(19) A. T. Amos and G. G. Hall, *Proc. Roy. Soc., Ser. A*, **263**, 483 (1961).
(20) A. T. Amos and L. C. Snyder, *J. Chem. Phys.*, **41**, 1733 (1964).
(21) L. C. Snyder and A. T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).
(22) J. Q. Adams, S. K. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).
(23) C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc., London*, 751 (1965).
(24) A. W. Salotto and L. Burnelle, *J. Chem. Phys.*, **53**, 333 (1970).
(25) D. Bordeaux and J. Lajzerowicz, *Acta Crystallogr., Sect. B*, **30**, 790 (1974).
(26) J. C. A. Boeyens and G. J. Kruger, *Acta Crystallogr., Sect. B*, **26**, 668 (1970).
(27) A. W. Salotto and L. Burnelle, *Chem. Phys. Lett.*, **3**, 80 (1969).
(28) F. W. Dalby, *Can. J. Phys.*, **36**, 1336 (1958).
(29) G. Chapelet-Letourneux, H. Lemaire, R. Lenk, M.-A. Marechal, and A. Rassat, *Buss. Soc. Chim. Fr.*, 3963 (1968).
(30) B. Andersen and P. Andersen, *Acta Chem. Scand.*, **20**, 2728 (1966).
(31) A. Caplomont, B. Choin, and J. Lajzerowicz-Bonneteau, *J. Chem. Phys.*, **60**, 2530 (1974).
(32) R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1695 (1957).
(33) B. V. Cheney and R. E. Christoffersen, *J. Chem. Phys.*, **56**, 3503 (1972). For a discussion of electron populations and bond orders in an FSGO basis, see L. L. Shipman and R. E. Christoffersen, *Chem. Phys. Lett.*, **15**, 469 (1972).
(34) C. L. Hamilton and H. M. McConnell, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, p 115.
(35) These values are within 2% of the experimental values and were chosen to aid comparison to other molecules in which the same geometric parameter choices were made.
(36) H. Hayat and B. L. Silver, *J. Phys. Chem.*, **77**, 72 (1973).
(37) O. Kikuchi, *Bull. Chem. Soc. Jap.*, **42**, 1187 (1969).
(38) O. Kikuchi, *Bull. Chem. Soc. Jap.*, **42**, 47 (1969).
(39) O. H. Griffith, P. J. Dehlinger, and S. P. Van, *J. Membrane Biol.*, **15**, 159 (1974).
(40) I. A. Abronin, N. A. Sysoeva, G. M. Zhidomirov, A. L. Buchachenko, and N. D. Churylkin, *Zh. Strukt. Khim.*, **12**, 985 (1971).
(41) P_N^{SD} and P_O^{SD} are taken to be the diagonal elements of the spin density matrix, P_{tt}^{SD}, where t represents nitrogen or oxygen π-type orbitals taken in a symmetrically orthonormalized basis (see ref 48 for a discussion of the application of symmetrical orthonormalized bases to the analogous problem of Mulliken-type electron population analysis). Thus, the quantity utilized here is not the true spin density, which is given by

$$\rho^{SD} = \sum_{r,s} P_{rs}^{SD} \chi_r \chi_s$$

but rather represents a type of "spin occupation number." Other contributions, arising from off-diagonal $\mathbf{P}^{SD}$ elements which are affected by planarity or lack thereof, are hence not included in the Mulliken-type analysis utilized here.
(42) $E_s/ea_0 = 5.142 \times 10^9$ V/cm.
(43) O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, **43**, 2909 (1965).
(44) R.-M. Dupeyre, H. Lamaire, and A. Rassat, *Tetrahedron Lett.*, **27**, 1781 (1964).
(45) R. Briere, H. Lemaire, and A. Rassat, *Tetrahedron Lett.*, **27**, 1775 (1964).
(46) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
(47) A. H. Cohen and B. M. Hoffman, *J. Amer. Chem. Soc.*, **95**, 2061 (1973).
(48) These parameters were determined through discussions on the nature of diffuse π^* orbitals with J. A. Ryan. Also see J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).
(49) The relationship $P_N^{SD}(f) + P^{SD}(f) \simeq 1.0$ is also found to hold using basis set C. Hence, the use of eq 18 is justified.

