A General Definition of Ring Substituent Positions

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Abstract. Starting from the concept of the mean plane of a general nonplanar N-membered ring, the substituent orientation angles α and β are derived. These angles define the position of a ring substituent in an unambiguous way, the angle α indicating the direction of the ring-substituent bond relative to the mean plane (perpendicular, inclined or parallel) and the angle β revealing whether the bond vector is directed inward (towards the geometrical center of the ring) or outward (away from the geometrical center). The orientation angle α allows a generalization of the terms "axial" and "equatorial" including Barton's original specification of these terms and vivifying their semantics. Unlike earlier descriptions of ring substituent orientations the new definitions completely avoid terms like "quasi-axial", "quasi-equatorial", etc. Examples are given which show their usefulness in discussions of steric effects.

INTRODUCTION

One of the principal concepts of conformational analysis is the distinction between axial and equatorial bonds for nonplanar ring compounds. Already in 1936, Kohlrausch[1] pointed out that the Raman spectra of monohalogenated cyclohexanes could be explained by assuming two types of CH bonds for the methylene groups of the cyclohexane chair. Six CH bonds should be oriented parallel to the threefold symmetry axis, while the six other CH bonds should form an angle of either 109°28′ or 70°32′ with the same axis provided that all carbon atoms are tetrahedral. Hardly one decade later, Kohlrausch's idea was confirmed by electron diffraction studies of dihalogeno-cyclohexanes performed by O. Hassel.[2] Additional experimental evidence was found in the thermodynamic properties of methyl and ethyl substituted cyclohexanes.[3] However, the major impact on the conformational analysis of cyclohexane derivatives developed from the work of Derek H. R. Barton, who was awarded together with Odd Hassel the 1969 Nobel Prize in Chemistry for his contributions in the field of stereochemistry. In a pioneering paper published in 1950,[4] Barton demonstrated the stereochemical consequences of the existence of two classes of CH bonds. Furthermore, he showed that these more subtle aspects of stereochemistry play an important role in the reactions of substituted cyclohexanes or compounds like steroids where the cyclohexane chair is incorporated into the molecular framework.

HISTORICAL BACKGROUND OF THE DEFINITIONS "AXIAL" AND "EQUATORIAL"

When a continuously growing wealth of experimental data gave further proof of the usefulness of the new stereochemical concept, it was felt that there was a need for a verbal distinction between the two CH bond classes. O. Hassel[2] had used the letter ε (symbolizing the greek word for "standing") for CH bonds parallel to the threefold axis of the cyclohexane chair and the letter κ (symbolizing the greek word for "reclining") for the radially extending CH bonds. But the greek origin of these designations was somewhat difficult to remember. Therefore, Barton[4] suggested, in analogy to geographical descriptions, the terms "polar" and "equatorial" for the

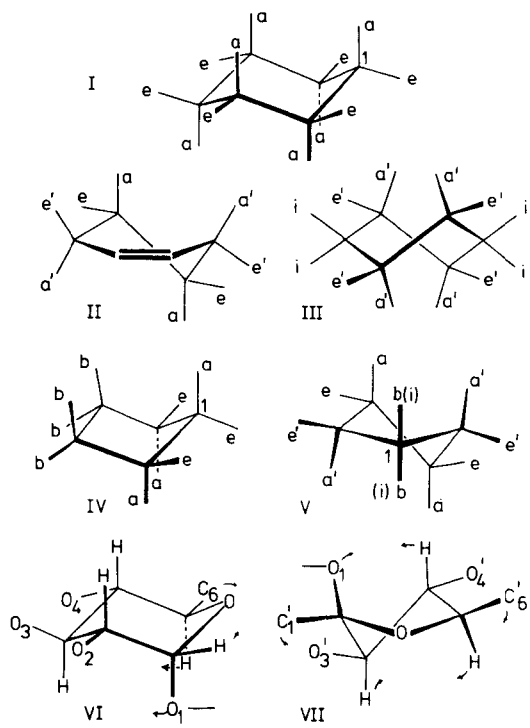

Fig. 1. Substituent positions in six-membered and five-membered ring conformations: chair (I). half-chair (II), twist-boat (III), envelope (IV), half-chair or twist-form (V), pyranoid ring (VI), and furanoid ring (VII) of sucrose. (Arrows in VI and VII indicate distortions.)

two types of CH bonds should be used. His definitions were based on the orientation of the CH bond vectors with regard to a plane which he described as "containing essentially the six carbon atoms" of the cyclohexane chair. Thus, the polar CH bonds should be those which are perpendicular to this plane, while the equatorial bonds should lie approximately in the plane. Although Barton's definitions were generally accepted, the word "polar" was somewhat unfortunate, since it could be misunderstood in the discussion of the stereochemical and electropolar characteristics of cyclohexane sub-

stituents. For this reason, it was decided[5] to change the term "polar" to "axial", thus indicating that the CH bonds designated in this way are parallel to the main symmetry axis of the cylohexane chair. Henceforth, the abreviations "a" and "e" were used for axial and equatorial bonds (see I, Fig. 1).

