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SHORT COMMUNICATION

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Ring asymmetry parameters from out-of-plane atomic displacements.

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Abstract

Formulae are given for calculating ring asymmetry parameters and e.s.d.'s from the out-of-plane displacements of the atoms of a ring.

The *asymmetry parameters* have been proposed by Duax, Weeks & Rohrer (1976) to give a quantitative evaluation of how a ring of any size deviates from ideal symmetry and to help in describing its conformation. These parameters are calculated as r.m.s.'s of the sums of mirror-related torsion angles (ΔC_S) or r.m.s.'s of the differences of twofold-axis-related torsion angles (ΔC_2).

Similar parameters, but directly connected with Cremer & Pople's (1975) total *puckering amplitude*, can be defined using the perpendicular displacements of the atoms from the mean plane through them. These parameters, which could be called *displacement asymmetry parameters*, are defined, together with their e.s.d.'s, by the following equations, where n is the number of the atoms of the ring, r_i is the perpendicular displacement of atom i from the mean plane and R_i is its distance from the center of the ring (the nomenclature is that proposed by Duax *et al.*).

Writing

$$\sin\varphi_i = r_i/R_i$$

where φ_i is the angle the vector $\mathbf{R}_i$ forms with the mean plane through the ring,

$$A_i = \sin\varphi_i - \sin\varphi_i'$$

$$B_i = \sin\varphi_i + \sin\varphi_i'$$

$$C_i = \frac{1}{R_i^2}\left\{\sigma^2(r_i) + \left[\frac{\sin\varphi_i}{R_i}\,\sigma(R_i)\right]^2\right\}$$

$$D = \sin^2\varphi_a \left\{\left[\frac{\sigma(r_a)}{R_a}\right]^2 + \left[\frac{\sin\varphi_a}{R_a}\,\sigma(R_a)\right]^2\right\}$$

$$S_1 = \sum_{i=1}^{m} A_i^2, \qquad S_2 = \sum_{i=1}^{m} B_i^2$$

$$S_3 = \sum_{i=1}^{m} A_i^2(C_i + C_i'), \quad S_4 = \sum_{i=1}^{m} B_i^2(C_i + C_i'),$$

all the possible cases are as follows.

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(i) Mirror plane through vertex a:

$$\Delta C_S(a) = (S_1/m)^{1/2}$$

$$\sigma[\Delta C_S(a)] = S_3^{1/2}/[m\,\Delta C_S(a)]$$

$m = (n-2)/2$ for n even

$m = (n-1)/2$ for n odd.

(ii) Mirror plane intersecting the a–a' bond:*

$$\Delta C_S(a-a') = (S_1/m)^{1/2}$$

$$\sigma[\Delta C_S(a-a')] = S_3^{1/2}/[m\Delta C_S(a-a')]$$

$m = n/2$ for n even.

(iii) Twofold axis through vertex a (n even):

$$\Delta C_2(a) = [(\sin^2\varphi_a + \sin^2\varphi_a'' + S_2)/(m+2)]^{1/2}$$

$$\sigma[\Delta C_2(a)] = (D + D'' + S_4)^{1/2}/[(m+2)\,\Delta C_2(a)]$$

$m = (n-2)/2$.

(iv) Twofold axis through vertex a (n odd):

$$\Delta C_2(a) = [(\sin^2\varphi_a + S_2)/(m+1)]^{1/2}$$

$$\sigma[\Delta C_2(a)] = (D + S_4)^{1/2}/[(m+1)\,\Delta C_2(a)]$$

$m = (n-1)/2$.

(v) Twofold axis intersecting the a–a' bond:*

$$\Delta C_2(a-a') = S_2^{1/2}/m$$

$$\sigma[\Delta C_2(a-a')] = S_4^{1/2}/[m\Delta C_2(a-a')]$$

$m = n/2$ for n even.

It is worth noticing that the displacement asymmetry parameters are dimensionless.

In Table 1 two simple examples are illustrated, taken from the neutron diffraction study of sucrose by Brown & Levy (1973). From the data quoted in the table it is easy to obtain a quantitative evaluation of the departure from ideal symmetry in the two cases: *i.e.* a twist form with the twist axis through oxygen for the furanoid ring and a distorted chair for the pyranoid ring. In both these cases the values of the e.s.d.'s show that the departures from ideal symmetries are statistically significant.

