The Conformation of Six-Membered Rings Described by Puckering Coordinates Derived from Endocyclic Torsion Angles[†]

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Abstract: The interrelation between the endocyclic torsion angles ϕ_j ($j = 0-5$) in a six-membered ring is given by a truncated Fourier series, $\phi_j = \Phi_2 \cos(P_2 + 4\pi j/6) + \Phi_3 \cos(\pi j)$. It is deduced from a set of 8451 experimentally determined six-membered ring conformations extracted from the Cambridge Structural Database that this equation reproduces the observed endocyclic torsions within 1°, except for sulfur-containing rings where the margins appear to be slightly larger. These findings are corroborated by an analysis of six-membered rings generated by molecular mechanics. The ring puckering coordinates Φ_2, P_2, and Φ_3 map out the conformations attainable by six-membered rings on the surface of a sphere. Thus, a convenient and pictorial description of conformational space accessible to six-membered rings is obtained. A comparison is made with the well-known Cremer–Pople ring puckering formalism. It is shown that, especially in the case of nonequilateral rings, the present method is more consistent with internal angular characteristics (e.g., local flattening) displayed by six-membered rings than the Cremer–Pople formalism.

Introduction

The description of nonplanar medium-sized nonaromatic rings is a problem with a long history[1] in conformational analysis. The foundations for its (quantitative) solution in the case of five-membered rings were laid by Kilpatrick, Pitzer, and Spitzer[2] in their 1947 discussion of the molecular structure of cyclopentane. In this now famous introduction of the concept of pseudorotation, they described the nonplanarity of the five-membered ring using the following expression for the perpendicular displacement z_j of the jth carbon from the plane of the unpuckered ring:

$$z_j = \sqrt{\frac{2}{5}} q \cos[2(F_{KPS} + 2\pi j/5)] \qquad (1)$$

Thus the conformation of the five-membered ring is characterized *quantitatively* by two puckering coordinates: q (=the amplitude of puckering) and F_{KPS} (=the phase angle of pseudorotation).

Although the usefulness of the (q, F_{KPS}) coordinate system was generally recognized, application of the model of Kilpatrick et al.[2] to a general five-membered ring with unequal bond lengths and angles appeared not to be straightforward. The difficulties resulting from determining the plane of reference were largely overcome by Altona et al.[3-5] who found that the endocyclic torsion angles in a five-membered ring system are interrelated by a function very similar to eq 1 and hence yield a quantitative description of the ring conformation based on internal instead of Cartesian coordinates.

Of course, next to the five-membered ring a considerable number of studies[6-17] were directed toward the conformation of other medium-sized rings. However, it took to 1975 before a general and exact definition of ring puckering coordinates was reported by Cremer and Pople.[18] By defining a unique mean plane for an arbitrary puckered N-membered ring, they were able to provide an exact parameterization of the ring puckering relative to this plane yielding $(N - 3)$ amplitude and phase coordinates which are generalizations of those introduced by Kilpatrick et al. (vide supra). These $(N - 3)$ puckering coordinates determine the ring conformation in a unique and exact fashion. However, it should be realized that this is only so under the implicit assumption[19] that all bond lengths as well as $(N - 3)$ bond angles are known.

For the six-membered ring, the three puckering coordinates defined by the Cremer–Pople (CP) algorithm[18]

$$z_j = \sqrt{\frac{2}{6}} q_2 \cos[F_{CP} + 4\pi(j-1)/6] + \sqrt{\frac{1}{6}} q_3(-1)^{j-1} \qquad (2)$$

describe[20] the conformational space accessible to the ring in a pseudorotational subspace of dimension two (i.e., a puckering amplitude, q_2, and a phase angle, F_{CP}) and an inversional subspace of dimension one (i.e., a puckering amplitude, q_3). Every ring conformation described in terms of this conformational space can be viewed[11,20] mathematically as a linear combination of the basis forms, i.e., boat, twist–boat, and chair. This cylindrical system of puckering coordinates may be reworked[10,18] to a spherical polar set (Q_{CP}, Θ_{CP}, F_{CP}) in which $Q_{CP} = (q_2^2 + q_3^2)^{1/2}$, the total puckering amplitude, and $\Theta_{CP} = \arctan(q_2/q_3)$. Thus, all types of puckering (for a given total amplitude Q_{CP}) can be mapped on the surface of a globe. It is the latter representation, originally proposed by Hendrickson,[7] that provides a practical framework for describing the conformation of six-membered rings.[10,18,21-23]

Notwithstanding its preciseness and other merits, the CP method does also have some drawbacks and limitations.[23,24]

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(3) Geise, H. J.; Altona, C.; Romers, C. *Tetrahedron Lett.* **1967**, 1383.

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(6) Hendrickson, J. B. *J. Am. Chem. Soc.* **1961**, *83*, 4537.

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(11) Dunitz, J. D. *Tetrahedron* **1972**, *28*, 5459.

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(19) Cremer, D. *Acta Cryst.* **1984**, *B40*, 498.

(20) Cremer, D. *Isr. J. Chem.* **1980**, *20*, 12.

(21) Boeyens, J. C. A. *J. Cryst. Mol. Struct.* **1978**, *8*, 317.