With the rapid development of conformational analysis in the fifties, attempts were made to extend the concept of a,e-bonds to six-membered ring conformations other than the highly symmetrical chair. Discussing the half-chair form of cyclohexene (II, Fig. 1), Barton[6] introduced the designations "quasi-equatorial" (symbolized by e′) and "quasi-axial" (symbolized by a′) for the CH bonds in α-position to the CC double bond. Application of these names or similar word creations like "pseudo-axial", "pseudo-equatorial", "axial-like" and "equatorial-like", etc. to conformations of cyclopentane,[7] cycloheptane[8] and cyclononane[9] followed. The retention of the term "axial" for these hydrocarbon rings, of course, was misleading. For example, the axial-like exocyclic bonds of the cyclohexene half-chair are not parallel to the main symmetry axis which is twofold and intersects the CC double bond and the opposite CC single bond, thus being almost perpendicular to the axial-like bonds. Nevertheless, the term "axial" was retained in order to point out the similarity of certain five-, seven-, or nine-membered ring conformations to the cyclohexane chair.

Besides the tendency to "discover" the chair-like features of a given conformation of a N-membered ring, Barton's original concept of describing the orientation of the exocyclic ring bonds was partially employed. This demanded the definition of a reference plane constituted by the positions of some or all ring atoms. Thus, for the envelope conformation of cyclopentane (IV, Fig. 1), the plane of the four adjacent atoms C(2), C(3), C(4), and C(5) was chosen as a reference. Accordingly, the CH bonds of the atom at the apex of the envelope as well as those of atoms C(2) and C(5) could be described as lying in planes either almost parallel to the reference plane (e-bonds) or almost perpendicular to the reference plane (a-bonds). This description was similar to the one which was based on the chair-like features of the envelope. But with regard to the methylene groups in positions 3 and 4, a new designation became necessary: With the choice of the reference plane 2–3–4–5, the four CH bonds are equalized in a geometrical sense, being neither axial nor equatorial. In order to indicate that the reference plane bisects the HCH angles the term "bisectional" was introduced for the CH bonds in positions 3 and 4.[10]

The other cyclopentane conformation of interest, namely the twist or half-chair form (V), was described in a similar way. The reference plane was chosen as the plane of C(1), C(2), and C(5) containing the twofold symmetry axis. Consequently, atom 1 possesses two bisectional bonds while all other exocyclic bonds can be termed a, e, a′ or e′ with regard to the plane 1–2–5. Later, it was felt that the CH bonds on the axis carbon should be distinguished from the other exocyclic bonds and the term "isoclinal" (equal dip or inclination) was proposed.[11]

PROBLEM OF THE REFERENCE PLANE

Considering the manifold of conformations possible for cyclic compounds it becomes clear that none of the rationales used for the definition of substituent positions of the cyclohexane chair can be generalized in a well-defined manner. For example, the chair-like character of a twist-boat form of a six-membered ring (III) certainly is dubious. Also, the concept of the reference plane is rather vague, since most ring forms without any symmetry at all seldom contain atom arrangements with four or more atoms exactly lying in one plane. Therefore, much effort was made especially by crystallographers to find planes which are common to as many ring atoms as possible. By means of a least-squares analysis of the position coordinates, it was attempted to calculate a ring plane for which the out-of-plane deviations of the atoms constituting the plane become minimal.[12] Although such a procedure is mathematically straightforward, it includes three disadvantages which make it difficult to use in stereochemical discussions:

(1) Normally, there exists several four-atom least-squares planes for a puckered N-membered ring which differ only slightly with regard to the calculated standard deviations. For the five- or six-atom least-squares planes the out-of-plane deviations increase which makes it difficult to use one of them. Accordingly, the choice of the reference plane is somewhat arbitrary.

(2) The use of the calculated reference plane necessitates three specifications, namely (a) about the ring atoms constituting the plane, (b) about the orientation of the plane, and (c) about the quality of the plane. Specifications (b) and (c) are given in mathematical terms and cannot be utilized in stereochemical discussions without a drawing of some sort showing the plane and the positions of the ring atoms relative to the reference plane.

(3) If an interconversional mode like ring inversion or pseudorotation is discussed, for each conformation traversed in the conformational process a new reference plane has to be defined. Hence, the determination of ring substituent positions is not consistent and does not reflect the continuous changes of these positions during the internal ring motion.

CONCEPT OF THE MEAN RING PLANE

At this point, it is useful to recall Barton's original proposal to define a plane "containing essentially the six carbon atoms" of the cyclohexane chair. This requirement, of course, cannot be rigorously fulfilled, since there is no plane which contains all six atoms of the chair form. Obviously, Barton thought of some kind of an average plane suitable for all carbon atoms of the ring.

