

figure of merit. This  $E$  map contained all 22 non-hydrogen atoms to be found. For the modified cardenolide structure, the  $E$  map calculated for the phase set with the second-highest combined figure of merit showed 31 atoms of the total 35 non-hydrogen atoms of the molecule. It is important to remark that the translations of the correctly positioned molecules did not coincide with the translations of the structural fragments selected from the normal  $E$  map. The modification of  $E$  values is easily incorporated in existing

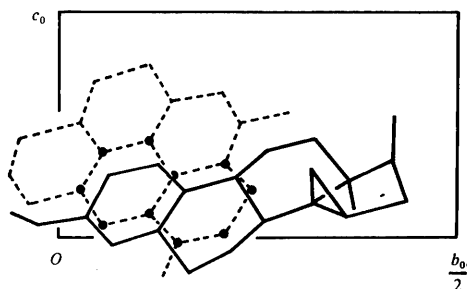


Fig. 1. Comparison of  $E$  maps of 3-methoxy-14 $\alpha$ ,15 $\alpha$ -oxido-estra-1,3,5(10)-triene-17 $\alpha$ -ol. The peaks of the best  $E$  map calculated with the  $E_{\text{obs}}(hkl)$  are connected by dotted lines representing a grid. The solid black circles mark the peaks which were used for the calculation of the  $E_{\text{frag}}(hkl)$ . The solid lines connect the 22 highest peaks in the  $E$  map with the third-highest combined figure of merit calculated with the  $E_m(hkl)$ . All these peaks correspond to atoms.

direct-methods programs and is an interesting alternative to the above-mentioned methods.

### References

- BEURSKENS, P. T., BOESBURG, H. M. & BEURSKENS, G. (1980). *TRADIR*. Strengthened translation functions. Univ. of Nijmegen, the Netherlands.
- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH. E. M. & PRICK, P. A. J. (1980). *DIRDIF*. Direct methods for difference structures. Univ. of Nijmegen, the Netherlands.
- HOPPE, W. (1957a). *Acta Cryst.* **10**, 750–754.
- HOPPE, W. (1957b). *Z. Elektrochem.* **61**, 1076–1083.
- HUBER, R. (1965). *Acta Cryst.* **19**, 353–356.
- KARLE, J. (1972). *Acta Cryst.* **B28**, 820–824.
- MAIN, P. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 97–105. Copenhagen: Munksgaard.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.
- MESSERSCHMIDT, A. & MEGGES, R. (1982). *Acta Cryst.* Submitted.
- MESSERSCHMIDT, A. & SCHUBERT, S. (1982). *Acta Cryst.* Submitted.
- NORDMAN, C. E. (1966). *Trans. Am. Crystallogr. Assoc.* **2**, 65–74.
- SHELDRIK, G. M. (1976). Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1982). **A38**, 869–870

**On the estimated standard deviation of the atom-to-plane distance.** By TETSUZO ITO, *The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan*

(Received 6 May 1982; accepted 15 June 1982)

### Abstract

An expression is given for the estimated standard deviation of the atom-to-plane distance of an atom defining the least-squares plane.

Two least-squares methods have been proposed to determine the best-plane parameters and their error matrix (variance-covariance matrix): one is a method of undetermined multiplier (Ito, 1981a, hereinafter called paper I), and the other is an elimination method (Ito, 1981b, paper II). Although the two methods give identical results in a general case, the elimination method has an advantage that it can deal with a plane defined with only three atoms.

In paper I, an expression is given for the estimated standard deviation of the atom-to-plane distance of the  $i$ th atom.\*

\* As will be explained in the following,  $\sigma_1$  of (11) and  $\sigma_2$  of (1) are the estimated standard deviations of the atom-to-plane distance of an atom defining and not defining the plane, respectively.

$$\sigma_2^2(d_i) = ({}^d\mathbf{M}_0)_{ii} + \tilde{\mathbf{y}}_i {}^n\mathbf{M}\mathbf{y}_i, \quad (1)$$

where  ${}^d\mathbf{M}_0$  is the error matrix for the atom-to-plane distances originating from the atomic positional errors,  $\tilde{\mathbf{y}}_i$  (transpose of  $\mathbf{y}_i$ ) is an atomic coordinate matrix:

$$\tilde{\mathbf{y}}_i \equiv (x_i y_i z_i - 1), \quad (2)$$

and  ${}^n\mathbf{M}$  is the error matrix for the four plane parameters,

$$\tilde{\mathbf{n}} \equiv (m_1 m_2 m_3 d_0), \quad (3)$$

which is obtained through the best-plane calculations. Expression (1) has been derived under the assumption that the atomic coordinates and the plane parameters are not correlated. Therefore, it is applicable only to atoms not defining the plane. The assumption is not valid for the plane-defining atoms because their coordinates are used to determine the plane parameters. Particularly in the case of a three-atom plane, the correlation is perfect; since the three atoms necessarily lie on the plane, their atom-to-plane distances of zero should have zero standard deviations, which is evidently in contradiction with (1).

