3282	3018	3697	1601	897	631
	0·002	0·002	0·003	3926	3926	3926	3926	1997	1011	742
C	−0·060	0·240	0·170	3·6	3811	3505	4293	1859	1041	733
	0·005	0·005	0·006	4559	4559	4559	4559	2319	1174	862

Table *A*3. *Structure factor data for the trial structure*

h	k	l	F_{obs}	F_{cal}	A_{cal}	B_{cal}	$\sin\theta/\lambda$	f(S)	f(C)	f(O)
0	0	2	5·71	5·97	3·83	4·59	0·2184	10·69	3·34	5·32
0	1	1	13·40	13·95	12·58	6·03	0·1604	12·41	4·18	6·31
0	1	−1	13·86	15·23	14·62	−4·24	0·1326	13·31	4·64	6·76
0	1	2	4·78	4·85	4·28	2·27	0·2561	9·80	2·91	4·72
0	1	−2	7·17	7·09	6·96	−1·34	0·2220	10·60	3·30	5·26
0	1	−3	6·00	5·84	5·73	1·11	0·3238	8·64	2·32	3·79
0	2	0	10·35	10·04	9·14	−4·16	0·1973	11·29	3·62	5·68
0	2	1	10·81	11·20	11·13	−1·23	0·2429	10·09	3·05	4·92
0	−2	1	4·67	4·96	4·95	0·30	0·2067	11·02	3·49	5·52
0	2	2	7·75	7·49	7·37	1·31	0·3208	8·68	2·34	3·83
0	2	−2	7·26	7·39	6·30	3·85	0·2652	9·61	2·82	4·58
0	2	3	5·07	4·22	4·19	0·46	0·4132	7·72	1·91	2·90
0	2	−3	9·14	8·42	8·18	1·97	0·3490	8·33	2·17	3·50
0	3	1	9·89	9·98	9·79	−1·92	0·3343	8·51	2·26	3·67
0	3	−1	2·79	2·39	2·19	−0·97	0·2955	9·06	2·54	4·15
0	3	2	7·87	7·35	7·11	1·89	0·3997	7·83	1·95	3·01
0	3	−2	4·73	5·43	4·18	3·47	0·3330	8·52	2·26	3·68
0	3	3	3·96	3·51	3·10	1·66	0·4813	7·19	1·72	2·44
0	−3	3	7·56	7·15	6·81	−2·16	0·3979	7·85	1·96	3·03
1	0	0	18·56	21·46	20·94	4·68	0·1029	14·24	5·09	7·21
1	0	2	4·71	4·66	4·65	−0·20	0·2643	9·63	2·83	4·60
1	0	−2	9·52	9·94	7·71	−6·28	0·2161	10·76	3·37	5·36
1	1	0	17·50	18·11	16·93	6·43	0·1751	11·95	3·94	6·06
−1	1	0	10·41	11·31	11·09	−2·20	0·1000	14·33	5·13	7·25
1	1	1	15·11	8·52	5·82	6·22	0·2290	10·42	3·21	5·15
−1	1	1	13·67	13·93	13·81	−1·86	0·1421	13·00	4·48	6·61
1	−1	1	8·02	8·92	8·56	−2·50	0·1537	12·63	4·29	6·42
1	1	−1	18·01	18·59	18·31	−3·22	0·1809	11·77	3·86	5·96
1	1	2	2·31	2·21	2·14	−0·57	0·3132	8·79	2·40	3·92
−1	1	2	8·93	10·03	9·95	1·30	0·2330	10·32	3·17	5·08
1	−1	2	9·76	10·05	9·51	−3·22	0·2472	9·99	3·01	4·86
1	1	−2	10·05	10·02	8·15	−5·82	0·2421	10·11	3·06	4·94
1	1	3	5·88	5·03	4·25	−2·71	0·4093	7·75	1·92	2·93
−1	1	3	5·34	5·29	5·24	0·69	0·3349	8·50	2·25	3·66
1	−1	3	9·24	8·27	8·27	0·07	0·3499	8·32	2·17	3·49
1	1	−3	3·44	3·09	2·96	−0·86	0·3292	8·57	2·29	3·73
1	2	0	10·56	9·75	9·66	1·29	0·2649	9·62	2·82	4·59

Table *A*3 (*cont.*)

h	*k*	*l*	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	*f*(S)	*f*(C)	*f*(O)
−1	2	0	6·29	6·28	3·81	−5·00	0·1699	12·11	4·03	6·15
1	2	1	6·51	6·18	5·86	1·97	0·3099	8·84	2·42	3·96
−1	2	1	13·76	13·50	11·57	−6·95	0·2077	10·99	3·48	5·50
1	−2	1	5·33	5·94	3·57	−4·75	0·1961	11·32	3·64	5·70
1	2	−1	9·12	9·27	9·17	−1·34	0·2611	9·69	2·86	4·64
1	2	2	4·07	3·58	3·56	−0·33	0·3818	7·99	2·02	3·17
−1	2	2	12·38	11·97	11·96	−0·31	0·2851	9·24	2·63	4·30
1	−2	2	10·06	10·91	9·38	−5·57	0·2681	9·55	2·79	4·54
1	2	−2	6·21	6·01	5·96	−0·79	0·3000	8·99	2·50	4·09
1	2	3	4·40	4·07	3·85	−1·32	0·4683	7·29	1·75	2·52
−1	2	3	6·67	6·84	6·40	2·42	0·3785	8·02	2·03	3·20
1	−2	3	10·07	9·31	9·30	−0·25	0·3593	8·22	2·12	3·39
1	2	−3	6·06	5·11	5·05	0·80	0·3684	8·12	2·07	3·30
1	3	0	8·36	7·34	7·00	−2·22	0·3594	8·22	2·12	3·39
1	−3	0	6·26	5·76	4·81	3·16	0·2593	9·73	2·88	4·67
1	3	1	8·24	6·82	6·81	0·38	0·3989	7·84	1·95	3·02
−1	3	1	10·59	9·73	8·96	−3·80	0·2925	9·11	2·56	4·19
1	−3	1	4·93	4·74	4·39	−1·80	0·2697	9·52	2·77	4·52
1	3	−1	5·75	4·50	3·91	−2·22	0·3509	8·31	2·16	3·48
1	3	2	5·19	4·31	4·16	1·12	0·4614	7·34	1·77	2·56
−1	3	2	10·12	8·97	8·96	0·35	0·3575	8·24	2·13	3·41
1	−3	2	7·38	7·50	7·06	−2·52	0·3195	8·70	2·35	3·84
1	3	−2	3·31	3·03	2·82	1·11	0·3754	8·05	2·04	3·23
1	3	3	3·18	2·45	2·44	0·23	0·5390	6·76	1·62	2·16
−1	3	3	5·94	5·32	4·85	2·18	0·4403	7·51	1·82	2·70
1	−3	3	7·50	6·56	6·56	−0·10	0·3940	7·88	1·97	3·06
1	3	−3	4·98	5·27	4·74	2·32	0·4272	7·61	1·86	2·79
2	0	0	7·29	8·56	8·46	1·26	0·2058	11·04	3·50	5·53
2	0	2	7·55	7·31	7·25	−0·97	0·3364	8·48	2·24	3·64
2	0	−2	9·38	9·69	9·57	−1·51	0·2587	9·74	2·88	4·68
2	1	0	9·70	9·77	8·43	4·95	0·2697	9·52	2·77	4·52
−2	1	0	3·04	3·69	3·29	1·67	0·1773	11·88	3·91	6·02
2	1	1	3·44	3·71	3·35	1·60	0·3167	8·74	2·37	3·88
−2	1	1	9·36	9·00	6·87	−5·81	0·1893	11·52	3·73	5·81
2	−1	1	10·40	10·51	8·22	−6·54	0·2255	10·51	3·26	5·20
2	1	−1	12·66	13·39	13·34	1·11	0·2627	9·66	2·84	4·62
2	1	2	4·65	3·92	3·58	−1·59	0·3895	7·92	1·99	3·10
−2	1	2	13·28	11·74	11·23	−3·43	0·2532	9·86	2·94	4·76
2	−1	2	11·78	11·07	10·86	−2·13	0·3068	8·88	2·45	4·00
2	1	−2	10·74	10·33	9·50	−4·06	0·2986	9·01	2·51	4·11
2	1	3	5·50	4·52	4·37	−1·15	0·4764	7·23	1·73	2·47
−2	1	3	9·21	8·49	8·42	1·05	0·3410	8·42	2·22	3·59
2	−1	3	7·89	7·35	7·09	1·95	0·4015	7·82	1·94	3·00
2	1	−3	4·68	4·37	3·44	−2·69	0·3649	8·16	2·09	3·34
2	2	0	6·99	6·65	5·75	3·34	0·3502	8·32	2·16	3·49
2	−2	0	2·64	2·89	2·89	−0·01	0·1999	11·21	3·58	5·64
2	2	1	2·83	2·54	2·40	0·81	0·3927	7·89	1·97	3·07
−2	2	1	9·45	9·50	6·97	−6·45	0·2202	10·65	3·32	5·29
2	−2	1	8·93	8·79	7·00	−5·31	0·2352	10·27	3·14	5·05
2	2	−1	8·78	9·28	9·20	1·21	0·3388	8·45	2·23	3·62
2	2	3	4·92	4·01	3·83	−1·19	0·5377	6·77	1·62	2·17
2	2	−3	4·88	4·15	3·85	−1·56	0·4133	7·72	1·91	2·90
2	3	0	5·76	4·83	4·81	0·42	0·4381	7·52	1·83	2·71
2	−3	0	7·02	7·10	7·01	−1·15	0·2608	9·70	2·86	4·65
2	3	1	4·32	3·41	3·40	0·34	0·4771	7·22	1·73	2·46
−2	3	1	6·39	6·33	6·24	−1·11	0·2839	9·26	2·64	4·31
2	−3	1	9·38	8·70	8·65	−0·87	0·2816	9·30	2·66	4·35
2	3	−1	6·05	5·06	5·03	−0·53	0·4244	7·63	1·87	2·81
2	3	2	3·44	2·72	2·70	−0·38	0·5359	6·79	1·62	2·17
−2	3	2	7·49	7·09	6·99	−1·16	0·3420	8·41	2·21	3·58
2	−3	2	7·55	7·04	6·96	1·08	0·3382	8·46	2·23	3·62
2	3	−2	4·39	3·82	3·79	−0·48	0·4383	7·52	1·83	2·71
2	3	3	3·27	2·51	2·48	−0·35	0·6088	6·25	1·53	1·92
−2	3	3	5·79	5·74	5·71	0·60	0·4210	7·66	1·88	2·84
2	−3	3	4·75	4·01	3·93	0·76	0·4164	7·70	1·90	2·88
2	3	−3	3·82	3·30	3·25	0·56	0·4774	7·22	1·73	2·46
3	0	0	5·43	5·60	4·84	−2·82	0·3087	8·86	2·43	3·98
3	0	2	7·87	6·86	6·82	0·73	0·4215	7·66	1·88	2·84
−3	0	2	7·20	6·78	6·36	−2·35	0·3290	8·57	2·29	3·73
3	1	0	5·11	4·64	4·58	0·74	0·3688	8·12	2·07	3·30

Table *A*3 (*cont.*)

h	*k*	*l*	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	*f*(S)	*f*(C)	*f*(O)
3	−1	0	5·18	5·64	3·95	−4·02	0·2721	9·48	2·75	4·48
3	1	1	5·00	4·35	4·31	−0·57	0·4115	7·74	1·91	2·91
−3	1	1	3·41	3·40	2·54	−2·26	0·2696	9·52	2·77	4·52
3	−1	1	9·91	9·39	8·60	−3·76	0·3150	8·76	2·39	3·90
3	1	−1	7·30	6·70	6·55	1·44	0·3557	8·26	2·13	3·43
3	1	2	4·63	4·21	4·20	−0·27	0·4760	7·23	1·74	2·47
−3	1	2	9·02	8·49	7·08	−4·68	0·3085	8·86	2·44	3·98
3	−1	2	8·64	8·03	8·02	0·39	0·3851	7·96	2·00	3·14
3	1	−2	7·79	7·16	7·14	−0·44	0·3753	8·06	2·04	3·23
3	1	3	3·63	2·97	2·95	0·29	0·5546	6·65	1·60	2·10
−3	1	3	9·88	8·61	8·57	−0·91	0·3762	8·05	2·04	3·22
3	−1	3	4·72	4·57	4·27	1·64	0·4703	7·28	1·75	2·50
3	1	−3	5·96	4·92	4·65	−1·62	0·4231	7·64	1·87	2·82
3	2	0	3·90	3·42	2·92	1·78	0·4429	7·49	1·82	2·68
3	−2	0	7·09	6·89	6·64	−1·81	0·2688	9·54	2·78	4·53
3	2	1	2·70	2·12	2·05	−0·55	0·4833	7·18	1·72	2·43
3	−2	1	8·50	8·06	8·02	−0·86	0·3056	8·90	2·46	4·02
3	2	−1	6·61	6·27	5·90	2·14	0·4273	7·61	1·86	2·79
3	2	2	3·46	3·16	2·91	−1·23	0·5430	6·73	1·61	2·14
−3	2	2	6·90	7·27	6·84	−2·47	0·3186	8·71	2·36	3·85
3	−2	2	6·96	6·03	5·98	0·73	0·3720	8·09	2·06	3·27
3	2	−2	8·44	6·74	6·73	−0·51	0·4392	7·52	1·83	2·71
3	2	3	3·68	2·87	2·86	−0·29	0·6165	6·19	1·52	1·90
−3	2	3	8·95	7·15	7·14	−0·32	0·3898	7·92	1·98	3·10
3	−2	3	4·03	3·65	3·64	0·25	0·4552	7·39	1·78	2·60
3	2	−3	5·53	4·54	4·09	−1·96	0·4765	7·23	1·73	2·47
3	3	0	2·58	2·41	2·29	0·75	0·5252	6·87	1·64	2·22
−3	3	0	10·62	10·23	10·11	1·55	0·2999	8·99	2·50	4·10
3	3	1	2·66	1·89	1·81	−0·54	0·5633	6·58	1·58	2·07
−3	3	1	6·37	6·89	6·27	2·86	0·3110	8·82	2·42	3·95
3	−3	1	9·53	9·06	8·74	2·39	0·3271	8·60	2·30	3·75
3	3	−1	4·82	3·95	3·81	1·03	0·5081	6·99	1·67	2·30
3	3	2	3·14	2·43	2·28	−0·83	0·6186	6·17	1·51	1·89
−3	3	2	4·55	3·84	3·84	0·23	0·3569	8·24	2·13	3·42
3	−3	2	5·17	4·71	4·05	2·42	0·3846	7·97	2·00	3·15
3	3	−2	4·92	4·24	4·24	−0·07	0·5142	6·95	1·66	2·27
−3	3	3	5·41	4·28	4·16	−1·02	0·4264	7·62	1·86	2·80
3	−3	3	2·50	2·13	2·11	−0·28	0·4612	7·35	1·77	2·56
3	3	−3	3·74	3·16	3·09	−0·65	0·5426	6·74	1·61	2·14