There is only one plane unique for all six atoms, that is the plane which passes through the geometrical center of the ring and which contains the three C_2-axes of an ideal cyclohexane chair. It can easily be verified that the out-of-plane displacements of the ring atoms measured with regard to the new reference plane cancel each other out. Considering this as a specification of the reference plane applicable in a more general sense, we will describe the plane of the C_2-axes of the chair, henceforth called the "mean-plane" of the ring, in mathematical terms. For this purpose, a Cartesian coordinate system is established by choosing the geometrical center of the ring as the origin and the direction of the z-axis to be perpendicular to the mean plane. The y-axis may conveniently be defined to pass through the projection of atom position 1 onto the mean plane. Then, in case of the cyclohexane chair, the x-axis bisects the bonds between atoms 2 and 3 and between 5 and 6. The relationship between the out-of-plane displacements z_i can be expressed by (1):

$$z_1 = z_3 = z_5 = -z_2 = -z_4 = -z_6. \qquad (1)$$

Now, let us assume that we have to transform some arbitrary plane in (x, y, z)-space into the mean plane of the cyclohexane chair.[13] In general, there are three mathematical operations necessary for the transformation, namely a translation along the z-axis and rotations around the x- and y-axis. The transformation is completed if the following conditions hold for the displacements of the chair atoms with regard to the transformed plane:[13,14]

$$\sum_{j=1}^{N} z_j = 0, \tag{2}$$

$$\sum_{j=1}^{N} z_j \cos[2\pi(j-1)/N] = 0, \tag{3}$$

$$\sum_{j=1}^{N} z_j \sin[2\pi(j-1)/N] = 0, \tag{4}$$

where $N = 6$ determines the ring size. By substituting the z_j values of (1) into Eqs. (2), (3) and (4) it can easily be seen that the latter define the mean plane of the chair uniquely. Furthermore, conditions (2)–(4) may be used quite generally for any puckered N-membered ring where it makes no difference whether the ring is symmetric or not.

Provided the Cartesian or internal coordinates of a ring are known, a simple mathematical procedure based on Eqs. (2)–(4) leads to the determination of the mean plane.[14,15] On the other hand, if one always considers that the z-displacements have to cancel each other out, it is also possible to get a qualitative idea of the mean plane of a given ring conformation, which is sufficient for qualitative stereochemical discussions. Thus, for the cylopentane envelope, one can derive just by inspection:

$$z_1 > 0; \quad z_2 = z_5 < 0; \quad z_3 = z_4 > 0 \tag{5}$$

and, similarly, for the cyclopentane half-chair:

$$z_1 = 0; \quad z_2 = -z_5; \quad z_3 = -z_4. \tag{6}$$

The concept of the mean ring plane provides the major advantage of placing the conformational analysis of nonplanar rings on a well-defined mathematical basis. For example, it leads to a useful generalization of the definition of ring puckering parameters which was first proposed by Kilpatrick, Pitzer and Spitzer[16] for the conformational modes of the cyclopentane ring. Since we have presented the mathematical foundations of these parameters elsewhere,[14] we shall just sketch the major conclusions of the performed generalization.

RING PUCKERING PARAMETERS

If we consider the six displacements z_j of a six-membered ring, we need six equations to define their precise value. Since three of these equations are already used to fix the orientation of a unique mean plane of the ring, we are left with three equations. They can be solved if three auxiliary parameters are introduced, i.e. for a general N-membered ring just N-3 parameters are necessary to fix the N out-of-plane displacements, once the mean ring plane has been determined. In the special case of the cyclohexane chair, obviously only one parameter suffices to evaluate the z_j-values of Eq. (1). This parameter is called the puckering amplitude q_3 of the chair, since it provides a measure for the degree of out-of-plane puckering.[14] As for the description of the boat and twistboat form of cyclohexane, two additional parameters are necessary. They are chosen in such a way that they reflect the conformational relationship between the two cyclohexane conformations evident in the fact that they are interconvertable by pseudorotation. Accordingly, one parameter presents the pseudorotation puckering amplitude q_2 and the other the pseudorotation phase angle ϕ_2. The mathematical analysis reveals that the puckering parameters q_2, ϕ_2, and q_3 are sufficient to describe any nonplanar conformation of a general six-membered ring. This is expressed by saying that the puckering coordinates q_2, ϕ_2, q_3 span the conformational space of a six-membered ring which contains one pseudorotational subspace of dimension two (q_2, ϕ_2) and one inversional subspace of dimension one (q_3).