A General Definition of Ring Puckering Coordinates

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Abstract: A unique mean plane is defined for a general monocyclic puckered ring. The geometry of the puckering relative to this plane is described by amplitude and phase coordinates which are generalizations of those introduced for cyclopentane by Kilpatrick, Pitzer, and Spitzer. Unlike earlier treatments based on torsion angles, no mathematical approximations are involved. A short treatment of the four-, five-, and six-membered ring demonstrates the usefulness of this concept. Finally, an example is given of the analysis of crystallographic structural data in terms of these coordinates.

Although the nonplanar character of closed rings in many cyclic compounds has been widely recognized for many years, there remain some difficulties in its quantitative specification. An important first step was taken by Kilpatrick, Pitzer, and Spitzer in their 1947 discussion of the molecular structure of cyclopentane.[1] Starting with the normal modes of out-of-plane motions of a planar regular pentagon,[2] they pointed out that displacement of the jth carbon atom perpendicular to the plane could be written

$$z_j = (2/5)^{1/2} q \cos (2\psi + 4\pi(j - 1)/5) \qquad (1)$$

where q is a puckering amplitude and ψ is a phase angle describing various kinds of puckering. By considering changes in an empirical potential energy for displacements perpendicular to the original planar form, they gave reasons to believe that the lowest energy was obtained for a nonzero value of q (finite puckering) but that this minimum was largely independent of ψ. Motion involving a change in ψ at constant q was described as pseudorotation. Subsequent refinement of this work has involved models in which constraints to require constant bond lengths are imposed[3,4] and extensions to larger rings[5-7] and some heterocyclic systems are considered.[8]

Although the correctness of the model of Kilpatrick, *et al.*,[1] and the utility of the (q, ψ) coordinate system is generally accepted, application to a general five-membered ring with unequal bond lengths and angles is not straightforward. Given the Cartesian coordinates for the five atoms (as from a crystal structure), determination of puckering displacements z_j requires specification of the plane $z = 0$. A least-squares choice (minimization of Σz_j^2) is one possibility, but the five displacements relative to this plane cannot generally be expressed in terms of two parameters q and ψ according to eq 1.

An attempt to define a generalized set of puckering cordinates which avoids these difficulties was made by Geise, Altona, Romers, and Sundaralingam.[9-11] Their quantitative description of puckering in five-membered rings involves the five torsion angles θ_j rather than displacements perpendicular to some plane. These torsion angles are directly derivable from the atomic coordinates and are all zero in the planar form. They proposed a relationship of the form[11]

$$\theta_j = \theta_m \cos (P + 4\pi(j - 1)/5) \qquad (2)$$

for these torsion angles where again θ_m is an amplitude and P is a phase angle. Given values for the five θ_j, the phase P is obtained from

$$\tan P = \frac{\theta_3 + \theta_5 - \theta_2 - \theta_4}{2\theta_1(\sin {}^1/_5\pi + \sin {}^2/_5\pi)} \quad (3)$$

(a consequence of eq 2) and then θ_m follows from (2) for one particular atom (actually atom 1). This procedure has been used to obtain such puckering coordinates for a large number of five-membered rings.[11]

Although the method of Geise, *et al.*, can be applied directly to any five-membered ring given only the torsion angles, it is nevertheless subject to certain disadvantages. These arise because the relations in (2) are only approximate and the full set of torsion angles cannot be expressed exactly in terms of two parameters in this way. Consequently, the puckering amplitude calculated by the above procedure will depend somewhat on which atom is chosen as number one. The approximation is fairly good provided that the puckering is not too large, but it would clearly be desirable to avoid such difficulties if possible.

More recently, Dunitz[12] has given a further discussion of ring-puckering and torsion angles. He showed that, for infinitesimal displacements of a regular pentagon from planarity, there is a direct linear relationship between torsion angles and displacements, so that the amplitudes and phases in (2) can be rigorously related to those in the original expression 1 of Kilpatrick, *et al.*[1] However, for finite displacements q such as those found in cyclopentane, there are significant deviations from these linear relationships.

