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The standard deviations of Cremer–Pople ring-puckering coordinates.

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Abstract

A method is presented for calculating standard deviations of Cremer–Pople ring-puckering coordinates.

The puckering of an N-membered ring ($N > 3$) may be described mathematically by the coordinates devised by Cremer & Pople (1975). A method is presented here for calculating the standard deviations of these quantities. For convenience, it is assumed that the atomic coordinates are expressed relative to an arbitrary set of Cartesian axes with the origin at the geometrical center of the ring. Thus, if the position vector of the jth atom is $\mathbf{R}_j$, then

$$\sum_{j=1}^{N} \mathbf{R}_j = 0. \tag{1}$$

Cremer & Pople define a mean plane containing vectors $\mathbf{R}'$ and $\mathbf{R}''$ given by

$$\mathbf{R}' = \sum_{j=1}^{N} \mathbf{R}_j \sin[2\pi(j-1)/N], \tag{2}$$

$$\mathbf{R}'' = \sum_{j=1}^{N} \mathbf{R}_j \cos[2\pi(j-1)/N]. \tag{3}$$

The perpendicular displacement of the jth atom from this plane, ζ_j, is

$$\zeta_j = \mathbf{R}_j.\mathbf{T}/|\mathbf{T}|, \tag{4}$$

where

$$\mathbf{T} = \mathbf{R}' \times \mathbf{R}''. \tag{5}$$

When N is odd, the Cremer–Pople puckering coordinates are then q_m and $\varphi_m[m = 2, 3, \ldots, (N-1)/2]$ in the formulae

$$q_m \cos \varphi_m = (2/N)^{1/2} \sum_{j=1}^{N} \zeta_j \cos[2\pi m(j-1)/N] \tag{6}$$

and

$$q_m \sin \varphi_m = -(2/N)^{1/2} \sum_{j=1}^{N} \zeta_j \sin[2\pi m(j-1)/N]. \tag{7}$$

When N is even, there is an additional puckering coordinate:

$$q_{N/2} = N^{-1/2} \sum_{j=1}^{N} (-1)^{j-1} \zeta_j. \tag{8}$$

The variances of $q_m[= \sigma^2(q_m)]$ and $\varphi_m[= \sigma^2(\varphi_m)]$ are given by

$$\begin{aligned} \sigma^2(q_m) &= \sum_j \sum_k (\partial q_m/\partial p_j)(\partial q_m/\partial p_k) \operatorname{cov}(p_j,p_k), \\ \sigma^2(\varphi_m) &= \sum_j \sum_k (\partial \varphi_m/\partial p_j)(\partial \varphi_m/\partial p_k) \operatorname{cov}(p_j,p_k), \end{aligned} \tag{9}$$

where the p_j, p_k are the ring-atom coordinates, and $\operatorname{cov}(p_j,p_k)$ is the covariance of p_j and p_k. If the covariances are not available from the least-squares correlation matrix, it is necessary to assume that the atomic coordinates are independent, *i.e.*

$$\operatorname{cov}(p_j,p_k) = 0 \qquad (p_j \neq p_k), \tag{10}$$

$$\operatorname{cov}(p_j,p_k) = \sigma^2(p_k) \quad (p_j = p_k) \tag{11}$$

[$\sigma^2(p_k)$ = variance of p_k]. Consequently, (9) may be written

$$\begin{aligned} \sigma^2(q_m) &= \sum_k (\partial q_m/\partial p_k)^2 \sigma^2(p_k), \\ \sigma^2(\varphi_m) &= \sum_k (\partial \varphi_m/\partial p_k)^2 \sigma^2(p_k). \end{aligned} \tag{12}$$

In order to calculate the required standard deviations, it is therefore necessary to evaluate the partial derivatives of q_m and φ_m with respect to the ring-atom coordinates. If the atomic coordinates of the jth atom relative to the arbitrary set of Cartesian axes are (x_j,y_j,z_j), and the components of $\mathbf{T}$ are X, Y and Z, *i.e.*

$$\mathbf{R}_j = x_j \mathbf{i} + y_j \mathbf{j} + z_j \mathbf{k}, \tag{13}$$

$$\mathbf{T} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k}, \tag{14}$$

then (4) may be rewritten as

$$\zeta_j = (x_j X + y_j Y + z_j Z)/|\mathbf{T}|. \tag{15}$$

From (14),

$$|\mathbf{T}| = (X^2 + Y^2 + Z^2)^{1/2} \tag{16}$$

and from (2), (3), (13) and (14),

$$X = \sum_{i=1}^{N} \sum_{j=1}^{N} S_{ij} y_i z_j, \tag{17}$$

$$Y = \sum_{i=1}^{N} \sum_{j=1}^{N} S_{ij} z_i x_j, \tag{18}$$

$$Z = \sum_{i=1}^{N} \sum_{j=1}^{N} S_{ij} x_i y_j, \tag{19}$$

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where

$$S_{ij} = \sin[2\pi(i-1)/N]\cos[2\pi(j-1)/N] - \cos[2\pi(i-1)/N]\sin[2\pi(j-1)/N]. \quad (20)$$

Then,

$$\partial X/\partial x_j = \partial Y/\partial y_j = \partial Z/\partial z_j = 0, \quad (21)$$

$$-\partial X/\partial y_j = \partial Y/\partial x_j = \sum_{i=1}^{N} S_{ij} z_i, \quad (22)$$

$$-\partial Y/\partial z_j = \partial Z/\partial y_j = \sum_{i=1}^{N} S_{ij} x_i, \quad (23)$$

$$-\partial Z/\partial x_j = \partial X/\partial z_j = \sum_{i=1}^{N} S_{ij} y_i \quad (24)$$

(note that $S_{ij} = -S_{ji}$).