Table *A*4. *Interatomic distances* (Å), *angles* (°) *and e.s.d.'s*

Intramolecular distances		Intramolecular angles		Intermolecular distances < 4·5	
S–O	1·640 (13)	O–S–C	117·04 (102)	C···O	3·466 (29)
S–C	1·788 (29)	S–O–C	32·99 (63)	C···O	3·827 (34)
O–C	2·925 (33)	S–C–O	29·97 (57)	O···S	4·172 (14)
				C···S	4·290 (27)
				C···S	4·471 (27)

Table *A*5. *Fourier block round the* S *atom* (*in* 30*th*)

	X = −1			*X* = 0			*X* = 1		
	Z = −1	*Z* = 0	*Z* = 1	*Z* = −1	*Z* = 0	*Z* = 1	*Z* = −1	*Z* = 0	*Z* = 1
Y = −1	11·84	12·48	11·27	12·45	13·30	12·20	11·13	12·06	11·28
Y = 0	12·62	13·39	12·17	13·52	14·53	13·41	12·36	13·46	12·62
Y = 1	11·30	12·09	11·09	12·35	13·36	12·42	11·53	12·62	11·89

Table *A*6. *Sums and discrepancy*

$\sum \lvert F_{obs} \rvert$	1039·27	Number of atoms	3
$\sum \lvert F_{calc} \rvert$	989·45	Number of parameters	25
$\sum \lvert \Delta F \rvert$	89·36	Number of reflexions	146
R	0·086	$\sum [w(\Delta F)^2]$	115

Table *A7. Details of the* 9×9 *block-diagonal least-squares matrices*

Atom: S

Original matrix elements $\times 10^{-2}$

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Vector
1086	638	490	−574	−210	−59	−1151
	1262	563	−625	−109	−154	−1314
		916	−240	−218	−172	−1266
			2552	−117	−218	−251
				1958	−481	177
					2253	−225

Inverse matrix elements $\times 10^{8}$

						Shifts
1516	−460	−450	192	102	14	−0·00605
	1360	−534	183	−8	56	−0·00642
		1696	−57	133	104	−0·00915
			484	72	75	−0·00516
				575	142	−0·00223
					494	−0·00327

Atom: O

Original matrix elements $\times 10^{-1}$

x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Vector
7547	−3212	−810	−27	−41	−40	95	−225	205	−169
	8665	−790	48	164	61	−82	205	−217	134
		6083	−113	−109	−33	205	−80	123	−62
			1028	575	454	−669	−224	−109	−293
				1208	484	−711	−46	−189	−199
					795	−280	−268	−194	−199
						2299	−218	−92	172
							1815	−561	36
								1934	−21

Inverse matrix elements $\times 10^{7}$

									Shifts
163	63	30	4	−11	8	−8	12	−9	−0·00223
	142	27	5	−19	−1	−5	−6	4	0·00081
		173	13	1	−7	−13	4	−10	−0·00166
			1678	−373	−538	326	180	71	−0·02498
				1377	−535	250	−41	59	−0·00194
					2016	−42	274	196	−0·01395
						622	149	112	−0·00258
							708	244	−0·00563
								625	−0·00541

Atom: C

Original matrix elements $\times 10^{-1}$

x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Vector
2856	−1139	−328	−77	9	28	25	8	13	−241
	3138	−233	12	38	−4	17	13	−55	139
		2282	4	−27	−6	13	56	−8	−178
			363	211	147	−241	−93	−7	6
				441	171	−275	−42	−41	−4
					265	−82	−71	−69	−83
						842	−14	−83	−20
							589	−164	67
								682	−106

Inverse matrix elements $\times 10^{7}$

									Shifts
429	161	77	151	−56	−95	−3	−11	−9	−0·00853
	383	62	40	−66	7	−21	−9	21	0·00010
		457	−17	27	−24	−11	−51	−6	−0·00923
			4757	−1090	−1534	866	526	60	0·01421
				3974	−1657	842	−30	151	0·00796
					5886	−341	503	564	−0·04805
						1712	281	299	−0·00173
							2011	570	0·00401
								1708	−0·01892

Table *A*8. *Least-squares shifts and estimated standard deviations* (*all values* $\times 10^5$)

Method: Full matrix

		x	y	z	β_{11} / U_{11}	β_{22} / U_{22}	β_{33} / U_{33}	β_{12} / U_{12}	β_{13} / U_{13}	β_{23} / U_{23}
S	Δ	0	0	0	−1047	−1335	−1254	−617	−322	−335
	σ	0	0	0	458	467	498	237	291	265
	Δ				−1252	−1734	−1333	−770	−362	−394
	σ				548	606	529	296	328	312
O	Δ	−240	123	−168	−2420	−509	−1517	−346	−334	−550
	σ	403	372	422	1401	1273	1486	835	965	826
	Δ				−2889	−667	−1617	−430	−379	−646
	σ				1676	1655	1579	1042	1087	971
C	Δ	−839	−67	−936	−145	469	−2425	−205	59	−472
	σ	651	619	684	2285	2043	2621	1326	1467	1518
	Δ				−171	609	−2559	−248	71	−558
	σ				2732	2657	2781	1652	1652	1782

Scale shift = 0·072 σ = 0·021

Method: Blocks of 9 × 9 per atom

		x	y	z	β_{11} / U_{11}	β_{22} / U_{22}	β_{33} / U_{33}	β_{12} / U_{12}	β_{13} / U_{13}	β_{23} / U_{23}
S	Δ	0	0	0	−605	−642	−915	−516	−223	−327
	σ	0	0	0	380	359	401	214	234	217
	Δ				−723	−835	−971	−643	−251	−384
	σ				454	468	426	268	264	254
O	Δ	−223	81	−166	−2498	−194	−1395	−258	−563	−541
	σ	394	367	405	1263	1144	1384	769	820	770
	Δ				−2988	−252	−1481	−322	−635	−636
	σ				1511	1488	1470	959	925	905
C	Δ	−853	10	−923	1421	796	−4805	−173	401	−1892
	σ	638	603	659	2126	1943	2365	1275	1382	1274
	Δ				1700	1035	−5103	−216	452	−2223
	σ				2543	2528	2512	1591	1558	1497

Adjusted β_{ij} and U_{ij} shifts for a scale shift of 0·0773

S	$(\Delta\beta)'$	−1222	−1209	−1610	−817	−391	−445
	$(\Delta U)'$	−1462	−1573	−1710	−1019	−441	−523
O	$(\Delta\beta)'$	−3115	−761	−2090	−559	−732	−660
	$(\Delta U)'$	−3727	−991	−2220	−697	−825	−776
C	$(\Delta\beta)'$	804	228	−5500	−474	232	−2010
	$(\Delta U)'$	962	297	−5842	−592	262	−2363

Method: Blocks of 3 × 3 and 6 × 6 per atom

		x	y	z	β_{11} / U_{11}	β_{22} / U_{22}	β_{33} / U_{33}	β_{12} / U_{12}	β_{13} / U_{13}	β_{23} / U_{23}
S	Δ	0	0	0	−605	−642	−915	−516	−223	−327
	σ	0	0	0	380	359	401	214	234	217
	Δ				−723	−835	−971	−643	−251	−384
	σ				454	468	426	268	264	254
O	Δ	−208	66	−121	−2487	−183	−1385	−275	−528	−572
	σ	393	366	404	1262	1143	1384	768	819	769
	Δ				−2976	−238	−1471	−343	−595	−673
	σ				1510	1486	1470	958	923	904
C	Δ	−932	37	−912	1661	806	−5057	−172	296	−1946
	σ	634	602	658	2113	1939	2360	1275	1380	1273
	Δ				1987	1048	−5371	−215	333	−2288
	σ				2528	2522	2506	1590	1556	1496

Adjusted β_{ij} and U_{ij} shifts for a scale shift of 0·0773

S	$(\Delta\beta)'$	−1222	−1209	−1610	−817	−391	−445
	$(\Delta U)'$	−1462	−1573	−1710	−1019	−441	−523
O	$(\Delta\beta)'$	−3105	−751	−2080	−576	−696	−691
	$(\Delta U)'$	−3714	−976	−2209	−719	−785	−812
C	$(\Delta\beta)'$	1044	238	−5752	−474	127	−2065
	$(\Delta U)'$	1249	310	−6109	−591	143	−2427

APPENDIX *B*

Test case $P\bar{1}$

Table *B*1. *Crystal data*

Direct cell		Reciprocal cell			
a	8·10 Å	a^*	0·1239 Å^{-1}	$F(000)$	60·0
b	5·90	b^*	0·1699	Scale	1·0
c	4·80	c^*	0·2096	Weights	as listed
α	86·00°	α^*	93·93°	Relaxation factor	1·0
β	85·00	β^*	94·94	Occupancy factors	1·0
γ	89·00	γ^*	90·66	Restricted parameters	occup. (S, O)
V	227·95 Å^3	V^*	0·00439 Å^{-3}		

Table *B*2. *Parameters of the trial structure*

	x	y	z	B	$U\times 10^5$	Occupancy
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$			
S	0·240	0·050	0·238	2·5	3166	1·0
	0·002	0·002	0·003			fixed
O	0·160	0·295	0·361	2·8	3546	1·0
	0·003	0·002	0·004			fixed
C	0·290	−0·255	0·354	3·0	3800	1·0
	0·005	0·005	0·006			variable

Table *B*3. *Structure factor data for the trial structure*

h	k	l	F_{obs}	F_{cal}	$\sin\theta/\lambda$	f(S)	f(C)	f(O)	$\sqrt{w}$
0	0	2	−19·21	−22·64	0·2096	10·93	3·45	5·47	0·14
0	1	1	−3·77	−6·07	0·1303	13·38	4·67	6·80	0·44
0	−1	1	14·52	14·39	0·1394	13·09	4·53	6·66	0·17
0	1	2	−15·08	−14·89	0·2207	10·63	3·31	5·28	0·17
0	1	−2	−18·02	−18·80	0·2315	10·36	3·18	5·11	0·14
0	1	3	−4·04	−1·76	0·3200	8·69	2·35	3·84	0·43
0	−1	3	−8·11	−6·73	0·3313	8·54	2·27	3·70	0·27
0	2	0	0·48	1·29	0·1699	12·11	4·03	6·15	0·86
0	2	1	3·83	2·61	0·1934	11·40	3·67	5·75	0·44
0	2	−1	19·37	18·21	0·2057	11·05	3·51	5·54	0·13
0	2	2	−17·81	−15·96	0·2606	9·70	2·86	4·65	0·14
0	2	−2	−4·57	−5·34	0·2787	9·35	2·69	4·39	0·40
0	2	3	−0·66	−0·38	0·3470	8·35	2·18	3·52	0·82
0	2	−3	−17·19	−15·77	0·3675	8·13	2·08	3·31	0·15
0	3	1	−15·32	−15·75	0·2689	9·54	2·78	4·53	0·16
0	3	−1	8·99	9·16	0·2821	9·29	2·65	4·34	0·25
0	3	2	−9·80	−10·77	0·3187	8·71	2·36	3·85	0·23
0	−3	2	−4·29	−6·18	0·3409	8·42	2·22	3·59	0·41
0	3	3	9·53	10·30	0·3910	7·91	1·98	3·09	0·24
0	−3	3	−8·28	−6·97	0·4181	7·68	1·89	2·86	0·27
1	0	0	6·28	7·29	0·0620	15·32	5·64	7·70	0·32
1	0	2	9·03	8·86	0·2134	10·83	3·41	5·41	0·25
−1	0	2	−8·92	−11·69	0·2237	10·56	3·28	5·23	0·25
1	1	0	−11·29	−10·69	0·1046	14·19	5·06	7·19	0·21
−1	1	0	7·53	9·95	0·1057	14·15	5·04	7·17	0·28
1	1	1	−22·43	−25·97	0·1399	13·07	4·52	6·65	0·12
−1	1	1	13·91	13·87	0·1485	12·80	4·38	6·51	0·18
1	−1	1	−12·10	−13·32	0·1492	12·78	4·37	6·49	0·20
1	1	−1	25·50	28·98	0·1558	12·56	4·26	6·39	0·11
1	1	2	2·74	5·64	0·2241	10·55	3·27	5·23	0·52
−1	1	2	6·56	4·16	0·2343	10·29	3·15	5·06	0·31
1	−1	2	−16·57	−16·49	0·2352	10·27	3·14	5·05	0·15
1	1	−2	5·99	3·53	0·2440	10·06	3·04	4·91	0·33
1	1	3	10·69	10·67	0·3206	8·69	2·35	3·83	0·22
−1	1	3	−16·97	−15·01	0·3313	8·54	2·27	3·70	0·15
1	−1	3	12·74	13·25	0·3322	8·53	2·27	3·69	0·19
1	1	−3	−11·23	−11·67	0·3418	8·41	2·21	3·58	0·21