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(24) Petit, G. H.; Dillen, J.; Geise, H. J. *Acta Cryst.* **1983**, *B39*, 648.

Reconstruction[25-28] of the ring (e.g., in atom coordinates) from the CP puckering coordinates is not straightforward unless the endocyclic valence angles are known. The required reference plane makes the method virtually impossible to apply to internal coordinates derived from, e.g., NMR. Moreover, in rings with significantly different endocyclic bond lengths and bond angles, the CP formalism has been shown[23] to lead to conclusions which are not consistent with other criteria accepted in stereochemistry. It was for these reasons that an alternative ring puckering description based on angular characteristics of the ring was looked for. The present paper discusses a method in which the puckering coordinates are derived from endocyclic torsion angles and which overcomes, at least partially, the difficulties mentioned above.

Results

By virtue of their periodicity, the endocyclic torsion angles (ϕ_j, $j = 0, 1, .., 5$) in a six-membered ring can be described[29] exactly by a Fourier series:

$$\phi_j = \Phi_0 + \Phi_1 \cos (P_1 + 2\pi j/6) + \Phi_2\cos (P_2 + 4\pi j/6) + \Phi_3 \cos (\pi j) \quad (3)$$

The parameters $\Phi_0 - \Phi_3$, P_1, and P_2 in eq 3 can be evaluated by Fourier inversion:

$$\Phi_0 = \frac{1}{6}\sum_{j=0}^{5} \phi_j \cos (\pi j/3) \quad (4)$$

$$\Phi_1 \cos P_1 = \frac{1}{3}\sum_{j=0}^{5} \phi_j \cos (\pi j/3) \quad (5)$$

$$\Phi_1 \sin P_1 = -\frac{1}{3}\sum_{j=0}^{5} \phi_j \sin (\pi j/3) \quad (6)$$

$$\Phi_2 \cos P_2 = \frac{1}{3}\sum_{j=0}^{5} \phi_j \cos (2\pi j/3) \quad (7)$$

$$\Phi_2 \sin P_2 = -\frac{1}{3}\sum_{j=0}^{5} \phi_j \sin (2\pi j/3) \quad (8)$$

$$\Phi_3 = \frac{1}{6}\sum_{j=0}^{5} \phi_j \cos (\pi j) \quad (9)$$

Of course, for a given ring the values of P_1 and P_2 as well as the sign of Φ_3 depend on the choice of the origin torsion angle ϕ_0. For a unique description of the six-membered ring conformation by means of eq 3, it is therefore necessary to define the endocyclic torsion angle numbering scheme. Following Cremer end Pople,[18] ring atom 1 is the atom with the lowest number according to IUPAC rules (e.g., heteroatom in heterocycles; see also Boeyens[21] for useful extensions); the rest of the ring atoms are then numbered 2 to 6 in clockwise order. For the purpose of eq 3, the endocyclic torsion about the bond between atom 6 and atom 1 is defined as ϕ_0; the torsion about the bond between atom 1 and atom 2, ϕ_1; and so forth.

For the sake of exploring the characteristics of eq 3, a dataset of experimentally determined six-membered ring conformations was extracted from the Cambridge Structural Datafile[30,31] (CSD). A search for cyclohexane, cyclohexene, tetrahydropyran, piperidine, thiane, and 4-oxathiane fragments (with no linkages between the ring atoms apart from the ring itself) yielded, after removal of those entries containing errors and/or with reported esd's(C–C) > 0.03 Å, a dataset with the Cartesian coordinates of 8451 six-membered rings. The latter dataset was used to calculate the endocyclic torsion angles which in turn led, by means of eq 4–9,

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Table I. Mean Values for Parameters Φ_0, Φ_1 (cf. Eq 3) and Rms Deviation between Observed and Calculated (by Eq 10) Endocyclic Torsion Angles as Determined from a Selection of Six-Membered Rings Taken from the Cambridge Structural Datafile (See Text)

ring type	no. of ring fragments	$\Phi_0{}^a$	$\Phi_1{}^a$	rms deviation[b]
all rings	8451	-0.00 (0.38)	0.99 (0.73)	0.77 (0.55)
(cyclohexane)	3515	-0.00 (0.45)	0.95 (0.73)	0.77 (0.58)
(cyclohexene)	1340	-0.01 (0.27)	1.15 (0.72)	0.87 (0.49)
(piperidine, N)	1789	-0.02 (0.36)	0.86 (0.68)	0.68 (0.51)
(tetrahydropyran, O)	1673	-0.00 (0.35)	0.98 (0.61)	0.75 (0.48)
(thiane, S)	124	-0.04 (0.22)	2.44 (1.16)	1.73 (0.83)
(oxathiane, O, S)	10	-0.08 (0.08)	2.14 (1.17)	1.52 (0.83)

[a] Average value (in degrees); standard deviation between brackets. [b] Average rms deviation between observed and recalculated endocyclic torsion angles (in degrees); standard deviation between brackets.

to the parameters $\Phi_0 - \Phi_3$, P_1, and P_2 (as defined in eq 3) for each ring fragment. Analysis of the data thus obtained shows that the magnitude of the parameters Φ_0 and Φ_1 is in general very small: Table I lists for Φ_0 an overall mean value of -0.00° (standard deviation = 0.38°) and for Φ_1 an overall mean value of 0.99° (standard deviation = 0.73°). The table also suggests that the mean values of Φ_0 and Φ_1 hardly depend on the type of six-membered ring; only in the case of sulfur-containing rings does Φ_1 appear to be on average slightly larger than in the rest of the examined rings.

