Nos. 331, 332, I.U.Cr. *World List of Crystallographic Computer Programs.*
COULSON, C. A. (1953). *Valence*, p. 205. London: Oxford University Press.
CRAVEN, B. M. & JEFFREY, G. A. (1959*a*). *Acta Cryst.* **12**, 754.
CRAVEN, B. M. & JEFFREY, G. A. (1959*b*). *Nature, Lond.* **183**, 676.
CRAVEN, B. M. (1959). *J. Phys. Chem.* **63**, 1296.
CRAVEN, B. M. (1962). Private communication. Program No. 374, I.U.Cr. *World List of Crystallographic Computer Programs.*
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 72.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.
DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96.
GOODKOOP, J. A. & MACGILLAVRY, C. H. (1957). *Acta Cryst.* **10**, 125.
KARLE, I. L. & KARLE, J. (1954). *J. Chem. Phys.* **22**, 43.
HANDLER, G. S. & ANDERSON, J. H. (1958). *Tetrahedron*, **2**, 345.
JEFFREY, G. A. & SAX, M. (1963). *Acta Cryst.* **16**, 430.
MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 737.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd Ed., pp. 126–128, 130–134, 136–142, 276. Ithaca: Cornell University Press.
SAX, M. (1963). *Acta Cryst.* **16**, 439.
SCHAPIRO, P. (1962*a*). Private communication. Program No. 353, I.U.Cr. *World List of Crystallographic Computer Programs.*
SCHAPIRO, P. (1962*b*). Private communication, Program No. 347, I.U.Cr. *World List of Crystallographic Computer Programs.*
SHEARER, H. M. M. & VAND, V. (1956). *Acta Cryst.* **9**, 379.
SHENSTONE, F. S. & VICKERY, J. R. (1956). *Nature, Lond.* **177**, 94.
SHIONO, R. (1962). Private communication. Programs Nos. 323, 330, I.U.Cr. *World List of Crystallographic Computer Programs.*
SOMAYAJULU, G. R. (1959). *J. Chem. Phys.* **31**, 919.
VAINSHTEIN, B. K. & PINSKER, Z. G. (1950). *Dokl. Akad. Nauk SSSR*, **72**, 53.
VAND, V. (1953). *Acta Cryst.* **6**, 797.

Acta Cryst. (1963). **16**, 1204

On the Least-Squares Analysis of the Rigid Body Vibrations of Non-Centrosymmetrical Molecules

BY G. S. PAWLEY*

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 4 *March* 1963)

The need for refinement of the origin of the mean-square rotational tensor ω_{ij} for non-centrosymmetrical molecules is investigated. The equations for the least-squares procedure are given, but a cruder method is used to establish that the refinement is important to obtain meaningful results. This is used on results for azulene, maleic anhydride and succinimide. Azulene presents a particular problem for which a special refinement is suggested.

Robertson, Shearer, Sim & Watson (1962) use the method of Cruickshank (1956) to analyse the anisotropic temperature factors obtained from the least-squares refinement of azulene. This gives the translational and rotational mean-square displacement tensors T_{ij} and ω_{ij}.

Previously Cruickshank (1957*a*, *b*) had applied this method to naphthalene and anthracene with considerable success. In both of these examples the molecule is centrosymmetrical, and therefore there is no ambiguity of choice for the origin of the molecular axes. This origin must clearly be at the centre of symmetry. The rotational tensors obtained by Cruickshank are therefore in the inertial coordinate system, describing rotations about the centre of symmetry.

However, azulene presents a different problem. The crystal belongs to the space group $P2_1/a$, and as there are only two molecules in the unit cell, this suggests a centrosymmetrical molecule placed about one quarter of the crystal symmetry centres. But the azulene molecule has no centre of symmetry and is found to exist in the crystal randomly in two orientations related to each other by the crystal centre of symmetry.