Table *B*3 (*cont.*)

h	*k*	*l*	F_{obs}	F_{cal}	sin θ/λ	*f*(S)	*f*(C)	*f*(O)	$\sqrt{w}$
1	2	0	−10·34	−10·34	0·1802	11·79	3·87	5·97	0·22
−1	2	0	4·75	6·14	0·1815	11·75	3·85	5·95	0·39
1	2	1	−5·69	−5·95	0·1997	11·22	3·58	5·64	0·35
−1	2	1	14·24	12·87	0·2064	11·02	3·50	5·52	0·17
1	−2	1	−1·11	−1·91	0·2127	10·85	3·41	5·42	0·73
1	2	−1	1·53	2·89	0·2168	10·74	3·36	5·35	0·66
1	2	2	−6·40	−5·54	0·2632	9·65	2·84	4·61	0·32
−1	2	2	−0·65	−0·21	0·2725	9·47	2·74	4·48	0·82
1	−2	2	−18·07	−17·35	0·2820	9·29	2·66	4·34	0·14
1	2	−2	21·76	20·01	0·2890	9·17	2·59	4·24	0·12
1	2	3	15·88	15·81	0·3474	8·35	2·18	3·52	0·16
−1	2	3	−17·36	−15·67	0·3576	8·24	2·12	3·41	0·15
1	−2	3	6·42	6·23	0·3685	8·12	2·07	3·30	0·32
1	2	−3	−10·72	−10·61	0·3769	8·04	2·04	3·22	0·22
1	3	0	−10·83	−9·81	0·2616	9·68	2·85	4·64	0·22
−1	3	0	17·19	16·87	0·2630	9·65	2·84	4·62	0·15
1	3	1	−16·18	−13·73	0·2732	9·45	2·74	4·47	0·16
−1	3	1	14·58	13·98	0·2786	9·35	2·69	4·39	0·17
1	−3	1	−15·73	−14·90	0·2876	9·20	2·61	4·26	0·16
1	3	−1	8·23	7·78	0·2902	9·15	2·58	4·23	0·27
1	3	2	11·90	9·92	0·3207	8·68	2·35	3·83	0·20
−1	3	2	−15·68	−16·99	0·3287	8·58	2·29	3·73	0·16
1	−3	2	−6·82	−6·07	0·3438	8·39	2·20	3·56	0·31
1	3	−2	10·11	9·56	0·3492	8·33	2·17	3·50	0·23
1	3	3	9·63	9·22	0·3911	7·91	1·98	3·09	0·24
−1	3	3	−4·91	−3·68	0·4005	7·83	1·95	3·01	0·38
1	−3	3	1·03	2·75	0·4191	7·68	1·89	2·85	0·74
1	3	−3	−1·25	−3·17	0·4262	7·62	1·87	2·80	0·71
2	0	0	−34·95	−39·55	0·1239	13·58	4·77	6·90	0·08
2	0	2	22·85	24·39	0·2341	10·30	3·15	5·06	0·12
−2	0	2	11·57	13·69	0·2525	9·87	2·95	4·77	0·21
2	1	0	−33·58	−36·57	0·1495	12·77	4·37	6·49	0·08
−2	1	0	−5·63	−5·63	0·1511	12·72	4·34	6·46	0·35
2	1	1	8·94	10·46	0·1728	12·02	3·98	6·10	0·25
−2	1	1	−8·14	−4·64	0·1866	11·60	3·77	5·86	0·27
2	−1	1	−15·20	−16·27	0·1811	11·77	3·85	5·96	0·16
2	1	−1	1·74	0·80	0·1918	11·45	3·70	5·77	0·63
2	1	2	18·43	18·02	0·2436	10·07	3·05	4·91	0·14
−2	1	2	18·57	16·35	0·2623	9·67	2·85	4·63	0·14
2	−1	2	9·31	9·10	0·2544	9·83	2·93	4·75	0·24
2	1	−2	14·24	17·38	0·2705	9·51	2·76	4·50	0·17
2	1	3	−1·37	−3·71	0·3329	8·52	2·26	3·68	0·69
−2	1	3	3·84	2·41	0·3532	8·28	2·15	3·46	0·44
2	−1	3	13·66	14·12	0·3444	8·38	2·20	3·55	0·18
2	1	−3	−3·57	−0·04	0·3627	8·18	2·10	3·36	0·46
2	2	0	−1·09	−3·52	0·2092	10·95	3·46	5·48	0·73
−2	2	0	−11·06	−10·32	0·2115	10·88	3·43	5·44	0·21
2	2	1	1·16	1·51	0·2237	10·56	3·28	5·23	0·72
−2	2	1	2·80	4·88	0·2356	10·26	3·14	5·04	0·52
2	−2	1	−10·94	−10·87	0·2364	10·24	3·13	5·03	0·22
2	2	−1	−19·09	−18·49	0·2437	10·07	3·04	4·91	0·14
2	2	3	3·82	3·43	0·3586	8·23	2·12	3·40	0·44
−2	2	3	−4·14	−5·64	0·3781	8·03	2·03	3·21	0·42
2	−2	3	13·85	12·44	0·3797	8·01	2·02	3·19	0·18
2	2	−3	11·88	11·36	0·3958	7·87	1·96	3·05	0·20
2	3	0	−8·04	−6·83	0·2821	9·29	2·65	4·34	0·27
−2	3	0	−15·82	−15·89	0·2847	9·25	2·63	4·30	0·16
2	3	1	8·23	5·85	0·2910	9·14	2·58	4·21	0·27
−2	3	1	20·25	21·44	0·3010	8·97	2·49	4·08	0·13
2	−3	1	−13·14	−12·23	0·3057	8·90	2·46	4·02	0·19
2	3	−1	−12·11	−10·95	0·3106	8·83	2·42	3·96	0·20
2	3	2	12·39	11·73	0·3343	8·51	2·26	3·67	0·19
−2	3	2	5·03	4·36	0·3495	8·33	2·17	3·50	0·37
2	−3	2	8·68	9·49	0·3575	8·24	2·13	3·41	0·26
2	3	−2	3·06	4·24	0·3679	8·13	2·07	3·31	0·50
2	3	3	−5·64	−5·01	0·4010	7·82	1·95	3·00	0·35
−2	3	3	−8·03	−9·93	0·4191	7·68	1·89	2·85	0·27
2	−3	3	5·12	4·14	0·4292	7·60	1·86	2·78	0·37
2	3	−3	11·57	10·19	0·4429	7·49	1·82	2·68	0·21
3	0	0	−7·98	−9·91	0·1859	11·62	3·78	5·87	0·27

Table *B*3 (*cont.*)

h	*k*	*l*	F_{obs}	F_{cal}	sin θ/λ	*f*(S)	*f*(C)	*f*(O)	$\sqrt{w}$
3	0	2	2·02	3·55	0·2679	9·56	2·79	4·54	0·60
3	0	−2	0·22	2·98	0·2919	9·12	2·57	4·20	0·93
3	1	0	−1·16	−0·62	0·2035	11·11	3·53	5·57	0·72
3	−1	0	−1·70	−1·30	0·2053	11·06	3·51	5·54	0·64
3	1	1	28·07	30·72	0·2187	10·69	3·34	5·32	0·10
−3	1	1	−13·50	−11·71	0·2351	10·27	3·14	5·05	0·18
3	−1	1	1·76	1·31	0·2258	10·50	3·25	5·20	0·63
3	1	−1	−22·64	−24·97	0·2387	10·19	3·10	4·99	0·12
3	1	2	−8·16	−8·67	0·2760	9·40	2·71	4·42	0·27
−3	1	2	−6·42	−4·54	0·3006	8·98	2·50	4·09	0·32
3	−1	2	16·72	16·86	0·2860	9·22	2·62	4·28	0·15
3	1	−2	1·25	5·04	0·3074	8·88	2·44	4·00	0·71
3	1	3	−10·93	−10·24	0·3557	8·26	2·13	3·43	0·22
−3	1	3	15·92	16·33	0·3840	7·97	2·01	3·15	0·16
3	−1	3	−9·25	−8·12	0·3669	8·14	2·08	3·32	0·24
3	1	−3	5·35	6·31	0·3925	7·90	1·98	3·07	0·36
3	2	0	14·38	11·38	0·2504	9·92	2·97	4·81	0·17
3	−2	0	−7·74	−9·64	0·2533	9·86	2·94	4·76	0·28
3	2	1	4·90	7·27	0·2606	9·70	2·86	4·65	0·38
−3	2	1	−14·89	−14·25	0·2758	9·41	2·71	4·43	0·17
3	−2	1	9·25	9·39	0·2724	9·47	2·75	4·48	0·24
3	2	−1	−8·98	−10·85	0·2819	9·29	2·66	4·34	0·25
3	2	2	1·73	0·94	0·3083	8·86	2·44	3·99	0·63
−3	2	2	7·64	9·16	0·3316	8·54	2·27	3·70	0·28
3	−2	2	11·38	9·47	0·3260	8·61	2·31	3·77	0·21
3	2	−2	−14·84	−11·69	0·3439	8·39	2·20	3·56	0·17
3	2	3	−13·99	−10·80	0·3797	8·01	2·02	3·19	0·18
−3	2	3	10·19	8·86	0·4072	7·77	1·93	2·95	0·23
3	−2	3	−3·50	−3·75	0·4003	7·83	1·95	3·01	0·46
3	2	−3	9·96	10·44	0·4230	7·64	1·87	2·82	0·23
3	3	0	8·72	8·29	0·3137	8·78	2·40	3·92	0·26
−3	3	0	−19·57	−19·44	0·3172	8·73	2·37	3·87	0·13
3	3	1	7·60	6·27	0·3200	8·69	2·35	3·84	0·28
−3	3	1	−6·36	−6·44	0·3336	8·51	2·26	3·68	0·32
3	−3	1	13·18	12·95	0·3345	8·50	2·25	3·66	0·19
3	3	−1	−3·06	−3·30	0·3412	8·42	2·21	3·59	0·50
3	3	2	−4·03	−1·60	0·3582	8·23	2·12	3·40	0·43
3	3	2	12·08	14·63	0·3794	8·02	2·02	3·19	0·20
3	−3	2	7·99	7·50	0·3810	8·00	2·02	3·18	0·27
3	3	−2	−13·81	−12·78	0·3955	7·87	1·96	3·05	0·18
3	3	3	−12·40	−10·72	0·4198	7·67	1·88	2·85	0·19
−3	3	3	2·83	0·78	0·4456	7·47	1·81	2·66	0·51
3	−3	3	−3·06	−3·88	0·4476	7·45	1·80	2·65	0·50
3	3	−3	4·07	5·92	0·4673	7·30	1·76	2·52	0·42

Table *B*4. *Interatomic distances* (Å), *angles* (°) *and e.s.d.'s*

Intramolecular distances		Intramolecular angles		Intermolecular distances <4·5	
S–O	1·696 (20)	O–S–C	142·04 (148)	O···C	2·870 (34)
				O···O	3·739 (38)*
S–C	1·894 (32)	S–O–C	20·06 (82)	O···C	3·785 (46)
				S···O	4·116 (26)
C–O	3·396 (33)	S–C–O	17·90 (74)	S···C	4·208 (32)
				O···O	4·436 (35)*
				S···O	4·452 (24)
				S···S	4·468 (31)*

* Indicates that e.s.d. includes a factor of $\sqrt{2}$ since atoms are related.

Table *B*5. *Fourier block round the* S *atom* (*in* 30*th*)

	X=7			*X*=8			*X*=9		
	Z=7	*Z*=8	*Z*=9	*Z*=7	*Z*=8	*Z*=9	*Z*=7	*Z*=8	*Z*=9
Y=0	7·75	6·97	5·18	7·51	6·70	4·92	6·07	5·35	3·86
Y=1	9·49	8·54	6·36	9·23	8·28	6·16	7·50	6·70	4·97
Y=2	9·65	8·66	6·45	9·40	8·45	6·34	7·68	6·90	5·21

Table *B*6. *Sums and discrepancy*

$\sum \lvert F_{obs} \rvert$	1530·04	Number of atoms	3
$\sum \lvert F_{calc} \rvert$	1538·42	Number of parameters	14
$\sum \lvert \Delta F \rvert$	195·16	Number of reflexions	151
R	0·128	$\sum [w(\Delta F)^2]$	52

Table *B*7. *Details of the* 4×4 *block-diagonal matrices*

Atom: S

Original matrix elements ×10⁻²

x	y	z	B	Vector
5403	611	−181	−0·11	1616
	3678	420	1·91	316
		3723	−4·74	−2395
			0·10	3·6

Inverse matrix elements ×10⁸

				Shifts
190	−34	15	1581	0·00265
	286	−43	−7569	0·00113
		293	14781	−0·00638
			10873000	0·0371

Atom: O

Original matrix elements ×10⁻²

x	y	z	B	Vector
999	134	−9	−0·09	214
	616	114	0·240	240
		537	0·321	599
			0·025	−0·90

Atom: C

Original matrix elements ×10⁻²

x	y	z	B	Occupancy	Vector
272	4	−11	0·246	−3·98	−140
	200	15	−0·160	2·15	−114
		159	−0·002	−0·54	−278
			0·011	−0·14	1·21
				2·59	10·2

Table *B*8. *Least-squares shifts and estimated standard deviations* (x, y, z, U ×10⁵)

Method: Full matrix

		x	y	z	B	U	Occupancy
S	Δ	332	54	−553	−0·46	−582	–
	σ	88	114	115	0·51	645	
O	Δ	135	141	950	−0·42	−533	–
	σ	206	262	301	0·67	852	
C	Δ	−750	−550	−407	2·30	2923	0·202
	σ	386	455	555	1·31	1664	0·077

Scale shift = 0·058 σ = 0·050

Method: Blocks of 4×4 for S and O, and 5×5 for C

		x	y	z	B	U	Occupancy
S	Δ	265	113	−638	0·037	47	–
	σ	85	105	106	0·204	258	
O	Δ	198	160	1115	−0·515	−652	–
	σ	199	259	273	0·393	498	
C	Δ	−575	−367	−1644	4·887	6189	0·300
	σ	380	441	493	1·043	1322	0·069

Adjusted B and U shifts for a scale shift of 0·125

S	−0·953	−1207
O	−1·505	−1906
C	3·897	4935

APPENDIX C

Test case $P\,2_1/c$

Table C1. *Crystal data*

Direct cell		Reciprocal cell			
a	8·64 Å	a^*	0·1175 Å^{-1}	$F(000)$	120·0
b	8·00	b^*	0·1250	Scale	1·0
c	6·00	c^*	0·1692	Weights	1·0
α	90·00°	α^*	90·00°	Relaxation factor	1·0
β	100·00	β^*	80·00	Occupancy factors	1·0
γ	90·00	γ^*	90·00	Restricted parameters	none
V	408·42 Å^3	V^*	0·00245 Å^{-3}		

Table C2. *Parameters of the trial structure* (U, β_{ij} *and* $U_{ij} \times 10^5$)

	x	y	z	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	U	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0·165	0·021	0·194	2·7	932	1055	1933	0	233	0
	0·002	0·002	0·001	3420	3420	3420	3420	0	594	0
O	0·390	0·190	0·318	2·5	863	977	1790	0	216	0
	0·002	0·002	0·003	3166	3166	3166	3166	0	550	0
C	0·344	0·100	0·150	3·0	1036	1172	2148	0	259	0
	0·005	0·005	0·006	3800	3800	3800	3800	0	660	0