The small mean values observed for Φ_0 and Φ_1 suggest that the terms in which they occur in eq 3 can be neglected at the cost of introducing a marginal systematic error. It is noted in passing that such a neglect is analogous to the situation in five-membered rings where (small) systematic deviations of the endocyclic torsion angles from the well-known pseudorotation equation proposed by Altona et al.[3-5] were shown[32] to stem from disregarding the same first two terms in the corresponding Fourier expansion. Thus, for the six-membered ring, eq 3 reduces to

$$\phi_j = \Phi_2 \cos (P_2 + 4\pi j/6) + \Phi_3 \cos (\pi j) \quad (10)$$

where $j = 0, 1, ..., 5$.

The validity of eq 10 may be tested by determining the differences between the values of ϕ_0, ϕ_1, ..., ϕ_5 in the observed molecule and the corresponding values recalculated by eq 10 using the ring-puckering parameters Φ_2, P_2, and Φ_3 (calculated using eq 7–9); the root-mean-square deviation between experimental and (re-)calculated torsion angles yields a "figure of merit" for how well eq 10 describes the conformation of the six-membered ring. The last column in Table I lists the mean value of these "figures of merit" calculated for the aforementioned dataset of experimentally determined ring conformations. The data show that eq 10 reproduces the experimental torsion angles quite well: the mean of the rms deviations between calculated and observed endocyclic torsions is well below 1° except for the sulfur-containing rings in which they appear to be slightly larger (but still below 2°). Notably, the mean value of the rms deviations observed in tetrahydropyran rings is comparable to the rms deviations found[33] in five-membered furanose rings upon application of the analogous Altona–Sundaralingam formalism.[5] Of course, the somewhat

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Table II. Mean Values for Parameters Φ_0, Φ_1 (cf. Eq 3) and Rms Deviation between Observed and Calculated (By Equation 10) Endocyclic Torsion Angles as Determined from Sets (F_{CP} = 0°, 10°, 20°, ..., 350°) of Six-Membered Ring Conformations with Given Cremer–Pople Puckering Coordinates (Q_{CP}, Θ_{CP}) and Generated by Molecular Mechanics (MM2)

ring type	Q_{CP}	Θ_{CP}	$\Phi_0{}^a$	$\Phi_1{}^a$	rms deviation^b
⬡	0.56	7.2	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
	0.56	51.5	0.00 (0.10)	0.02 (0.00)	0.09 (0.04)
	0.56	90.0	0.00 (0.35)	0.00 (0.00)	0.31 (0.17)
	0.75	90.0	0.00 (0.55)	0.00 (0.00)	0.48 (0.26)
⬡O	0.56	7.2	0.00 (0.03)	0.25 (0.01)	0.18 (0.01)
	0.56	51.5	−0.00 (0.27)	1.12 (0.05)	0.84 (0.06)
	0.56	90.0	−0.00 (0.46)	1.01 (0.17)	0.85 (0.12)
	0.75	90.0	−0.00 (0.72)	1.34 (0.14)	1.17 (0.21)
⬡S	0.69	8.6	−0.00 (0.02)	2.04 (0.24)	1.44 (0.17)
	0.69	52.0	−0.00 (0.22)	1.80 (0.96)	1.31 (0.64)
	0.69	90.0	0.00 (0.50)	2.33 (0.24)	1.72 (0.19)
	0.88	90.0	0.00 (0.74)	2.63 (0.25)	1.99 (0.24)
⬡O,S	0.67	5.2	−0.00 (0.06)	1.29 (0.32)	0.91 (0.23)
	0.67	52.0	0.00 (0.38)	3.08 (0.66)	2.22 (0.46)
	0.67	90.0	−0.00 (0.53)	3.48 (0.45)	2.52 (0.30)
	0.90	90.0	−0.00 (0.89)	4.20 (0.34)	3.10 (0.24)

^{a}Cf. eq 3; mean value (in degrees, averaged over F_{CP}), standard deviation in parentheses. ^{b}Average rms deviation between observed and recalculated (by eq 10) endocyclic torsion angles (in degrees); standard deviation in parentheses.

larger rms deviations noted for thiane and oxathiane rings relate directly to the neglect of the Φ_1 term in eq 10 in particular, the amplitude of which (Φ_1) being on average larger in sulfur-containing rings than in the remainder (vide supra).

For purpose of a more systematic analysis, sets of six-membered ring conformations were generated by molecular mechanics calculations. The construction of cyclohexane, tetrahydropyran, thiane, and 4-oxathiane rings with particular CP-puckering parameters (denoted Q_{CP}, Θ_{CP}, and F_{CP}) was facilitated[26] by the restricted motion option in the well-known MM2 program.[34] Thus, sets of chair-like, envelope-like, and (twist-)boat-like rings with CP phase angles (F_{CP}) varying from 0° to 350° in 10° steps were obtained. Mean values of Φ_0 and Φ_1 as well as the rms deviation between observed torsion angles and those recalculated by eq 10 for these sets of ring conformations are collected in Table II.

