unacceptable interatomic distances, fits naturally the space groups $P\overline{6}2c$ and $P6_3/mmc$ already discussed. It makes the space group $P6_3mc$ rather unlikely though not impossible.

The modulation in this case thus could well be a long-range order in the orientations of the MoO_4 tetrahedra oriented approximately with their peaks upward over one half of the modulation period and downward over the other half of the period. Above the transition point at 440°C, the tetrahedra will presumably be distributed at random among the possible orientations.

It seems possible that this distribution stems to some extent from rotational freedom of the anion (see also Bredig, 1943). However, this cannot be decided from our data.

The model proposed here agrees well with predictions of Fischmeister (1962) based on steric calculations carried out for the high temperature modifications of a series of sulphates. The structure of these sulphates also belongs to the basic structure type. Using steric as well as thermodynamic evidence, Fischmeister proposed three possible structure types:

(i) two possible orientations of the anion tetrahedra, pointing either upward or downward along the **c** direction, are randomly distributed among the anion positions,

(ii) domains are present in which the orientation of all tetrahedra is the same,

(iii) a superstructure is present.

In all of these cases at least two anions with weight $\frac{1}{2}$ must be superposed in order to get the average structure. Our model of the modulated structure can be described as a special case of (ii) or a generalization of (iii).

Since the average modulated structure has been shown to be essentially identical to the hexagonal high temperature form, the latter is not likely to possess Eysel's high K_2SO_4 structure either. We believe that it represents Fischmeister's type (i).

K_2WO_4, Rb_2WO_4

The above interpretation applies equally well to these compounds. In the case of K_2WO_4 a superstructure with $\kappa=\frac{1}{4}$ seems to be possible. Some reflexions with $l=4$, which were absent in K_2MoO_4 are present here with very weak intensities.

We thank Professor P. M. de Wolff for his valuable advice and criticism, Mr G. M. Fraase Storm for his skillful technical assistance and Dr A. S. Koster for putting the diffraction patterns of Rb_2WO_4 and K_2WO_4 at our disposal.

References

AKKER, A. W. M. VAN DEN, KOSTER, A. S. & RIECK, G. D. (1970). *J. Appl. Cryst.* **3**, 389–392.
BREDIG, M. A. (1943). *J. Phys. Chem.* **47**, 587–590.
BROUNS, E., VISSER, J. W. & DE WOLFF, P. M. (1964). *Acta Cryst.* **17**, 614.
DUBBELDAM, G. C. & DE WOLFF, P. M. (1969). *Acta Cryst.* B**25**, 2665–2667.
EYSEL, W. (1971). Habilitationsschrift, Technische Hochschule Aachen.
EYSEL, W. & HAHN, T. (1970). *Z. Kristallogr.* **131**, 322–341.
FISCHMEISTER, H. F. (1962). *Mh. Chem.* **93**, 420–434.
GATEHOUSE, B. M. & LEVERETT, P. (1969). *J. Chem. Soc.* (*A*), pp. 849–854.
HOSHINO, S. & MOTEGI, H. (1967). *Jap. J. Appl. Phys.* **6**, 708–718.
KOOLS, F. X. N. M., KOSTER, A. S. & RIECK, G. D. (1970). *Acta Cryst.* B**26**, 1974–1977.

Acta Cryst. (1973). B**29**, 589

Least-squares Refinement and the Weighted Difference Synthesis

BY J. D. DUNITZ AND P. SEILER

Laboratory of Organic Chemistry, Swiss Federal Institute of Technology, 8006 *Zürich, Switzerland*

(*Received* 2 *November* 1972; *accepted* 10 *November* 1972)

The weights to be assigned in least-squares refinements of crystal structures are discussed in terms of a weighted difference synthesis in which electron density differences close to atomic centres are regarded as more important than those in other regions. Least-squares refinement with suitably modified weights is shown to produce more acceptable atomic parameters in certain cases than those obtained with experimental weights.

Relation between least-squares refinement and difference synthesis

Suppose that we wish to refine the parameters describing a crystal structure by the method of least squares and that we have at our disposal a set of experimental F_o values of uniform quality and free from systematic error. It is easily shown that minimization of

$$Q=\sum_h w(\mathbf{h})[F_o(\mathbf{h})-F_c(\mathbf{h})]^2 \qquad (1)$$

with unit weights $[w(\mathbf{h})=1]$ is equivalent to minimizing the integral of the difference density squared over the unit-cell volume. From the relationship between the electron density distribution $\varrho(\mathbf{x})$ and its Fourier coefficients $F(\mathbf{h})$ we have

$$\sum_h [F_o(\mathbf{h})-F_c(\mathbf{h})]\exp(-2\pi i\mathbf{h}\,.\,\mathbf{x}) = \varrho_o(\mathbf{x})-\varrho_c(\mathbf{x})=\delta(\mathbf{x})$$

$$\sum_h [F_o(\mathbf{h})-F_c(\mathbf{h})]^2\cos(2\pi\mathbf{h}\,.\,\mathbf{u})=D(\mathbf{u}) = \int\delta(\mathbf{x})\delta(\mathbf{x}-\mathbf{u})\mathrm{d}\mathbf{x}$$

$$\sum_h [F_o(\mathbf{h})-F_c(\mathbf{h})]^2=D(0)=\int\delta^2(\mathbf{x})\mathrm{d}\mathbf{x}\,. \qquad (2)$$