The aim of this paper is to propose a general definition of ring-puckering coordinates which parallels the cyclopentane treatment of Kilpatrick, *et al.*, but which can be applied without approximation to any cyclic molecule given only the coordinates of the nuclear positions of the atoms in the ring. This requires specification of an appropriate mean plane. We give the mathematical details for a ring of general size in the following section and then discuss certain qualitative features of the coordinates introduced. Finally, we give an example of application of the method to the determination of such coordinates for a compound where an accurate crystallographic structure is available.

Mathematical Formulation

Let us suppose that the positions of the nuclei of N atoms forming a puckered ring are specified by Cartesian coordinates (X_j, Y_j, Z_j) or position vectors $\mathbf{R}_j$ $(j = 1, 2, \ldots, N)$. Initially these may be with respect to any origin, but it is convenient in the subsequent development to move the origin to the geometrical center (center of mass if the N nuclei all have the same mass). With this origin, the position vectors satisfy

$$\sum_{j=1}^{N} \mathbf{R}_j = 0 \quad (4)$$

To set up a system of puckering coordinates, it is desirable to specify the displacement of each nucleus from some suitably defined mean plane. This plane will be chosen to pass through the central origin. Further a new set of Cartesian coordinates (x,y,z) with respect to molecular axes can be chosen so that the origin is at the center and the z axis is perpendicular to this plane. The y axis may be chosen conveniently to pass through the projection of nuclear position 1 onto this plane. These new molecular coordinates will be a simple linear transformation of the original coordinates (X,Y,Z) with respect to space-fixed axes.

The orientation of the mean plane $(z = 0)$ is not yet fixed. This may be specified in the following manner. The puckering with respect to the plane $z = 0$ can be partly described by the N coordinates z_j. By virtue of eq 4 and the requirement that the new origin is at the geometrical center, it follows that

$$\sum_{j=1}^{N} z_j = 0 \quad (5)$$

We now impose the additional conditions

$$\sum_{j=1}^{N} z_j \cos [2\pi(j-1)/N] = 0 \quad (6)$$

$$\sum_{j=1}^{N} z_j \sin [2\pi(j-1)/N] = 0 \quad (7)$$

Equations 6 and 7 are sufficient to fix the mean plane uniquely. In the special case of small puckering displacements of a regular planar polygon, they correspond to the condition that the displacements z_j are such as to lead to no overall angular momentum.[2] However, the same conditions may be used more generally for finite displacements, nonequivalent atoms, and any bond lengths and angles. Further, it is easily confirmed that these conditions are the same whichever atom in the ring is number one.

The orientation of the mean plane can now be determined for the position vectors $\mathbf{R}_j$ in the following manner. Define new vectors

$$\mathbf{R}' = \sum_{j=1}^{N} \mathbf{R}_j \sin [2\pi(j-1)/N] \quad (8)$$

$$\mathbf{R}'' = \sum_{j=1}^{N} \mathbf{R}_j \cos [2\pi(j-1)/N] \quad (9)$$

Then the unit vector

$$\mathbf{n} = \mathbf{R}' \times \mathbf{R}''/|\mathbf{R}' \times \mathbf{R}''| \quad (10)$$

will be perpendicular to $\mathbf{R}'$ and $\mathbf{R}''$. This will be chosen as the molecular z axis. Since the components of $\mathbf{R}'$ and $\mathbf{R}''$ along $\mathbf{n}$ are zero, it follows that (6) and (7) are satisfied. The positive direction of $\mathbf{n}$ defines a "topside" of the ring (above the face with clockwise numbering).

The components of the unit vector $\mathbf{n}$ with respect to the space-fixed axes may be obtained directly from the components (X_j,Y_j,Z_j) of $\mathbf{R}_j$ using (8), (9), and (10). The full set of displacements from the mean plane are then given by the scalar products

$$z_j = \mathbf{R}_j \cdot \mathbf{n} \quad (11)$$

These will automatically satisfy (5), (6), and (7).