Robertson *et al.* (1962) used this centre as the origin for the tensor ω_{ij}, and obtained the results

---

* Now at the Department of Chemistry, Harvard University, Cambridge, Massachusetts, U.S.A.

$$T_{ij} = \begin{bmatrix} 6\cdot53 & 0\cdot12 & 0\cdot48 \\ & 4\cdot57 & 0\cdot37 \\ & & 3\cdot37 \end{bmatrix} \text{Å}^2.10^{-2}$$

$$\omega_{ij} = \begin{bmatrix} 17\cdot10 & 0\cdot45 & 2\cdot46 \\ & 13\cdot40 & -2\cdot63 \\ & & 27\cdot83 \end{bmatrix} \text{deg}^2 \qquad (1)$$

with an estimated standard deviation of the U_{ij} of 0·0107 Å^2.

It would seem most reasonable to choose the centre of gravity of the molecule as the origin for the tensor ω_{ij}, which is near to but not quite coincident with the crystal centre of symmetry. With this ambiguity of choice of origin it is of interest to find how the tensors T_{ij} and ω_{ij} vary with the choice of origin.

These tensors were calculated, by means of a program written for the EDSAC by D. G. Watson, with origins at 1, 2 and 3 Å from the crystal symmetry centre towards the atom A (Fig. 1, Robertson *et al.*, 1962). The first of these gave

$$T_{ij} = \begin{bmatrix} 6\cdot24 & 0\cdot52 & -0\cdot40 \\ & 5\cdot21 & -0\cdot44 \\ & & 5\cdot74 \end{bmatrix}$$

$$\omega_{ij} = \begin{bmatrix} 1\cdot86 & -2\cdot54 & 1\cdot77 \\ & 3\cdot93 & -2\cdot79 \\ & & 17\cdot34 \end{bmatrix} \qquad (2)$$

which has estimated standard deviations of all components less than those given by Robertson *et al.* The estimated standard deviation of the U_{ij} was 0·00934.

At 2 and 3 Å towards A the tensors

$$T_{ij} = \begin{bmatrix} 6\cdot55 & 0\cdot49 & -0\cdot42 \\ & 5\cdot41 & -0\cdot38 \\ & & 5\cdot98 \end{bmatrix}$$

$$\omega_{ij} = \begin{bmatrix} -1\cdot31 & -2\cdot05 & 1\cdot14 \\ & 1\cdot67 & -1\cdot32 \\ & & 8\cdot82 \end{bmatrix} \qquad (3)$$

and

$$T_{ij} = \begin{bmatrix} 6\cdot66 & 0\cdot47 & -0\cdot44 \\ & 5\cdot26 & -0\cdot39 \\ & & 6\cdot01 \end{bmatrix}$$

$$\omega_{ij} = \begin{bmatrix} -1\cdot96 & -1\cdot56 & 0\cdot78 \\ & 0\cdot99 & -0\cdot79 \\ & & 5\cdot51 \end{bmatrix} \qquad (4)$$

respectively were obtained. These have some negative diagonal components which are physically impossible and therefore cannot be expected to fit the experimental results.

This analysis implies that the optimum choice of origin lies between the crystal symmetry centre and the atom A and within 1 Å of the former. The differences between (1) and (2), especially in ω_{11}, suggest that the choice of origin in non-centrosymmetrical molecules is of great importance in obtaining meaningful results. This origin should be chosen to fit the experimental results as accurately as possible.

This can best be done by a least-squares refinement, which involves finding the best fit to the experimental results of the two tensors T_{ij} and ω_{ij} each with six independent components, where the origin of ω_{ij} is given by $R(X, Y, Z)$. X, Y and Z are the only variables additional to those dealt with by Cruickshank (1956). This enlarges the least-squares matrix, making it 15 by 15, which contains the 12 by 12 matrix of Cruickshank, **M**. We see later that the new components of this matrix are functions of R and ω_{ij}, which means that the best fit cannot be obtained by solving one matrix equation. Instead, the matrix has to be set up a number of times, each time using the values of R and ω_{ij} found from the previous solution. Therefore initial values of R and ω_{ij} must be given, and some criterion to terminate the refinement.