Analysis of the ring puckering parameters shows that Φ_0 oscillates around 0° as a function of F_{CP}. Hence, averaging Φ_0 over the total pseudorotation circuit (F_{CP} = 0–350°) causes the mean value to collapse to zero, the standard deviation being a measure of the amplitude of the oscillation. For all boat/twist-boat pseudorotation circuits (Θ_{CP} = 90°), Φ_0 reaches its extremes at the twist-boat conformations; for boat conformations Φ_0 is 0° (or very close to 0°). For cyclohexane this is also true for all other pseudorotation circuits characterized by $\Theta_{CP} \neq 90°$; however, heterocyclic rings do not display such a straightforward interpretable behavior at $\Theta_{CP} \neq 90°$. Table II shows that for all molecules the standard deviation of the mean value of Φ_0 attains its maximum value at Θ_{CP} = 90° and correlates positively with Q_{CP}. Moreover, Φ_0 appears to be rather insensitive to nonequilaterality of the ring: the maximum attained value in cyclohexane (at Q_{CP} = 0.75 Å, Θ_{CP} = 90°) equals ±0.77°, whereas that in 4-oxathiane (at Q_{CP} = 0.9 Å, Θ_{CP} = 90°) equals ±1.42°. All in all, it may be concluded that the Φ_0 term in eq 3 plays indeed only a minor role. Notably, within a particular pseudorotation circuit (Θ_{CP} = constant), Φ_1 appears to be much less dependent on the type of conformation (cf. Table II). Instead, nonequilaterality appears to be the dominant factor with Φ_1 being larger in the boat/twist-boat itinerary than in the more chair-like conformations.

The cumulative effect of the neglect of these two parameters is reflected in the mean rms deviation between the torsions ob-
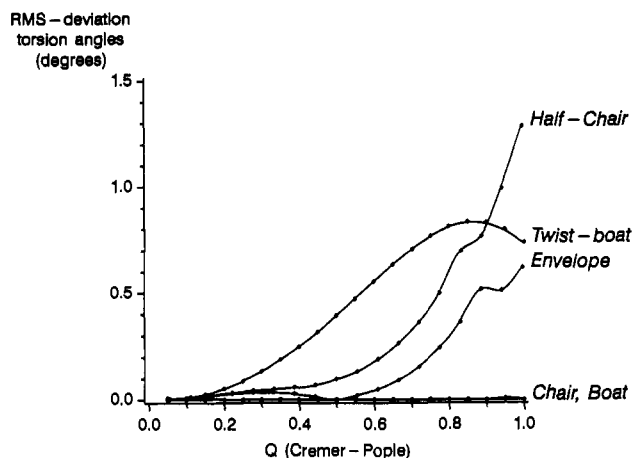
(34) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *12*, 395.

Figure 1. Rms deviations between "observed" (i.e., generated by MM2) and recalculated (by eq 10) endocyclic torsion angles determined for five canonical six-membered ring conformations as a function of Q_{CP} (in Å).

served in the rings generated by MM2 and the corresponding torsions subsequently recalculated by eq 10. As can be gleaned from the last column in Table II, overall (i.e., mean) deviations from eq 10 increase going from chair-like to (twist-)boat-like conformations. Moreover, the MM2-generated six-membered ring dataset indicates that eq 10 is nearly exact for equilateral rings, but there is a clear trend in the mean rms deviations as the latter become larger in case the ring is "more nonequilateral". These findings were elaborated for the equilateral ring formed by cyclohexane. For five classical conformations, i.e., the chair, envelope, half-chair, boat, and twist-boat, the rms deviations between "observed" (i.e., generated by MM2) and recalculated (by eq 10) endocyclic torsion angles were determined as a function of the total puckering amplitude Q_{CP}. The results are given in Figure 1, and it is seen that the error introduced by the neglect of the first two terms of the Fourier series depends on the conformation (i.e., F_{CP} and Θ_{CP}): for chairs and boats eq 10 is virtually exact; for the remaining conformations the error in general becomes larger as Q_{CP} increases, i.e., as the ring becomes more puckered. As the total puckering amplitude, Q_{CP}, of cyclohexane-type rings commonly occurs in the 0.50–0.80 Å interval, it is inferred that the intrinsic error of eq 10 when applied to this type of rings is 0.0–0.8°.

Having established that eq 10 reproduces the endocyclic torsion angles in six-membered rings to a satisfactory degree, a closer look at this equation is in order. The first term in eq 10 corresponds to the description given by Buys and Geise[9] for the boat/twist-boat itinerary of six-membered rings, whereas the second term delineates the torsion angle dependence in the undistorted chair as defined by Bucourt.[35] Hence, eq 10 effectively describes the conformation of a given six-membered ring as a linear combination of these basis forms (vide infra). At this point it is noted in passing that there are some exceptional ring systems that cannot be described in terms of the formalism denoted by eq 10. It turns out that some (but not all!) six-membered rings that are part of a polycyclic compound display rather large (up to 15°) Φ_0 and/or Φ_1 terms in eq 3. This situation occurs especially in cases where the six-membered ring under consideration is, in fact, a bicyclo[3.1.0]hexanoid ring. Of course, one can debate whether, for example, an epoxide of a five-membered ring compound should indeed be treated as a six-membered ring; the fact is, that for this type of molecule, eq 10 may break down.

