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Group Theory of Ring Pucker

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Abstract

It is shown that a group-theoretical definition of the conformation of puckered rings, in terms of the normal modes of displacement on regular polygons, is equivalent to the description in terms of puckering coordinates, referred to a mean plane. This means that the conformation of a general N-membered ring is completely defined by the one-dimensional symmetrical displacements of the regular polygon and that practical conformational analysis is always possible in terms of the uniquely defined mean plane. The displacement modes, fixed by group theory, provide a natural basis set for the analysis of complex conformations as a linear combination of the primitive types representing these modes.

Introduction

Interest in the puckering of cyclic molecular fragments developed out of the conformational analyses of the cycloalkanes (Hendrickson, 1961, 1964, 1967; Dale, 1973) into a topic of general importance for crystallography and molecular mechanics. Quantitative description of ring puckering is a non-trivial problem in three dimensions that requires $3N$ parameters for the characterization of a puckered N-membered ring. The set of Cartesian coordinates (x_j, y_j, z_j) for each atom j would be such a set, but with limited descriptive power owing to the large number of parameters involved. It was first shown by Kilpatrick, Pitzer & Spitzer (1947) that the conformation of any puckered form of cyclopentane can be specified in terms of two parameters only – an amplitude and a phase angle. These parameters relate to the out-of-plane displacements required to generate the puckered form from the planar configuration. Generalization of the concept to the larger cycloalkanes was formulated by Pickett and others (Pickett & Strauss, 1970, 1971; Bocian, Pickett, Rounds & Strauss, 1975; Strauss, 1971).

The puckered forms of an N-membered ring are generated by the set of N displacements perpendicular to a regular planar polygon. This one-dimensional description is unique for the smaller rings ($N \leq 12$). The description involves a maximum of N parameters. In fact, any puckered form is fully characterized by $N-3$ symmetry-adapted coordinates. The application of the model to a general N-membered ring is, however, not immediate. Early attempts (Adams, Geise & Bartell, 1970; Geise, Adams & Bartell, 1969) to define a generalized set of coordinates for five-membered rings required a number of approximations and were limited by the extent of puckering.

A general definition of ring-puckering coordinates was given by Cremer & Pople (1975) for any type of cyclic compound. The method relies on the definition of a unique mean plane for a general monocyclic puckered ring. The geometry of the puckering relative to this plane is described by a set of $N-3$ puckering parameters, which are generalizations of the amplitudes and phases of cyclopentane conformations, introduced by Kilpatrick *et al.* (1947). The $N-3$ parameters are defined in terms of the atomic coordinates perpendicular to the mean plane only. The method has been of practical importance in crystallography as the basis of conformational analysis and the nomenclature for six-, seven- and eight-membered-ring conformations (Boeyens, 1978; Boessenkool & Boeyens, 1980; Evans & Boeyens, 1988).

We now demonstrate the one-to-one correspondence between the $N-3$ symmetry-adapted coordinates of Pickett & Strauss (1971) and the puckering parameters of Cremer & Pople (1975). The expressions for ring-puckering coordinates as out-of-plane displacement modes are derived directly from group-theoretical representations to demonstrate the general applicability of the model.

Mathematical derivation

Following Pickett & Strauss (1971) the puckered conformation of an N-membered ring may be generated by out-of-plane displacements of the atoms of the planar ring. This polygon, of D_{Nh} symmetry, and the set of N displacements can be used as the basis for an irreducible representation, as in vibrational analysis. The character tables for N even and odd, presented in Appendix 1, directly produce the irreducible representations of the required displacements as

$$\Gamma(\text{even}) = B_{2(g,u)} + E_{2u} + \ldots + E_{(N/2-1)(u,g)}$$

$$\Gamma(\text{odd}) = E''_2 + \ldots + E''_{(N-1)/2}.$$

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For each irreducible representation, the out-of-plane coordinates of each ring atom, z_j, are written in terms of symmetry-adapted coordinates.

The $B_{2(g,u)}$ representation produces the out-of-plane displacements

$$z_j = (-1)^j Q,$$

where Q transforms as $B_{2(g,u)}$.

The E_m representations produce displacements

$$z_j = \rho_m \cos(2\pi jm/N + \varphi_m),$$

where $\rho_m\cos\varphi_m$ and $\rho_m\sin\varphi_m$ transform together as E_m, $j = 1,...,N$, $m = 2,...,(N-1)/2$ (N odd); $m = 2,...,(N/2)-1$ (N even). This expression is based on the out-of-plane normal coordinates of a thin circular rod (Love, 1927):

$$z(\theta) = \rho_m \cos(m\theta - \varphi_m), \quad m = 2,3,....$$

The out-of-plane displacements of a general conformation may now be expressed as a linear combination of the irreducible representations of individual modes of out-of-plane displacement.