Let $r_0(x_0, y_0, z_0)$ be the position coordinates of an atom with respect to the origin of the molecular coordinate system, and let $r(x, y, z)$ be the position coordinates with respect to the origin of the tensor ω_{ij}. Thus

$$x = x_0 - X \text{ etc.}$$

Let us simplify the usual notation by putting 1, 2, 3, 4, 5 and 6 as subscripts for ij = 11, 22, 33, 23, 31 and 12 respectively for the components of the tensors. Equations of the type (2·3) of Cruickshank (1956) are then written

$$\begin{aligned} U_1 &= T_1 + z^2\omega_2 + y^2\omega_3 - 2yz\omega_4 \\ U_4 &= T_4 - yz\omega_1 - x^2\omega_4 + xy\omega_5 + zx\omega_6 \,. \end{aligned} \qquad (5)$$

Equations (2·5) to (2·8) are here applicable, to which must be added

$$\begin{aligned} \left(\frac{\partial U_1}{\partial X}\right) &= 0 \\ \left(\frac{\partial U_2}{\partial X}\right) &= -2x\omega_3 + 2z\omega_5 \\ \left(\frac{\partial U_3}{\partial X}\right) &= -2x\omega_2 + 2y\omega_6 \\ \left(\frac{\partial U_4}{\partial X}\right) &= 2x\omega_4 - y\omega_5 - z\omega_6 \\ \left(\frac{\partial U_5}{\partial X}\right) &= z\omega_2 - y\omega_4 \\ \left(\frac{\partial U_6}{\partial X}\right) &= y\omega_3 - z\omega_4 \,. \end{aligned} \qquad (6)$$

The normal equations written in matrix form are

$$\left[\begin{array}{c|lll}
 & 0 & 2z\omega_4-2y\omega_3 & 2y\omega_4-2z\omega_2 \\
 & 2z\omega_5-2x\omega_3 & 0 & 2x\omega_5-2z\omega_1 \\
 & 2y\omega_6-2x\omega_2 & 2x\omega_6-2y\omega_1 & 0 \\
 & 2x\omega_4-y\omega_5-z\omega_6 & z\omega_1-x\omega_5 & y\omega_1-x\omega_6 \\
 & z\omega_2-y\omega_4 & 2y\omega_5-z\omega_6-x\omega_4 & x\omega_2-y\omega_6 \\
 & y\omega_3-z\omega_4 & x\omega_3-z\omega_5 & 2z\omega_6-x\omega_4-y\omega_5 \\
\mathbf{M} & \begin{array}{l}[2y^2(y\omega_6-x\omega_2)\\ \;+2z^2(z\omega_5-x\omega_3)\\ \;+yz(y\omega_5+z\omega_6-2x\omega_4)]\end{array} & \begin{array}{l}[2y^2(x\omega_6-y\omega_1)\\ \;+yz(x\omega_5-z\omega_1)]\end{array} & \begin{array}{l}[2z^2(x\omega_5-z\omega_1)\\ \;+yz(x\omega_6-y\omega_1)]\end{array} \\
 & \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\
 & \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\
 & \begin{array}{l}[x^2(y\omega_5+z\omega_6-2x\omega_4)\\ \;+xy(z\omega_2-y\omega_4)\\ \;+zx(y\omega_3-z\omega_4)]\end{array} & \begin{array}{l}[4yz(y\omega_3-z\omega_4)\\ \;+x^2(x\omega_5-z\omega_1)\\ \;+zx(x\omega_3-z\omega_5)\\ \;+xy(2y\omega_5-z\omega_6-x\omega_4)]\end{array} & \begin{array}{l}[4yz(z\omega_2-y\omega_4)\\ \;+x^2(x\omega_6-y\omega_1)\\ \;+xy(x\omega_2-y\omega_6)\\ \;+zx(2z\omega_6-y\omega_5-x\omega_4)]\end{array} \\
 & \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\
 & \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\
\hline
 & \begin{array}{l}[4(x\omega_3-z\omega_5)^2\\ \;+4(x\omega_2-y\omega_6)^2\\ \;+(2x\omega_4-y\omega_5-z\omega_6)^2\\ \;+(z\omega_2-y\omega_4)^2\\ \;+(y\omega_3-z\omega_4)^2]\end{array} & \begin{array}{l}[4(x\omega_2-y\omega_6)(y\omega_1-x\omega_6)\\ \;+(2x\omega_4-y\omega_5-z\omega_6)\\ \quad(z\omega_1-x\omega_5)\\ \;+(2y\omega_5-x\omega_6-x\omega_4)\\ \quad(z\omega_2-y\omega_4)\\ \;+(y\omega_3-z\omega_4)(x\omega_3-z\omega_5)]\end{array} & \cdots\cdots\cdots \\
 & \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\
 & \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots
\end{array}\right]$$