Weighted difference synthesis

In minimizing the integral on the right hand side of (2), differences between $\varrho_o(\mathbf{x})$ and $\varrho_c(\mathbf{x})$ at all positions $\mathbf{x}$ throughout the unit cell have equal weight. In certain circumstances, however, we may choose to regard some regions of $\varrho_o(\mathbf{x})$ and $\varrho_c(\mathbf{x})$ as more relevant than others to the problem under consideration. For example, we may be more interested in fitting the distributions close to the atomic centres than in fitting the outer regions. This would be the case if we want atomic positions that correspond to positions of maximum electron density rather than to centroids of asymmetric density distributions, or if we want vibrational parameters that are as far as possible free from the disturbing effects of valency electrons. We may then wish to introduce an appropriate function that assigns high weight to difference density close to atomic centres, low weight to difference density that we regard as irrelevant for our purposes.

If $\varrho_o(\mathbf{x})$ and $\varrho_c(\mathbf{x})$ are taken as sums of atomic distributions, *i.e.*

$$\varrho(\mathbf{x})=\sum_j \varrho_j(\mathbf{x}-\mathbf{x}_j)$$

the quantity to be minimized is then

$$D'(0)=\sum_j\int\delta_j^2(\mathbf{x}-\mathbf{x}_j)\exp[-2q(\mathbf{x}-\mathbf{x}_j)^2] \qquad (3)$$

where the weighting function is conveniently taken as Gaussian. This is equivalent to multiplying the peaks of $\varrho_o(\mathbf{x})$ and $\varrho_c(\mathbf{x})$ by Gaussian functions $\exp[-q(\mathbf{x}-\mathbf{x}_j)]^2$ with appropriate modification of their Fourier coefficients.

Modified least-squares refinement

Suppose that the 'natural' atomic peaks are also roughly Gaussian in shape:

$$\varrho_{oj}(\mathbf{x}-\mathbf{x}_j)\sim\varrho_{cj}(\mathbf{x}-\mathbf{x}_j)\sim A\exp[-p(\mathbf{x}-\mathbf{x}_j)^2]\,.$$

The form factor (including isotropic temperature factor) of the scattering centres is then proportional to

$$f(\mathbf{h})=A\left(\frac{\pi}{p}\right)^{3/2}\exp\left[\frac{-\pi^2h^2}{p}\right]$$

using a standard definite integral (Dwight, 1957, formula 863·3) where $h=2\sin\theta/\lambda$.

The weighted atomic peaks are then

$$\varrho'_{oj}(\mathbf{x}-\mathbf{x}_j)\sim\varrho_j(\mathbf{x}-\mathbf{x}_j)\sim A\exp[-(p+q)(\mathbf{x}-\mathbf{x}_j)^2]$$

corresponding to modified form factors

$$f'(\mathbf{h})=A\left(\frac{\pi}{p+q}\right)^{3/2}\exp\left[-\frac{\pi^2h^2}{p+q}\right].$$

Thus, to the extent that all atoms can be assumed to have similar form factors, the ratio of modified to unmodified Fourier coefficients is

$$\frac{F'(\mathbf{h})}{F(\mathbf{h})}=\frac{f'(\mathbf{h})}{f(\mathbf{h})}=\left(\frac{p}{p+q}\right)^{3/2}\exp\left[\frac{\pi^2h^2q}{p(p+q)}\right].$$

In order to achieve minimization of (3) the experimental weights in the corresponding least-squares analysis have to be multiplied by a function that depends on the desired degree of sharpening, and the expression to be minimized is then not (1) but

$$Q'=\sum_h w'(\mathbf{h})[F_o(\mathbf{h})-F_c(\mathbf{h})]^2 \qquad (4)$$

where

$$w'(\mathbf{h})=w(\mathbf{h})\exp[r\sin^2\theta/\lambda^2]$$

with

$$r=\frac{8\pi^2q}{p(p+q)}\,.$$

The maximum permissible value of r, corresponding to a δ function for $\varrho'(\mathbf{x}-\mathbf{x}_j)$, is $8\pi^2/p$.

Choice of modified 'weights'

The approximation of treating atomic peaks as symmetrical Gaussian functions holds reasonably well, and typical values of p for second-row atoms are in the range 3–4 Å^{-2} (Stout & Jensen, 1968), or even smaller if thermal motion is large. The value of q is chosen to give the desired degree of sharpening. With $q=9$ Å^{-2}, $\delta^2(\mathbf{x})$ is reduced to 5% of its value at radial distance 0·41 Å from the atomic centre. With $p=3$ Å^{-2}, $q=9$ Å^{-2} we obtain $r\sim20$ Å^2. Alternatively, we could derive a reasonable value of r, and hence of q, from the overall form factor combined with the overall isotropic temperature factor. In light-atom structures $f_j\exp[-B\sin^2\theta/\lambda^2]$ is approximately reproduced by a Gaussian function $z_j\exp[-B'\sin^2\theta/\lambda^2]$, corresponding to an average atom with density fall-off given by $\exp[-px^2]$ where $p=4\pi^2/B'$. Note that if $p=q$ then

$$r=\frac{8\pi^2q}{p(p+q)}=\frac{4\pi^2}{p}=B'$$

showing that the weighted least-squares expression $\sum\frac{1}{f(\mathbf{h})}[F_o(\mathbf{h})-F_c(\mathbf{h})]^2$ discussed by Cochran (1948) corresponds to minimization of $D'(0)$ (equation 3) with atomic peaks exactly twice as sharp as those of the natural electron density distribution. We see that, depending on how much weight we assign to the outer regions of the atomic peaks, we may choose a somewhat larger or smaller value of q. Thus the modified weights in the corresponding least-squares analysis depend not only on the experimental weights but also on which features of the electron density are regarded as of most importance for the atomic parameters in question.