The atom-to-plane distances  $\mathbf{d}$  of the  $n$  atoms defining the plane are dependent on the least-squares adjustments of the plane parameters  $\Delta \mathbf{n}$  through the relationship,

$$\mathbf{d} = \mathbf{d}^{(0)} - \mathbf{Y} \Delta \mathbf{n}, \quad (4)$$

where

$$\bar{\mathbf{d}} \equiv (d_1 d_2 \dots d_n), \quad (5)$$

$$\tilde{\mathbf{Y}} \equiv (\mathbf{y}_1 \mathbf{y}_2 \dots \mathbf{y}_n), \quad (6)$$

and  $\mathbf{d}^{(0)}$  denotes the distances before adjustments. Substituting the least-squares solution [equations (20a) and (23) of paper I]

$$\Delta \mathbf{n} = {}^n \mathbf{M} \tilde{\mathbf{Y}} \mathbf{W} \mathbf{d}^{(0)} \quad (7)$$

into (4), we obtain the relationship

$$\mathbf{d} \bar{\mathbf{d}} = \mathbf{d}^{(0)} \bar{\mathbf{d}}^{(0)} - \mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}} \mathbf{W} \mathbf{d}^{(0)} \bar{\mathbf{d}}^{(0)} - \mathbf{d}^{(0)} \bar{\mathbf{d}}^{(0)} \mathbf{W} \mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}} + \mathbf{Y} \Delta \mathbf{n} \Delta \bar{\mathbf{n}} \tilde{\mathbf{Y}}, \quad (8)$$

where  $\mathbf{W}$  is the weight matrix defined by

$$\mathbf{W} = {}^d \mathbf{M}_0^{-1}. \quad (9)$$

The error matrix for  $\mathbf{d}$  can readily be obtained from (8) with the aid of (9) as

$${}^d \mathbf{M}_1 = {}^d \mathbf{M}_0 - \mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}} \mathbf{W} {}^d \mathbf{M}_0 - {}^d \mathbf{M}_0 \mathbf{W} \mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}} + \mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}} = {}^d \mathbf{M}_0 - \mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}}. \quad (10)$$

The diagonal element of  ${}^d \mathbf{M}_1$  is the variance of the atom-to-plane distance of the plane-defining atom,

$$\sigma_i^2(d_i) = ({}^d \mathbf{M}_0)_{ii} - \tilde{\mathbf{y}}_i {}^n \mathbf{M} \mathbf{y}_i. \quad (11)$$

It should be noted that (11) is the same as (1) except that the sign of the second term is reversed.

Expression (11) may be checked for a three-atom plane. In this case reference must be made to the elimination method of paper II. It can generally be shown that

$$\mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}} = \mathbf{Y}_e {}^p \mathbf{M} \tilde{\mathbf{Y}}_e, \quad (12)$$

where  $\mathbf{Y}_e$  is the derivative matrix [equation (12) of paper II] after one of the plane parameters has been eliminated, and  ${}^p \mathbf{M}$  is the error matrix for the remaining three plane parameters which is given by

$${}^p \mathbf{M} = (\tilde{\mathbf{Y}}_e \mathbf{W} \mathbf{Y}_e)^{-1}. \quad (13)$$

Now, since  $\mathbf{Y}_e^{-1}$  is defined for a three-atom plane, (12) together with (13) gives

$$\mathbf{Y} {}^n \mathbf{M} \tilde{\mathbf{Y}} = \mathbf{W}^{-1} = {}^d \mathbf{M}_0, \quad (14)$$

that is, from (10),

$${}^d \mathbf{M}_1 = 0, \quad (15)$$

for a three-atom plane, which is the expected result.

The Fortran program BP70 of paper II has been modified according to (11) for the plane-defining atoms.

A simple example of a four-atom group will serve for illustration. The four atoms are located at  $A(1,0,0)$ ,  $B(0,1,0)$ ,  $C(-1,0,0)$  and  $D(0,-1,0.01)$  in a Cartesian coordinate system in Å units, with a common isotropic standard deviation of 0.01 Å. If we define a plane with three atoms  $A$ ,  $B$  and  $C$ , the plane evidently coincides with the  $x,y$  plane through the origin, and atom  $D$  not defining the plane is out of the plane by 0.01 Å, with the standard deviation  $\sigma_2$  of (1) of 0.02 Å; atom  $D$  is coplanar within the standard deviation.

On the other hand, if we define a plane with all the four atoms, the best plane inclines by 0.29 (57)° from the  $x,y$  plane, with the origin-to plane distance of 0.0025 (50) Å. Atoms  $A$  and  $C$ , and  $B$  and  $D$  are out of the plane by 0.0025 Å in opposite directions, with a common standard deviation  $\sigma_1$  of equation (11) of 0.005 Å; the four atoms are again planar within the standard deviations.

$$\chi^2 \equiv \sum [d_i / \sigma_1(d_i)]^2 \quad (16)$$

for the four atoms is 1.00 for one degree of freedom, which also confirms the planarity. However, such statistical tests based on the ratios  $d/\sigma$  must be used with caution, because any groups of atoms would hardly be planar, if the atomic positions are determined with very high precision. In other words, the atom-to-plane distances themselves are also important to test planarity (e.g.  $d$  less than  $\pm 0.005$  Å).

## References

- ITO, T. (1981a). *Acta Cryst.* **A37**, 621–624.  
 ITO, T. (1981b). *Sci. Pap. Inst. Phys. Chem. Res. Saitama*, **75**, 55–58.

*Acta Cryst.* (1982). **A38**, 870–871

**Magnétoélectricité et pyroconductivité.** Par JEAN SIVARDIÈRE, *Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble CEDEX, France* et ALEX WAIN TAL, *Laboratoire Louis Néel, CNRS, 166 X, 38042 Grenoble CEDEX, France*

(Reçu le 19 janvier 1982, accepté le 27 mai 1982)

## Abstract

Magnetolectric classes in which the magnetolectric tensor is non-symmetrical allow the existence of spontaneous electrical currents.

Les 58 classes magnétoélectriques ont été énumérées par Indenbom (1960; voir aussi Cracknell, 1975), qui a précisé la forme du tenseur magnétoélectrique dans chacune d'elles. La théorie des représentations permet d'obtenir simplement ces résultats (Bertaut, 1968; Sivardièrre & Waintal, 1969; Sivardièrre, 1969).