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

References

ADAMS, W. J., GEISE, H. J. & BARTELL, L. S. (1970). *J. Am. Chem. Soc.* **92**, 5013–5019.

BOCIAN, D. F., PICKETT, H. M., ROUNDS, T. C. & STRAUSS, H. L. (1975). *J. Am. Chem. Soc.* **97**, 687–695.

BOESSENKOOL, I. K. & BOEYENS, J. C. A. (1980). *J. Cryst. Mol. Struct.* **10**, 11–18.

BOEYENS, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

DALE, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.

DURELL, C. V. & ROBSON, A. (1959) *Advanced Trigonometry*, pp. 125–126. London: G. Bell.

EVANS, D. G. & BOEYENS, J. C. A. (1988). *Acta Cryst.* B**44**, 663–671.

GEISE, H. J., ADAMS, W. J. & BARTELL, L. S. (1969). *Tetrahedron*, **25**, 3045–3052.

HENDRICKSON, J. B. (1961). *J. Am. Chem. Soc.* **83**, 4537–4547.

HENDRICKSON, J. B. (1964). *J. Am. Chem. Soc.* **86**, 4854–4866.

HENDRICKSON, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7036–7046, 7047–7061.

KILPATRICK, J. E., PITZER, K. S. & SPITZER, R. (1947). *J. Am. Chem. Soc.* **69**, 2483–2488.

LOVE, A. E. H. (1927). *A Treatise on the Mathematical Theory of Elasticity*, Section 293*b*. Cambridge Univ. Press.

PICKETT, H. M. & STRAUSS, H. L. (1970). *J. Am. Chem. Soc.* **92**, 7281–7284.

PICKETT, H. M. & STRAUSS, H. L. (1971). *J. Chem. Phys.* **55**, 324–334.

STRAUSS, H. L. (1971). *J. Chem. Educ.* **48**, 221–223.

WILSON, E. B., DECIUS, J. C. & CROSS, D. C. (1955). *Molecular Vibrations*. New York: McGraw-Hill.

Acta Cryst. (1989). B**45**, 581–590

Conformational Analysis of Ring Pucker

BY DEBORAH G. EVANS AND JAN C. A. BOEYENS

Department of Chemistry, University of the Witwatersrand, PO Wits, 2050 Johannesburg, South Africa

(*Received* 5 *October* 1988; *accepted* 6 *July* 1989)

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.

0108-7681/89/060581-10$03.00

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-

rotational cycles on $(N-3)$-dimensional surfaces. These surfaces have been represented by a circle for five-, a sphere for six-, a torus for seven- and a family of tori on a unit sphere for eight-membered rings. The transformation from crystallographic atomic coordinates to conformational type is achieved by mapping the derived parameters of the general ring onto the appropriate surface as a function of puckering parameters. The conformational type is then assigned on account of the proximity to a symmetrical form, previously located in the surface. This method is adequate for the special case where the ring corresponds to a symmetrical form. More often, however, the general ring does not map exactly onto a symmetrical form.

The conformation of a heterocyclic ring with various substituents need also not adopt a conformation energetically favourable for unsubstituted cycloalkanes, especially not in the crystal where packing forces may be significant. It is here that the assignment of conformational type becomes largely descriptive. A ring conformation could be described as intermediate between at least two classical forms, with the share of contributing forms estimated by their distance on the surface from the calculated surface site of the cyclic fragment. A quantitative measure of this distance on the surface should generate the coefficients in a linear combination of symmetrical forms. A quantitative expression for the deviation of an actual conformation from symmetrical types in the neighbourhood has been proposed before as the Euclidean distance between the points in $(N-3)$-dimensional space (Evans & Boeyens, 1988). Although this is a useful guide, it is sensitive to the degree of pucker, and has no theoretical basis.

A better description of the intermediate forms has now been established, based on the group-theoretic model of Pickett & Strauss (1971) and the puckering equations of Cremer & Pople (1975). It is suggested that the normal modes of displacement, at different values of phase angle, and not the recognized symmetrical forms be used as a basis for representing any conformation as a linear combination of these basic forms. The coefficients are independent of the atomic numbering scheme and the amplitude of pucker. The ring conformation is readily visualized as a combination of the puckered shapes of the basis forms in the correct relative proportions.