Table C3. *Structure factor data for the trial structure*

h	k	l	F_{obs}	F_{cal}	$\sin\theta/\lambda$	f(S)	f(C)	f(O)
0	0	2	−50·27	−53·87	0·1692	12·13	4·04	6·16
0	1	1	27·60	23·83	0·1052	14·17	5·05	7·18
0	1	2	2·15	3·92	0·1804	11·79	3·86	5·97
0	1	3	−33·32	−29·43	0·2614	9·69	2·85	4·64
0	2	0	40·05	36·46	0·1250	13·55	4·75	6·88
0	2	1	−39·46	−39·41	0·1509	12·72	4·34	6·47
0	2	2	−16·47	−20·31	0·2104	10·91	3·44	5·46
0	2	3	4·92	4·16	0·2830	9·28	2·65	4·33
0	3	1	18·89	17·76	0·2057	11·04	3·51	5·54
0	3	2	−21·87	−22·33	0·2526	9·87	2·95	4·77
0	3	3	−32·45	−29·94	0·3156	8·76	2·38	3·89
1	0	0	−4·00	−5·09	0·0588	15·38	5·68	7·72
1	0	2	−29·08	−26·91	0·1885	11·54	3·74	5·83
1	0	−2	30·75	22·41	0·1692	12·13	4·04	6·16
1	1	0	−32·31	−34·06	0·0858	14·74	5·34	7·44
1	1	1	−50·38	−49·39	0·1275	13·47	4·72	6·84
1	1	−1	69·88	66·81	0·1131	13·92	4·94	7·06
1	1	2	6·31	4·55	0·1986	11·25	3·60	5·66
1	1	−2	25·03	23·80	0·1804	11·79	3·86	5·97
1	1	3	−5·16	−1·66	0·2775	9·37	2·70	4·40
1	1	−3	−24·51	−27·38	0·2581	9·76	2·89	4·69
1	2	0	30·10	35·85	0·1381	13·13	4·55	6·68
1	2	1	4·05	5·58	0·1672	12·19	4·07	6·19
1	2	−1	−19·11	−19·04	0·1566	12·54	4·24	6·37
1	2	2	−43·87	−48·62	0·2262	10·49	3·25	5·19
1	2	−2	15·47	9·54	0·2104	10·91	3·44	5·46
1	2	3	4·61	6·96	0·2978	9·02	2·52	4·12
1	2	−3	8·70	5·05	0·2799	9·33	2·68	4·37
1	3	0	−21·71	−18·13	0·1965	11·31	3·63	5·69
1	3	1	−13·86	−13·93	0·2179	10·71	3·35	5·33
1	3	−1	17·75	17·99	0·2099	10·93	3·45	5·47
1	3	2	9·32	11·86	0·2659	9·60	2·81	4·57
1	3	−2	5·80	3·18	0·2526	9·87	2·95	4·77
1	3	3	0·41	4·73	0·3290	8·57	2·29	3·73
1	3	−3	−7·74	−13·11	0·3128	8·79	2·40	3·93
2	0	0	−36·99	−27·62	0·1175	13·79	4·87	7·00
2	0	2	−11·91	−12·13	0·2222	10·60	3·30	5·26
2	0	−2	45·70	42·11	0·1885	11·54	3·74	5·83
2	1	0	24·68	27·31	0·1331	13·29	4·63	6·76

Table C3 (*cont.*)

h	k	l	F_{obs}	F_{cal}	$\sin\theta/\lambda$	f(S)	f(C)	f(O)
2	1	1	−30·69	−30·92	0·1683	12·16	4·05	6·17
2	1	−1	2·82	9·72	0·1464	12·87	4·42	6·54
2	1	2	−4·64	−3·27	0·2308	10·38	3·19	5·12
2	1	−2	−22·10	−17·96	0·1986	11·25	3·60	5·66
2	1	3	25·49	26·90	0·3042	8·92	2·47	4·04
2	1	−3	13·28	2·72	0·2680	9·56	2·79	4·54
2	2	0	−27·85	−25·54	0·1716	12·06	4·00	6·12
2	2	1	5·99	3·79	0·2001	11·21	3·58	5·63
2	2	−1	−12·95	−8·86	0·1821	11·74	3·84	5·94
2	2	−2	26·02	22·11	0·2262	10·49	3·25	5·19
2	2	3	8·61	6·62	0·3229	8·65	2·33	3·80
2	2	−3	8·41	8·35	0·2890	9·17	2·59	4·24
2	3	0	−9·30	−10·33	0·2213	10·62	3·31	5·27
2	3	1	−46·87	−45·40	0·2441	10·06	3·04	4·91
2	3	−1	36·41	41·01	0·2295	10·41	3·21	5·14
2	3	2	16·99	14·50	0·2907	9·14	2·58	4·22
2	3	−2	1·20	3·90	0·2659	9·60	2·81	4·57
2	3	3	21·50	18·40	0·3518	8·30	2·16	3·47
2	3	−3	−0·63	−5·38	0·3210	8·68	2·34	3·83
3	0	0	−15·10	−19·02	0·1763	11·91	3·93	6·04
3	0	2	21·08	24·42	0·2647	9·62	2·82	4·59
3	0	−2	1·25	9·57	0·2222	10·60	3·30	5·26
3	1	0	−14·48	−19·25	0·1870	11·59	3·76	5·85
3	1	1	−12·89	−17·04	0·2175	10·72	3·35	5·34
3	1	−1	−9·59	−0·41	0·1923	11·43	3·69	5·77
3	1	2	11·07	11·24	0·2720	9·48	2·75	4·48
3	1	−2	4·82	6·94	0·2308	10·38	3·19	5·12
3	1	3	22·00	19·51	0·3391	8·45	2·23	3·61
3	1	−3	21·91	20·14	0·2896	9·16	2·59	4·23
3	2	0	−34·48	−39·75	0·2161	10·76	3·37	5·36
3	2	1	−1·32	−1·41	0·2430	10·09	3·05	4·92
3	2	−1	12·24	8·39	0·2206	10·64	3·32	5·28
3	2	2	19·09	16·09	0·2928	9·11	2·56	4·19
3	2	−2	28·02	36·04	0·2549	9·82	2·92	4·74
3	2	3	−8·15	−8·28	0·3559	8·25	2·13	3·43
3	2	−3	−6·98	−1·25	0·3092	8·85	2·43	3·97
3	3	0	7·04	3·75	0·2574	9·77	2·90	4·70
3	3	1	2·84	1·45	0·2803	9·32	2·67	4·36
3	3	−1	−20·89	−19·96	0·2612	9·69	2·86	4·64
3	3	2	−3·53	−3·53	0·3244	8·63	2·32	3·78
3	3	−2	−3·24	−0·66	0·2907	9·14	2·58	4·22
3	3	3	11·76	13·52	0·3824	7·99	2·01	3·17
3	3	−3	21·42	19·12	0·3393	8·44	2·23	3·61

Table C4. *Interatomic distances* (Å), *angles* (°) *and e.s.d.'s*

Intramolecular distances		Intramolecular angles		Intermolecular distances < 4·0	
S–O	2·379 (23)	O–S–C	30·44 (140)	O···C	2·688 (42)
				O···O ×2	3·150 (35)* [10]†
S–C	1·733 (46)	S–O–C	44·78 (195)	S···S	3·370 (28)* [26]
				C···C	3·841 (83)* [87]
O–C	1·246 (41)	S–C–O	104·78 (267)	C···C ×2	3·842 (75)* [50]
				S···O	3·967 (22)
				O···C	3·990 (44)

* Indicates that e.s.d. includes a factor of $\sqrt{2}$ since atoms are related.
† [ ] are e.s.d.'s calculated with proper covariance terms for symmetry-related atoms.

Table C5. *Fourier block round the* S *atom* (*in* 30*th*)

	$X=4$			$X=5$			$X=6$		
	$Z=4$	$Z=5$	$Z=6$	$Z=4$	$Z=5$	$Z=6$	$Z=4$	$Z=5$	$Z=6$
$Y=0$	5·55	6·50	6·49	6·29	7·41	7·40	6·15	7·24	7·24
$Y=1$	5·56	6·50	6·48	6·40	7·49	7·46	6·41	7·48	7·44
$Y=2$	4·73	5·48	5·45	5·54	6·42	6·35	5·71	6·57	6·49

Table C6. *Sums and discrepancy*

$\sum \lvert F_{obs} \rvert$	1523·57	Number of atoms	3
$\sum \lvert F_{calc} \rvert$	1492·62	Number of parameters	28
$\sum \lvert \Delta F \rvert$	248·62	Number of reflexions	82
R	0·163	$\sum_i [w(\Delta F)^2]$	1196

Table C7. *Details of the 9×9 block diagonal least-squares matrices*

Atom: S

Original matrix elements $\times 10^{-2}$

x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Vector $\times 10^{-1}$
44933	−256	−4678	−510	−52	−465	248	329	389	4460
	38590	96	246	626	544	−429	21	−304	600
		37045	164	243	298	389	−930	−441	−4012
			8392	3366	3718	95	−1029	−103	486
				6765	3187	75	−213	−44	80
					6112	123	−703	−108	50
						14428	−207	−1136	510
							14872	245	−282
								11108	−207

Inverse matrix elements $\times 10^{9}$

									Shifts
226	1	28	11	−12	15	−5	−2	−7	0·00899
	260	0	8	−20	−18	8	−1	8	0·00167
		274	5	−8	−8	−7	16	9	−0·00982
			1754	−494	−801	−1	76	5	0·00783
				2101	−799	−2	−42	−4	−0·00135
					2550	−11	52	10	−0·00259
						699	8	71	0·00348
							681	−12	−0·00223
								909	−0·00208

Atom: O

Original matrix elements $\times 10^{-2}$

x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Vector
11710	−87	−928	136	11	49	−247	−137	31	−8335
	9674	−88	138	103	413	−9	42	−189	−7345
		8553	−69	100	15	31	98	−796	−5705
			1820	819	693	13	−353	19	28
				1618	657	17	−144	17	1229
					1100	17	−233	16	−888
						2957	37	−259	3007
							2773	34	2578
								2433	356

Atom: C

Original matrix elements $\times 10^{-2}$

x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Vector
4524	5	−389	18	−2	−9	21	−1	1	−12828
	3784	2	−24	−22	−53	−12	−17	2	−4615
		3389	0	4	1	1	−17	74	5447
			720	290	270	−2	−102	1	−526
				564	225	0	−64	−2	−176
					462	−2	−93	2	−277
						1168	2	−95	2528
							1080	−3	206
								956	137

Table C8. *Least-squares shifts and estimated standard deviations (all values* $\times 10^5$)

Method: Full matrix

		x	y	z	β_{11} / U_{11}	β_{22} / U_{22}	β_{33} / U_{33}	β_{12} / U_{12}	β_{13} / U_{13}	β_{23} / U_{23}
S	Δ	488	61	−921	−107	−90	−236	−26	−17	−20
	σ	363	291	273	1211	824	869	565	549	497
	Δ				−382	−290	−415	−90	−43	−46
	σ				4444	2673	1538	1948	1398	1190
O	Δ	−655	−731	−1294	−72	−296	525	507	488	−20
	σ	568	711	855	1640	2117	3585	1018	1356	1392
	Δ				−259	−948	937	1748	1241	−50
	σ				6013	6868	6335	3511	3455	3334
C	Δ	−2006	−1378	−14	235	3	−150	421	30	−400
	σ	1236	1314	1396	3688	3669	5478	2472	2566	2196
	Δ				856	30	−258	1445	77	−957
	σ				13533	11904	9694	8523	6542	5268

Scale shift = 0·036 σ = 0·050

Method: Blocks of 9 × 9 per atom

		x	y	z	β_{11} / U_{11}	β_{22} / U_{22}	β_{33} / U_{33}	β_{12} / U_{12}	β_{13} / U_{13}	β_{23} / U_{23}
S	Δ	899	167	−982	783	−135	−259	348	−223	−208
	σ	224	240	246	623	682	752	394	388	449
	Δ				2872	−437	−459	1199	−569	−497
	σ				2287	2212	1329	1358	989	1075
O	Δ	−747	−743	−789	108	1359	−1186	941	906	−75
	σ	438	484	520	1341	1417	1749	871	908	975
	Δ				398	4405	−2099	3246	2307	−180
	σ				4920	4595	3094	3003	2314	2335
C	Δ	−2732	−1219	1288	−536	113	−508	2221	99	272
	σ	703	766	813	2095	2326	2601	1383	1448	1530
	Δ				−1967	365	−899	7660	251	652
	σ				7685	7543	4601	4769	3688	3664

Adjusted β_{ij} and U_{ij} shifts for a scale shift of −0·0132

S	$(\Delta\beta)'$				861	−47	−98	348	−204	−208
	$(\Delta U)'$				3157	−151	−173	1200	−519	−497
O	$(\Delta\beta)'$				186	1447	−1025	941	925	−75
	$(\Delta U)'$				683	4691	−1813	3246	2357	−180
C	$(\Delta\beta)'$				−459	201	−347	2221	118	272
	$(\Delta U)'$				−1682	651	−614	7660	301	652

Method: Blocks of 3 × 3 and 6 × 6 per atom

		x	y	z	β_{11} / U_{11}	β_{22} / U_{22}	β_{33} / U_{33}	β_{12} / U_{12}	β_{13} / U_{13}	β_{23} / U_{23}
S	Δ	893	164	−971	750	−100	−349	339	−149	−145
	σ	224	240	246	623	682	751	394	388	449
	Δ				2750	−323	−617	1168	−379	−348
	σ				2286	2211	1329	1357	989	1074
O	Δ	−777	−773	−759	147	1383	−1561	1028	873	243
	σ	437	479	511	1340	1415	1734	870	908	959
	Δ				541	4485	−2761	3544	2224	581
	σ				4915	4589	3067	3000	2312	2297
C	Δ	−2722	−1216	1295	−673	148	−251	2193	111	364
	σ	703	765	813	2095	2326	2599	1383	1448	1529
	Δ				−2470	480	−443	7563	281	871
	σ				7684	7543	4597	4769	3687	3661

Adjusted β_{ij} and U_{ij} shifts for a scale shift of −0·0132

S	$(\Delta\beta)'$				827	−12	−188	339	−129	−145
	$(\Delta U)'$				3035	−38	−332	1168	−330	−348
O	$(\Delta\beta)'$				225	1471	−1400	1028	893	243
	$(\Delta U)'$				826	4770	−2476	3544	2274	581
C	$(\Delta\beta)'$				−596	236	−89	2193	130	364
	$(\Delta U)'$				−2184	765	−158	7563	331	871