We may now define generalized ring-puckering coordinates in the following manner. If the number of atoms in the ring N is odd and $N > 3$, define q_m and ϕ_m by

$$q_m \cos \phi_m = (2/N)^{1/2} \sum_{j=1}^{N} z_j \cos [2\pi m(j-1)/N] \quad (12)$$

$$q_m \sin \phi_m = -(2/N)^{1/2} \sum_{j=1}^{N} z_j \sin [2\pi m(j-1)/N] \quad (13)$$

These formulas apply for $m = 2, 3, \ldots, (N-1)/2$. They represent a set of puckering coordinates with amplitudes q_m $(q_m \geq 0)$ and phase angles ϕ_m $(0 \leq \phi_m < 2\pi)$. If the number of atoms N in the ring is even, the coordinates in (12) and (13) apply up to $m = {}^1/_2N - 1$ and then there is a single puckering coordinate

$$q_{N/2} = N^{-1/2} \sum_{j=1}^{N} z_j \cos [(j-1)\pi] = N^{-1/2} \sum_{j=1}^{N} (-1)^{j-1} z_j \quad (14)$$

Unlike the other q amplitudes, this q value can have either sign. The total number of ring-puckering coordinates is $N - 3$. It should be noted that the index $j - 1$ appears in (12)–(14) so that the corresponding angles appearing in these formulas are zero for atom 1 which will be treated as the apex of the ring.

Equations 5–7 and 12–14 constitute a set of N linear equations for the N displacements z_j. They may be solved

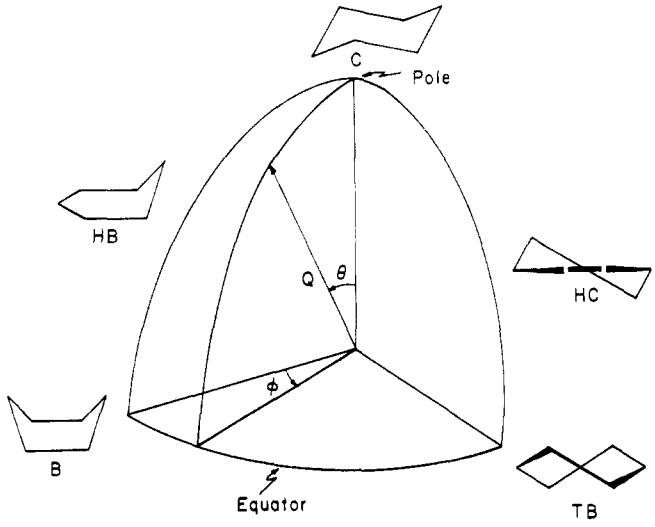


Figure 1. One octant of the sphere on which the conformations of six-membered rings can be mapped (for a constant Q). Special conformations are indicated: C = chair for $\theta = 0°$, $\phi = 0°$; B = boat for $\theta = 90°$, $\phi = 0°$; TB = twist boat for $\theta = 90°$, $\phi = 90°$; HB = half-boat; HC = half-chair.

to give expressions for z_j in terms of the puckering coordinates q_m and ϕ_m. The results are

$$z_j = (2/N)^{1/2} \sum_{m=2}^{1/2(N-1)} q_m \cos [\phi_m + 2\pi m(j-1)/N] \quad (N \text{ odd}) \tag{15}$$

and

$$z_j = (2/N)^{1/2} \sum_{m=2}^{N/2-1} q_m \cos [\phi_m + 2\pi m(j-1)/N] + N^{-1/2} q_{N/2}(-1)^{j-1} \quad (N \text{ even}) \tag{16}$$

The normalization factors in the definitions in eq 12–14 are such that

$$\sum_{j=1}^{N} z_j^2 = \sum_m q_m^2 = Q^2 \tag{17}$$

the quantity Q (≥ 0) may be termed a *total puckering amplitude.*

It is useful to consider the coordinates more explicitly for some small rings. The smallest ring showing puckering is $N = 4$ and, in this case, the mean plane is that which is equidistant from all four atoms so that

$$z_1 = -z_2 = z_3 = -z_4 \tag{18}$$

The single q coordinate is $2z_1$ and may have either sign.