Thus, for a general conformation,

$$z_j = (-1)^j Q + \sum_m \rho_m \cos(2\pi jm/N + \varphi_m) \quad (N \text{ even})$$

$$z_j = \sum_m \rho_m \cos(2\pi jm/N + \varphi_m). \quad (N \text{ odd})$$

The expression for each z_j is a linear sum over all possible m values. We can thus consider only one value of m without loss of generality.

$$z_j = \rho_m \cos(2\pi jm/N + \varphi_m).$$

Consider

$$\sum_j z_j \cos(2\pi jm/N) \tag{1}$$

and

$$\sum_j z_j \sin(2\pi jm/N). \tag{2}$$

Substitution for z_j in these expressions gives (1) as

$$\sum_j \rho_m \cos(2\pi jm/N + \varphi_m)\cos(2\pi jm/N)$$

or

$$\sum_j \rho_m \cos\varphi_m \cos^2(2\pi jm/N) - \sum_j \rho_m \sin\varphi_m \cos(2\pi jm/N)\sin(2\pi jm/N)$$

and (2) as

$$\sum_j \rho_m \cos(2\pi jm/N + \varphi_m)\sin(2\pi jm/N)$$

or

$$\sum_j \rho_m \cos\varphi_m \cos(2\pi jm/N)\sin(2\pi jm/N) - \sum_j \rho_m \sin\varphi_m \sin^2(2\pi jm/N).$$

$\sum_j \cos^2(2\pi jm/N)$, $\sum_j \sin^2(2\pi jm/N)$ and $\sum_j \sin(2\pi jm/N)\cos(2\pi jm/N)$ can be expressed as $\frac{1}{2}\sum_j[1 + \cos(4\pi jm/N)]$, $\frac{1}{2}\sum_j[1 - \cos(4\pi jm/N)]$ and $\frac{1}{2}\sum_j \sin(4\pi jm/N)$, respectively.

$\sum_j \cos(4\pi jm/N)$ and $\sum_j \sin(4\pi jm/N) = 0$, as shown in Appendix 2.

Expression (1) therefore reduces to $(N/2)\rho_m\cos\varphi_m$ and (2) reduces to $-(N/2)\rho_m\sin\varphi_m$.

Hence,

$$(N/2)\rho_m \cos\varphi_m = \sum_j z_j \cos(2\pi jm/N) \tag{3}$$

and

$$(N/2)\rho_m \sin\varphi_m = -\sum_j z_j \sin(2\pi jm/N) \tag{4}$$

$$\sum_j z_j^2 = \sum_j \rho_m^2 \cos^2(2\pi jm/N + \varphi_m) = (N/2)\rho_m^2.$$

The coordinates ρ_m may be normalized so that

$$\sum_m \rho_m^2 = \sum_j z_j^2.$$

With the normalized coordinates, (3) and (4) become

$$\rho_m \cos\varphi_m = (2/N)^{1/2} \sum_j z_j \cos(2\pi jm/N)$$

$$\rho_m \sin\varphi_m = -(2/N)^{1/2} \sum_j z_j \sin(2\pi jm/N).$$

To ensure a direct correlation between atom 1 and φ_m, it is necessary to replace j by $(j-1)$ in the expressions above, without changing their meaning:

$$\rho_m \cos\varphi_m = (2/N)^{1/2} \sum_j z_j \cos\{[2\pi(j-1)]m/N\}$$

$$\rho_m \sin\varphi_m = -(2/N)^{1/2} \sum_j z_j \sin\{[2\pi(j-1)]m/N\}.$$

These expressions are those given by Cremer & Pople (1975) to define a set of generalized ring-puckering coordinates. The one-to-one correspondence of the φ_m values and of ρ_m with their q_m is clearly evident. These expressions hold true for any $N > 3$. For N even, the symmetry coordinate Q is included. When $\rho_m = 0$; $\forall\ m = 2,3,4...,(N/2) - 1$.

$$z_j = (-1)^j Q$$

$$z_j^2 = (-1)^{2j} Q^2$$

$$\sum_j z_j^2 = Q^2 \sum_{j=1}^{N} (-1)^{2j} = NQ^2. \tag{5}$$

But

$$\sum_j z_j^2 = Q \sum (-1)^j z_j. \tag{6}$$

Equating (5) and (6), one gets

$$(1/N)\sum_j (-1)^j z_j = Q.$$

Once again the value of Q must be normalized

$$\sum z_j^2 = Q^2.$$

Replacing Q by the normalized value, one gets

$$Q = (1/N^{1/2})\sum_j (-1)^j z_j.$$

j must be replaced by $(j-1)$ to correspond with the atomic number of the previous expressions:

$$Q = (1/N^{1/2})\sum_j (-1)^{j-1} z_j.$$

Q is the same as the parameter $q_{N/2}$ of Cremer & Pople (1975).