APPENDIX *D*

Test case $Pmn2_1$

Table *D*1. *Crystal data*

Direct cell		Reciprocal cell			
a	9·00 Å	a^*	0·1111 Å^{-1}	$F(000)$	120·0
b	11·70	b^*	0·0855	Scale	1·0
c	4·00	c^*	0·2500	Weights	1·0
α	90·00°	α^*	90·00°	Relaxation factor	1·0
β	90·00	β^*	90·00	Occupancy factors	1·0
γ	90·00	γ^*	90·00	Restricted parameters	z(S)
V	421·20 Å^3	V^*	0·00237 Å^{-3}		

Table *D*2. *Parameters of the trial structure*

	x	y	z	B	$U\times 10^5$
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$		
S	0·2640	0·2320	0·0	2·0	2533
	0·0005	0·0005	0·0		
O	0·3220	0·0940	−0·0750	2·8	3546
	0·0008	0·0010	0·0007		
C	0·2000	0·3780	0·0740	3·2	4053
	0·0010	0·0014	0·0012		

Table *D*3. *Structure factor data for the trial structure*

h	k	l	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	f(S)	f(C)	f(O)
0	0	2	51·83	50·65	50·38	−5·27	0·2500	9·93	2·98	4·81
0	0	8	1·50	1·51	1·50	0·10	1·0000	3·56	1·11	1·37
0	1	1	69·07	74·83	1·06	74·82	0·1321	13·32	4·64	6·77
0	1	2	17·65	17·87	7·55	−16·20	0·2536	9·85	2·94	4·76
0	1	3	24·67	25·42	1·22	25·39	0·3774	8·03	2·03	3·21
0	2	0	41·76	44·82	−44·82	0·00	0·0855	14·75	5·35	7·44
0	2	1	22·90	23·94	17·39	16·46	0·1514	12·70	4·33	6·46
0	2	2	26·43	29·39	−29·07	−4·37	0·2642	9·63	2·83	4·60
0	2	3	14·85	13·72	12·51	5·65	0·3846	7·97	2·00	3·15
0	3	1	11·12	14·29	5·05	−13·37	0·1791	11·83	3·88	5·99
0	3	2	10·41	11·15	−8·93	6·68	0·2810	9·31	2·67	4·35
0	3	3	21·36	20·26	4·10	−19·84	0·3963	7·86	1·96	3·04
0	30	0	0·40	0·36	0·36	0·00	1·2821	2·39	0·84	1·16
0	31	0	0·10	0·12	0·12	0·00	1·3248	2·28	0·80	1·12
1	1	0	7·51	7·87	0·00	−7·87	0·0701	15·14	5·55	7·62
1	1	1	12·47	12·12	−11·87	2·43	0·1433	12·96	4·47	6·59
1	1	2	5·68	6·12	−4·63	−3·99	0·2596	9·72	2·87	4·67
1	1	3	2·19	2·13	−0·91	1·92	0·3815	8·00	2·02	3·17
1	2	0	17·30	18·54	0·00	−18·54	0·1019	14·27	5·10	7·22
1	2	1	1·83	1·98	0·73	1·84	0·1613	12·38	4·17	6·29
1	2	2	6·43	6·34	−2·64	−5·77	0·2700	9·52	2·77	4·51
1	2	3	2·37	2·28	1·81	1·39	0·3886	7·93	1·99	3·11
1	3	0	3·18	2·70	0·00	−2·70	0·1397	13·08	4·52	6·65
1	3	1	4·71	5·40	5·38	0·40	0·1875	11·57	3·76	5·85
1	3	2	6·56	6·21	−6·20	0·28	0·2864	9·22	2·62	4·28
1	3	3	0·98	0·98	0·94	0·28	0·4002	7·83	1·95	3·01
2	0	0	84·31	86·11	−86·11	0·00	0·1111	13·99	4·97	7·09
2	0	2	42·40	41·48	−41·45	1·65	0·2736	9·45	2·73	4·46
2	1	0	9·15	8·90	−8·90	0·00	0·1190	13·74	4·85	6·97
2	1	1	55·75	58·48	0·14	−58·48	0·1726	12·03	3·98	6·10
2	1	2	9·92	11·03	−4·93	9·86	0·2769	9·39	2·70	4·41
2	1	3	20·98	23·55	−0·05	−23·54	0·3934	7·89	1·97	3·07
2	2	0	37·78	41·79	41·79	0·00	0·1402	13·06	4·52	6·64
2	2	1	13·68	14·82	−10·35	−10·61	0·1878	11·56	3·75	5·84
2	2	3	8·81	9·50	−8·05	−5·04	0·4003	7·83	1·95	3·01
2	3	0	8·83	9·88	9·88	−0·00	0·1697	12·12	4·03	6·15
2	3	1	18·21	20·33	−2·06	20·22	0·2107	10·90	3·44	5·45

Table *D3* (*cont.*)

h	*k*	*l*	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	*f*(S)	*f*(C)	*f*(O)
2	3	2	8·73	9·43	8·30	−4·46	0·3021	8·96	2·48	4·07
2	3	3	21·96	19·39	−1·70	19·31	0·4116	7·74	1·91	2·91
3	1	0	15·16	15·86	−0·00	15·86	0·1721	12·04	3·99	6·11
3	1	1	21·24	21·50	21·13	−3·95	0·2127	10·85	3·42	5·42
3	1	2	12·52	12·77	8·82	9·23	0·3035	8·94	2·47	4·05
3	1	3	3·34	3·82	2·02	−3·25	0·4126	7·73	1·91	2·91
3	2	0	34·05	32·57	0·00	32·57	0·1873	11·58	3·76	5·85
3	2	1	4·74	5·11	−3·98	−3·20	0·2252	10·52	3·26	5·21
3	2	2	12·48	12·20	4·19	11·46	0·3124	8·80	2·41	3·93
3	2	3	5·63	5·77	−5·11	−2·69	0·4192	7·68	1·89	2·85
3	3	0	5·14	1·42	0·00	1·42	0·2103	10·92	3·45	5·46
3	3	1	9·70	10·85	−10·80	−0·95	0·2446	10·05	3·03	4·90
3	3	2	12·07	12·16	11·80	−2·93	0·3267	8·60	2·30	3·76
3	3	3	2·41	2·57	−2·41	−0·90	0·4299	7·59	1·85	2·77
5	6	4	3·58	3·81	−0·92	−3·69	0·6268	6·11	1·51	1·87
6	5	4	5·32	5·01	−4·41	2·38	0·6378	6·03	1·49	1·85
6	8	4	4·70	4·74	−4·73	0·34	0·6914	5·63	1·44	1·73
6	8	5	4·00	4·63	−0·75	4·57	0·7865	4·92	1·34	1·58
6	9	4	5·90	6·07	−5·98	−1·07	0·7135	5·46	1·41	1·69
6	9	5	1·80	2·01	−0·62	−1·91	0·8060	4·78	1·32	1·56
7	8	4	3·20	3·46	0·16	−3·46	0·7198	5·41	1·41	1·68
7	8	5	2·10	2·19	2·16	−0·37	0·8116	4·74	1·31	1·55
7	9	4	2·10	2·29	0·46	2·24	0·7411	5·25	1·38	1·65
7	9	5	2·10	2·05	2·03	0·28	0·8305	4·61	1·29	1·53
7	9	6	1·00	0·98	0·05	0·98	0·9283	3·97	1·19	1·44
7	10	5	1·00	0·97	−0·97	−0·04	0·8512	4·47	1·27	1·51
7	10	6	1·00	1·14	−0·07	1·14	0·9468	3·86	1·17	1·42
8	9	5	1·50	1·49	0·56	1·38	0·8580	4·42	1·26	1·50
8	9	6	1·50	1·67	1·67	0·13	0·9529	3·82	1·16	1·41
8	10	5	2·00	2·15	−0·09	2·15	0·8779	4·29	1·24	1·48
8	10	6	0·40	0·40	−0·39	0·09	0·9709	3·72	1·14	1·40
8	10	7	0·80	0·74	−0·00	0·74	1·0704	3·20	1·04	1·32
8	11	6	0·80	1·09	−1·09	0·07	0·9905	3·61	1·12	1·38
8	11	7	0·10	0·19	−0·00	−0·19	1·0882	3·12	1·02	1·30
9	10	6	1·10	1·11	−0·01	−1·11	0·9976	3·57	1·12	1·38
9	10	7	0·05	0·20	0·20	0·02	1·0946	3·09	1·02	1·30
9	11	6	0·30	0·31	0·00	0·31	1·0166	3·47	1·10	1·36
9	11	7	0·50	0·55	0·55	0·02	1·1120	3·02	1·00	1·29
9	11	8	0·10	0·11	−0·00	0·11	1·2128	2·61	0·90	1·21
9	12	7	0·20	0·20	−0·20	0·01	1·1308	2·94	0·98	1·27
9	12	8	0·30	0·31	−0·02	0·31	1·2300	2·55	0·89	1·20
10	11	7	0·10	0·12	0·01	0·12	1·1381	2·91	0·97	1·27
10	11	8	0·30	0·27	0·27	−0·00	1·2368	2·53	0·88	1·19
10	12	7	0·50	0·48	−0·00	0·48	1·1564	2·83	0·96	1·25
10	12	8	0·05	0·05	−0·05	0·02	1·2536	2·48	0·86	1·18
24	0	0	0·10	0·13	−0·13	0·00	1·3333	2·26	0·79	1·12

Table *D4*. *Interatomic distances* (Å), *angles* (°) *and e.s.d.'s*

Intramolecular distances		Intramolecular angles		Intermolecular distances <4·0	
S–O	1·723 (13)	O–S–C	179·00 (52)	O···O	3·204 (14)*
S–C	1·827 (17)	S–O–C	0·51 (27)	O···O ×2	3·243 (17)*
O–C	3·550 (19)	S–C–O	0·48 (25)	C···C	3·600 (18)*
				C···C ×2	3·600 (27)*

* Indicates that e.s.d. includes a factor of 1/2 since the atoms are related.

Table *D5*. *Fourier block round the* S *atom* (*in* 30*th*)

	X=7			*X*=8			*X*=9		
	Z=−1	*Z*=0	*Z*=1	*Z*=−1	*Z*=0	*Z*=1	*Z*=−1	*Z*=0	*Z*=1
Y=6	4·90	5·05	4·50	5·62	5·77	5·23	5·68	5·86	5·31
Y=7	5·15	5·50	5·04	5·73	6·31	5·69	5·30	5·69	5·35
Y=8	4·63	5·01	4·81	4·68	5·07	4·94	4·33	4·89	4·71

Table *D6. Sums and discrepancy*

$\sum \lvert F_{obs} \rvert$	912·74	Number of atoms	3
$\sum \lvert F_{calc} \rvert$	943·19	Number of parameters	12
$\sum \lvert \Delta F \rvert$	59·72	Number of reflexions	83
R	0·065	$\sum [w(\Delta F)^2]$	140

Table *D7. Details of the* 4×4 *block diagonal least-squares matrices*

Atom: S

Original matrix elements $\times 10^{-2}$ | Vector

x	y	B	
23833	−164	−3·65	−2893
	22477	−4·20	−288
		1·29	32

Inverse matrix elements $\times 10^{10}$ | Shifts

4198	33	11958	−0·00118
	4452	14563	−0·00010
		77462000	0·243

Atom: O

Original matrix elements $\times 10^{-2}$ | Vector

x	y	z	B	
3283	237	−82	0·031	619
	4976	38	−1·688	−4557
		1265	−2·880	119
			0·101	−3·9

Atom: C

Original matrix elements $\times 10^{-2}$ | Vector

x	y	z	B	
1422	−61	−23	0·997	75
	2495	49	−0·778	2390
		817	0·276	65
			0·026	0·6

Table *D8. Least-squares shifts and estimated standard deviations* (x, y, z, $U \times 10^5$)

Method: Full matrix

		x	y	z	B	U
S	Δ	−133	51	0	−0·112	−141
	σ	116	167	0	0·147	186
O	Δ	20	−290	−63	−1·371	−1734
	σ	299	344	638	0·663	843
C	Δ	77	452	−153	−0·259	−322
	σ	439	438	776	1·178	1487

Scale shift $= 0{\cdot}0405$ $\sigma = 0{\cdot}0134$

Method: Blocks of 4×4 per atom

		x	y	z	B	U
S	Δ	−118	−10	0	0·243	308
	σ	91	94	0	0·123	156
O	Δ	258	−946	16	−0·543	−688
	σ	245	200	408	0·458	580
C	Δ	60	972	7	0·494	625
	σ	377	282	492	0·890	1127

Adjusted B and U shifts for a scale shift of 0·048

S	−0·164	−207
O	−0·950	−1204
C	0·086	109

APPENDIX *E*

Test case $P6_122$

Table *E*1. *Crystal data*

	Direct cell		Reciprocal cell		
a	8·53 Å	a^*	0·1354 Å^{-1}	$F(000)$	216·0
b	8·53	b^*	0·1354	Scale	1·0
c	20·37	c^*	0·0491	Weights	as listed
α	90·00°	α^*	90·00°	Relaxation factor	1·0
β	90·00	β^*	90·00	Occupancy factors	1·0
γ	120·00	γ^*	60·00	Restricted parameters	$\{y, z, \beta_{22}, \beta_{23}$(S) $\{y, z, \beta_{22}, \beta_{23}$(O)
V	1283·57 Å^3	V^*	0·000779 Å^{-3}		

Table *E*2. *Parameters of the trial structure* (U, β_{ij} *and* $U_{ij} \times 10^5$)

		x	y	z	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					U	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S*	in 6(*b*)	0·202	0·798	0·91667	2·0	916	916	121	458	0	0
					2533	2533	2533	2533	1267	0	0
O	in 6(*a*)	0·498	0·498	0·66667	2·0	916	916	121	458	0	0
					2533	2533	2533	2533	1267	0	0
C	in 12(*c*)	0·488	0·096	0·038	2·5	(to be refined isotropically)					
					3166						

* Results are presented for the two following cases: (*a*) excluding, and (*b*) including the anomalous dispersion components $\Delta f'$ and $\Delta f''$ of atom S.