$$\times\left[\begin{array}{c} T_1\\ T_2\\ T_3\\ T_4\\ T_5\\ T_6\\ \omega_1\\ \omega_2\\ \omega_3\\ \omega_4\\ \omega_5\\ \omega_6\\ \hline X\\ \\ \\ Y\\ Z \end{array}\right] = \left[\begin{array}{l} U_1\\ U_2\\ U_3\\ U_4\\ U_5\\ U_6\\ y^2U_3+z^2U_2-yzU_4\\ z^2U_1+x^2U_3-zxU_5\\ x^2U_2+y^2U_1-xyU_6\\ -x^2U_4+xyU_5+zxU_6-2yzU_1\\ -y^2U_5+yzU_6+xyU_4-2zxU_2\\ -z^2U_6+zxU_4+yzU_5-2xyU_3\\ \hline [2U_2(z\omega_5-x\omega_3)+2U_3(y\omega_6-x\omega_2)\\ +U_4(2x\omega_4-y\omega_5-z\omega_6)\\ +U_5(z\omega_2-y\omega_4)+U_6(y\omega_3-z\omega_4)]\\ \quad\cdots\cdots\cdots\cdots\\ \quad\cdots\cdots\cdots\cdots \end{array}\right] \tag{7}$$

where **M**, the matrix of Cruickshank, requires rearrangement for the different order of the variables. Here a line of dots denotes a similar matrix element.

As the terms of this equation are rather cumbersome, it seemed wise first to use a somewhat crude but easily programmed method, based on trial and error. The variables were altered by predetermined steps after finding which direction of alteration would diminish the sum

$$\Sigma(U_{\text{obs}}-U_{\text{calc}})^2.$$

When the values of the variables oscillated, the steps were reduced and the process continued.

The results for azulene were the first to be analysed. The origin of the mean-square rotational tensor of azulene was confined to the molecule plane, and during the refinement moved 0·53 Å from the crystal symmetry centre to the point marked $\ast$ in Fig. 1. The resulting tensors were

$$T_{ij} = \begin{bmatrix} 5{\cdot}940 & 0{\cdot}608 & -0{\cdot}375 \\ & 4{\cdot}910 & -0{\cdot}503 \\ & & 5{\cdot}315 \end{bmatrix} \text{Å}^2.10^{-2}$$

$$\omega_{ij} = \begin{bmatrix} 7{\cdot}77 & -1{\cdot}56 & 1{\cdot}77 \\ & 6{\cdot}94 & -4{\cdot}06 \\ & & 24{\cdot}61 \end{bmatrix} \text{deg}^2 \qquad (8)$$

giving an estimated standard deviation of the U_{ij} of 0·00815 Å^2. This is a better fit with experiment than that found by Robertson *et al.*, being significant on the 2% level of the *F*-distribution.

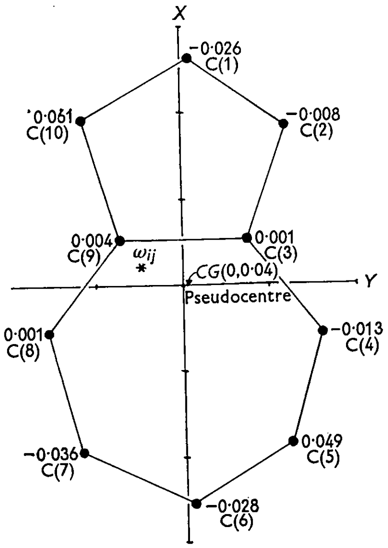

Fig. 1. Azulene, showing the axes used by Robertson *et al.* (1962), the centre of gravity of the molecule, the deviations in Å from the mean molecular plane, and the best origin for ω_{ij} in the molecular plane.