Analogous to the CP formalism, the puckering parameters (Φ_2, P_2, Φ_3) in eq 10 may be replaced by a spherical polar set (Q, Θ, P_2), where Q is the total puckering amplitude

$$Q = \sqrt{\Phi_2{}^2 + \Phi_3{}^2} \qquad (11)$$

and

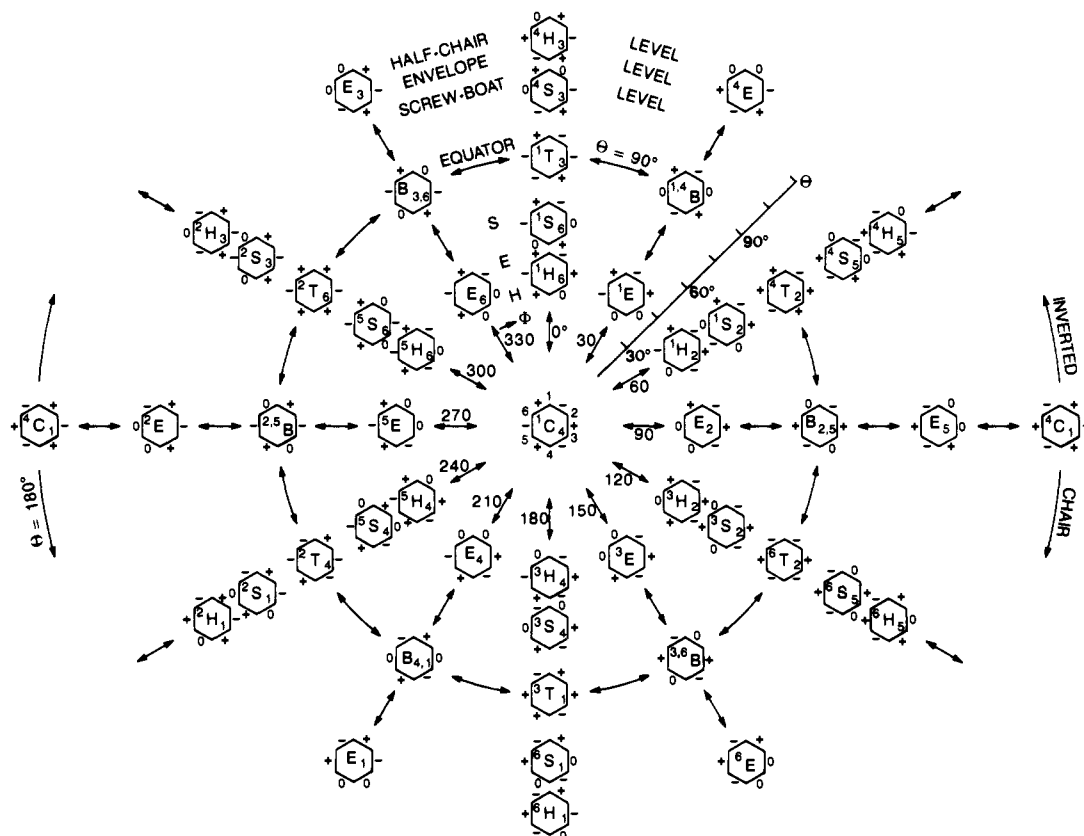$$\Theta = \arctan(\Phi_2/\Phi_3) \qquad (12)$$

Figure 2. Polar projection of the sphere depicting conformational space accessible to six-membered rings. Hexagons denote the canonical conformations (see text); symbols on the sides of the hexagons indicate the signs of the endocyclic torsion angles.

with $0 \leq \Theta \leq \pi$.

For a given amplitude Q, this transformation enables one to map out the conformations accessible to six-membered rings on the surface of a sphere. The poles, at $\Theta = 0°$ or $180°$, correspond to the canonical chair conformations. The equator ($\Theta = 90°$) represents the pseudorotational pathway for the flexible boat/twist-boat interconversions; specific forms are characterized by the phase angle P_2: the six boat conformations occur at $P_2 = 30°$, $90°$, $150°$, $210°$, $270°$, $330°$, whereas the six twist-boat conformations occur at $P_2 = 0°$, $60°$, $120°$, $180°$, $240°$, $300°$ (note that these positions are shifted by $30°$ with respect to the corresponding CP phase angle). Other commonly described conformations are located at specific points on the northern or southern hemisphere. Following the terminology proposed by Boeyens,[21] half-chairs are characterized by $\tan \Theta = \pm 1$, $P_2 = n\cdot60°$ (n = 0–5); envelopes (or sofas) by $\tan \Theta = \pm 2/\sqrt{3}$, $P_2 = 30° + n\cdot60°$ (n = 0–5); and screw-boat (or 1,3-diplanar forms) by $\tan \Theta = \pm 2$, $P_2 = n\cdot60°$ (n = 0–5). For an overview, the surface of the sphere is depicted in Figure 2 in a two-dimensional polar projection. In this figure the hexagons represent the canonical conformations boat (B), twist-boat (T), chair (C), half-chair (H), envelope (E), and screw-boat (S). The hexagons also carry the notation introduced by Bucourt[35] to indicate the signs of the endocyclic torsion angles in the depicted conformations.