Table *E*3. *Structure factor data for the trial structure*

* Indicates unobserved reflexion

h	k	l	F_{obs}	F_{cal}	A_{cal}	B_{cal}	$\sin\theta/\lambda$	f(S)	f(C)	f(O)	$\sqrt{w}$
0	0	6	39·40	29·36	−29·36	0·00	0·1473	12·84	4·40	6·53	3·51
0	0	12	48·44	43·14	43·14	−0·00	0·2946	9·08	2·55	4·17	2·38
0	1	0	43·20	43·04	−43·04	0·00	0·0677	15·19	5·58	7·64	5·27
0	1	1	57·36	59·55	−59·55	0·00	0·0720	15·10	5·52	7·60	5·27
0	1	2	76·96	96·07	96·07	−0·00	0·0836	14·80	5·37	7·46	4·83
0	1	3	53·04	52·41	−52·41	−0·00	0·1000	14·33	5·13	7·25	4·30
0	1	4	9·88	12·77	12·77	0·00	0·1193	13·73	4·84	6·97	2·62
0	1	5	44·88	39·31	−39·31	−0·00	0·1402	13·06	4·52	6·64	3·70
*0	1	6	7·48	8·57	−8·57	0·00	0·1621	12·36	4·15	6·28	
0	1	7	34·56	30·20	30·20	0·00	0·1847	11·66	3·80	5·89	2·98
0	1	8	14·40	7·29	−7·29	0·01	0·2077	10·99	3·48	5·50	2·67
0	1	9	17·96	14·56	14·56	0·00	0·2310	10·37	3·19	5·11	2·50
0	1	10	20·40	22·32	22·32	0·01	0·2546	9·83	2·93	4·74	2·23
0	1	11	22·24	18·26	18·26	0·01	0·2784	9·36	2·69	4·39	2·21
*0	1	12	6·68	2·95	−2·95	−0·00	0·3022	8·95	2·48	4·06	
0	2	0	35·64	33·28	33·28	0·00	0·1354	13·22	4·59	6·72	3·81
0	2	1	21·64	19·69	19·69	0·00	0·1376	13·15	4·56	6·68	3·37
0	2	2	39·36	38·17	−38·17	−0·00	0·1440	12·94	4·45	6·58	3·37
0	2	3	54·12	50·91	−50·91	0·00	0·1541	12·62	4·29	6·41	3·38
0	2	4	36·00	33·41	33·41	−0·00	0·1672	12·20	4·07	6·19	3·05
0	2	5	13·28	14·18	−14·18	−0·00	0·1827	11·72	3·83	5·93	2·28
0	2	6	60·28	60·68	60·68	0·00	0·2000	11·21	3·58	5·63	2·88
0	2	7	26·76	24·59	−24·59	0·00	0·2187	10·69	3·34	5·32	2·48
0	2	8	19·68	15·51	15·51	0·00	0·2385	10·19	3·10	4·99	2·62
0	2	9	40·08	34·34	34·34	0·00	0·2591	9·73	2·88	4·67	2·40
0	2	10	16·84	13·20	−13·20	−0·00	0·2803	9·32	2·67	4·36	2·21
0	2	11	8·40	3·71	−3·71	−0·00	0·3020	8·96	2·49	4·07	2·58
0	3	0	52·48	47·37	−47·37	0·00	0·2031	11·12	3·54	5·58	3·05
0	3	1	24·48	20·39	−20·39	−0·00	0·2045	11·08	3·52	5·56	2·91
0	3	2	7·68	6·88	6·88	−0·00	0·2089	10·95	3·46	5·48	2·52
0	3	3	33·76	30·33	30·33	0·00	0·2160	10·76	3·37	5·36	2·70
0	3	4	28·00	26·84	26·84	0·00	0·2255	10·51	3·26	5·20	2·71

Table *E*3 (*cont*).

h	*k*	*l*	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	*f*(S)	*f*(C)	*f*(O)	$\sqrt{w}$
0	3	5	11·20	9·60	−9·60	−0·00	0·2373	10·22	3·12	5·01	2·15
0	3	6	20·28	13·84	13·84	0·00	0·2508	9·91	2·97	4·80	2·67
*0	3	7	6·56	1·35	1·35	0·00	0·2660	9·59	2·81	4·57	
0	3	8	41·93	40·98	40·98	0·00	0·2825	9·28	2·65	4·33	2·19
0	3	9	53·32	44·12	−44·12	0·00	0·3001	8·99	2·50	4·09	2·31
0	4	0	10·56	16·31	16·31	0·00	0·2707	9·50	2·76	4·50	1·72
0	4	1	28·08	29·40	29·40	−0·00	0·2718	9·48	2·75	4·48	1·99
0	4	2	10·88	5·03	5·03	0·00	0·2752	9·42	2·72	4·44	2·94
0	4	3	19·72	15·99	15·99	−0·00	0·2806	9·32	2·67	4·36	2·48
0	4	4	9·88	9·74	−9·74	0·00	0·2880	9·19	2·60	4·26	1·79
0	4	5	17·20	17·53	17·53	−0·00	0·2973	9·03	2·52	4·13	1·86
0	4	6	17·32	19·51	19·51	0·00	0·3082	8·86	2·44	3·99	2·13
1	1	0	40·08	36·91	−36·91	0·00	0·1172	13·79	4·87	7·00	3·98
1	1	1	44·48	42·22	36·57	−21·11	0·1198	13·71	4·83	6·96	3·99
*1	1	2	6·40	3·29	1·64	−2·85	0·1271	13·48	4·72	6·85	
1	1	3	17·60	14·24	0·00	14·24	0·1384	13·12	4·54	6·67	3·53
1	1	4	81·44	86·58	−43·29	−74·98	0·1529	12·65	4·31	6·43	3·37
*1	1	6	6·52	0·66	0·66	0·00	0·1882	11·55	3·75	5·83	
*1	1	7	7·36	6·53	−5·66	3·26	0·2080	10·98	3·48	5·50	
1	1	8	42·20	41·88	−20·95	36·27	0·2287	10·43	3·22	5·15	2·70
*1	1	9	8·44	6·76	0·00	−6·76	0·2501	9·93	2·97	4·81	
1	1	10	28·28	19·29	9·64	16·70	0·2720	9·48	2·75	4·48	2·11
1	1	11	11·92	7·87	−6·82	−3·93	0·2944	9·08	2·55	4·17	2·02
1	2	0	27·84	22·47	22·47	0·00	0·1791	11·83	3·88	5·99	3·15
1	2	1	29·28	27·11	−6·72	−26·27	0·1808	11·78	3·86	5·96	2·88
1	2	2	39·36	36·73	−27·41	−24·44	0·1857	11·63	3·78	5·88	3·04
1	2	3	19·48	17·36	13·90	−10·40	0·1936	11·39	3·67	5·74	2·75
1	2	4	24·32	24·87	6·90	23·90	0·2042	11·09	3·52	5·56	2·55
1	2	5	33·28	27·50	8·06	26·29	0·2171	10·73	3·36	5·34	2·80
1	2	6	46·08	42·56	−40·17	−14·05	0·2319	10·35	3·18	5·10	2·55
1	2	7	42·44	36·05	8·57	35·02	0·2482	9·97	3·00	4·84	2·53
*1	2	8	9·00	12·03	0·34	−12·03	0·2658	9·60	2·81	4·57	
1	2	9	12·96	11·42	10·03	5·47	0·2844	9·25	2·63	4·31	2·05
1	2	10	16·12	17·06	−15·05	8·04	0·3038	8·93	2·47	4·04	2·01
1	3	0	15·96	15·64	−15·64	0·00	0·2440	10·06	3·04	4·91	2·23
1	3	1	17·88	15·91	−5·70	−14·85	0·2453	10·04	3·03	4·89	2·22
1	3	2	43·32	40·57	13·69	38·19	0·2489	9·95	2·99	4·83	2·41
1	3	3	7·28	4·38	0·67	4·33	0·2549	9·82	2·92	4·74	0·00
1	3	4	20·52	23·97	−23·62	4·06	0·2631	9·65	2·84	4·61	2·04
1	3	5	11·56	11·28	−7·26	8·63	0·2732	9·46	2·74	4·47	2·20
1	3	6	13·68	10·59	4·01	9·80	0·2850	9·24	2·63	4·30	2·17
1	3	7	24·64	20·28	19·85	4·12	0·2985	9·01	2·51	4·11	2·16
1	3	8	32·80	27·17	−19·19	−19·24	0·3132	8·79	2·40	3·92	1·95
*1	4	0	6·72	0·72	−0·72	0·00	0·3102	8·83	2·42	3·96	
1	4	1	20·04	19·04	5·89	18·10	0·3111	8·82	2·41	3·95	1·86
1	4	2	14·68	13·09	−11·98	5·27	0·3140	8·78	2·39	3·91	2·17
2	2	0	48·00	51·22	51·22	0·00	0·2345	10·29	3·15	5·06	2·43
2	2	1	27·68	25·87	−22·40	12·94	0·2357	10·26	3·14	5·04	2·63
*2	2	2	7·68	5·94	2·97	−5·15	0·2396	10·17	3·09	4·98	
2	2	3	12·64	10·36	−0·00	10·36	0·2458	10·02	3·02	4·88	2·36
2	2	4	7·72	5·17	−2·58	−4·48	0·2542	9·84	2·93	4·75	2·32
2	2	5	47·48	41·27	−35·74	−20·64	0·2646	9·62	2·82	4·59	2·36
2	2	6	10·40	1·37	−1·37	0·00	0·2769	9·39	2·70	4·41	2·51
2	2	7	15·60	14·56	12·61	−7·28	0·2907	9·14	2·58	4·22	2·14
2	2	8	16·64	19·10	−9·55	16·54	0·3058	8·90	2·46	4·02	1·69
2	3	0	27·08	27·13	−27·13	0·00	0·2950	9·07	2·54	4·16	2·12
*2	3	1	8·08	5·11	−4·14	3·00	0·2960	9·05	2·53	4·15	
2	3	2	22·92	23·01	18·41	−13·81	0·2991	9·00	2·51	4·11	2·31
2	3	3	40·36	35·90	−35·59	−4·76	0·3041	8·93	2·47	4·04	2·19
2	3	4	16·92	13·86	−2·95	−13·54	0·3109	8·82	2·42	3·95	1·91

Table *E*3 (*cont*).

With anomalous dispersion

h	*k*	*l*	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	*f*(S)†	*f*(C)	*f*(O)	$\sqrt{w}$
0	0	6	39·40	31·76	−31·38	−4·94	0·1473	13·19	4·40	6·53	3·51
0	0	12	48·44	45·12	44·91	4·34	0·2946	9·43	2·55	4·17	2·38
0	1	0	43·20	43·20	−43·20	−0·39	0·0677	15·54	5·58	7·64	5·27
0	1	1	57·36	60·66	−60·60	−2·59	0·0720	15·45	5·52	7·60	5·27
0	1	2	76·96	96·86	96·84	1·90	0·0836	15·15	5·37	7·46	4·83
0	1	3	53·04	53·38	−53·33	−2·26	0·1000	14·68	5·13	7·25	4·30
0	1	4	9·88	12·15	12·01	−1·87	0·1193	14·08	4·84	6·97	2·62
0	1	5	44·88	40·41	−40·33	−2·52	0·1402	13·41	4·52	6·64	3·70
*0	1	6	7·48	8·42	−8·42	0·37	0·1621	12·71	4·15	6·28	
0	1	7	34·56	31·29	31·20	2·45	0·1847	12·01	3·80	5·89	2·98
0	1	8	14·40	8·20	−8·01	−1·76	0·2077	11·34	3·48	5·50	2·67
0	1	9	17·96	15·54	15·40	2·08	0·2310	10·72	3·19	5·11	2·50
0	1	10	20·40	24·07	23·01	1·70	0·2546	10·18	2·93	4·74	2·23
0	1	11	22·24	19·31	19·18	2·25	0·2784	9·71	2·69	4·39	2·21
*0	1	12	6·68	3·10	−3·09	−0·33	0·3022	9·30	2·48	4·06	
0	2	0	35·64	32·48	32·41	−2·14	0·1354	13·57	4·59	6·72	3·81
0	2	1	21·64	19·95	19·94	0·61	0·1376	13·50	4·56	6·68	3·37
0	2	2	39·36	39·01	−38·96	−1·95	0·1440	13·29	4·45	6·58	3·37
0	2	3	54·12	52·41	−52·30	−3·39	0·1541	12·97	4·29	6·41	3·38
0	2	4	36·00	34·24	34·19	1·92	0·1672	12·55	4·07	6·19	3·05
0	2	5	13·28	13·95	−13·94	0·59	0·1827	12·07	3·83	5·93	2·28
0	2	6	60·28	61·55	61·52	2·05	0·2000	11·56	3·58	5·63	2·88
0	2	7	26·76	24·83	−24·82	−0·57	0·2187	11·04	3·34	5·32	2·48
0	2	8	19·68	16·34	16·24	1·82	0·2385	10·54	3·10	4·99	2·62
0	2	9	40·08	35·74	35·61	3·11	0·2591	10·08	2·88	4·67	2·40
0	2	10	16·84	14·02	−13·91	−1·74	0·2803	9·67	2·67	4·36	2·21
0	2	11	8·40	3·96	−3·93	−0·53	0·3020	9·31	2·49	4·07	2·58
0	3	0	52·48	48·28	−48·23	−2·12	0·2031	11·47	3·54	5·58	3·05
0	3	1	24·48	20·63	−20·62	−0·56	0·2045	11·43	3·52	5·56	2·91
0	3	2	7·68	6·43	6·23	−1·61	0·2089	11·30	3·46	5·48	2·52
0	3	3	33·76	31·92	31·73	3·46	0·2160	11·11	3·37	5·36	2·70
0	3	4	28·00	27·53	27·49	1·59	0·2255	10·86	3·26	5·20	2·71
0	3	5	11·20	9·84	−9·82	−0·54	0·2373	10·57	3·12	5·01	2·15
0	3	6	20·28	14·80	14·66	2·03	0·2508	10·26	2·97	4·80	2·67
*0	3	7	6·56	1·66	1·57	0·53	0·2660	9·94	2·81	4·57	
0	3	8	41·93	41·62	41·59	1·50	0·2825	9·63	2·65	4·33	2·19
0	3	9	53·32	45·52	−45·41	−3·17	0·3001	9·34	2·50	4·09	2·31
0	4	0	10·56	16·29	16·29	−0·05	0·2707	9·85	2·76	4·50	1·72
0	4	1	28·08	30·46	30·37	2·37	0·2718	9·83	2·75	4·48	1·99
0	4	2	10·88	5·92	5·70	1·63	0·2752	9·77	2·72	4·44	2·94
0	4	3	19·72	16·80	16·71	1·77	0·2806	9·67	2·67	4·36	2·48
0	4	4	9·88	10·52	−10·40	−1·61	0·2880	9·54	2·60	4·26	1·79
0	4	5	17·20	18·62	18·47	2·31	0·2973	9·38	2·52	4·13	1·86
0	4	6	17·32	19·53	19·53	0·05	0·3082	9·21	2·44	3·99	2·13
1	1	0	40·08	37·31	−37·30	−0·96	0·1172	14·14	4·87	7·00	3·98
1	1	1	44·48	42·99	38·09	−19·93	0·1198	14·06	4·83	6·96	3·99
*1	1	2	6·40	5·39	4·83	−2·41	0·1271	13·83	4·72	6·85	
1	1	3	17·60	14·24	0·00	14·24	0·1384	13·47	4·54	6·67	3·53
1	1	4	81·44	87·83	−41·35	−77·48	0·1529	13·00	4·31	6·43	3·37
*1	1	6	6·52	1·38	1·03	0·92	0·1882	11·90	3·75	5·83	
*1	1	7	7·36	7·42	−7·10	2·14	0·2080	11·33	3·48	5·50	
1	1	8	42·20	43·10	−23·91	35·86	0·2287	10·78	3·22	5·15	2·70
*1	1	9	8·44	6·76	0·00	−6·76	0·2501	10·28	2·97	4·81	
1	1	10	28·28	20·54	7·89	18·96	0·2720	9·83	2·75	4·48	2·11
1	1	11	11·92	8·64	−6·59	−5·59	0·2944	9·43	2·55	4·17	2·02
1	2	0	27·84	23·70	23·55	2·66	0·1791	12·18	3·88	5·99	3·15
1	2	1	29·28	27·77	−4·13	−27·46	0·1808	12·13	3·86	5·96	2·88
1	2	2	39·36	37·81	−27·93	−25·49	0·1857	11·98	3·78	5·88	3·04
1	2	3	19·48	17·34	13·93	−10·33	0·1936	11·74	3·67	5·74	2·75
1	2	4	24·32	26·02	7·25	24·99	0·2042	11·44	3·52	5·56	2·55
1	2	5	33·28	27·76	5·45	27·22	0·2171	11·08	3·36	5·34	2·80
1	2	6	46·08	44·43	−41·21	−16·60	0·2319	10·70	3·18	5·10	2·55
1	2	7	42·44	36·65	6·13	36·14	0·2482	10·32	3·00	4·84	2·53
*1	2	8	9·00	11·09	0·83	−11·06	0·2658	9·95	2·81	4·57	
1	2	9	12·96	11·37	10·00	5·41	0·2844	9·60	2·63	4·31	2·05
1	2	10	16·12	16·91	−15·37	7·05	0·3038	9·28	2·47	4·04	2·01
1	3	0	15·96	16·10	−16·07	−1·04	0·2440	10·41	3·04	4·91	2·23
1	3	1	17·88	17·30	−5·55	−16·39	0·2453	10·39	3·03	4·89	2·22
1	3	2	43·32	42·31	11·88	40·61	0·2489	10·30	2·99	4·83	2·41

