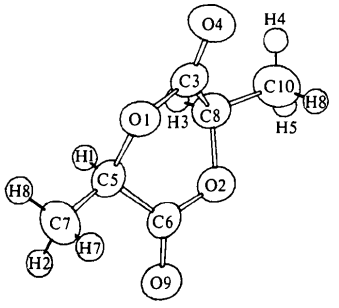

Fig. 1. The D-,D-lactide molecule showing the atomic numbering.

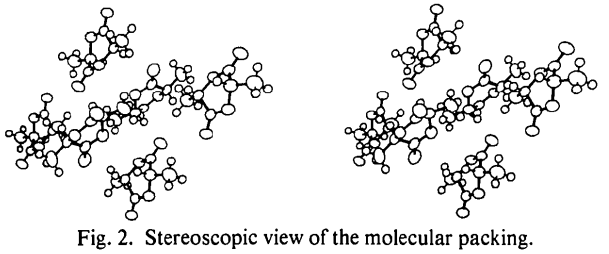

Fig. 2. Stereoscopic view of the molecular packing.

interpreted by Holten *et al.* (1971) are in agreement with our results. Therefore, in principle, polymers derived from the title compound may contain longer isotactic sequences.

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SHORT COMMUNICATIONS

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Standard deviations obtained from block-diagonal least-squares matrices.

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Abstract

It is demonstrated that the estimated standard deviations of parameters obtained from partial-matrix least-squares refinement are smaller than, or equal to, the corresponding standard deviations obtained from full-matrix refinement.

It is the purpose of this note to demonstrate that a standard deviation obtained from a diagonal, or from any form of block-diagonal, least-squares refinement is a *minimum*

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estimate that will generally be smaller than the e.s.d. obtained from a full-matrix refinement. While this concept is by no means new (see, *e.g.*, Hodgson & Rollett, 1963; Dunitz, 1979), we have not before seen it proved except for the diagonal case (Sparks, 1958).

Consider the full matrix of normal equations, **A**, which is positive definite and Hermitian (in this case, **A** is real and symmetric). Let us partition **A** as follows:

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} \\ \mathbf{A}_{21} & \mathbf{A}_{22} \end{pmatrix}, \tag{1}$$

where $\mathbf{A}_{11}$ and $\mathbf{A}_{22}$ are square matrices of orders n_1 and n_2. We similarly partition the inverse matrix:

$$\mathbf{A}^{-1} = \mathbf{B} = \begin{pmatrix} \mathbf{B}_{11} & \mathbf{B}_{12} \\ \mathbf{B}_{21} & \mathbf{B}_{22} \end{pmatrix}, \tag{2}$$

where again $\mathbf{B}_{11}$ and $\mathbf{B}_{22}$ are square matrices of orders n_1 and n_2. The elements of $\mathbf{A}^{-1}$ (b_{ij}) are the variance and covariance terms for the various parameters x_i. We shall show here that the determinant of any principal minor of **B**, such as det $\mathbf{B}_{11}$, is greater than or equal to (det $\mathbf{A}_{11})^{-1}$. More generally the evaluation of $(\mathbf{A}_{11})^{-1}$, which is obtained by any blocked-matrix approximation to **A**, yields a set of variances which are less than or equal to the diagonal elements of $\mathbf{B}_{11}$ as obtained from the *complete* **A** matrix.

Since **A** is Hermitian positive definite, we can write the Cholesky factorizations

$$\mathbf{A} = \mathbf{R}\mathbf{R}^*; \quad \mathbf{A}^{-1} = (\mathbf{R}^{-1})^* \, \mathbf{R}^{-1}, \tag{3}$$

where **R** and $\mathbf{R}^{-1}$ are right-triangular ($r_{ij} = 0$ for $i > j$) and where $\mathbf{R}^*$ is left-triangular and has elements i, j equal to r_{ji}; all the diagonal elements r_{ii} are positive (see, *e.g.*, Franklin, 1968, pp. 203–208). We then partition **R** and $\mathbf{R}^{-1}$:

$$\mathbf{R} = \begin{pmatrix} \mathbf{R}_{11} & \mathbf{R}_{12} \\ \mathbf{0} & \mathbf{R}_{22} \end{pmatrix}, \quad \mathbf{R}^{-1} = \begin{pmatrix} \mathbf{S}_{11} & \mathbf{S}_{12} \\ \mathbf{0} & \mathbf{S}_{22} \end{pmatrix}, \tag{4}$$

where $\mathbf{R}_{11}$ and $\mathbf{S}_{11}$ are square (and right-triangular) matrices of order n_1.