High-order refinement

Least-squares refinements based only on high-order reflexions have been reported in some cases (*e.g* Stewart & Jensen, 1969; O'Connell, 1969; Collins & Hoard, 1970) to yield atomic coordinates that are closer to the true atomic positions (*i.e.* as determined by neutron diffraction) than those derived from refinements including all observed reflexions. High-order refinements have also been reported to give improved values of thermal parameters (Coppens & Vos, 1971). We can expect to find differences between the results of least-squares refinements with different weighting systems if the electron density peaks are not centrosymmetric, as could arise from asymmetric charge distributions or from anharmonic vibrations of the atoms. The effects of such asymmetry have been discussed by Dawson (1964), who showed that the use of spherical f functions in unit-weight least-squares analysis can lead to spurious shifts in atomic positions of *circa* 0·02 Å and to apparent anisotropy in thermal parameters.

High-order refinements are implicitly based on discontinous weighting systems, with a sudden change from zero to unit (or experimental) weights at some arbitrary radius in reciprocal space. The corresponding peak-weighting functions obtained by Fourier transformation of discontinous step functions are not as smooth nor as readily interpretable as Gaussian functions. In addition to a sharp, central peak, they contain high-frequency ripples of considerable amplitude, which may give relatively high weight to features of the difference density at some distance from the atomic centres. We believe that the modified least-squares refinement based on expression (4) is, in general, to be preferred to high-order refinement.

Experience with modified weights

We have carried out a number of least-squares refinements with various weighting schemes (unit, experimental, modified) for three crystal structures.

(*a*) 1,4,7,10,13,16-Hexaoxacyclooctadecane, $C_{12}H_{24}O_6$ ($a=8{\cdot}295$, $b=20{\cdot}230$, $c=8{\cdot}490$ Å, $Pbca$, $Z=4$).

(*b*) Potassium thiocyanate complex, $C_{12}H_{24}O_6$.KNCS ($a=8{\cdot}190$, $b=14{\cdot}285$, $c=7{\cdot}775$ Å, $\beta=99{\cdot}19°$, $P2_1/c$, $Z=2$).

(*c*) Sodium thiocyanate complex, $C_{12}H_{24}O_6$.NaNCS ($a=12{\cdot}316$, $b=13{\cdot}737$, $c=11{\cdot}215$ Å, $\beta=105{\cdot}32°$, $P2_1/c$, $Z=4$).

Full details of these structures will be given else-

Table 1. *Analysis of results of least-squares analysis with experimental and modified weighting systems for for crystal structures* (*a*) (*b*) (*c*)

For numbering system see Fig. 1.

Uncomplexed ligand (*a*)

Bond	Experimental weights	Modified weights $r=20$ Å^2	$r=36$ Å^2
C(2)–C(3)	1·496 (2) Å	1·505 (3) Å	1·506 (2) Å
C(5)–C(6)	1·489 (2)	1·504 (2)	1·509 (2)
C(8)–C(9)	1·491 (2)	1·504 (2)	1·505 (2)
C(2)–O(1)	1·420 (2)	1·416 (2)	1·414 (2)
C(3)–O(4)	1·424 (2)	1·412 (2)	1·408 (2)
C(5)–O(4)	1·415 (2)	1·408 (2)	1·403 (2)
C(6)–O(7)	1·410 (2)	1·407 (2)	1·405 (2)
C(8)–O(7)	1·417 (2)	1·411 (2)	1·407 (2)
C(9)–O(1)′	1·429 (2)	1·426 (2)	1·426 (2)
$\langle d(\mathrm{C{-}C})\rangle$	1·492 Å	1·504 Å	1·507 Å
$\langle d(\mathrm{C{-}O})\rangle$	1·419	1·413	1·411
R (%)	4·01	4·67	5·22
R_{H} (%)	4·18	3·40	2·23
$\langle (U^o_{ij}-U^c_{ij})^2\rangle^{1/2}$	0·00444 Å^2	0·00424 Å^2	0·00444 Å^2
$\sin\theta/\lambda$ range	0–0·704 Å^{-1}		

Potassium complex (*b*)