For an odd-membered ring like cyclopentane, there are $(N-3)/2$ parameter pairs (q, ϕ) corresponding to the same number of different pseudorotational modes of the ring. In the case of an even-membered ring like cyclohexane, $(N-4)/2$ pseudorotation pairs (q, ϕ) exist plus the single puckering amplitude which describes the inversion of a chair-like form. If the total $(N-3)$-dimensional conformational space is spanned by the ring puckering coordinates, it follows that $N-3$ unique types of ring conformations can be defined which are located at the

Table 1. Ring Puckering Parameters and Unique Interconversional Modes of a N-membered Ring

Ring size N	Puckering Coordinates	Pseudorotation Modes	(q, ϕ)-Pairs	Inversion Modes	q-amplitude
3[a]	—	—	—	—	—
4	1	—	—	1	q_2
5	2	1	q_2, ϕ_2	—	—
6	3	1	q_2, ϕ_2	1	q_3
7	4	2	q_2, ϕ_2 q_3, ϕ_3	—	—
8	5	2	q_2, ϕ_2 q_3, ϕ_3	1	q_4
9	6	3	q_2, ϕ_2 q_3, ϕ_3 q_4, ϕ_4	—	—
10	7	3	q_2, ϕ_2 q_3, ϕ_3 q_4, ϕ_4	1	q_5
..	.	.	...		

a. The pair (q_1, ϕ_1) belongs to the three-membered ring and, accordingly, is not defined.

Table 2. Basis Conformations of a N-membered Ring ($N \leqq 8$)

Ring Size N	Definition	Descriptive Name	Descriptive Symbol
4	$q_2 \neq 0$	puckered form	
5	$q_2 > 0; \phi_2 = 0$	envelope	
	$q_2 > 0; \phi_2 = \pi/2$	twist form	
6	$q_3 = 0; q_2 > 0; \phi_2 = 0$	boat	
	$q_3 = 0; q_2 > 0; \phi_2 = \pi/2$	twist-boat	
	$q_2 = 0; q_3 \neq 0$	chair	
7	$q_3 = 0; q_2 > 0; \phi_2 = 0$	boat	
	$q_3 = 0; q_2 > 0; \phi_2 = \pi/2$	twist-boat	
	$q_2 = 0; q_3 > 0; \phi_3 = 0$	chair	
	$q_2 = 0; q_3 > 0; \phi_3 = \pi/2$	twist-chair	
8	$q_4 = q_3 = 0; q_2 > 0; \phi_2 = 0$	boat-boat	
	$q_4 = q_3 = 0; q_2 > 0; \phi_2 = \pi/2$	twist-boat	
	$q_4 = q_2 = 0; q_3 > 0; \phi_3 = 0$	long-chair	
	$q_4 = q_2 = 0; q_3 > 0; \phi_3 = \pi/2$	twist-chair	
	$q_3 = q_2 = 0; q_4 \neq 0$	crown	

space axes. Every other ring form out of the total conformational space can be mathematically viewed as a linear combination of the basis forms. In this way, the search for the "chair-like" or "boat-like" features of a general six-membered ring conformation becomes meaningful. In Tables 1 and 2, we have summarized the consequences of the concept of ring puckering coordinates for small and medium sized rings.

SUBSTITUENT ORIENTATION ANGLES

Besides the advantage of deriving a set of unique puckering coordinates which facilitates the analysis of ring conformations, the concept of the mean ring plane also provides the possibility of defining the orientation of exocyclic ring bonds in an unambiguous way. If s is a unit vector pointing from a ring atom to the corresponding substituent S, a *substituent orientation angle* α ($0 < \alpha < \pi$) may be defined by

$$\cos \alpha = \boldsymbol{s} \cdot \boldsymbol{n} \tag{7}$$

where $\boldsymbol{n}$ is the unit vector perpendicular to the mean plane, thus coinciding with the direction of the $+z$-axis. If α is near zero, this means that the unit vector $\boldsymbol{s}$ is approximately parallel to the z-axis and the substituent axial above the ring plane. Also, if α is near 180°, the orientation is axial below the plane. Values near 90° correspond to equatorial orientations.

Certainly, terms like "quasi-axial", quasi-equatorial", etc., could be assigned to certain ranges of the angle α. However, we shall not propose such definitions, since these terms have been used in connection with other reference planes than the mean ring plane. Instead, we stick to the terms axial and equatorial and suggest applying them in the following way:

(1) In order to indicate that the substituent position is described with regard to the mean plane of the ring in a well-defined way, all terms are supplied with the prefix g- (standing for geometrical).

(2) In addition, a second prefix to the position term, being either t- or b-, is introduced which indicates whether the substituent is on the *t*opside ($+z$-axis) or the *b*ottomside ($-z$-axis) of the ring.

(3) For $0° \leqq \alpha \leqq 30°$, we call the substituent orientation "t-g-axial", for $150° \leqq \alpha \leqq 180°$, "b-g-axial".

(4) For $60° \leqq \alpha < 90°$, the substituent position is described as "t-g-equatorial", for $90° < \alpha \leqq 120°$, as "b-g-equatorial". If $\alpha = 90°$ the first prefix can be suppressed.