A Fortran 77 routine has been written to calculate systematically these parameters for rings up to 40 atoms and is currently used in a general program system (Nardelli, 1982). Listings of this program are available from the author on request.

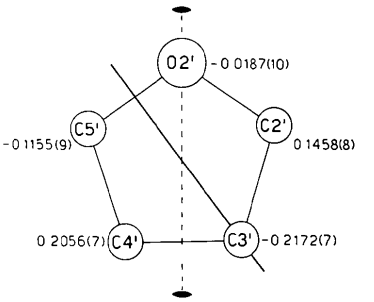
The idea of calculating asymmetry parameters from atomic displacements arose from a private discussion with Professor A. Kálmán (Budapest) during the fourth Joint Meeting of the Italian and Yugoslavian Crystallographic Associations (Bled, 30 May–3 June 1982).

* Obviously, when n is odd, only mirrors or twofold axes through vertices can be considered.

Table 1. *Puckering and asymmetry parameters of simple rings*

The numerical values in the figures are the perpendicular displacements (Å) of the atoms from the mean planes through the rings. E.s.d.'s are given in parentheses.

(*a*) Furanoid ring of sucrose (data from Brown & Levy, 1973)



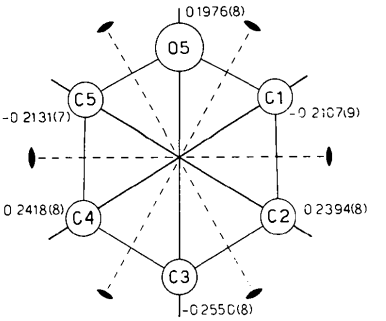
Puckering parameters

$q_2 = 0{\cdot}353\ (1)$ Å, $\varphi_2 = 265{\cdot}2\ (2)°$

Asymmetry parameters

$\Delta C_S(O2') = 0{\cdot}2779\ (6)$	$\Delta C_2(O2') = 0{\cdot}0872\ (3)$
$\Delta C_S(C2') = 0{\cdot}2106\ (7)$	$\Delta C_2(C2') = 0{\cdot}1408\ (4)$
$\Delta C_S(C3') = 0{\cdot}0629\ (7)$	$\Delta C_2(C3') = 0{\cdot}1781\ (4)$
$\Delta C_S(C4') = 0{\cdot}1089\ (7)$	$\Delta C_2(C4') = 0{\cdot}1629\ (4)$
$\Delta C_S(C5') = 0{\cdot}2391\ (7)$	$\Delta C_2(C5') = 0{\cdot}1077\ (4)$

(*b*) Pyranoid ring of sucrose (data from Brown & Levy, 1973)



Puckering parameters

$q_2 = 0{\cdot}050\ (1)$ Å, $q_3 = 0{\cdot}554\ (1)$ Å, $\varphi_2 = 183\ (1)°$

$Q = 0{\cdot}557\ (1)$ Å, $\theta_2 = 5{\cdot}1\ (1)°$

Asymmetry parameters

$\Delta C_S(O5) = 0{\cdot}0015\ (6)$	$\Delta C_S(O5\text{–}C5) = 0{\cdot}3146\ (5)$
$\Delta C_S(C1) = 0{\cdot}0244\ (6)$	$\Delta C_S(O5\text{–}C1) = 0{\cdot}3147\ (5)$
$\Delta C_S(C2) = 0{\cdot}0259\ (6)$	$\Delta C_S(C1\text{–}C2) = 0{\cdot}3140\ (5)$
$\Delta C_2(O5) = 0{\cdot}2489\ (4)$	$\Delta C_2(O5\text{–}C5) = 0{\cdot}0131\ (5)$
$\Delta C_2(C1) = 0{\cdot}2484\ (4)$	$\Delta C_2(O5\text{–}C1) = 0{\cdot}0111\ (5)$
$\Delta C_2(C2) = 0{\cdot}2483\ (4)$	$\Delta C_2(C1\text{–}C2) = 0{\cdot}0238\ (5)$

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