Bond	Experimental weights	$r=14$ Å^2	$r=36$ Å^2
C(2)–C(3)	1·489 (2) Å	1·497 (3) Å	1·493 (3) Å
C(5)–C(6)	1·495 (3)	1·507 (4)	1·509 (5)
C(8)–C(9)	1·493 (2)	1·507 (3)	1·508 (3)
C(2)–O(1)	1·411 (2)	1·418 (2)	1·420 (3)
C(3)–O(4)	1·415 (2)	1·414 (2)	1·410 (3)
C(5)–O(4)	1·421 (2)	1·418 (3)	1·413 (3)
C(6)–O(7)	1·414 (2)	1·418 (2)	1·423 (2)
C(8)–O(7)	1·419 (2)	1·417 (2)	1·415 (3)
C(9)–O(1)′	1·425 (2)	1·424 (2)	1·425 (3)
$\langle d(\mathrm{C{-}C})\rangle$	1·492 Å	1·504 Å	1·503 Å
$\langle d(\mathrm{C{-}O})\rangle$	1·418	1·418	1·418
R (%)	3·46	4·21	4·55
R_{H} (%)	4·69	5·79	5·85
$\langle (U^o_{ij}-U^c_{ij})^2\rangle^{1/2}$	0·00402 Å^2	0·00398 Å^2	0·00418 Å^2
$\sin\theta/\lambda$ range	0–0·682 Å^{-1}		

Sodium complex (*c*)

Bond	Experimental weights	Modified weights $r=18$ Å^2	$r=36$ Å^2
C(2)—C(3)	1·487 (3) Å	1·496 (2) Å	1·497 (2) Å
C(5)—C(6)	1·492 (4)	1·495 (2)	1·497 (2)
C(8)—C(9)	1·489 (3)	1·509 (2)	1·509 (2)
C(11)–C(12)	1·485 (4)	1·491 (3)	1·491 (3)
C(14)–C(15)	1·472 (5)	1·510 (3)	1·511 (3)
C(17)–C(18)	1·504 (4)	1·507 (2)	1·510 (2)
C(2)—O(1)	1·422 (3)	1·420 (2)	1·421 (1)
C(3)—O(4)	1·416 (3)	1·412 (2)	1·413 (2)
C(5)—O(4)	1·425 (3)	1·425 (2)	1·425 (2)
C(6)—O(7)	1·419 (3)	1·423 (1)	1·423 (1)
C(8)—O(7)	1·420 (3)	1·411 (2)	1·410 (2)
C(9)—O(10)	1·434 (3)	1·424 (2)	1·423 (2)
C(11)–O(10)	1·424 (3)	1·424 (2)	1·426 (2)
C(12)–O(13)	1·421 (4)	1·437 (3)	1·437 (2)
C(14)–O(13)	1·408 (4)	1·415 (3)	1·418 (2)
C(15)–O(16)	1·438 (4)	1·430 (3)	1·432 (2)
C(17)–O(16)	1·428 (4)	1·428 (3)	1·426 (3)
C(18)–O(1)	1·427 (3)	1·421 (2)	1·419 (2)
$\langle d(\mathrm{C{-}C})\rangle$	1·488 Å	1·501 Å	1·503 Å
$\langle d(\mathrm{C{-}O})\rangle$	1·424	1·423	1·423
R (%)	5·18	6·80	8·10
R_{H} (%)	8·17	6·09	5·28
$\langle (U^o_{ij}-U^c_{ij})^2\rangle^{1/2}$	0·00711 Å^2	0·00603 Å^2	0·00627 Å^2
$\sin\theta/\lambda$ range	0–0·617 Å^{-1}		

where (Seiler, Phizackerley, Dobler & Dunitz, 1972, unpublished), and we merely note here that intensity data for all three crystals were measured with a four-circle diffractometer (Hilger & Watts Y290) under similar conditions (graphite monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan with background measured for each reflexion separately). Experimental weights were assigned in accordance with our usual laboratory practice, in which allowance is made for various kinds of experimental error.

The least-squares refinements, some results of which are summarized in Table 1, were based on structure models containing all atoms including hydrogens (positions of H atoms calculated from stereochemical considerations and held constant during individual refinement cycles). In structure (*b*) the thiocyanate group is disordered, occupying two antiparallel orientations at random, and the parameters describing this group were held constant in the modified least-squares refinements, which are not appropriate for treating disordered groups of atoms.

Since it is almost impossible to draw any conclusions directly from the positional parameters obtained by the various least-squares refinements, we base our discussion mainly on the C–C and C–O bond distances calculated from these parameters. It should be kept in mind that the true internuclear distances in these structures are not known. As expectation values for the uncomplexed hexa-ether we may adopt the values d(C–C) = 1·523 Å and d(C–O) = 1·423 Å found in 1,4-dioxane by gas-phase electron diffraction (Davis & Hassel, 1963). These distances may be somewhat different in the alkali cation complexes, and slight differences, of the order of 0·01 Å, perhaps, can also be anticipated between chemically equivalent but crystallographically non-equivalent bonds. Moreover, the thermal vibration parameters for all three crystal structures are quite large and sometimes highly anisotropic. Analyses of these parameters in terms of rigid-body libration and translation (Schomaker & Trueblood, 1968) leads to only modest agreement between observed and calculated U_{ij} values for crystals (*a*) and (*b*) and to poor agreement for the Na complex (*c*) (see Table 1). In all three cases, and especially in (*c*), the observed bond distances are slightly shortened as a result of rigid-body and intramolecular motions. Nevertheless, in spite of these uncertainties and gaps in our knowledge, a comparison of the results of the different least-squares refinements leads to some interesting conclusions.