Replacing ρ_m and Q with the normalized values, one finds the expressions for the out-of-plane displacements as defined by Cremer & Pople (1975):

$$z_j = N^{-1/2}(-1)^{j-1}Q + (2/N)^{1/2}\sum_m \rho_m \times \cos[2\pi m(j-1)/N + \varphi_m] \qquad (N \text{ even})$$

$$z_j = (2/N)^{1/2}\sum_m \rho_m \cos[2\pi m(j-1)/N + \varphi_m] \qquad (N \text{ odd}).$$

Discussion

Pickett & Strauss (1971) approached the conformational analysis of puckered rings on the basis of symmetry-allowed displacements normal to the planes of regular D_{Nh} polygons, whereas Cremer & Pople (1975) presented a method to reduce the pucker of actual rings to displacements from an idealized polygon in the mean ring plane – *i.e.* the inverse operation. The two methods have now been shown to be consistent and the special conditions imposed by Cremer & Pople (1975) to define a unique plane to be natural consequences of the group theory.

Only perpendicular displacements are considered to operate on the fully symmetrical polygon. The same assumption applies during the inverse operation, which consequently always results in a conformation that projects as a regular polygon on the mean plane, irrespective of variations in bond length.

The theoretical basis of the Cremer & Pople (1975) ring-puckering coordinates now provides insights into their number and nature. Group theory illustrates how $N-3$ parameters specify the positions of N atoms in a one-dimensional projection. Each symmetrical conformation and its ring-puckering parameters must correspond to characteristic values of ρ_m and φ_m of the E_m representation. This group-theoretical basis therefore dictates a fixed relationship with symmetry type and the observed alternation of the symmetry elements C_s and C_2 along the pseudorotational paths is also rationalized.

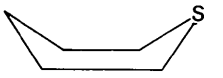
The model is a one-dimensional description of a three-dimensional phenomenon and extension of the group-theoretical arguments to general N-membered rings must be exercised with caution. As an example,

Table 1. *Cartesian and puckering coordinates of the hypothetical* SC_5 *boat configuration*

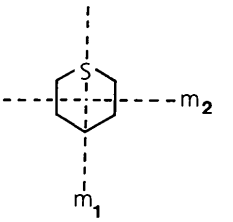
	Cartesian coordinates			Puckering coordinates		
S	0·00	1·70	0·50	0.00	1·59	0.50
C1	1·40	0·75	−0·25	1·40	0·64	−0.25
C2	1·25	−0·75	−0·25	1·25	−0·86	−0·25
C3	0·00	−1·05	0·50	0·00	−1·16	0·50
C4	−1·25	−0·75	−0·25	−1·25	−0·86	−0·25
C5	−1·40	0·75	−0·25	−1·40	0·64	−0·25

Puckering parameters
$q_2 = 0{\cdot}87$ Å
$q_3 = 0$ Å
$\varphi_2 = 0°$

consider the hypothetical heterocyclic six-membered ring:



puckered according to the details specified in Table 1. Its puckering parameters are the same as those of the cyclohexane boat form. The $\varphi_2 = 0$ indicates a mirror plane through S, perpendicular to another mirror plane



Clearly, m_2 is a pseudo mirror plane. The symmetry refers only to the z_j displacements and not to the ring as a three-dimensional chemical object. This limitation, however, detracts very little from the general practical utility of the model.

The total pucker of a ring results from a linear combination of symmetry-adapted primitive normal modes, identified by the irreducible representations of the D_{Nh} point group. Each coefficient in the expansion specifies the contribution from a symmetry class, or primitive mode, and collectively they provide a natural basis set for conformational analysis.

The B_2 class represents the contribution from crown forms, for even-membered rings only, and each two-dimensional E_m representation adds two contributing forms which often constitute a pseudorotational pair. A general conformation is therefore made up of contributions from $N-3$ primitive forms, consistent with the number of irreducible representations. The characterization of these primitive forms and their incorporation into a scheme for quantitative analysis of ring pucker will be the topic of a subsequent communication.