For $N = 5$, there is just one amplitude–phase pair, (q, ϕ), and the displacement expressions (eq 15) become

$$z_j = (2/5)^{1/2} q \cos [\phi + 4\pi(j-1)/5] \tag{19}$$

This is just expression 1 used by Kilpatrick, *et al.*[1] (except for renumbering and the fact that ϕ in (19) corresponds to 2ψ in (1)). In terms of the original cyclopentane model[1] (parallel displacements for a regular planar pentagon), values $\phi = 0, 36, 72°, \ldots$ correspond to ten envelope (E) conformations I with C_s symmetry while $\phi = 18, 54, 90°, \ldots$ give ten twist (T) conformations II with C_2 symmetry. This nomenclature can be carried over to the general five-membered ring with different lengths and angles using the phase ϕ defined in this paper. Thus a "pure envelope" conformation with apex at 1 ($\phi = 0$ or 180°) would be such that

$$z_2 = z_5 \qquad z_3 = z_4 \tag{20}$$

and a "pure twist" with axis through 1 ($\phi = 90$ or 270°) would have

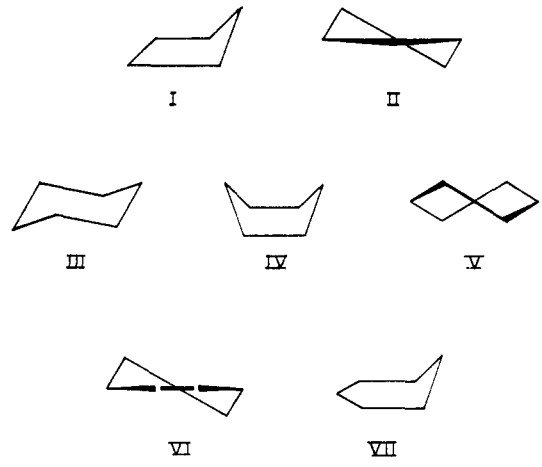
$$z_1 = z_2 + z_5 = z_3 + z_4 = 0 \tag{21}$$

However, it should be noted that for the general ring with unequal lengths and angles, the conditions in (20) do not necessarily imply coplanarity of atoms 2, 3, 4, and 5.

For six-membered rings ($N = 6$), there are three puckering degrees of freedom. These are described by a single amplitude–phase pair (q_2, ϕ_2) and a single puckering coordinate q_3. Alternatively, these coordinates may be replaced[13,14] by a "spherical polar set" (Q, θ, ϕ), where Q is the total puckering amplitude and θ is an angle ($0 \leq \theta \leq \pi$) such that

$$q_2 = Q \sin \theta \qquad q_3 = Q \cos \theta \tag{22}$$

This coordinate system permits the mapping of all types of puckering (for a given amplitude Q) on the surface of a sphere (Figure 1). The analysis of this paper allows every puckered ring with $N = 6$ to be located precisely on this surface.



The polar positions ($\theta = 0$ or 180°) correspond to a chair conformation III with $q_2 = 0$ and $q_3 = \pm Q$. For this conformation, the displacements relative to the mean plane are given by

$$z_1 = -z_2 = +z_3 = -z_4 = +z_5 = -z_6 = 6^{-1/2} q_3 \tag{23}$$

For the special case of a puckered chair with equal bond lengths R and tetrahedral bond angles, the displacement z_1 is $(1/6)R$ and the amplitude q_3 is $(1/6)^{1/2}R$.

The positions on the equator of the sphere (Figure 1) have $\theta = 90°$ so that $q_3 = 0$ and $q_2 = Q$. As the phase angle ϕ varies, the conformation traverses a series of six boat conformations IV ($\phi = 0, 60, 120, 180, 240, 300°$) and six twist-boat conformations V ($\phi = 30, 90, 150, 210, 270, 330°$). These can be interconverted by a pseudorotational path. Certain other commonly described conformations can also be located on this diagram. Thus the half-chair VI is intermediate between III and V. For small displacements of a regular hexagon (small Q), it can be shown that $\tan \theta = (3/2)^{1/2}$ and $\phi = 90°$ maintains copolanarity of atoms 4, 5, 6, and 1, so this angular deviation (θ, ϕ) may be taken as a more general definition of the half-chair. Similarly, the envelope or half-boat VII is intermediate between III and IV. In this case, coplanarity of atoms 2, 3, 4, 5, and 6 is maintained for small Q if $\tan \theta = 2^{1/2}$ and $\phi = 0$.