The above given description of conformational space accessible to six-membered rings in three coordinates (Q, Θ, P_2) is convenient and pictorial. However, it is noted that, as[19,24] in the analogous CP description, in a real molecule (e.g., cyclohexane) each conformation adopts its own particular value of Q. This means that conformational space for such a given molecule is not a sphere[24] but rather resembles a flattened pumpkin.

Discussion

The Cremer–Pople formalism enjoys a great popularity and has indeed become the de facto standard for describing six-

membered ring conformations.[21,22,36] Nevertheless, in the past several empirically derived methods to calculate puckering coordinates for six-membered rings from endocyclic torsion angles have been proposed and tested by various authors.[9,17,23] However, the latter relationships described only part of the conformational space available to the ring[9] or used rather complicated formulas.[17,23] Diez et al.[37,38] worked out a relationship between endocyclic torsion angles and the CP ring puckering coordinates assuming infinitesimal displacements from a planar reference conformation. They showed that under these conditions the CP equation can be transformed into a generalized torsion angle expression closely related to the Fourier series model (eq 3) of Cano et al.[29] In fact, for six-membered rings an expression equivalent to eq 10 was suggested, but a serious test of the application of this expression to the experimental and/or theoretical torsion angles of six-membered rings was not published.

Obviously, the truncated Fourier (TF) description given by eq 10 and the corresponding CP formalism are to some extent interrelated. Scrutiny of the TF and CP data obtained for the six-membered rings generated by MM2 (vide supra) shows that for the equilateral cyclohexane ring the relation

$$F_{CP} = P_2 - 30° \qquad (13)$$

holds for all conformations (Q_{CP}, Θ_{CP}) within $0.2°$ (worst case). The relationships between the CP-puckering coordinates q_2, q_3, and, by implication, Q_{CP} and Θ_{CP}, on the one hand, and the corresponding TF-puckering coordinates Φ_2, Φ_3, Q, and Θ, on the other hand, are less straightforward. This is exemplified by Figure 3 in which for five canonical conformations Q is plotted as a function of Q_{CP}. It is found that for a particular conformation

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(36) French, A. D.; Brady, J. W. *Computer Modeling of Carbohydrate Molecules*, French, A. D.; Brady, J. W., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1990; Chapter 1, p 1.

(37) Diez, E.; Esteban, A. L.; Guilleme, J.; Bermejo, F. L. *J. Mol. Struct.* 1981, 70, 61.

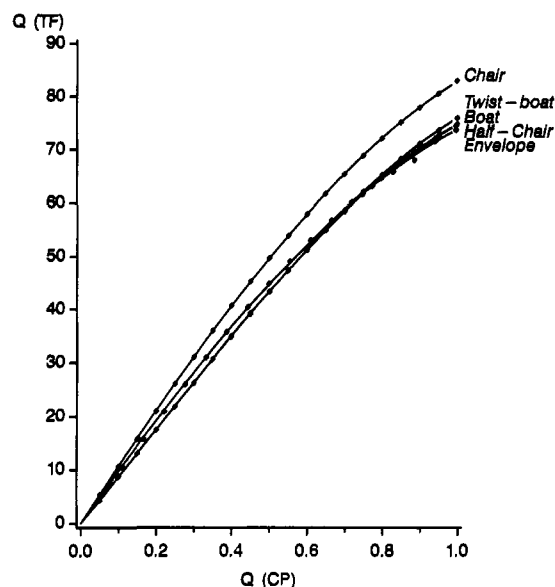(38) Diez, E.; Esteban, A. L.; Bermejo, F.; Altona, C.; Leeuw, F. A. A. M. de *J. Mol. Struct.* 1984, 125, 49.

Figure 3. Functional dependence between the total puckering amplitudes defined by the TF formalism (Q, in degrees) and the CP formalism (Q_{CP}, in Å), respectively, as determined for five canonical cyclohexane conformations generated by MM2.
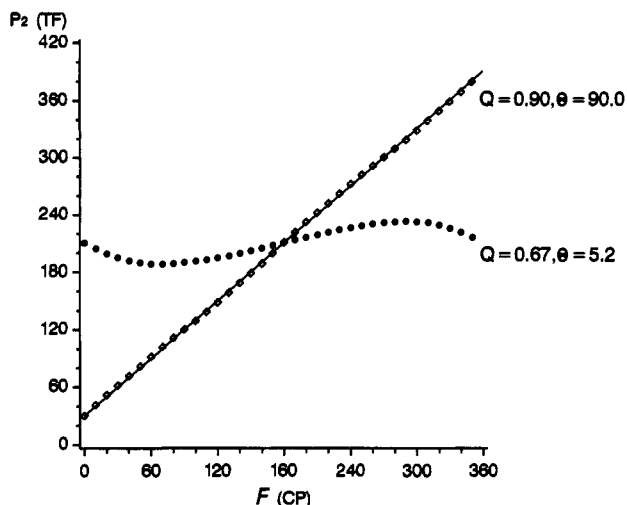

