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Note

Stereographic representation of the Cremer–Pople ring-puckering parameters for pyranoid rings*

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The concept of ring-puckering parameters has proven very useful for describing the conformational relationships of the sugar rings in nucleosides and nucleotides[1]. A general definition of ring-puckering that can be applied without approximation to any cyclic molecule, given only the coordinates of the atoms, was provided by Cremer and Pople[2]. The conformation of the five-membered ring is simply represented, as

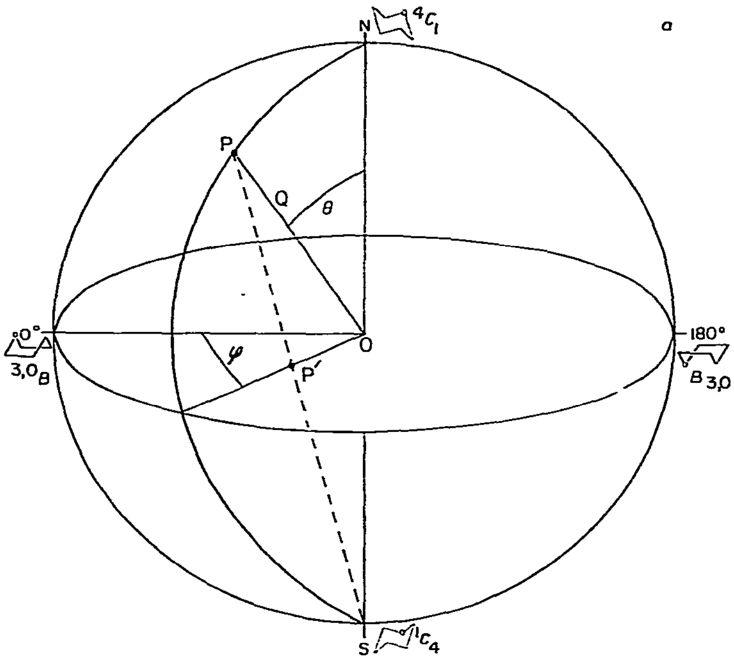

Fig. 1(*a*) The spherical-coordinate system of the Cremer and Pople puckering parameters for six-membered rings.

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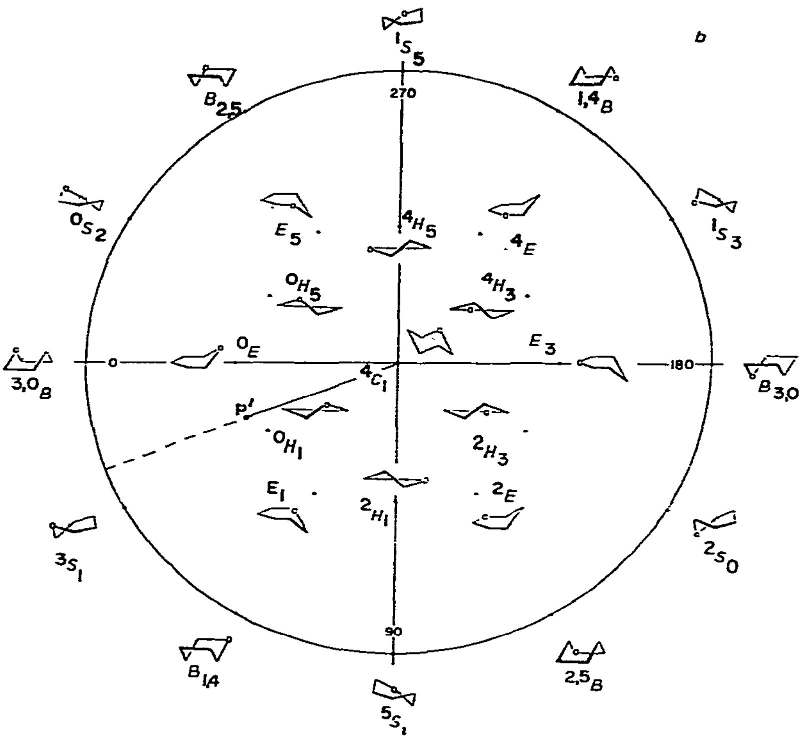

Fig. 1(*b*) Stereogram of the puckering parameters for a pyranoid ring. The *E* and *H* conformations are those of the upper hemisphere of Fig. 1a, namely, distorted ${}^4C_1$ conformations. Those of the lower hemisphere, namely, distorted ${}^1C_4$, are related by symmetry at the center of the circle. That is. ${}^0E$ becomes ${}^3E$, and ${}^0H_1$ becomes ${}^3H_4$ for ${}^1C_4$ distortions.

it involves only an amplitude and a phase angle. The Cremer and Pople parameters for five-membered rings differ only slightly from those of Altona and Sundaralingam[3], the approximation for which is small for small amplitudes of puckering.