Table *E*3 (*cont.*)

h	*k*	*l*	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	*f*(S)†	*f*(C)	*f*(O)	$\sqrt{w}$
1	3	3	7·28	4·20	0·60	4·16	0·2549	10·17	2·92	4·74	0·00
1	3	4	20·52	26·80	−26·56	3·60	0·2631	10·00	2·84	4·61	2·04
1	3	5	11·56	11·37	−8·41	7·66	0·2732	9·81	2·74	4·47	2·20
1	3	6	13·68	11·67	4·42	10·80	0·2850	9·59	2·63	4·30	2·17
1	3	7	24·64	20·48	19·71	5·57	0·2985	9·36	2·51	4·11	2·16
1	3	8	32·80	27·71	−17·50	−21·48	0·3132	9·14	2·40	3·92	1·95
*1	4	0	6·72	0·82	−0·80	−0·19	0·3102	9·18	2·42	3·96	
1	4	1	20·04	20·41	4·37	19·94	0·3111	9·17	2·41	3·95	1·86
1	4	2	14·68	14·45	−13·63	4·80	0·3140	9·13	2·39	3·91	2·17
2	2	0	48·00	52·20	52·15	2·27	0·2345	10·64	3·15	5·06	2·43
2	2	1	27·68	27·05	−24·61	11·22	0·2357	10·61	3·14	5·04	2·63
*2	2	2	7·68	6·52	4·22	−4·97	0·2396	10·52	3·09	4·98	
2	2	3	12·64	10·36	−0·00	10·36	0·2458	10·37	3·02	4·88	2·36
2	2	4	7·72	5·75	−1·81	−5·46	0·2542	10·19	2·93	4·75	2·32
2	2	5	47·48	42·37	−35·37	−23·33	0·2646	9·97	2·82	4·59	2·36
2	2	6	10·40	3·13	−2·25	−2·17	0·2769	9·74	2·70	4·41	2·51
2	2	7	15·60	15·74	14·69	−5·66	0·2907	9·49	2·58	4·22	2·14
2	2	8	16·64	19·57	−10·72	16·38	0·3058	9·25	2·46	4·02	1·69
2	3	0	27·08	27·96	−27·90	−1·89	0·2950	9·42	2·54	4·16	2·12
*2	3	1	8·08	4·51	−3·63	2·68	0·2960	9·40	2·53	4·15	
2	3	2	22·92	24·35	20·12	−13·73	0·2991	9·35	2·51	4·11	2·31
2	3	3	40·36	37·65	−36·83	−7·82	0·3041	9·28	2·47	4·04	2·19
2	3	4	16·92	14·89	−1·80	−14·78	0·3109	9·17	2·42	3·95	1·91

* indicates unobserved reflexion † includes $\Delta f'$(S)

Table *E*4. *Interatomic distances* (Å) < 4·5

O–C ×2	1·175	S–O ×2	2·827	O–C ×2	4·297
S–C ×2	1·683	C–C	3·128		
C–C	2·100	S–C ×2	3·510		

Table *E*5. *Fourier block round the* S *atom* (*in* 30*th*)

Phases calculated ignoring the anomalous dispersion. Number of reflexions included in the Fourier summations is 314, in addition to F(000).

	X=5			*X*=6			*X*=7		
	Z=26	*Z*=27	*Z*=28	*Z*=26	*Z*=27	*Z*=28	*Z*=26	*Z*=27	*Z*=28
Y=23	1·17	8·04	7·65	1·35	8·10	7·79	0·77	6·08	6·08
Y=24	0·84	7·69	7·61	1·33	8·87	8·87	1·05	7·79	8·10
Y=25	0·26	5·70	5·70	0·87	7·61	7·69	0·91	7·65	8·04

Table *E*6. *Sums and discrepancy*

(For the observed reflexions only.)

	Without dispersion	With dispersion		
$\sum \lvert F_{obs} \rvert$	2314·52	2314·52	Number of atoms	3
$\sum \lvert F_{calc} \rvert$	2146·69	2212·38	Number of parameters	15
$\sum \lvert \Delta F \rvert$	273·64	240·04	Number of observed reflexions	81
R	0·118	0·104	(Number of unobserved reflexions	
$\sum [w(\Delta F)^2]$	$1{\cdot}74 \times 10^4$	$1{\cdot}59 \times 10^4$	excluded from the sums	11)

Table *E*7. *Details of the block diagonal least-squares matrices*

(*a*) Excluding the anomalous dispersion

Atom: S ($y = -x$, $\beta_{22} = \beta_{11}$, $\beta_{23} = \beta_{13}$)

	Original matrix elements ×10⁻⁴				Vector ×10⁻⁴
x	β_{11}	β_{33}	β_{12}	β_{13}	
13834	94	389	173	−222	0·90
	3772	4951	−2313	−254	−25·25
		77076	−2388	−1480	−154·70
			2044	166	13·48
				6083	−8·88

Table *E*7 (*cont.*)

	Inverse matrix elements $\times 10^{11}$				Shifts
728	−182	0	−269	26	0·00014
	9257	−278	10163	35	−0·00542
		143	−149	27	−0·00174
			16246	−65	−0·00142
				1655	−0·00207

Atom: O ($y=x$, $\beta_{22}=\beta_{11}$, $\beta_{23}=-\beta_{13}$)

	Original matrix elements $\times 10^{-4}$				Vector $\times 10^{-4}$
x	β_{11}	β_{33}	β_{12}	β_{13}	
938	−8	−11	−2	106	3·05
	791	967	−508	4	4·71
		15355	−463	14	37·00
			520	−1	−0·96
				5975	15·16

Atom: C

	Original matrix elements $\times 10^{-4}$			Vector $\times 10^{-4}$
x	y	z	B	
1012	−501	3	−0·093	1·298
	1076	117	0·056	0·199
		9268	−0·531	39·723
			0·012	0·006

(*b*) Including the anomalous dispersion of the S atom

Atom: S ($y=-x$, $\beta_{22}=\beta_{11}$, $\beta_{23}=\beta_{13}$)

	Original matrix elements $\times 10^{-4}$				Vector $\times 10^{-4}$
x	β_{11}	β_{33}	β_{12}	β_{13}	
14299	−9	103	191	−220	2·66
	4064	5294	−2504	−263	−14·17
		82883	−2591	−1563	−113·14
			2204	171	7·91
				6477	−9·59

	Inverse matrix elements $\times 10^{11}$				Shifts
702	−121	1	−199	25	0·00016
	8722	−256	9616	34	−0·00192
		133	−136	25	−0·00128
			15325	−55	0·00004
				1554	−0·00186

Atom: O ($y=x$, $\beta_{22}=\beta_{11}$, $\beta_{23}=-\beta_{13}$)

	Original matrix elements $\times 10^{-4}$				Vector $\times 10^{-4}$
x	β_{11}	β_{33}	β_{12}	β_{13}	
941	−7	−8	−2	103	2·36
	757	874	−491	4	5·29
		14932	−416	12	36·46
			507	0	−1·36
				5903	13·63

Atom: C

	Original matrix elements $\times 10^{-4}$			Vector $\times 10^{-4}$
x	y	z	B	
1007	−497	−2	−0·092	1·701
	1068	122	0·062	0·053
		9086	−0·537	33·924
			0·012	0·003

Table *E*8. *Least-squares shifts and estimated standard deviations* (x, y, z, β_{ij}, U_{ij} *and* $U \times 10^5$)

(*a*) Excluding the anomalous dispersion

Method: Full matrix

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	Δ	9	$-\Delta x$	0	−1470	$\Delta\beta_{11}$	−298	−668	−322	$\Delta\beta_{13}$
	σ	147	σx	0	623	$\sigma\beta_{11}$	92	775	255	$\sigma\beta_{13}$
	Δ				−4065	ΔU_{11}	−6275	−1847	−2453	ΔU_{13}
	σ				1721	σU_{11}	1927	2142	1944	σU_{13}
O	Δ	309	Δx	0	−698	$\Delta\beta_{11}$	87	−532	114	$-\Delta\beta_{13}$
	σ	680	σx	0	1450	$\sigma\beta_{11}$	259	1672	303	$\sigma\beta_{13}$
	Δ				−1930	ΔU_{11}	1839	−1471	870	$-\Delta U_{13}$
	σ				4008	σU_{11}	5442	4624	2312	σU_{13}
					B	U				
C	Δ	−592	26	287	−3·15	−3985				
	σ	1033	886	301	2·52	3193				
	Scale shift = 0·0931				σ = 0·0261					

Method: One block per atom

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	Δ	14	$-\Delta x$	0	−542	$\Delta\beta_{11}$	−174	−142	−207	$\Delta\beta_{13}$
	σ	139	σx	0	49	$\sigma\beta_{11}$	62	655	209	$\sigma\beta_{13}$
	Δ				−1499	ΔU_{11}	−3665	−393	−1576	ΔU_{13}
	σ				136	σU_{11}	1294	1811	1594	σU_{13}
O	Δ	310	Δx	0	916	$\Delta\beta_{11}$	210	898	247	$-\Delta\beta_{13}$
	σ	531	σx	0	975	$\sigma\beta_{11}$	137	1172	210	$\sigma\beta_{13}$
	Δ				2534	ΔU_{11}	4420	2482	1885	$-\Delta U_{13}$
	σ				2696	σU_{11}	2883	3240	1605	σU_{13}
					B	U				
C	Δ	152	39	432	0·687	871				
	σ	587	569	170	1·488	1885				

Adjusted thermal parameters for a scale shift of 0·096

S	$(\Delta\beta)'$	−1371	$\Delta\beta_{11}'$	−283	−556	−207	$\Delta\beta_{13}'$
	$(\Delta U)'$	−3790	$\Delta U_{11}'$	−5956	−1538	−1576	$\Delta U_{13}'$
O	$(\Delta\beta)'$	87	$\Delta\beta_{11}'$	101	484	247	$-\Delta\beta_{13}'$
	$(\Delta U)'$	243	$\Delta U_{11}'$	2129	1337	1885	$-\Delta U_{13}'$
C	$(\Delta B)'$, $(\Delta U)'$	−1·121	−1420				

(*b*) Including the anomalous dispersion of the S atom

Method: Full matrix

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	Δ	12	$-\Delta x$	0	−1153	$\Delta\beta_{11}$	−262	−497	−263	$\Delta\beta_{13}$
	σ	138	σx	0	579	$\sigma\beta_{11}$	85	718	236	$\sigma\beta_{13}$
	Δ				−3189	ΔU_{11}	−5503	−1373	−2005	ΔU_{13}
	σ				1600	σU_{11}	1777	1986	1802	σU_{13}
O	Δ	335	Δx	0	−572	$\Delta\beta_{11}$	82	−370	108	$-\Delta\beta_{13}$
	σ	649	σx	0	1412	$\sigma\beta_{11}$	249	1614	291	$\sigma\beta_{13}$
	Δ				−1582	ΔU_{11}	1732	−1024	827	$-\Delta U_{13}$
	σ				3905	σU_{11}	5237	4462	2222	σU_{13}
					B	U				
C	Δ	−437	13	240	−3·21	−4070				
	σ	987	851	289	2·42	3065				
	Scale shift = 0·1014				σ = 0·0247					

Method: One block per atom

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	Δ	16	$-\Delta x$	0	−192	$\Delta\beta_{11}$	−128	4	−186	$\Delta\beta_{13}$
	σ	130	σx	0	459	$\sigma\beta_{11}$	57	609	194	$\sigma\beta_{13}$
	Δ				−530	ΔU_{11}	−2684	11	−1420	ΔU_{13}
	σ				1270	σU_{11}	1193	1683	1477	σU_{13}

Table *E*8 (*cont.*)