APPENDIX 1

Character tables for the D_{Nh} point groups [adapted from Wilson, Decius & Cross (1955) and Pickett & Strauss (1971)]

D_{Nh} (N odd)

D_{Nh}	E	$2S_N(N-1)/2$	$2C_N^2$	$2S_N(N-3)/2$	...	σ_h	NC_2'	$N\sigma_v$	
A_1'	1	1	1	1	...	1	1	1	
A_2'	1	1	1	1	...	1	−1	−1	R_z
A_1''	1	−1	1	−1	...	−1	1	−1	
A_2''	1	−1	1	−1	...	−1	−1	1	T_z
E_1''	2	$2\cos(\pi/N)$	$2\cos(4\pi/N)$	$2\cos(3\pi/N)$	...	−2	0	0	$R_{x,y}$
E_2'	2	$2\cos(2\pi/N)$	$2\cos(2\times 4\pi/N)$	$2\cos(6\pi/N)$	...	+2	0	0	
⋮				⋮					
$E_{(N-1)/2}''$	2	$\pm 2\cos[(\pi/N)(N-1)/2]$	$2\cos[(4\pi/N)(N-1)/2]$	$\pm 2\cos[3/2(N-1)(\pi/N)]$	...	−2	0	0	
$E_{(N-1)/2}'$	2	$\mp 2\cos[(\pi/N)(N-1)/2]$	$2\cos[(4\pi/N)(N-1)/2]$	$\mp 2\cos[3/2(N-1)(\pi/N)]$	...	+2	0	0	
⋮				⋮					
E_1'	2	$-2\cos(\pi/N)$	$2\cos(4\pi/N)$	$-2\cos(3\pi/N)$	...	+2	0	0	$T_{x,y}$

D_{Nh} (N even)

D_{Nh}	E	$2C_N$	$2C_N^2$	...	$C_N N/2 = C_2$	$N/2C_2$	$N/2C_2'$	i	$2S_N N/2-1$	$2S_N N/2-2$	...	σ_h	$N/2\sigma_d$	$N/2\sigma_v$	
A_{1g}	1	1	1	+1	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	+1	1	−1	−1	1	1	1	1	1	−1	−1	R_z
B_{1g}	1	−1	1	±1	$(-1)^{N/2}$	1	−1	1	−1	1	±1	$(-1)^{N/2}$	1	−1	
B_{2g}	1	−1	1	±1	$(-1)^{N/2}$	−1	1	1	−1	1	±1	$(-1)^{N/2}$	−1	1	
E_{1g}	2	$2\cos(2\pi/N)$	$2\cos[(2\pi/N)2]$	...	−2	0	0	2	$2\cos(2\pi/N)$	$2\cos[(2\pi/N)2]$	...	−2	0	0	$R_{x,y}$
⋮								⋮							
E_{kg}	2	$2\cos[(2\pi/N)k]$	$2\cos[(2\pi/N)2k]$	...	$2(-1)^k$	0	0	2	$2\cos[(2\pi/N)k]$	$2\cos[(2\pi/N)2k]$	...	$2(-1)^k$	0	0	
⋮								⋮							
$E_{[(N/2)-1]g}$	2	$-2\cos(2\pi/N)$	$2\cos[(2\pi/N)2]$	...	$2(-1)^{(N/2-1)}$	0	0	2	$-2\cos(2\pi/N)$	$2\cos[(2\pi/N)2]$	...	$2(-1)^{(N/2-1)}$	0	0	
A_{1u}	1	1	1	+1	1	1	1	−1	−1	−1	−1	−1	−1	−1	
A_{2u}	1	1	1	+1	1	−1	−1	−1	−1	−1	−1	−1	1	1	T_z
B_{1u}	1	−1	1	±1	$(-1)^{N/2}$	1	−1	−1	1	−1	∓1	$(-1)^{N/2+1}$	−1	1	
B_{2u}	1	−1	1	±1	$(-1)^{N/2}$	−1	1	−1	1	−1	∓1	$(-1)^{N/2+1}$	1	−1	
E_{1u}	2	$2\cos(2\pi/N)$	$2\cos[(2\pi/N)2]$	...	−2	0	0	−2	$-2\cos(2\pi/N)$	$-2\cos[(2\pi/N)2]$	...	2	0	0	$T_{x,y}$
⋮								⋮							
E_{ku}	2	$2\cos[(2\pi/N)k]$	$2\cos[(2\pi/N)2k]$	...	$2(-1)^k$	0	0	−2	$-2\cos[(2\pi/N)k]$	$-2\cos[(2\pi/N)2k]$	...	$2(-1)^{k+1}$	0	0	
⋮								⋮							
$E_{[(N/2)-1]u}$	2	$-2\cos(2\pi/N)$	$2\cos[(2\pi/N)2]$	...	$2(-1)^{(N/2-1)}$	0	0	−2	$2\cos(2\pi/N)$	$-2\cos[(2\pi/N)2]$	...	$2(-1)^{N/2}$	0	0	