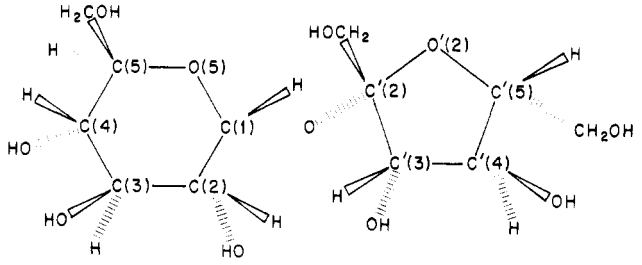
Example

The following example will demonstrate the usefulness of the ring-puckering parameters. From the reported neutron diffraction study of sucrose[15] (VIII), precise position coordinates of all atoms composing the two rings in the carbohy-

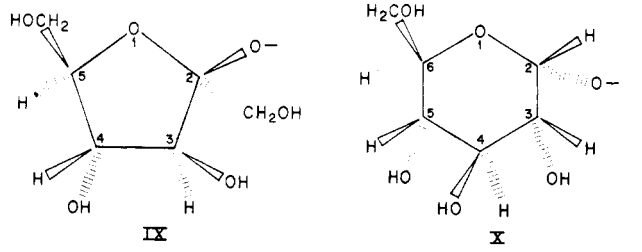
Table I. Coordinates and Puckering Parameters for the Furanoid and Pyranoid Ring of Sucrose after the Neutron Diffraction Analysis of Brown and Levy[15]

Atom		Cell coordinates[a]			Cartesian coordinates (x_j,y_j,z_j)[b]		
			Furanoid Ring of Sucrose				
O′(2)	1	0.2120	0.0944	0.3157	0	1.2111	−0.0189
C′(2)	2	0.1245	0.1926	0.3689	1.1622	0.4349	0.1461
C′(3)	3	0.0072	1.1907	0.2148	0.7425	−1.0012	−0.2174
C′(4)	4	0.0648	0.1665	0.0548	−0.7221	−1.0309	0.2057
C′(5)	5	0.1763	0.0613	0.1286	−1.1826	0.3861	−0.1154
			Puckering parameters: $q_2 = 0.353$, $\phi_2 = 265.1°$				
			Pyranoid Ring of Sucrose				
O(5)	1	0.3772	0.3988	0.3686	0	1.3839	0.1976
C(1)	2	0.2996	0.3579	0.4849	1.1997	0.7624	−0.2106
C(2)	3	0.3125	0.4747	0.6360	1.2356	−0.7040	0.2393
C(3)	4	0.2854	0.6367	0.5645	0.0110	−1.4564	−0.2550
C(4)	5	0.3740	0.6709	0.4420	−1.2300	−0.7208	0.2420
C(5)	6	0.3592	0.5511	0.2953	−1.2164	0.7350	−0.2133
			Puckering parameters: $q_2 = 0.050$, $\phi_2 = 183.7°$				
				$q_3 = 0.554$			
				$Q = 0.556$, $\theta = 5.2°$			

[a] Space group $p2_1$; $a = 10.8633$ Å, $b = 8.7050$ Å, $c = 7.7585$ Å, $\beta = 102.945°$ (ref 12). [b] All coordinates and puckering amplitudes in Å.