Figure 4. Plots of TF phase angles of pseudorotation (P_2) versus its CP counterparts (F_{CP}) for two MM2-generated pseudorotation circuits of 4-oxathiane (circles: $Q_{CP} = 0.67$ Å, $\Theta_{CP} = 5.2°$; diamonds: $Q_{CP} = 0.90$ Å, $\Theta_{CP} = 90°$). Solid line indicates the P_2/F_{CP} relation delineated by eq 13.

the functional dependence between Q and Q_{CP} is best described by a third degree polynomial expression; however, it is noted that the polynomial expressions differ for the different types of conformations. Such behavior is also noted for the remaining puckering coordinates. In other words, the TF-puckering amplitudes, Φ_n, are not just a function of the corresponding CP-puckering amplitudes, q_n, but instead a function of all CP-puckering coordinates (F_{CP}, q_2, and q_3). It follows that the simple relationships between torsion angles and displacement of a regular hexagon from planarity, as suggested by Dunitz,[11] do not hold for finite puckered six-membered rings.

In the case of nonequilateral rings, the interrelation between the TF and CP description is even more difficult to read. Here the problem concentrates on the relationship between the phase angles of pseudorotation P_2 and F_{CP}, respectively. To illustrate this point, plots of P_2 versus F_{CP} are displayed in Figure 4 for two pseudorotation circuits calculated by means of MM2 for 4-oxathiane: one at $\Theta_{CP} = 5.2°$, $Q_{CP} = 0.67$ Å, and the other one at $\Theta_{CP} = 90°$, $Q_{CP} = 0.90$ Å. It is seen that in the latter boat/twist-boat pseudorotation itinerary the relation between P_2 and
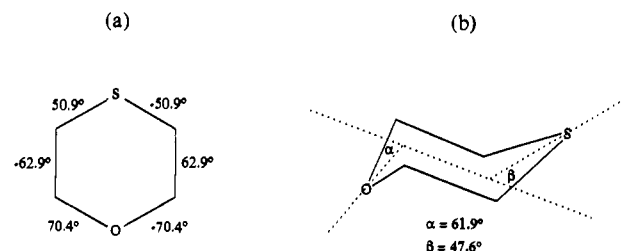
(a)   (b)

Figure 5. Endocyclic torsion angles (a) and interplanar angles (b) observed[39] in the 4-oxathiane ring of 4-oxathianum bis(carbomethoxy)-methylide.

F_{CP} sticks to eq 13 reasonably well (maximum deviation ±2°). However, in the chair-like conformations ($\Theta_{CP} = 5.2°$, $Q_{CP} = 0.67$ Å), the simple linear functional dependence as delineated by eq 13 is completely lost and replaced by a periodic function, amplitude 22°.

These findings imply that the conformational spaces spanned by the TF and the CP formalism, respectively, differ in a rather subtle way. From the validity of eq 13 it is inferred that for equilateral as well as nonequilateral rings the boat/twist-boat pseudorotational subspaces defined by the two formalisms are by and large the same. By the same token it is concluded that for equilateral six-membered rings the inversional subspaces (i.e., chair forms) defined by the two formalisms are identical. However, for nonequilateral rings this is no longer true; in this case the undistorted chair defined by the TF formalism may differ substantially from the undistorted chair delineated by the CP formalism. This is easily recognized when it is realized that the TF formalism defines the undistorted chair in terms of its endocyclic torsion angles: all torsions adopt the same absolute value; only the signs of the torsions alternate along the ring. The CP formalism defines the undistorted ring in terms of equal but alternately signed z-displacements of the ring atoms from the CP mean plane. Only for six-membered rings with true D_{3d} symmetry, like the cyclohexane chair, do the two definitions yield identical conformations; however, in nonequilateral rings this identity is lost.

The 4-oxathiane ring observed in the X-ray structure of 4-oxathianum bis(carbomethoxy)methylide[39] (Figure 5) is a good example of the latter feature. The CP-puckering coordinates for this ring are calculated as $q_2 = 0.002$ Å, $F_{CP} = 180°$, $q_3 = 0.648$ Å; hence for all practical purposes the ring is an undistorted chair in terms of the CP formalism. Figure 5a shows that the endocyclic torsion angles along the ring vary substantially in absolute value. The TF-puckering coordinates calculated for this 4-oxathiane ring amount to $\Phi_2 = 11.2°$, $P_2 = 210°$, and $\Phi_3 = 61.4°$. The interpretation of the latter puckering coordinates (i.e., the ring conformation is a linear combination of the ^SC_O and $B_{S,O}$ forms) is in accordance with the internal puckering phenomena locally observed within the 4-oxathiane ring; the C–S–C part is obviously less puckered than the C–O–C part of the molecule (cf. Figure 5b). In other words, the ring is definitely not an undistorted chair as defined by the TF formalism, thereby demonstrating that the definitions of the undistorted chair differ in the case of nonequilateral rings. Which one of the two definitions of an undistorted chair is the "correct" one is a matter of preference. However, it is noted that in this way the CP definition may be at odds with other criteria[35] commonly accepted in stereochemistry (see also below).