From (3) and (4), we see that

$$\mathbf{A}_{11} = \mathbf{R}_{11}(\mathbf{R}_{11})^* + \mathbf{R}_{12}(\mathbf{R}_{12})^* \tag{5}$$

and

$$\mathbf{B}_{11} = (\mathbf{S}_{11})^* \, \mathbf{S}_{11}. \tag{6}$$

Hence, det $\mathbf{B}_{11} = (\det \mathbf{R}_{11})^{-2}$.

We now write equation (5) as follows:

$$\mathbf{A}_{11} = \mathbf{R}_{11}(\mathbf{I} + \mathbf{Q})(\mathbf{R}_{11})^*, \tag{7}$$

where **Q** is a positive semidefinite matrix:

$$\mathbf{Q} = \mathbf{S}_{11} \, \mathbf{R}_{12}(\mathbf{R}_{12})^* \, (\mathbf{S}_{11})^*. \tag{8}$$

We then have

$$\det(\mathbf{I} + \mathbf{Q}) \geq 1, \tag{9}$$

with equality only if $\mathbf{Q} = \mathbf{0}$, *i.e.*, only if $\mathbf{R}_{12} = \mathbf{0}$ – or, since $\mathbf{A}_{12} = \mathbf{R}_{12}(\mathbf{R}_{22})^*$, only if $\mathbf{A}_{12} = \mathbf{0}$.

From (6), (7), and (9) we obtain

$$\begin{aligned} \det \mathbf{A}_{11} &= (\det \mathbf{R}_{11})^2 \det(\mathbf{I} + \mathbf{Q}) \\ \det \mathbf{A}_{11} &\geq (\det \mathbf{R}_{11})^2 \\ \det \mathbf{A}_{11} &\geq (\det \mathbf{B}_{11})^{-1}; \end{aligned} \tag{10}$$

or, as we set out to demonstrate,

$$\det \mathbf{B}_{11} \geq (\det \mathbf{A}_{11})^{-1}. \tag{11}$$

By permutation of indices, the inequality (11) can be extended to *all* the principal minors. Consider an $n \times n$ permutation matrix **P** which, by the multiplication $\mathbf{P}^T\mathbf{A}\mathbf{P}$, interchanges any desired rows and columns of **A**. Since $\mathbf{P}^T\mathbf{P} = \mathbf{I}$, we have

$$(\mathbf{P}^T\mathbf{A}\mathbf{P})^{-1} = \mathbf{P}^T \, \mathbf{A}^{-1} \, \mathbf{P} = \mathbf{P}^T\mathbf{B}\mathbf{P}. \tag{12}$$

Let $k_1, \ldots, k_n$ be the resulting ordering of the rows and columns $1, \ldots, n$. The inequality (11) then implies, for any principal minor of order n_1,

$$\det(b_{k_i k_j}) \geq [\det(a_{k_i k_j})]^{-1} \; (i, j = 1, \ldots, n_1). \tag{13}$$

For example, if $n = 3$, $n_1 = 2$, and $k_1, k_2, k_3 = 3,1,2$, then

$$\begin{vmatrix} b_{33} & b_{31} \\ b_{13} & b_{11} \end{vmatrix} \geq \begin{vmatrix} a_{33} & a_{31} \\ a_{13} & a_{11} \end{vmatrix}^{-1}, \tag{14}$$

with equality only if $a_{12} = a_{32} = 0$.

Relationship (11) holds for any number of sub-matrices $\mathbf{A}_{11}$ of any order, including $n_1 = 1$ for the diagonal approximation. Clearly the extent of the inequality will depend upon the magnitudes of the off-diagonal elements within $\mathbf{A}_{12}$, and will be larger for more highly correlated parameters such as Gaussian coefficients B or U and atomic coordinates in oblique crystal systems. In particular, as Templeton (1959) has pointed out, neglect of off-diagonal elements will lead to coordinate e.s.d.'s that are underestimated by a factor $\cos a_i b_i$, where a_i and b_i are the real and reciprocal axes – plus, of course, by additional factors arising from any additional correlations. We repeat Dunitz's (1979) recommendation that highly correlated parameters be included, in so far as possible, in the same matrix block, to increase both the rate of convergence and the reliability of the resulting error estimates.

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