For the uncomplexed hexa-ether, refinement with experimental weights [Table 1(*a*) column 2] leads to C–C distances of 1·489–1·496 Å, mean 1·492 Å, and to C–O distances 1·410–1·429 Å, mean 1·419 Å. Very similar results are obtained with unit weights. When the experimental weights are multiplied by a modification function as in (4) with $r = 20$ Å^2, [Table 1(*a*), column 3] the C–C distances increase to a uniform value of 1·504 Å, while the C–O distances decrease slightly to 1·407–1·426 Å, mean 1·413 Å. Increasing r to 36 Å^2 [Table 1(*a*), column 4] leads to further small changes in the parameters, generally in the same sense as before. The thermal motion corrections to be applied here are of uncertain magnitude but they should lengthen C–C and C–O distances by roughly equal amounts. The difference $\langle d(\text{C–C})\rangle - \langle d(\text{C–O})\rangle$ is 0·073 Å with experimental weights, and 0·091–0·096 Å with modified weights. As discussed previously, the expected difference, by analogy with 1,4-dioxane, is 0·100 Å. The least-squares analysis with experimental (or unit) weights thus appears to lead to C–C distances that are too short and to C–O distances that are slightly too long, presumably because of bonding density effects, These systematic errors can apparently be reduced, to what extent we do not know, by using a suitably modified weighting system. It is worth noting that recent X-ray and neutron diffraction analyses of D-glucitol (Park, Jeffrey & Hamilton, 1971) give $\langle d(\text{C–C})\rangle_X = 1{\cdot}520$ Å, $\langle d(\text{C–C})\rangle_N = 1{\cdot}525$ Å, $\langle d(\text{C–O})\rangle_X = 1{\cdot}427$ Å, $\langle d(\text{C–O})\rangle_N = 1{\cdot}422$ Å, thus illustrating the same kind of systematic error.

Similar trends are also seen in the results obtained with the NaNCS and KNCS complexes. In both cases $\langle d(\text{C–C})\rangle$ increases from about 1·490 Å with experimental (or unit) weights to greater than 1·50 Å with modified weights; $\langle d(\text{C–O})\rangle$ remains almost constant at about 1·423–1·424 Å for the Na complex and 1·417–1·418 Å for the K complex.

Table 1 also suggests that the vibration parameters U_{ij} obtained with experimental weights can be slightly improved by introducing a modified weighting system. As a criterion we use here the quantity $\langle (U^o_{ij} - U^c_{ij})^2\rangle^{1/2}$ averaged over all vibration tensor components and over all atoms. This quantity is a measure of the good-

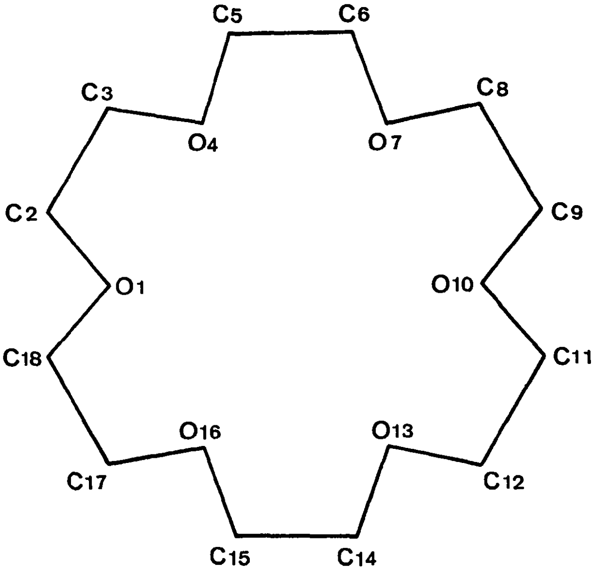


Fig. 1. Numbering system for 1,4,7,10,13,16-hexa-oxacyclo-octadecane (see Table 1).

ness-of-fit obtainable by adjusting translational and librational motions of a rigid body to the observed parameters. The improvement is most obvious for the Na complex.

There are two other advantages to be gained by using suitably modified instead of experimental weights in least-squares analysis. One is in faster convergence (provided the starting parameters are not too far from the final ones); the other is that, because of 'sharpening' of the atomic peaks, cross-terms between different atoms in the normal-equations matrix are reduced so much that 'block-diagonal' refinement converges rapidly to yield parameters almost identical to those obtained by full-matrix refinement. This represents a considerable saving in computation time.