Robertson *et al.* compare their results with those found for naphthalene. Their conclusion that the greatest amplitude of translational vibration is along the long axis of the molecule is upheld, although the fit with experiment for azulene is far poorer than that for naphthalene. They obtain in refinement an *R* index of 6·5% which is normally beyond suspicion. However they stress that as the structure is disordered this brings atoms of the molecule in one orientation very close to different atoms of the oppositely orientated molecule, for six out of the ten atoms. Consequently the least-squares method gives large errors for all bond lengths which involve these six atoms, and only three bond lengths have an error of 0·007 Å or less. Bonds involving one of the six atoms have errors greater than 0·019 Å, and bonds between pairs from these six atoms have errors greater than 0·026 Å.

The rotational tensor is most affected by the results of the outermost atoms, but these are the atoms which fall into pairs of overlapping atoms. Because of the proximity of the atoms of each pair, their parameters must suffer from interaction in the least-squares refinement.

In order to obtain a solution without these interactions, we should have to assume that the temperature parameters for all the atoms are determined by the two tensors, T_{ij} and ω_{ij}, and that the origin of ω_{ij} is not the centre of gravity of the molecule. There would then be one scale factor, thirty atomic coordinates, twelve tensor components and three coordinates for the origin of ω_{ij}, all to be refined, in all 46 instead of the 91 used by Robertson *et al.* The resulting *R* index would be larger than 6·5%, owing to the reduction in the number of parameters refined, and this might then renew doubts as to whether the structure really is disordered, since Robertson *et al.* quote an *R* index of 22·4%, with only isotropic temperature factors but with an ordered crystal structure.

Owing to the inaccuracies in the thermal parameters of azulene we cannot use this example to support the theory that the origin of ω_{ij} is not necessarily the centre of gravity of the molecule. Two other crystals, maleic anhydride and succinimide, whose structures have recently been determined by the least-squares method by Marsh, Ubell & Wilcox (1962) and Mason (1961), were chosen to continue the study. Orthogonal coordinates were taken along the *x*, *y* and *z* axes of these orthorhombic crystals, the centres of gravity, the principal inertia axes, and the U_{obs} were found, using the procedure described for azulene. The results were first analysed with the origin of ω_{ij} at the centres of gravity, and the results obtained are as follows.

For maleic anhydride,

$$T_{ij} = \begin{bmatrix} 5{\cdot}200 & 0{\cdot}202 & -0{\cdot}126 \\ & 6{\cdot}120 & 0{\cdot}601 \\ & & 6{\cdot}985 \end{bmatrix} \text{Å}^2.10^{-2}$$

$$\omega_{ij} = \begin{bmatrix} 34{\cdot}666 & 0{\cdot}931 & 6{\cdot}466 \\ & 41{\cdot}053 & -0{\cdot}487 \\ & & 15{\cdot}420 \end{bmatrix} \text{deg}^2 \qquad (9)$$

giving an estimated standard deviation of the U_{ij} of 0·00605 Å^2.

For succinimide,

$$T_{ij} = \begin{bmatrix} 1{\cdot}078 & 0{\cdot}144 & 0{\cdot}366 \\ & 1{\cdot}484 & 0{\cdot}201 \\ & & 2{\cdot}423 \end{bmatrix} \text{Å}^2.10^{-2}$$

$$\omega_{ij} = \begin{bmatrix} 4{\cdot}912 & -2{\cdot}165 & 2{\cdot}232 \\ & 25{\cdot}037 & 0{\cdot}094 \\ & & 36{\cdot}093 \end{bmatrix} \text{deg}^2 \qquad (10)$$

giving an estimated standard deviation of the U_{ij} of 0·00702 Å^2.