Clearly, these definitions include the original use of the terms axial ($\alpha = 0°$, 180°) and equatorial ($\alpha = 109.5°$, 70.5°) for the CH bonds of the cyclohexane chair. In addition, they vivify the semantics of these terms. Thus, the axial substituents are approximately parallel to the z-axis which defines the orientation of the reference plane, and the equatorial substituents lie in the equator of a local polar coordinate system spanned by s, α, and another angle not yet defined. The only substituent positions which are not covered by the rules (1) to (4) are those where the unit vector s is inclined by about 45° or 135° to the mean plane. We suggest the term "inclinal" for these substituents and add (5) to the substituent position rules:

(5) For $30° < \alpha < 60°$, substituents may be described as "t-g-inclinal" and, for $120° < \alpha < 150°$, as "b-g-inclinal".

With (5) all possible substituent positions are covered (Fig. 2). Hence, for any general N-membered ring, the orientation of the exocyclic bonds can be determined both in a qualitative and a quantitative manner. The usefulness of our concept shall be demonstrated for the five-membered ring depicted in the center of Fig. 3. This ring is formed by atoms of the type X, Y and Z and possesses the three *cis* substituents R, S, and T. We assume that, according to the rules of nomenclature, the atoms have to be numbered in the following way: R – X(1), S – Y(2), T – Z(3), Z(4), Y(5), clockwise around the ring. Consequently, the basis conformations $\phi_2 = 0°$ (envelope) and $\phi_2 = 90°$ (twist form) are unambiguously defined (see Fig. 3).[17]

Keeping the puckering amplitude q_2 to a fixed value larger than zero we will study the changes in the substituent positions for a complete pseudorotation itinerary ($\phi_2 = 0° \rightarrow 360°$). For this purpose, puckered forms of the five-membered ring are drawn at convenient intervals of $\pi/10$. By inspection of Fig. 3 we recognize that during

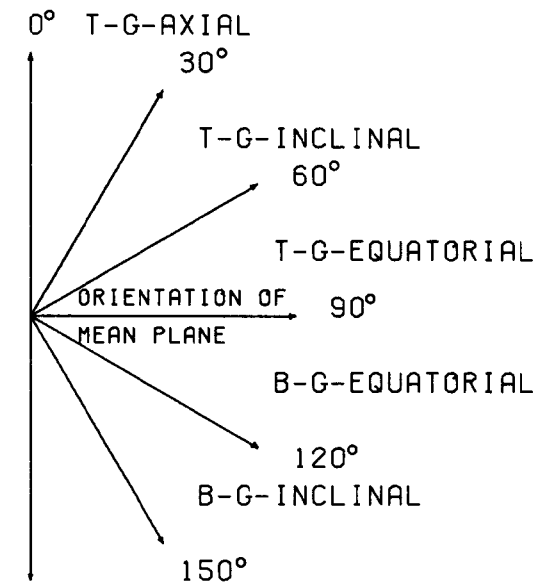

Fig. 2. Definition of substituent orientations relative to the mean plane of a ring.

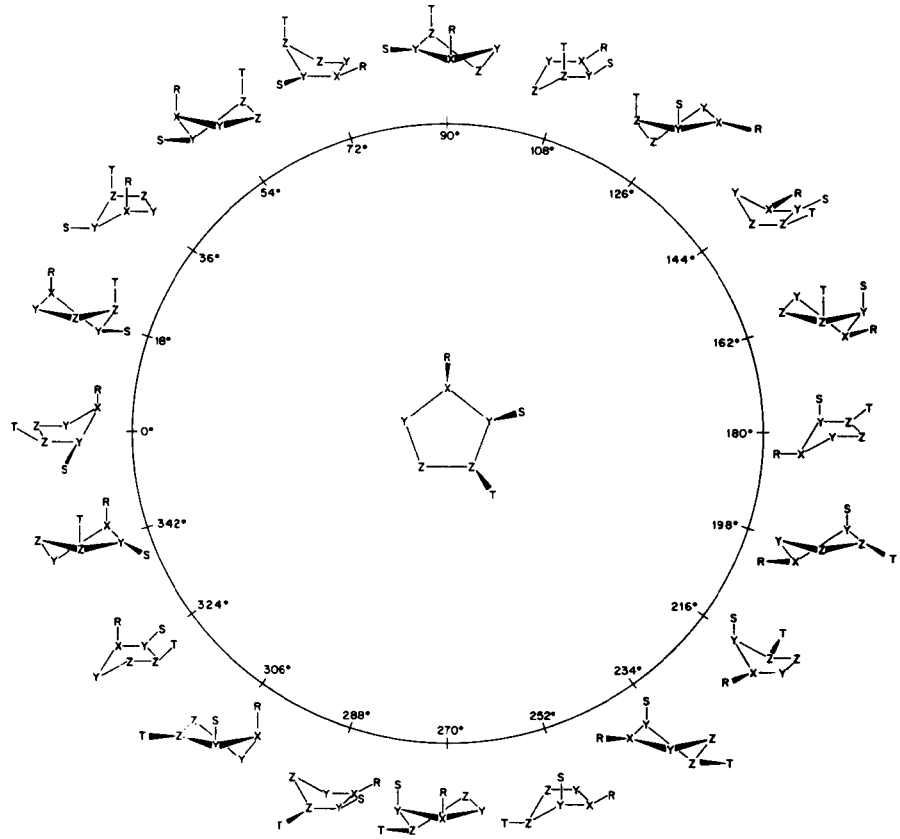

Fig. 3. Pseudorotation itinerary of a general five-membered ring.