One might expect that introduction of too extreme a modification function should lead to wildly erratic parameter shifts. Table 1 shows that the parameters hardly change at all on increasing the exponent r from 15–20 to 36 Å². With the larger value of r the ratio of modified to experimental weights is about 10^7 for high-order reflexions ($\sin\theta/\lambda \sim 0{\cdot}7$ Å^{-1}). A simple, practical method to ensure that the modified weighting function $w' = w \exp(r \sin^2\theta/\lambda^2)$ is not too extreme is to plot values of $\langle w'(\Delta F)^2\rangle$ in different $\sin\theta/\lambda$ ranges. One criterion for an appropriate weighting system is that there should be no pronounced variation of $\langle w'(\Delta F)^2\rangle$ with $\sin\theta/\lambda$. We find that with our 'experimental' weights ($r=0$) $\langle w(\Delta F^2)\rangle$ typically decreases somewhat with increasing $\sin\theta/\lambda$. For the Na complex (Table 2) the average at high $\sin\theta/\lambda$ is about 10% of the average at low $\sin\theta/\lambda$. When exponentially modified weighting systems are introduced the ratio $\langle w'\Delta^2\rangle/\langle w\Delta^2\rangle$ increases with increasing $\sin\theta/\lambda$ but, up to a certain limiting r value, the increase in this ratio is far less than the increase in the ratio of the weights, $\langle w'\rangle/\langle w\rangle$. This limiting value of r is about 18 Å² for the Na complex (Table 2) and somewhat different for the other two structures. At these limiting r values the plots of $\langle w'\Delta^2\rangle$ against $\sin\theta/\lambda$ are reasonably flat. Further increase in r (up to 36 Å²) brings a rapidly steeper increase in the ratio $\langle w'\Delta^2\rangle/\langle w\Delta^2\rangle$, but the atomic positional parameters suffer only very small changes in this range (see Table 1). The thermal parameters do change (up to *ca.* 10%) and, judging from the goodness-of-fit attainable by the rigid-body treatment, the changes are for the worse. Within limits, the harm done by introducing a too steeply rising exponential modification function does not appear to be excessive.

Comparison with neutron diffraction results

A more objective criterion for the improvement attainable by introducing exponentially modified weights into the least-squares analysis can be based on a comparison between results of X-ray and neutron diffraction. Whereas the atomic positions obtained by conventional least-squares analysis of X-ray data correspond to centroids of electron density distributions, those obtained with suitably modified weights should correspond more to centres of core electron distributions and hence should be in better agreement with nuclear positions as determined by neutron diffraction.

We have carried out some comparisons with data for *trans*-cyclodecane-1,6-diol, the crystal structure of which has been determined by X-ray followed by neutron diffraction (Ermer & Dunitz, 1971). The original X-ray analysis was carried out merely to provide a convenient starting point for the neutron analysis and no special precautions were taken to obtain highly accurate intensity data. Apart from hydrogen atoms (whose positions were estimated in the X-ray work from stereochemical considerations and held constant during the least-squares refinements discussed here), the asymmetric unit comprises 10 carbon and 2 oxygen atoms, for which the positional and vibration parameters were allowed to vary. With 'experimental weights' the quantity $Q = \langle(\mathbf{x}_j^{\mathrm{N}} - \mathbf{x}_j^{\mathrm{X}})^2\rangle^{1/2}$ was 0·023 Å, maximum deviation $|\mathbf{x}_j^{\mathrm{N}} - \mathbf{x}_j^{\mathrm{X}}|$ being 0·045 Å. With exponentially modified weights ($r=$ 11 Å²), Q was 0·017 Å, maximum deviation 0·023 Å, a considerable improvement. The quantities $Q' =$

Table 2. *Dependence of* $\langle\Delta^2\rangle$ $\langle w'\rangle$ *and* $\langle w'\Delta^2\rangle$ *on* $\sin\theta/\lambda$ *for three refinements with exponentially modified weighting systems* ($r=0$, 18, 36 Å²)

Data from analysis of sodium complex (*c*).

$\langle\sin\theta/\lambda\rangle$	0·21	0·32	0·38	0·43	0·47	0·51	0·54	0·57	0·60
$r=0$									
$\langle\Delta^2\rangle$	3·56	1·14	0·53	0·43	0·40	0·31	0·27	0·24	0·27
$\langle w\rangle$	9·22	11·7	13·8	13·1	14·4	15·3	14·6	13·9	13·0
$\langle w\Delta^2\rangle$	30·5	10·1	6·25	4·53	5·32	4·93	3·87	3·31	3·42
$r=18$ Å²									
$\langle\Delta^2\rangle$	16·5	4·28	1·19	0·43	0·38	0·20	0·14	0·12	0·10
$\langle w'\rangle$	$2{\cdot}07\times10$	$6{\cdot}96\times10$	$1{\cdot}74\times10^2$	$3{\cdot}30\times10^2$	$6{\cdot}98\times10^2$	$1{\cdot}41\times10^3$	$2{\cdot}55\times10^3$	$4{\cdot}61\times10^3$	$7{\cdot}76\times10^3$
$\langle w'\Delta^2\rangle$	$1{\cdot}51\times10^2$	$1{\cdot}62\times10^2$	$1{\cdot}73\times10^2$	$1{\cdot}34\times10^2$	$2{\cdot}42\times10^2$	$2{\cdot}88\times10^2$	$3{\cdot}39\times10^2$	$4{\cdot}93\times10^2$	$6{\cdot}61\times10^2$
$r=36$ Å²									
$\langle\Delta^2\rangle$	26·1	6·09	1·59	0·61	0·54	0·30	0·19	0·14	0·11
$\langle w'\rangle$	$5{\cdot}71\times10$	$4{\cdot}84\times10^2$	$2{\cdot}51\times10^3$	$9{\cdot}39\times10^3$	$3{\cdot}81\times10^4$	$1{\cdot}48\times10^5$	$5{\cdot}03\times10^5$	$1{\cdot}73\times10^6$	$5{\cdot}22\times10^6$
$\langle w'\Delta^2\rangle$	$4{\cdot}8\times10^2$	$1{\cdot}41\times10^3$	$3{\cdot}17\times10^3$	$5{\cdot}14\times10^3$	$1{\cdot}75\times10^4$	$4{\cdot}34\times10^4$	$8{\cdot}72\times10^4$	$2{\cdot}20\times10^5$	$4{\cdot}76\times10^5$
No. of reflexions	334	324	329	343	362	374	372	360	373