Note: When ($N/2$) is even, the columns under $N/2\sigma_v$ and $N/2\sigma_d$ are inverted. Out-of-plane displacements are represented by $\Gamma = A_{2u} + B_{2(g,u)} + E_{1g} + E_{2u} + E_{3g} + \cdots + E_{(N/2)-1(u,g)}$. Pickett & Strauss (1971) noted that A_{2u}, which represents T_z, and E_{1g}, which represents R_x and R_y, are of no conformational significance. Ignoring these representations is equivalent to the special conditions formulated by Cremer & Pople (1975) to avoid trivial translation or rotation of a ring. The symbol (g,u) reads g for $N/2$ odd and u for $N/2$ even.

APPENDIX 2

It is required that

$$\sum_j \cos(4\pi jm/N) \text{ and } \sum_j \sin(4\pi jm/N) = 0.$$

According to Durell & Robson (1959),

$$\sum_{n=0}^{N-1} \cos(\alpha + n\beta) = \cos[\alpha + (n-1)/2\beta] \times \sin(n\beta/2)/\sin(\beta/2)$$

and

$$\sum_{n=0}^{N-1} \sin(\alpha + n\beta) = \sin[\alpha + (n-1)/2\beta] \times \sin(n\beta/2)/\sin(\beta/2).$$

Hence

$$\sum_{j=1}^{N} \cos(4\pi jm/N) = \cos(4\pi m/N) + \ldots + \cos(4\pi m)$$
$$= \cos(4\pi m/N) + \ldots + \cos[4\pi m(N-1)/N] + \cos(0)$$
$$= \cos\left[\frac{N-1}{2}\left(\frac{4\pi m}{N}\right)\right] \times (\sin 2\pi m)/\sin(2\pi m/N)$$
$$= 0.$$

and

$$\sum_{j=1}^{N} \sin(4\pi jm/N) = \sin(4\pi m/N) + \ldots + \sin(4\pi m)$$
$$= \sin(0) + \ldots + \sin[4\pi m(N-1)/N]$$
$$= \sin\left[\frac{N-1}{2}\left(\frac{4\pi m}{N}\right)\right] \times \sin(2\pi m)/\sin(2\pi m/N)$$
$$= 0.$$

[These expressions hold if $\sin(2\pi m/N) \neq 0$; $m = 2,3,...,(N-1)/2$, N odd; $m = 2,3,...,(N/2)-1$, N even.]

However,

$$\sin[2\pi(m/N)] = 0$$
$$\Leftrightarrow 2m/N = K, \quad K \in \mathbb{N}$$
$$\Leftrightarrow N|2m$$

Since $m < N/2 \forall N > 3$, $\sin(2\pi m/N) \neq 0$.

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Conformational Analysis of Ring Pucker

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Abstract

The conformation of a general puckered ring is defined by a linear combination of normal atomic displacements, according to the irreducible representations of the D_{Nh} symmetry group. Each two-dimensional representation contributes two uniquely defined primitive modes, superimposed on a one-dimensional crown form that only exists for N even, adding up to $N-3$ primitive forms, for any N. The normalized linear coefficients are independent of the amplitude of pucker and of the ring numbering scheme. The formalism applies to any ring type and a quantitative characterization of conformations, intermediate between the conventional classical forms, is possible. It provides the basis for mapping conformations as a function of puckering parameters and a simple algorithm for the identification of the classical forms. The procedure relates general ring conformations to a few simple shapes, familiar to chemists, without losing the advantage of quantitative puckering analysis.

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Introduction

Group-theoretical analysis of the normal modes of displacement on N-membered polygons provides the basis of a quantitative formulation of ring pucker (Boeyens & Evans, 1989). These symmetry-adapted displacement coordinates are equivalent to the general puckering coordinates of Cremer & Pople (1975) which accurately describe the nature and extent of ring pucker. The description is quantitative and unique, but the interpretation of numerical values in terms of conformational nomenclature, familiar to chemists (boat, chair *etc.*) is not obvious. The relationship between puckering parameters and conformational type has been established for five- (Altona & Sundaralingam, 1972), six- (Boeyens, 1978), seven- (Boessenkool & Boeyens, 1980) and eight- (Evans & Boeyens, 1988) membered rings, by mapping the symmetrical (classical) forms in the field of puckering parameters. The classical forms, previously identified by energy calculations (Hendrickson, 1961, 1964, 1967), map out as pseudo-