For pyranoid rings, the Cremer and Pople puckering parameters take the form of the spherical polar set, Q, θ, and φ, which define the point P, on a sphere of radius Q, as shown in Fig. 1a. The *north-pole*, N, corresponds to the perfect ${}^4C_1$ chair, the *south-pole*, S, to the ${}^1C_4$ chair, and the equator to the pathway of the flexible boat–skew interconversions[4]. The latitude of P describes the degree of distortion from the perfect chair-form, and the longitude defines the nature of this distortion, whether it is in the direction of a boat, *B*, or skew, *S*, conformation[5]. Other points of special interest are the half-chair, *H*, conformations at $\theta = 50.8^{\circ}$ and $\varphi = (30 + n^{\pi}/3)^{\circ}$, and the half-boats, *E*, at $\theta = 54.7^{\circ}$ and $\varphi = n^{\pi}/3^{\circ}$. The radius of the sphere Q is a measure of the atomic displacements from a mean plane defined by three equations in the Cremer and Pople paper.

In calculating these parameters, the following conventions must be maintained in order to correspond to the Figures given in this paper. The ring-oxygen atom is atom 1, as recommended by IUPAC for organic molecules, the anomeric carbon atom

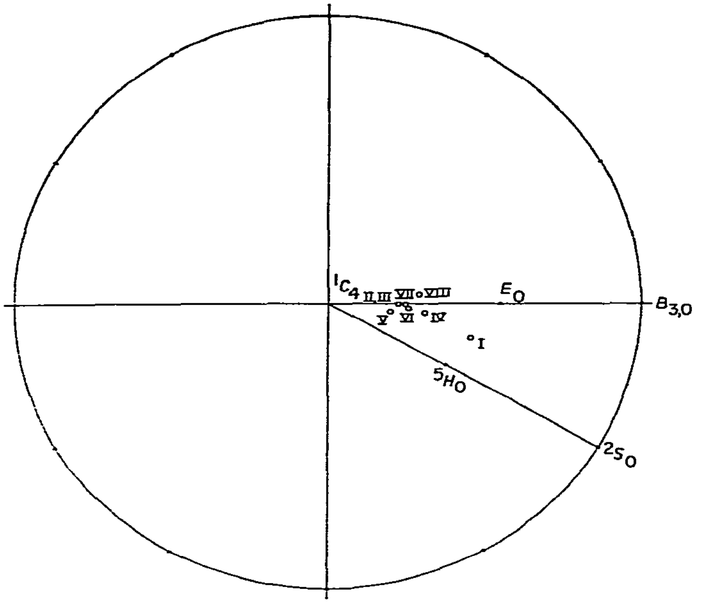

Fig. 2. Stereogram of the pyranoid-ring puckering parameters for the 1,6-anhydro and dianhydro sugars given in the key. Key: I, 1,6:2,3-dianhydro-β-D-gulopyranose[8]; II and III, 1,6-anhydro-β-D-glucopyranose[9,10]; IV, 1,6-anhydro-3,4-*O*-isopropylidene-β-D-talopyranose[11]; V, 2,3-di-*O*-acetyl-1,6-anhydro-β-D galactopyranose[12]; VI, 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose[13]; VII, 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose[14]; VIII, 3-ammonio-1,6-anhydro-3-deoxy-β-D-glucopyranose chloride monohydrate[15].

is atom 2, and thence the numbering is clockwise around the ring. The conformations in the Figures are described, however, in standard carbohydrate numbering. In a D-hexose and D-pentose having a $^{4}C_1$ ring, C-6 and O-4 are above and below the mean plane of the pyranose ring, respectively, in the classical Haworth convention.

A two-dimensional representation of the position of P by means of a stereographical projection is a convenience that is familiar to crystallographers[6] and geographers. If P lies in the northern hemisphere, it is represented by the point, P′, where the line PS, between P and the south pole, intersects the equatorial plane. If P is in the southern hemisphere, the line PN goes to the north pole. In Fig. 1b, the radius OP′ defines a small circle that measures the distortion from the ideal chair-conformation, and the intersection of the extension of OP′ with the equatorial circle defines the type of distortion. Ring interconversions between points on centric circles on the stereogram will follow pseudo-rotational pathways, whereas those in the direction of the radii will occur through flipping across potential barriers[7]. Systematic relationships in the puckering parameters of related pyranoid sugars may thereby by displayed very conveniently in computer-generated, two-dimensional plots*. For furanoid rings, $\theta = 90°$, and the stereogram becomes the pseudo-rotational circle of Altona and Sundaralingam[3].

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*A FORTRAN version of this program is available from the authors.

Fig. 2 illustrates the difference in the shape of the pyranoid ring in some 1,6-anhydro and dianhydro glycopyranose derivatives that have been studied by X-ray and neutron-diffraction methods[8-15]. The Q values range from 0.605 to 0.630, but were assumed to be equal for the purpose of this comparison.

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