$\langle(d_{ij}^{\mathrm{N}}-d_{ij}^{\mathrm{X}})^2\rangle^{1/2}$ expressed in terms of the agreement in corresponding bond distances are 0·013 Å for 'experimental' weights and 0·007 Å for modified weights. The estimated standard deviations in $\mathbf{x}_j^{\mathrm{N}}$ are about 0·003–4 Å and in $\mathbf{x}_j^{\mathrm{X}}$ about 0·006 Å.

Standard deviations

Sharpening the atomic peaks by applying a modification function is a poor substitute for sharpening *via* an appropriate experiment *e.g.* neutron diffraction or X-ray diffraction at low temperature, because the observational errors unavoidably present in the high-order reflexions increase in importance with the increased weight assigned to these reflexions. In the calculations described in this paper, the standard deviations of the atomic parameters have been estimated in the usual way *i.e.* by inversion of the least-squares normal equations, assuming the relative weights to be given by $w'(\mathbf{h})$ instead of $w(\mathbf{h})$ (equation 4). Certain rather obvious objections could be raised against this procedure and the standard deviations calculated by it are doubtless somewhat underestimated. A more detailed discussion of the problems concerning the 'weights' and estimates of standard deviation in least-squares analysis of X-ray diffraction data will be given elsewhere (Bürgi, 1972).

Conclusions

In X-ray analysis, as in many other fields of investigation, one can never get something for nothing. The improvement in the determination of atomic peak positions is paid for by sacrificing information about the electron density distribution in regions further from the atomic centres. The loss here is not a serious one, since this information is usually ignored anyway in routine least-squares analysis based on standard spherical form factors and, in any case, it can always be recovered later by difference synthesis. In fact, for atoms with asymmetric density distributions, it is just these outer regions that cause the apparent atomic centres, as determined by least-squares analysis, to drift away from the electron density maxima when low-order reflexions are included in the analysis with large weight. The improvement in the shapes of the vibrational tensors has to be offset against lower precision in the overall temperature and scale factors. Since these factors depend on the general fall-off of F^2 with increasing scattering angle, any down-weighting of low-order reflexions leads to increased uncertainty about the behaviour at low $\sin\theta/\lambda$. Again the loss is not serious since the overall temperature factor is not usually a quantity to which much physical significance can be ascribed. It is more often a kind of repository for collecting various kinds of systematic errors in the observations and imperfections in the model.

We have been assuming so far that the weights to be applied in expression (1) have been determined from an analysis of the experiment, and that we place more confidence in these weights than in the model used to obtain $F_c(\mathbf{h})$. We have shown that altering certain features of the model, *e.g.* peak shapes, has the effect of modifying the weights. The altered model really corresponds to a different experiment, one that we have not actually carried out, but one whose results can be inferred, in principle, by mathematical operations on the actual experimental data.

The opposite extreme point of view is to place no confidence whatsoever in the experimental weights, but to assign weights solely on the basis of the trends in $[\Delta F(h)]^2$. A weighting function is chosen so that $\langle w(\Delta F)^2\rangle$ is roughly constant for arbitrary subsets of the data. As discussed by Cruickshank (1970), weights chosen in this way lead to estimates of precision for the model parameters that 'allow for all random experimental errors, for such systematic experimental errors as cannot be paralleled in the calculated model, and for such defects of the model as are not paralleled in the experimental data'. The main weakness of this extreme point of view is that although the model has been tampered with, one does not know in what way and to what extent.

The concept of a modified weighting system does not eliminate this difficulty but it provides some insight into the interplay of certain kinds of systematic experimental error and certain defects in the model. For example, the distribution of $\langle w(\Delta F)^2\rangle$ shown in Table 2 could be ascribed to systematic errors in the experiment that affect low-order reflexions more severely than high-order ones, or to defects in the model, or possibly to both. Whatever the underlying cause, a possible response is to introduce a modifying function in the least-squares analysis that evens out the irregular behaviour in the data by 'sharpening' the atomic electron density peaks. But even if the distribution of $\langle w(\Delta F)^2\rangle$ against $\sin\theta/\lambda$ were flat, we may be more interested in certain parameters that describe the model *e.g.* atomic positions, than in others, *e.g.* bonding electron density, and may decide to use a modified weighting function $w'=w\exp(r\sin^2\theta/\lambda^2)$. The increase in w' with increasing $\sin\theta/\lambda$ can be offset by a corresponding reduction in $(\Delta F)^2$ for high-order reflexions so that the plot of $(w'\Delta^2\rangle$ remains nearly flat. In summary we see that the 'weights' in least-squares analysis depend not only on the experimental data but also on the model and on our attitude to it.

This work was carried out with the financial support of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. We are also grateful to Dr Hans-Beat Bürgi and Professor Peter J. Huber for helpful comments and criticisms.