VIII



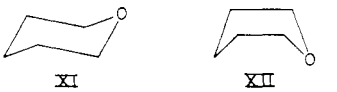
IX X

drate are known. In structure VIII, the original numbering is used. To describe the individual rings in accordance with the established IUPAC rules,[16] it is necessary to renumber the rings separately as in IX and X. In both the furanoid and pyranoid rings, oxygen is atom 1 and the carbon with the glycosidic linkage is atom 2. It should be noted that, to obtain clockwise numbering, the furanoid ring has been turned over in going from VIII to IX. (This will not, of course, change any of the puckering parameters.) Correspondence between these new numberings and the original ones follows by detailed comparison of VIII, IX, and X. According to the definitions of "top" and "bottom" of the rings given in the previous section, it is clear that the pyranoid ring is a substituent on the top of the furanoid ring. Also the furanoid ring is a substituent on the bottom of the pyranoid ring.

The evaluation of the puckering parameters proceeded in the way described above. After a transformation of the reported cell coordinates to Cartesian coordinates,[17] the geometrical center of each ring was found and a translation of the origin of the coordinate system to this pint was implemented. By eq 8, 9, and 10 the vector **n** was derived. This defines the new z direction and the mean ring plane. The projection of the position vector R_1 into this plane led to the positive y direction and the unit vector **m**, the cross product (**m** × **n**) to the unit vector **l**, and the new x direction. The scalar products of $\mathbf{R}_j$ with **l**, **m**, and **n** then gave the new set of x_j,y_j,z_j coordinates shown for both furanoid and pyranoid rings in Table I. Finally, the puckering parameters were evaluated from eq 12, 13, and 14. These are also given in Table I. (A Fortran computer routine which evaluates the coordinate set x_j,y_j,z_j and the puckering parameters will be published.[18])

For the furanoid ring, the ϕ_2 value (265°) is close to the value (270°) appropriate to one of the T forms with twist axis through the oxygen. This is also shown by the z_j coordinates ($z_1 \sim 0$, $z_2 + z_5 \sim 0$, $z_3 + z_4 \sim 0$, $z_2 > 0$). This twist form (or one with ϕ near 90°) seems to be the most stable conformation for oxolane[8,19,20] itself and many compounds containing this ring.[11] Indeed, the puckering amplitude for many such rings lies in a narrow range[19] near 0.35 Å.

The puckering amplitudes of the pyranoid ring describe a slightly distorted chair (XI) with $q_3 \gg q_2$. Indeed, the total puckering amplitude Q (0.56 Å) lies only slightly under the Q value of an ideal cyclohexane chair (0.63 Å for R(C-C) = 1.54 Å). The magnitude of the distortion is given by θ (5°) or better by tan θ which is very small. In order to find the direction of the distortion, we note that ϕ_2 is close to 180° which corresponds to an inverted boat conformation (XII). Therefore the pyranoid ring is distorted from the pure chair XI in the direction of XII and hence is flattened



XI XII

at the oxygen apex, allowing the C-O-C angle to increase to 115° while the other internal ring angles remain close to tetrahedral values. These conformational tendencies reflected by the puckering parameters are common for many pyranoid rings.[21]

Conclusion

The ring mean plane and consequent molecular Cartesian and puckering coordinates introduced in this paper should aid quantitative stereochemistry in a number of ways. In the first place, the type of puckering coordinates first applied to pseudorotation in cyclopentane by Kilpatrick, Pitzer, and Spitzer[1] can be generalized without approximation in any ring with heteroatoms and arbitrary bond angles. The new definitions are completely consistent with the original ones in molecules to which they applied. Second, the analysis applies to rings of any size and should

allow a more systematic description of the possible geometrical structures for larger rings containing seven or more atoms. The "spherical" coordinate system used for six-membered rings in which the total puckering amplitude is Q and the "distortion-type" is specified by two angular variables θ and ϕ can itself be generalized. Thus for an N ring, it should be possible to represent all types of puckering by location on the surface of a hypersphere in $N - 3$ dimensions. Finally, the definition of a unique mean plane passing through the geometrical center should permit a more quantitative approach to the description of substituent orientation relative to such a plane. Studies in these directions are in progress.[21]

