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Note

Puckering parameters for furanoid rings*

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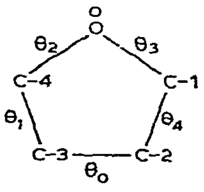
The concept of pseudorotation, and the description of ring conformations in terms of puckering parameters, have been most valuable in analyzing n.m.r. and crystal-structure data relating to the nucleosides and nucleotides[1]. Two types of puckering parameters are available for this purpose, those devised by Altona and Sundaralingam (A and S)[2] and those by Cremer and Pople (C and P)[3].

In the A and S treatment, the five ring-torsion angles θ_0–θ_4 in **1** are expressed in terms of the puckering parameters θ_m and P by the formula

$$\theta_j = \theta_m \cdot \cos(P + 4\pi j/5), \qquad j = 0, 1, \ldots, 4. \tag{1}$$



1

The value θ_m represents the maximum possible torsion-angle on the pseudorotational circuit, and is therefore a measure of the degree to which the ring is distorted from planarity. The term P indicates the direction of this distortion, namely, the point on the pseudorotational circuit at which the ring lies. Eq. *1* is necessarily an approximation, as the five torsion-angles cannot be expressed solely in terms of two variables.

The C and P parameters are q and ψ in the formula

$$z_j = (2/5)^{1/2}\, q \cdot \cos(\psi + 4\pi j/5), \qquad j = 0, 1, \ldots, 4, \tag{2}$$

where z_j is the perpendicular displacement of the jth ring atom in **1** from a uniquely defined, mean plane. Clearly, ψ is analogous to P in Eq. *1*, and q is similar to θ_m in

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that it describes the degree of puckering, $(2/5)^{1/2}q$ being the maximum possible atomic-displacement from the mean plane. Eq. *2* is identical in form to that used by Kilpatrick *et al.* in describing the pseudorotation of cyclopentane[4]. However, the definition of the mean plane in the C and P treatment is such that the formula is mathematically exact, irrespective of whether the ring bond-lengths are equal or not.

The derivation of the relationship between P and ψ is trivial, but is given here in order to emphasize that these parameters are not equal for a given ring, even allowing for the discrepancy arising from the approximation in the A and S formula. The $^3T_2$ and $^4T_3$ conformations[5] correspond to maximally positive values of θ_0 and θ_1 respectively, and if the A and S formula were exact they would always occur at P values of 0° for $^3T_2$ and 216° for $^4T_3$. In the C and P formula, the definition of the reference mean-plane is such that $z_0 = 0$, z_1 is positive for $^3T_2$ (that is, $\psi = 270°$), and z_0 is negative, $z_1 = 0$ for $^4T_3$ (that is, $\psi = 126°$). Consequently $\psi = P - 90 + \varepsilon$, where ε is the discrepancy due to the approximation in the A and S formula.

The value of ε depends on both the degree of puckering and the ring-bond-lengths, and cannot be analytically derived in the general case. In order to assess its importance, we have calculated the puckering parameters and ε values of 100 furanose rings, taken from the crystal structures of various nucleosides and nucleotides. Standard deviations were calculated for all quantities from the published e.s.d. values of the atomic coordinates (uncertainties in unit-cell parameters were neglected). In 73 of the 100 examples, ε exceeded three times its standard deviation. The most significant value encountered was for molecule A in the crystal structure of 2,2′-anhydro-1-(β-D-arabinofuranosyl)uracil[6], for which:

$$\begin{array}{ll} P = 227.1(3)°, & \theta_m = 29.3(2)°, \\ \psi = 134.1(3)°, & q = 0.274(2)\,\text{Å}. \\ \varepsilon = -3.1(1)°, & \end{array}$$

(Note that the e.s.d. of ε is invariably lower than that of P or ψ because of the large, positive covariance of these two parameters.)

Clearly, the error introduced by using the A and S formula is often greater than that inherent in the experimental measurements. Although the A and S parameters are conceptually simpler and are more easily related, in an approximate way, to the molecular geometry, the C and P parameters have the advantage that they define the ring conformation exactly and are, in general, to be preferred.

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