References

Bürgi, H. B. (1972). Umpublished work.
Cochran, W. (1948). *Acta Cryst.* **1**, 138–142.
Collins, D. M. & Hoard, J. L. (1970). *J. Amer. Chem. Soc.* **92**, 3761–3771.

Coppens, P. & Vos, A. (1971). *Acta Cryst.* **B27**, 146–158.

Cruickshank, D. W. J. (1970). In *Crystallographic Computing*. Edited by F. R. Ahmed, S. R. Hall and C. P. Huber, p. 195. Copenhagen: Munksgaard.

Davis, M. & Hassel, O. (1963). *Acta Chem. Scand.* **17**, 1181.

Dawson, B. (1964). *Acta Cryst.* **17**, 990–996.

Dwight, H. B. (1957). *Tables of Integrals and other Mathematical Data*, 3rd ed. New York and London: Macmillan.

Ermer, O. & Dunitz, J. D. (1971). *Chem. Commun.* pp. 178–179.

O'Connell, A. M. (1969). *Acta Cryst.* **B25**, 1273–1280.

Park, Y. J., Jeffrey, G. A. & Hamilton, W. C. (1971). *Acta Cryst.* **B27**, 2393–2401.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

Stewart, R. F. & Jensen, L. H. (1969). *Z. Kristallogr.* **128**, 133–147.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*, p. 375. New York: Macmillan.

Acta Cryst. (1973). B**29**, 595

The Molecular Structure of *o*-Carboxyphenyl Methyl Sulphoxide and *o*-Carboxyphenyl Methyl Selenium Oxide

By Birgitta Dahlén

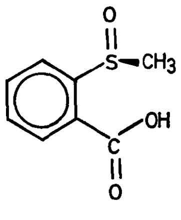
Crystallography Group, Swedish Medical Research Council Unit for Molecular Structure Analysis, University of Göteborg, Fack, S-400 33 Göteborg 33, Sweden

(*Received* 28 *June* 1972; *accepted* 14 *November* 1972)

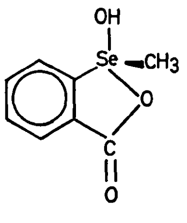
o-Carboxyphenyl methyl sulphoxide and *o*-carboxyphenyl methyl selenium oxide are monoclinic ($P2_1/c$) with cell dimensions $a=8{\cdot}979$, $b=11{\cdot}660$, $c=9{\cdot}554$ Å, $\beta=123{\cdot}62°$ and $a=8{\cdot}948$, $b=11{\cdot}445$, $c=9{\cdot}583$ Å, $\beta=122{\cdot}03°$ respectively. Although the two compounds show very similar atomic positions the molecular structures are essentially different. The hydroxyl hydrogen atom of the carboxyl group of the sulphur compound corresponds to the hydrogen atom attached to the selenium oxide oxygen, and there are several structural indications that there is ring closure by a Se–O bond. However, this bond is 2·378 Å which is 34% longer than a normal Se–O covalent bond. Both molecules are mainly planar except for the methyl group, which projects from the benzene ring plane. The molecules are linked together by a hydrogen bond from the hydroxyl oxygen to the oxygen attached to sulphur and selenium respectively in the adjacent molecule.

Introduction

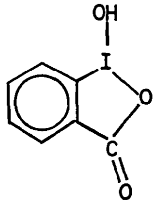
Organic sulphoxides of the type RR'SO can be resolved into optical antipodes. In connection with work on (I) Professor A. Fredga of Uppsala University recently synthesized an analogous selenium oxide (report in preparation). As some spectral data indicated that there might be a difference in the structure of these oxides, X-ray structure determinations of the two compounds were undertaken.



(I)



(II)



(III)

Experimental

Weissenberg photographs indicated that both compounds were monoclinic. The space group was determined as $P2_1/c$ from the systematic absences, $h0l$ for l odd and $0k0$ for k odd. The crystal data are as follows:

$C_8H_8O_3S$, *o*-Carboxyphenyl methyl sulphoxide
Molecular weight 184·21
Unit cell $a=8{\cdot}979$ (3), $b=11{\cdot}660$ (5), $c=9{\cdot}554$ (2) Å, $\beta=123{\cdot}62°(2)$
$V=832{\cdot}9$ Å^3
$Z=4$
$D_c=1{\cdot}469$ g cm^{-3}
$D_m=1{\cdot}469$ g cm^{-3}
$\mu=30{\cdot}73$ cm^{-1} for Cu $K\alpha$ radiation.

$C_8H_8O_3Se$, *o*-Carboxyphenyl methyl selenium oxide
Molecular weight 231·11
Unit cell $a=8{\cdot}948$ (5), $b=11{\cdot}445$ (6), $c=9{\cdot}583$ (6) Å
$\beta=122{\cdot}03°(5)$.
$V=831{\cdot}9$ Å^3
$Z=4$
$D_c=1{\cdot}845$ g cm^{-3}
$D_m=1{\cdot}840$ g cm^{-3}
$\mu=65{\cdot}57$ cm^{-1} for Cu $K\alpha$ radiation.

Intensity data for both compounds were collected on a Picker FACS I automatic diffractometer using graphite monochromated Cu $K\alpha$ radiation. Reflexions up