pseudorotation the substituents always stay on the topside of the molecule. This also holds for an inversion through the planar form. Furthermore, it appears as if certain ring forms have stronger 1,2- or 1,3-substituent interactions than others. A quantitative analysis of these observations is provided by evaluation of the substitutent orientation angle α. In Fig. 4, we have plotted the variation of α_R, α_S, and α_T as a function of the phase angle ϕ_2 for a constant puckering amplitude of $q_2 = 0.39$ Å taken from a quantum chemical study of cyclopentane.[18] Thus, the α-curves of Fig. 4 reflect the CH bond orientations in positions 1, 2, and 3 during the pseudorotation of cyclopentane.

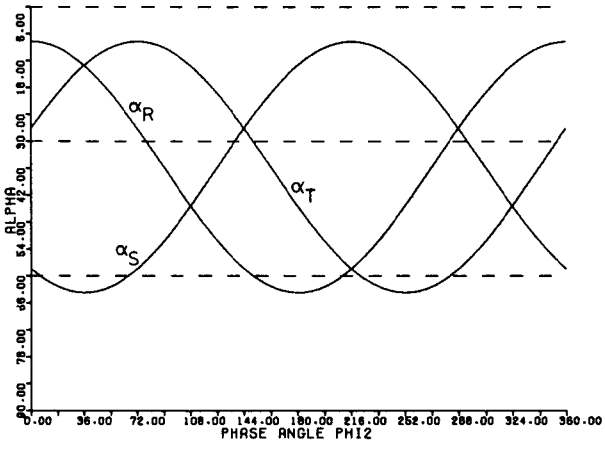

Fig. 4. The dependence of α_R, α_S and α_T on the pseudorotation phase angle calculated for the CH bonds of cyclopentane.

Evidently, the substituents R, S, and T steadily move up and down during pseudorotation. There is a phase shift of 144° and 288°, respectively, between the three curves which means R, S and T interchange their roles at intervals of $4\pi/5$. For $\phi_2 = 0°$, substituents R and T are in t-g-axial positions. Thus, some kind of 1,3-interaction can be expected for them. We note that a description of T as being "bisectional" disguises this stereochemical consequence. Maximal 1,3-interaction can be expected for the case where $\alpha_R = \alpha_T = 13°$ ($\phi_2 = 36°$). Then, the bonds XR and ZT are almost parallel.[19] A similar situation can be observed for $\phi_2 = 216°$ ($\alpha_R = \alpha_T = 58.3°$), but then, R and T are t-g-inclinal which means that their bonds point in completely different directions, thus avoiding unfavorable 1,3-interaction. These observations are quite general and can be made for most puckered ring compounds

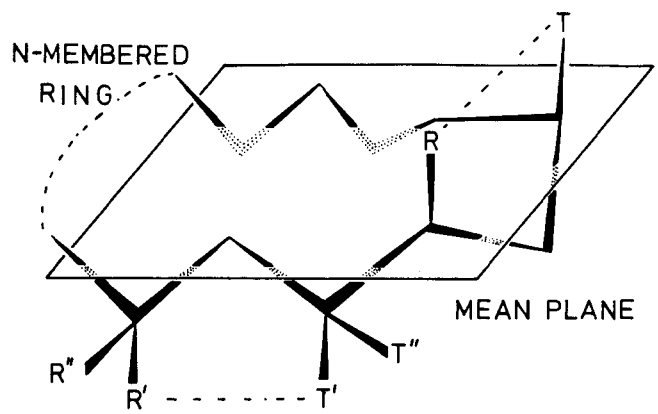

Fig. 5. 1,3-interactions in a general N-membered ring.

provided the substituent vectors are extending radially outward. This is indicated in Fig. 5.

Equal values of α can also be found for vicinal substituent pairs, for example, for $\phi_2 = 108°$ or 288° (R and S) and $\phi_2 = 144°$ or 324° (S and T). These are the conformations with unfavorable bond eclipsing between two t-g-inclinal substituents or two t-g-axial substituents.