The origin of ω_{ij} was then refined, and when the convergence was very slow the origin had moved by

0·332 Å and 0·448 Å for the two examples respectively. Figs. 2(*a*) and (*b*) show the two molecules, their intermediate and minor inertia axes, the deviation in Å from the maximum inertia plane, the centres of gravity and the origins of the tensors ω_{ij}, marked $\ast$. The divisions along the axes are in Å. The tensors obtained are, for maleic anhydride,

$$\begin{aligned} T_{ij} &= \begin{bmatrix} 4{\cdot}657 & 0{\cdot}207 & 0{\cdot}092 \\ & 6{\cdot}110 & 0{\cdot}616 \\ & & 6{\cdot}928 \end{bmatrix} \text{Å}^2.10^{-2} \\ \omega_{ij} &= \begin{bmatrix} 34{\cdot}680 & 2{\cdot}740 & 15{\cdot}610 \\ & 40{\cdot}000 & 2{\cdot}742 \\ & & 40{\cdot}280 \end{bmatrix} \text{deg}^2 \end{aligned} \tag{11}$$

with an estimated standard deviation of the U_{ij} of 0·00434 Å^2, and for succinimide,

$$\begin{aligned} T_{ij} &= \begin{bmatrix} 0{\cdot}758 & 0{\cdot}103 & 0{\cdot}392 \\ & 1{\cdot}609 & 0{\cdot}205 \\ & & 2{\cdot}470 \end{bmatrix} \text{Å}^2.10^{-2} \\ \omega_{ij} &= \begin{bmatrix} 2{\cdot}622 & -2{\cdot}521 & 3{\cdot}261 \\ & 24{\cdot}730 & 7{\cdot}199 \\ & & 46{\cdot}150 \end{bmatrix} \text{deg}^2 \end{aligned} \tag{12}$$

with an estimated standard deviation of the U_{ij} of 0·00602 Å^2.

The improvement thus obtained for maleic anhydride is significant at the 2% level, though for succinimide the improvement is significant at the 16% level. Although the latter level is high, the theory to be tested is that the origin of ω_{ij} is not *necessarily* the centre of gravity. In some cases therefore we should expect the origin to be very near if not coincident with the centre of gravity. Improvements will of course depend on the accuracy of the initial F_{obs} and the amount of refinement done. Maleic anhydride reached an R index of 5·5% for 479 reflexions, and succinimide reached 9·1% for 705 reflexions, somewhat poorer. The results here obtained are therefore considered to support the theory, and to justify investigation of the least-squares method.

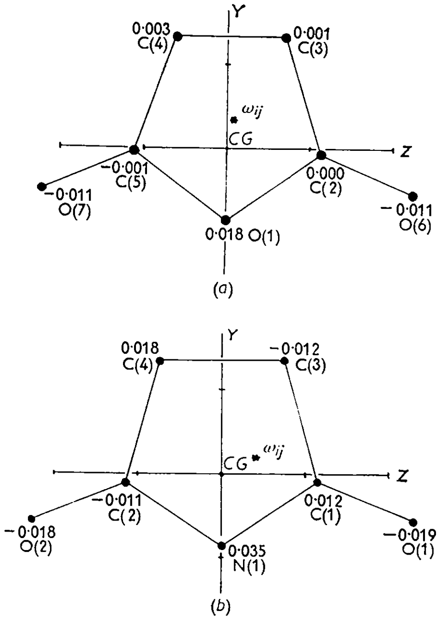

Fig. 2. (*a*) Maleic anhydride. (*b*) Succinimide. Each of these shows the inertia axes which intersect at the centre of gravity of the molecule, the deviations in Å from the plane of maximum inertia, and the best origin for ω_{ij} in this plane.

The author wishes to thank Dr M. V. Wilkes, F. R. S. for permission to use the EDSAC, on which the computations were done, Dr W. Cochran, F.R.S. for constant supervision, and the Department of Scientific and Industrial Research for the award of a Research Studentship, during the tenure of which this work was done.

References

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757.

Cruickshank, D. W. J. (1957*a*). *Acta Cryst.* **10**, 470.

Cruickshank, D. W. J. (1957*b*). *Acta Cryst.* **10**, 504.

Marsh, R. E., Ubell, E. & Wilcox, H. E. (1962). *Acta Cryst.* **15**, 35.

Mason, R. (1961). *Acta Cryst.* **14**, 720.

Robertson, J. M., Shearer, H. M. M., Sim, G A. & Watson, D. G. (1962). *Acta Cryst.* **15**, 1.