An even more extreme illustration of the difference between the TF and the CP formalism is the thiane ring observed in the X-ray structure of *trans*-2-methylthiane-1-(*p*-tosyl)imide.[40] Figure 6 summarizes the CP and TF interpretation, respectively, of the thiane ring conformation. As can be gleaned from the figure, the CP formalism describes the thiane ring as a linear

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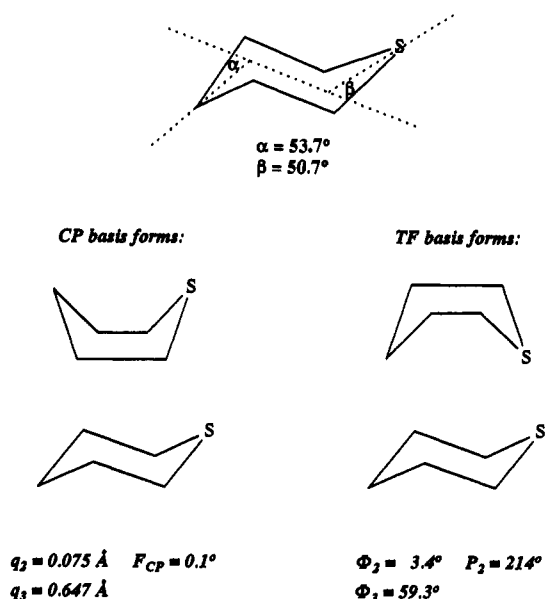
$\alpha = 53.7°$
$\beta = 50.7°$

CP basis forms: *TF basis forms:*

$q_2 = 0.075 \text{ Å}$ $F_{CP} = 0.1°$ $\Phi_2 = 3.4°$ $P_2 = 214°$
$q_3 = 0.647 \text{ Å}$ $\Phi_3 = 59.3°$

Figure 6. Interplanar angles (α, β) in the thiane ring observed[40] for *trans*-2-methylthiane-1-(*p*-tosyl)imide, indicating the flattening of the ring at the C–S–C apex. Lower part shows the basis forms that are part of the linear combinations prescribed by the CP (left) and TF (right) formalisms, respectively.

combination of the $^{S,4}B$ and the $^{S}C_4$ form, whereas the TF formalism takes it to be a combination of $B_{S,4}$ and $^{S}C_4$ forms. Again, based on the internal angular characteristics of the ring (the C–S–C apex less puckered than the C–C₄–C apex), one is inclined to prefer the TF interpretation. However, it should be stressed that from a mathematical point of view the CP interpretation is

correct. The discrepancies noted above stem from the difference in reference systems used by the two methods: the CP formalism employs an external reference plane, whereas the TF formalism is based on internal coordinates only. The examples given above just demonstrate the hazards inherent in using externally referenced puckering coordinates to interpret the internal angular characteristics of a six-membered ring.

Conclusion

The TF formalism delineated by eq 10 gives a description of six-membered ring conformations in terms of three ring puckering coordinates derived from the endocyclic torsion angles. As such, it relies solely on internal coordinates and is therefore not in need of an external reference plane, e.g., the mean plane in the CP formalism. This is an important feature since the determination of a reference plane requires the Cartesian coordinates of *all* ring atoms to be known which consequently makes it virtually impossible to apply the CP formalism to molecules in solution. Conversely, the TF formalism is in a sense geared to dealing with six-membered rings in solution as it utilizes torsion angle magnitudes which may be derived from NMR coupling constants. Especially with respect to the latter type of work, it is noted that the linear equation system given by eq 10 can still be solved for the three ring puckering coordinates if only three torsions are known. Admittedly, the TF formalism lacks the CP formalism's exactness, but its accuracy seems satisfactory for all practical purposes. More important, especially in nonequilateral rings, the TF method appears to be consistent with internal angular characteristics of rings such as local flattening, etc. It is for these reasons that the TF formalism may well serve existing stereochemical needs.

Kinetic Models for Gas-Phase Electron-Transfer Reactions between Nitrobenzenes

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Abstract: Rate constants for gas-phase electron-transfer reactions between substituted nitrobenzenes have been measured using ion cyclotron resonance spectroscopy. On the basis of the assumption that these reactions occur through the formation of an intermediate complex, a statistical model is used to interpret the reaction kinetics. The intersecting parabolas quantum mechanical model provides an alternative description of the energy surface. Energy barriers are found to be consistent for the two methods. The results for exothermic reactions are consistent with a Marcus theory analysis, but suggest that a zero-order potential energy surface may not be completely adequate for quantitative prediction of reaction rates.

Introduction

Electron-transfer reactions have long been studied in both solution and gas phases. In solution, they generally have an activation barrier that can be ascribed to structural deformation of the reactants (the inner-sphere reorganization energy) and the reorientation of solvent dipoles (the outer-sphere reorganization energy) upon the formation of the transition state. Early gas-phase studies mostly concentrated on reactions between rare gas cations or diatomic cations and small molecules (2–3 atoms) that had no analogous reactions in solution. Recently, systematic studies on

gas-phase electron-transfer reactions of metallocenes[1] and nitrobenzenes[2] which had been studied in solution phase have appeared.

Kinetics of gas-phase electron-transfer reactions are governed by, among other things, energy defects and Franck–Condon factors of the reacting pair.[3] At thermal energies the energy resonance

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