Up to this point, we have discussed the orientation of an exocyclic bond relative to the mean ring plane, not, however, its direction relative to the geometrical center. For example, substituents R and T for $\phi_2 = 36°$ may be bent either outward or inward by an amount of 13°. In the latter case, steric interactions would be significantly enhanced. In order to complete the description of substituent orientations, we introduce two sets of auxiliary vectors, namely the unit vectors $\boldsymbol{u}_j$ and $\boldsymbol{v}_j$ which can be derived from the position vectors $\boldsymbol{R}_j$ of the ring atoms (see Fig. 6):

$$\boldsymbol{U}_j = \boldsymbol{R}_j - (\boldsymbol{R}_j \cdot \boldsymbol{n}) \cdot \boldsymbol{n}, \tag{8}$$

$$\boldsymbol{u}_j = \boldsymbol{U}_j / |\boldsymbol{U}_j|, \tag{9}$$

$$\boldsymbol{v}_j = \boldsymbol{n} \times \boldsymbol{u}_j. \tag{10}$$

For atom j, the vector $\boldsymbol{u}_j$ points from the geometrical center to the projection of the position of atom j onto the mean plane. According to (10), the vector $\boldsymbol{v}_j$ is perpendicular to both $\boldsymbol{n}$ and $\boldsymbol{u}_j$. The orientation of $\boldsymbol{s}_j$ with regard to $\boldsymbol{u}_j$ and $\boldsymbol{v}_j$ is defined by the *substituent orientation angle* β:

$$\boldsymbol{s}_j \cdot \boldsymbol{u}_j = \sin\alpha \cos\beta, \tag{11}$$

$$\boldsymbol{s}_j \cdot \boldsymbol{v}_j = -\sin\alpha \sin\beta. \tag{12}$$

The angle β can take values between 0° and 360°. Values close to 0° or 360° indicate that the substituent is extending radially outward while values close to 180° are characteristic for an inward directed substituent.

In order to demonstrate the usefulness of the substituent orientation angles, we have calculated α- and β-values for the substituents of the furanoid and pyranoid ring of sucrose using the Cartesian coordinates of Table 3 which have been evaluated from reported neutron diffraction data[20] by means of Eqs. (2), (3), and (4). The angles are listed together with the relevant substituent designations and the ring puckering parameters in Table 4. For comparison, the substituent orientation angles of the corresponding conformations of cyclopentane[18] and cyclohexane have also been included in Table 4. All parameters have been computed with the program RING which is available from QCPE.[15]

The amplitude q_2, the phase angle ϕ_2, and the α-values indicate that the furanoid ring of sucrose can be consi-

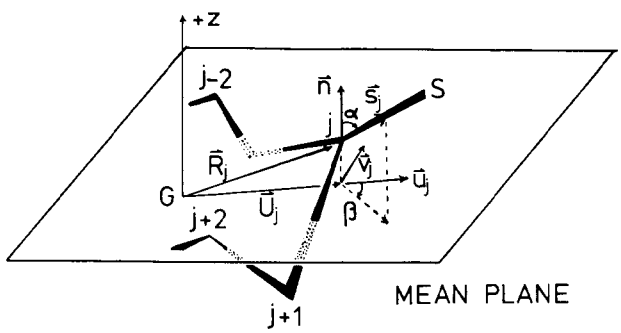

Fig. 6. Definition of the substituent orientation angle β by means of the unit vectors $\boldsymbol{n}$, $\boldsymbol{u}_j$ and $\boldsymbol{v}_j$. The substituent S is attached to ring atom j. (G: geometrical center of the ring; $\boldsymbol{R}_j$: position vector of atom j; $\boldsymbol{U}_j$: component of $\boldsymbol{R}_j$ in the mean plane.)

Table 3. Coordinates for the Substituent Atoms of the Furanoid and Pyranoid Ring of Sucrose after the Neutron Diffraction Analysis of Brown and Levy[a]

Position	Ringatom	Substituents	Cell Coordinates			Cartesian Coordinates (x_j, y_j, z_j)[b]		
				Furanoid Ring				
2	C'(2)	O(1)	0.1714	0.3463	0.3917	1.5992	0.4471	1.5058
		C'(1)	0.1030	0.1311	0.5438	2.2383	1.0368	−0.7507
3	C'(3)	O'(3)	−0.0737	0.3178	0.2045	1.5428	−2.0243	0.3159
		H	−0.0495	0.0884	0.2290	0.7837	−1.1085	−1.3137
4	C'(4)	H	0.0984	0.2772	0.0155	−0.7809	−1.2135	1.2863
		O'(4)	−0.0212	0.0973	−0.0890	−1.4725	−1.9989	−0.5111
5	C'(5)	C'(6)	0.2893	0.0819	0.0467	−2.2609	0.9301	0.7972
		H	0.1465	−0.0599	0.1133	−1.5479	0.4411	−1.1542
				Pyranoid Ring				
2	C(1)	H	0.3347	0.2451	0.5388	2.0018	1.3240	0.2935
		O(1)	0.1714	0.3463	0.3917	1.3498	0.8496	−1.6219
3	C(2)	H	0.4116	0.4693	0.7117	1.2246	−0.6994	1.3451
		O(2)	0.2295	0.4355	0.7477	2.4250	−1.3322	−0.2310
4	C(3)	O(3)	0.3080	0.7477	0.7028	−0.0286	−2.7852	0.2548
		H	0.1871	0.6448	0.4897	0.0071	−1.4797	−1.3522
5	C(4)	H	0.4717	0.6681	0.5218	−1.2289	−0.7588	1.3440
		O(4)	0.3488	0.8141	0.3563	−2.4249	−1.2748	−0.2627
6	C(5)	C(6)	0.4575	0.5708	0.1846	−2.3520	1.5368	0.4084
		H	0.2638	0.5613	0.2093	−1.3045	0.7665	−1.3126