Differentiation of (15) with respect to an atomic coordinate, p_k, gives

$$|\mathbf{T}|(\partial\zeta_j/\partial p_k) = x_j(\partial X/\partial p_k) + X(\partial x_j/\partial p_k) + y_j(\partial Y/\partial p_k) + Y(\partial y_j/\partial p_k) + z_j(\partial Z/\partial p_k) + Z(\partial z_j/\partial p_k) - \zeta_j(\partial|\mathbf{T}|/\partial p_k). \quad (25)$$

Each $(\partial\zeta_j/\partial p_k)$ may therefore be evaluated by using (21) through (25), and the additional relationships

$$\partial|\mathbf{T}|/\partial p_k = [X(\partial X/\partial p_k) + Y(\partial Y/\partial p_k) + Z(\partial Z/\partial p_k)]/|\mathbf{T}| \quad (26)$$

and

$$\partial x_j/\partial p_k = 0 \quad (p_k \neq x_j), \quad = 1 \quad (p_k = x_j), \text{ etc.} \quad (27)$$

Evaluation of the required derivatives is now straightforward. Differentiating (6) and (7),

$$\cos\varphi_m(\partial q_m/\partial p_k) - q_m\sin\varphi_m(\partial\varphi_m/\partial p_k) = (2/N)^{1/2}\sum_{j=1}^{N}(\partial\zeta_j/\partial p_k)\cos[2\pi m(j-1)/N], \quad (28)$$

$$\sin\varphi_m(\partial q_m/\partial p_k) + q_m\cos\varphi_m(\partial\varphi_m/\partial p_k) = -(2/N)^{1/2}\sum_{j=1}^{N}(\partial\zeta_j/\partial p_k)\sin[2\pi m(j-1)/N], \quad (29)$$

and solving the simultaneous equations for $(\partial q_m/\partial p_k)$ and $(\partial\varphi_m/\partial p_k)$, one gets

$$\partial\varphi_m/\partial p_k = -(2/N)^{1/2}\{\sin\varphi_m\sum_{j=1}^{N}(\partial\zeta_j/\partial p_k) \times\cos[2\pi m(j-1)/N] + \cos\varphi_m\sum_{j=1}^{N}(\partial\zeta_j/\partial p_k) \times\sin[2\pi m(j-1)/N]\}/q_m, \quad (30)$$

$$\partial q_m/\partial p_k = (2/N)^{1/2}\{\cos\varphi_m\sum_{j=1}^{N}(\partial\zeta_j/\partial p_k) \times\cos[2\pi m(j-1)/N] - \sin\varphi_m\sum_{j=1}^{N}(\partial\zeta_j/\partial p_k) \times\sin[2\pi m(j-1)/N]\}. \quad (31)$$

For the additional coordinate when N is even.

$$\partial q_{N/2}/\partial p_k = N^{-1/2}\sum_{j=1}^{N}(-1)^{j-1}(\partial\zeta_j/\partial p_k). \quad (32)$$

Cremer & Pople have shown that in the case of six-membered rings ($N = 6$), the three puckering coordinates (q_2,φ_2) and q_3 may be transformed into a 'spherical polar' set (Q,θ,φ), where

$$q_2 = Q\sin\theta, \quad (33)$$

$$q_3 = Q\cos\theta. \quad (34)$$

The variances of Q and θ can be related to those of q_2 and q_3 by the expressions

$$\sigma^2(Q) = (\partial Q/\partial q_2)^2\sigma^2(q_2) + (\partial Q/\partial q_3)^2\sigma^2(q_3), \quad (35)$$

$$\sigma^2(\theta) = (\partial\theta/\partial q_2)^2\sigma^2(q_2) + (\partial\theta/\partial q_3)^2\sigma^2(q_3). \quad (36)$$

Performing the differentiations and simplifying the resulting expressions, one gets

$$\sigma^2(Q) = \sin^2\theta\,\sigma^2(q_2) + \cos^2\theta\,\sigma^2(q_3), \quad (37)$$

$$\sigma^2(\theta) = [\cos^2\theta\,\sigma^2(q_2) + \sin^2\theta\,\sigma^2(q_3)]/Q^2. \quad (38)$$

When θ approaches 0 or 180° (corresponding to only slight distortions from the perfect chair form), φ becomes increasingly indeterminate, and this is reflected in very large estimated standard deviations, even for precisely determined structures. For example, the L-arabinopyranose rings in the neutron diffraction studies of β-DL-arabinopyranose (Takagi, Nordenson & Jeffrey, 1979) and β-L-arabinopyranose (Takagi & Jeffrey, 1977) have φ values differing by 23·2°, but this difference is only just significant:

β-DL-arabinopyranose: $Q = 0{\cdot}584$ (1) Å, $\theta = 2{\cdot}1$ (1)°, $\varphi = 140$ (3)°;

β-L-arabinopyranose: $Q = 0{\cdot}573$ (2) Å, $\theta = 1{\cdot}5$ (2)°, $\varphi = 116$ (7)°.

A program for performing these calculations is available from the author.

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