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References and Notes

(1) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947).
(2) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, N.Y., 1945.
(3) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959).
(4) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970).
(5) P. Hazebroek and L. J. Oosterhoff, *Discuss. Faraday Soc.*, **10**, 87 (1951).
(6) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); **85**, 4059 (1963); **86**, 4854 (1964); **89**, 7048 (1967).
(7) J. D. Dunitz and J. Waser, *J. Amer. Chem. Soc.*, **94**, 5645 (1972).
(8) H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, **25**, 3045 (1969).
(9) H. J. Geise, C. Altona, and C. Romers, *Tetrahedron Lett.*, **15**, 1383 (1967).
(10) C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, **24**, 13 (1968).
(11) C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, **94**, 8205 (1972).
(12) J. D. Dunitz, *Tetrahedron*, **28**, 5459 (1972).
(13) H. M. Pickett and H. L. Strauss, *J. Amer. Chem. Soc.*, **92**, 7281 (1970).
(14) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **55**, 324 (1971).
(15) G. M. Brown and H. A. Levy, *Acta Crystallogr., Sect. B*, **29**, 790 (1973).
(16) International Union of Pure and Applied Chemistry, Reports on Symbolism and Nomenclature, *J. Amer. Chem. Soc.*, **82**, 5517 (1960).
(17) J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press, Oxford, 1965.
(18) D. Cremer, QCPE, Indiana University, Bloomington, Ind., to be submitted for publication.
(19) A. Almenningen, H. M. Seip, and T. Willadsen, *Acta Chem. Scand.*, **23**, 2748 (1969).
(20) D. Cremer and J. A. Pople, *J. Amer. Chem. Soc.*, following paper in this issue.
(21) D. Cremer, unpublished work.

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXIII. Pseudorotation in Saturated Five-Membered Ring Compounds

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Abstract: *Ab initio* molecular orbital theory is used to study the potential surfaces associated with ring puckering in cyclopentane, oxolane, 1,3-dioxolane, and cyclopentanone. A geometrical model is used which has fixed bond lengths and fixed angular conformations for methylene groups, but all other degrees of freedom are varied. Extensive geometry exploration is carried out with the minimal STO-3G basis and a more limited study with the split valence 4-31G basis. Estimates are made of changes in the potential surface that would occur if the calculations were carried out using the polarized 6-31G* basis. It is found that the theory predicts puckering amplitudes in fair agreement with experimental data. For cyclopentane, all methods give nearly free pseudorotation. The oxolane surface also shows that a pseudorotational path is the favored route for conformational interconversion. The final results (6-31G* estimates) indicate a twist (T) conformation (C_2 symmetry) as the most stable form with a low barrier to pseudorotation into an envelope (E) conformation (C_s symmetry). Similar results with a somewhat higher barrier are obtained for 1,3-dioxolane. Cyclopentanone is also found to have its energy minimum in the twist (T) form, but in this case conformational interconversion occurs most easily along a path passing close to the planar skeleton form as a transition state, in good agreement with experimental findings. The qualitative factors underlying these results are analyzed in terms of the quantum mechanical calculations.

In 1947, Kilpatrick, Pitzer, and Spitzer[1] introduced the concept of pseudorotation to explain the high gas-phase entropy of cyclopentane. According to their thermodynamic data, they suggested that the cyclopentane ring is puckered rather than planar. This deformation, however, is not static but dynamic, the puckering displacements moving around the ring in a relatively free manner. Since that time, this pseudorotation phenomenon has been extensively documented by various experimental techniques,[2-5] not only for the hydrocarbon cyclopentane but also for various derivatives and compounds with one or more heteroatoms in the ring.[6-19] Unfortunately reliable information on the full pseudorotational potential and the populations of the various conformations is not easily derivable from experimental observation. It is therefore very desirable to develop quantum mechanical treatments of the phenomenon in five-membered ring compounds. This should aid the interpretation of the important structural features influencing the properties of such molecules.

The aim of this paper is to initiate a systematic *ab initio* molecular orbital theory of pseudorotation. This requires a geometrical procedure to allow for finite puckering displacements of five-membered rings, followed by quantum mechanical calculations of the appropriate potential surface. The molecules studied in detail are cyclopentane, oxolane, 1,3-dioxolane, and cyclopentanone.

I. The Geometry of Pseudorotation

The mathematical description of pseudorotation in a molecule such as cyclopentane is usually based on the out-