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	Δ	238	Δx	0	1063	$\Delta\beta_{11}$	208	931	226	$-\Delta\beta_{13}$
	σ	508	σx	0	951	$\sigma\beta_{11}$	132	1135	203	$\sigma\beta_{13}$
	Δ				2938	ΔU_{11}	4369	2575	1721	$-\Delta U_{13}$
	σ				2631	σU_{11}	2782	3139	1544	σU_{13}
					B	U				
C	Δ	200	52	375	0·437	553				
	σ	559	543	164	1·418	1796				
Adjusted thermal parameters for a scale shift of 0·105										
S	$(\Delta\beta)'$				−1080	$\Delta\beta_{11}'$	−245	−440	−186	$\Delta\beta_{13}'$
	$(\Delta U)'$				−2984	$\Delta U_{11}'$	−5138	−1216	−1420	$\Delta U_{13}'$
O	$(\Delta\beta)'$				175	$\Delta\beta_{11}'$	91	487	226	$-\Delta\beta_{13}'$
	$(\Delta U)'$				484	$\Delta U_{11}'$	1915	1348	1721	$-\Delta U_{13}'$
C	$(\Delta B)'$, $(\Delta U)'$				−1·501	−1901				

APPENDIX *F*

Test case $I\bar{4}3d$

Table *F*1. *Crystal data.*

Direct cell		Reciprocal cell			
a	11·00 Å	a^*	0·0909 Å^{-1}	$F(000)$	1152·0
b	11·00	b^*	0·0909	Scale	1·0
c	11·00	c^*	0·0909	Weights	1·0
α	90·00°	α^*	90·00°	Relaxation factor	1·0
β	90·00	β^*	90·00	Occupancy factors	1·0
γ	90·00	γ^*	90·00	Restricted parameters	O(1) y,z; O(2) x,y,z; C y,z
V	1331·00 Å^3	V^*	0·000751 Å^{-3}		

Table *F*2. *Parameters of the trial structure*

	x	y	z	B	$U\times10^5$
	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$		
S in 48(*e*)	0·121	0·169	0·301	2·1	2660
	0·001	0·001	0·001		
O(1) in 24(*d*)	−0·005	0·0	0·250	2·8	3546
	0·002	0·0	0·0		
O(2) in 12(*a*)	0·375	0·0	0·250	2·8	3546
	0·0	0·0	0·0		
C in 16(*c*)	0·258	0·258	0·258	3·0	3800
	0·005	0·005	0·005		

Table *F*3. *Structure factor data for the trial structure*

h	k	l	F_{obs}	F_{cal}	A_{cal}	B_{cal}	$\sin\theta/\lambda$	f(S)	f(C)	f(O)
4	0	0	12·43	2·85	2·85	−0·00	0·1818	11·74	3·84	5·94
8	0	0	54·42	58·29	58·29	−0·00	0·3636	8·17	2·09	3·35
12	0	0	12·20	8·02	−8·02	0·00	0·5455	6·72	1·61	2·13
3	1	0	23·91	23·12	−0·00	−23·12	0·1437	12·95	4·46	6·58
5	1	0	68·88	64·41	0·00	64·41	0·2318	10·35	3·18	5·10
7	1	0	71·27	73·32	0·00	73·32	0·3214	8·67	2·34	3·82
9	1	0	9·99	10·91	−0·00	−10·91	0·4116	7·74	1·91	2·91
11	1	0	43·52	40·88	−0·00	40·88	0·5021	7·03	1·68	2·33
2	2	0	61·46	66·15	66·15	0·00	0·1286	13·44	4·70	6·83
4	2	0	17·72	17·97	−17·97	−0·00	0·2033	11·11	3·54	5·58
6	2	0	45·26	53·75	−53·75	−0·00	0·2875	9·20	2·61	4·26
8	2	0	14·90	13·76	13·76	−0·00	0·3748	8·06	2·04	3·24

Table *F*3 (*cont.*)

h	*k*	*l*	F_{obs}	F_{cal}	A_{cal}	B_{cal}	sin θ/λ	*f*(S)	*f*(C)	*f*(O)
10	2	0	30·40	23·50	−23·50	−0·00	0·4635	7·33	1·76	2·54
2	1	1	132·01	129·89	52·49	−118·81	0·1113	13·98	4·96	7·09
10	1	1	40·88	43·63	−43·30	5·38	0·4591	7·36	1·78	2·57
2	4	2	193·88	201·32	−36·27	−198·02	0·2227	10·58	3·29	5·25
6	4	2	67·02	68·57	63·36	26·21	0·3402	8·43	2·22	3·60
8	4	2	61·48	60·65	8·02	−60·12	0·4166	7·70	1·89	2·87
3	2	1	132·40	131·18	4·91	131·09	0·1701	12·11	4·02	6·14
5	2	1	75·62	75·74	−42·88	62·43	0·2490	9·95	2·99	4·83
7	2	1	29·70	30·88	10·14	−29·17	0·3340	8·51	2·26	3·67
9	2	1	99·31	97·83	95·37	21·80	0·4215	7·66	1·88	2·84
3	4	1	73·35	72·45	72·44	0·62	0·2318	10·35	3·18	5·10
5	4	1	128·42	125·12	45·15	116·69	0·2946	9·08	2·55	4·17
7	4	1	47·24	47·23	−23·76	−40·82	0·3693	8·11	2·07	3·29
3	6	1	80·91	80·80	79·02	−16·88	0·3083	8·86	2·44	3·99
1	6	1	170·20	172·21	126·14	117·24	0·2802	9·32	2·67	4·37
5	6	1	40·91	40·83	−39·92	−8·58	0·3579	8·23	2·12	3·41
3	8	1	89·68	86·08	−8·96	85·61	0·3910	7·91	1·98	3·09
3	3	2	193·73	193·10	−192·83	10·28	0·2132	10·84	3·41	5·41
5	5	2	81·95	78·78	−0·70	78·77	0·3340	8·51	2·26	3·67
4	4	4	112·97	108·99	105·02	29·14	0·3149	8·77	2·39	3·90

Table *F*4. *Interatomic distances* (Å), *angles* (°) *and e.s.d.'s*

Intramolecular distances <4·0		Intramolecular angles		Intermolecular distances <3·0		
S–O(1)	2·386 (17)	O(1)–S——O(2)	90·72 (44)	S·····O(2)	×4	1·797 (11)
S–O(2)	3·403 (11)	O(1)–S——C	145·27 (182)	S·····C	×2	1·858 (56)
S–C	1·858 (56)	O(2)–S——C	65·16 (172)	S·····O(1)		2·386 (17)
C–O(2)	3·117 (55)	S——O(2)–C	32·75 (103)	S·····S	×2	2·511 (22)*
		S——C——O(2)	82·09 (188)	O(1)···O(1)		2·640 (44)*
				C·····O(1)	×3	2·667 (55)
				S·····O(1)	×2	2·739 (13)
				S·····S	×2	2·789 (22)*

* Indicates that e.s.d. includes a factor of $\sqrt{2}$ since the atoms are related.

Table *F*5. *Fourier block round the* S *atom* (*in* 30*th*)

Number of reflexions in the Fourier summations is 157, in addition to *F*(000).

	X=3			*X*=4			*X*=5		
	Z=8	*Z*=9	*Z*=10	*Z*=8	*Z*=9	*Z*=10	*Z*=8	*Z*=9	*Z*=10
Y=4	7·25	9·84	5·83	7·06	10·09	6·41	2·76	5·17	2·47
Y=5	10·10	12·82	8·33	10·27	13·62	9·53	5·90	8·45	5·34
Y=6	6·48	8·50	5·26	6·91	9·69	6·66	4·39	6·25	3·60

Table *F*6. *Sums and discrepancy*

$\sum \lvert F_{obs} \rvert$	2318·02	Number of atoms	4
$\sum \lvert F_{calc} \rvert$	2302·19	Number of parameters	10
$\sum \lvert \Delta F \rvert$	86·45	Number of reflexions	32
R	0·037	$\sum w(\Delta F)^2$	430

Table *F*7. *Details of the* 4×4 *block diagonal matrices*

Atom: S

Original matrix elements ×10⁻⁴				Vector ×10⁻²
x	*y*	*z*	*B*	
8970	338	904	0·300	−1166
	8082	995	3·699	629
		9558	2·262	−1087
			0·173	−0·35

Inverse matrix elements ×10¹⁰				Shifts
113	−3	−10	12	−0·00122
	127	−12	−2539	0·00098
		107	−1120	−0·00112
			5843000	−0·025

Table *F*7 (*cont.*)

Atom: O(1)

Original matrix elements $\times 10^{-2}$		Vector $\times 10^{-2}$
x	B	
52450	−1·17	1·9
	1·98	−0·23

Atom: O(2)

Original matrix elements		Vector
	B	
	58·26	2·2

Atom: C

Original matrix elements $\times 10^{-3}$		Vector
x	B	
4817	5·086	997
	0·0486	−6·1

Table *F*8. *Least-squares shifts and estimated standard deviations* (x, y, z, $U \times 10^5$)

Method: Full matrix

		x	y	z	B	U
S	Δ	−124	94	−123	−0·100	−127
	σ	48	51	50	0·210	266
O(1)	Δ	77	0	0	0·067	85
	σ	205	0	0	0·415	526
O(2)	Δ	0	0	0	−0·162	−205
	σ	0	0	0	0·602	761
C	Δ	−68	Δx	Δx	0·175	222
	σ	226	σx	σx	0·815	1032

Scale shift = 0·0083 σ = 0·0176

Method: One block per atom

		x	y	z	B	U
S	Δ	−122	98	−112	−0·025	−32
	σ	47	50	46	0·107	135
O(1)	Δ	4	0	0	−0·118	−149
	σ	193	0	0	0·314	398
O(2)	Δ	0	0	0	0·037	47
	σ	0	0	0	0·580	734
C	Δ	38	Δx	Δx	−0·165	−209
	σ	409	σx	σx	1·288	1632

Adjusted B and U shifts for a scale shift of 0·015

S	−0·167	−212
O(1)	−0·260	−329
O(2)	−0·105	−133
C	−0·307	−388

then

$$\sigma^2(X_i') = \sum_{j=1}^{3} T_{ij}^2 \, \sigma^2(x_j) \, .$$

The standard deviation of the bond AB is derived from

$$\begin{aligned}\sigma^2(AB) = \{&(\Delta X')^2[\sigma^2(X_A') + \sigma^2(X_B')] \\ &+ (\Delta Y')^2[\sigma^2(Y_A') + \sigma^2(Y_B')] \\ &+ (\Delta Z')^2[\sigma^2(Z_A') + \sigma^2(Z_B')]\}/(AB)^2 \, .\end{aligned}$$

(*b*) *Angles*

$$\sigma^2(\widehat{ABC}) = \frac{\sigma^2(A)}{(AB)^2} + \sigma^2(B)\left(\frac{1}{(AB)^2} - \frac{2\cos(\widehat{ABC})}{AB.BC} + \frac{1}{(BC)^2}\right) + \frac{\sigma^2(C)}{(BC)^2}$$

where

$$\sigma^2(A) = \tfrac{1}{3}[\sigma^2(X_A') + \sigma^2(Y_A') + \sigma^2(Z_A')] \, .$$

Precision of the numerical values

The quantities calculated, the crystallographic program systems which produced them, and the precision referred to the least significant digit quoted in each case, are as follows:

Quantities	Program systems	Precision
$V, a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*, V^*$	XRAY, NRC	±0
$\sin\theta/\lambda$	XRAY, NRC, LASL	±1
Interpolated f-values	XRAY, NRC, LASL	±3
F_c, A_c, B_c	XRAY, NRC, LASL	±7
$\sum \lvert F_o \rvert$	XRAY, NRC, LASL	±0
$\sum \lvert F_c \rvert$	XRAY, NRC, LASL	±18
$\sum \lvert \Delta F \rvert$	XRAY, NRC, LASL	±6
R	XRAY, NRC, LASL	±1
$\sum w(\Delta F)^2$	XRAY, NRC	±1
Interatomic distances	XRAY, NRC, LASL	±0
E.s.d.'s of distances	XRAY, NRC, LASL	±5
Valence angles	XRAY, NRC, LASL	±1
E.s.d.'s of angles	XRAY, NRC, LASL	±17
Electron densities	XRAY, NRC, LASL	±1
Least-squares matrices	XRAY, NRC, LASL	±15
Inverse matrices	NRC	–
L.S. shifts and e.s.d.'s		
(*a*) full matrix	XRAY, LASL	±15
(*b*) 9×9 block-diagonal	XRAY, NRC	±2
(*c*) 3×3 and 6×6 block-diagonal	NRC	–
(*d*) 4×4 and 5×5 block-diagonal	XRAY, NRC	±5

The authors wish to acknowledge the valuable assistance of Mrs M. E. Pippy and Mrs S. Byram of the National Research Council of Canada, and Misses J. Willis, S. Vogel, and M. Smith of the University of Maryland, and would like to thank Professor E. C. Lingafelter for helpful discussions. A.C.L. and J.M.S. also wish to acknowledge the financial support of the United States Atomic Energy Commission, and NASA grant NSG 398 to the University of Maryland respectively.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). The NRC Crystallographic System of Programs. *World List of Crystallographic Computer Programs*, 2nd ed. Appendix, p. 52.

CRUICKSHANK, D. W. J. (1970). *Least Squares Refinement of Atomic Parameters.* In *Crystallographic Computing*, p. 187. Copenhagen: Munksgaard.

CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

LARSON, A. C. (1971). LASL crystal structure programs (unpublished).

STEWART, J. M. (1970). *Standard Tests for Crystallographic Programs.* In *Crystallographic Computing*, p. 279. Copenhagen: Munksgaard.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY-70 System. University of Maryland, College Park, Md.

Acta Cryst. (1972). A**28**, 393

Strong Enantiomorph Discrimination *via* Calculated Cosine Invariants

BY HERBERT HAUPTMAN AND WILLIAM L. DUAX

Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, *U.S.A.*

(*Received* 17 *November* 1971 *and in revised form* 17 *February* 1972)

Using calculated values of the cosine invariants and the concept of orthogonal classes of phases, a procedure for decisive enantiomorph selection is described. The method, which is strongly dependent on a study of invariants of special type, facilitates the evaluation of an initial set of phases and provides a broad base for subsequent phase extension by one of the tangent techniques. Three applications of this new procedure are cited.

1. Introduction

If a structure invariant L has the value s for a crystal structure S then the value of the same structure invariant for the enantiomorphous structure S' is $-s$ (Hauptman & Karle, 1956). Thus if $s=0$ or π then L has the same value (0 or π) for both enantiomorphs and is not suitable for enantiomorph discrimination. If, on the other hand, $s\neq 0$ or π then, since the magnitude of s (or, equivalently, $\cos s$) is determined by the known magnitudes of the structure factors, the enantiomorph may be chosen by specifying arbitrarily