a. Space group $p2_1$; $a = 10.8633$ Å, $b = 8.7050$ Å, $c = 7.7585$ Å, $\beta = 102.945°$ (Ref. 20).
b. All coordinates in Å.

Table 4. Substituent Positions in the Furanoid and Pyranoid Ring of Sucrose Evaluated from the Cartesian Coordinates of Table 3.[a] (For Comparison, Substituent Poisitions in the Cyclopentane Twist[b] and Cyclohexane Chair Form are Given in Parentheses.)

Position	Ringatom	Substituents	α		β		Description
Furanoid Ring: $q_2 = 0.35$ Å, $\phi_2 = 265.2°$							
2	C'(2)	O(1)	17.8	(19.2)	18.9	(15.7)	t-g-axial
		C'(1)	126.0	(127.8)	351.3	(355.4)	b-g-inclinal
3	C'(3)	O'(3)	67.7	(62.3)	358.5	(358.6)	t-g-equatorial
		H	174.0	(170.9)	15.6	(13.6)	b-g-axial
4	C'(4)	H	10.1	(9.1)	342.7	(346.4)	t-g-axial
		O'(4)	120.3	(117.7)	2.7	(1.4)	b-g-inclinal
5	C'(5)	C'(6)	52.9	(52.2)	8.7	(4.6)	t-g-inclinal
		H	160.4	(160.8)	350.4	(344.3)	b-g-axial
Pyranoid Ring: $q_3 = 0.55$ Å, $q_2 = 0.05$ Å, $\phi_2 = 183.1°$							
2	C(1)	H	62.8	(70.6)	357.4	(360.0)	t-g-equatorial
		O(1)	173.0	(180.0)	2.3	(0)	b-g-axial
3	C(2)	H	0.6	(0)	172.9	(0)	t-g-axial
		O(2)	109.3	(109.5)	358.2	(360.0)	b-g-equatorial
4	C(3)	O(3)	69.0	(70.6)	2.1	(0)	t-g-equatorial
		H	178.8	(180.0)	10.1	(0)	b-g-axial
5	C(4)	H	2.0	(0)	298.7	(360.0)	t-g-axial
		O(4)	111.0	(109.5)	5.5	(0)	b-g-equatorial
6	C(5)	C(6)	65.9	(70.6)	4.1	(0)	t-g-equatorial
		H	175.1	(180.0)	348.5	(360.0)	b-g-axial

a. Puckering parameters are taken from Ref. 14.
b. Puckering parameters of the cyclopentane twist form are $q_2 = 0.39$ Å, $\phi_2 = 270.0°$. See Ref. 18.

dered as a slightly distorted half-chair (VII, Fig. 1). The substituent orientations closely resemble those of twisted cyclopentane ($\phi_2 = 270°$, Fig. 4). As for the pyranoid ring, the calculated α-values are typical for a chair conformation (VI, Fig. 1) which is confirmed by $q_3 \gg q_2$.[14] Distortions resulting from steric repulsions are indicated by the α-values of the three b-g-axial substituents (1,3-interactions) and by the β-values of the equatorial substituents (1,2-interactions). The latter are slightly bent forward towards the front part of the chair containing the ring oxygen. The same can also be observed for the equatorial and inclinal substituents of the furanoid ring. Certainly, this has to do with the steric crowding in the back parts of the two rings as well as with the two hydrogen bonds between the two rings.[20]

CONCLUSION

By means of the concept of the mean ring plane, useful definitions of the orientations of ring substituents can be derived. A quantitative description of the substituent positions is possible with the substituent orientation angles α and β. The new definitions are quite general. They can be applied without restriction to any general N-membered ring. Furthermore, they have the advantage of being completely consistent with Barton's original specification of the terms "axial" and "equatorial". They allow vague descriptions like "quasi-axial", "quasi-equatorial", etc. to be abandoned. Steric effects resulting from substituent interactions can be meaningfully discussed with the aid of the individual substituent orientation angles.[21]

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$$z_j' = z_j + c_1 + c_2 \cdot \cos[2\pi(j-1)/N] + c_3 \cdot \sin[2\pi(j-1)/N]$$

where c_1 determines a shift along the z-axis and the trigonometric terms correspond to rotation around the x-axis and the y-axis, respectively. Only if c_1, c_2, and c_3 vanish due to a transformation, does the arbitrary plane coincide with the mean plane of the ring.
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