Description of ring pucker

The conformations of a general N-membered ring may be generated by the out-of-plane displacements of the flat polygon. According to this model, the out-of-plane displacements of a general ring may be generated as as linear combination of the normal mode displacements (Boeyens & Evans, 1989; Pickett & Strauss, 1971), represented by

$$\Gamma = B_{2(u,g)} + \sum_m E_{m(g,u)}.$$

The $B_{2(u,g)}$ representation only occurs for N even, with basis

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

Each mode of this representation is a multiple of the form

$$z_j = (-1)^{j-1}. \qquad (1)$$

$E_{m(g,u)}$, or E''_m for odd N, represents displacements

$$z_j = \rho_m \cos[\varphi_m + (2\pi m/N)(j-1)].$$

Each mode of this representation is a linear combination of two mutually orthogonal forms

$$z_j = \cos[(2\pi m/N)(j-1)] \qquad (2)$$

$$z_j = \sin[(2\pi m/N)(j-1)]. \qquad (3)$$

Every conformation is a linear combination of these normal modes and hence a linear combination of the sets of displacements (1)–(3) (N even) or (2)–(3) (N odd), for each m. The same result is obtained from the Cremer & Pople (1975) analysis (Boeyens & Evans, 1989).

For an arbitrary conformation, the out-of-plane displacements are therefore given by the Cremer & Pople (1975) equations

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

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

where q, ρ_m, φ_m are the normalized puckering parameters or symmetry-adapted coordinates.

These expressions may be written in a number of equivalent ways, one of which gives

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

It has already been recognized for six- and seven-membered rings that the coefficients $\rho_m\cos\varphi_m$, $\rho_m\sin\varphi_m$ and q carry the planar ring into the normal modes where $z_j = \frac{\cos}{\sin}[(2\pi m/N)(j-1)$ and $(-1)^{j-1}/2^{1/2}$, respectively (Bocian, Pickett, Rounds & Strauss, 1975; Pickett & Strauss, 1970; Strauss, 1971). The Cremer & Pople (1975) equations are an explicit statement of this fact. All ring conformations can be reduced to linear combinations of the normal modes of the E_m representations (and the B_{2u} representation for N even) (Boeyens & Evans, 1989).

The fundamental primitive forms and their relative out-of-plane atomic displacements for five- to eight-membered rings are described in Fig. 1 and Table 1.

A number of forms equivalent to these normal modes exist, differing only in the value of the phase angle. For each m, any linear combination of forms with

$$z_j = \begin{matrix}\cos\\ \sin\end{matrix}[(2\pi m/N)(j-1)]$$

is also a normal mode of E_m. The equivalent forms at phase angles φ_m have

$$z_j = \cos\varphi_m \cos[(2\pi m/N)(j-1)] - \sin\varphi_m \sin[(2\pi m/N)(j-1)].$$

Consider the forms $^{1,4}B$, $^6T_2$ and $B_{2,5}$ in the nomenclature of Boeyens (1978) for $N = 6$, with z_j of

$^{1,4}B$: $\cos[4\pi/6(j-1)]$

$^6T_2$: $\sin[4\pi/6(j-1)]$

$B_{2,5}$: $\cos 60° \times {}^{1,4}B - \sin 60° \times {}^6T_2$.

$^{1,4}B$ is equivalent to $B_{2,5}$, although they differ in phase angle by 60°. The equivalent forms are themselves normal modes of E_m and should be part of the extended basis set. Each conformation will still be expressed as a linear combination of $N-3$ normal modes, two from each E_m representation, but now chosen to have phase angles closest to that of the ring of interest.

Mathematical formulation

The set of normal modes, whose z_j are given by $(-1)^{j-1}/2^{1/2}$, $\cos[(2\pi m/N)(j-1)]$, $\sin[(2\pi m/N)(j-1)]$ are linearly independent (see Appendix). These modes can therefore form a suitable basis for conformational type.

Group-theoretical analysis shows that the set of forms equivalent to the cos form and sin form of each m are separated by a constant amount. Given any arbitrary ring, its φ_m value will lie between those of a 'cos-type' form and a 'sin-type' form.

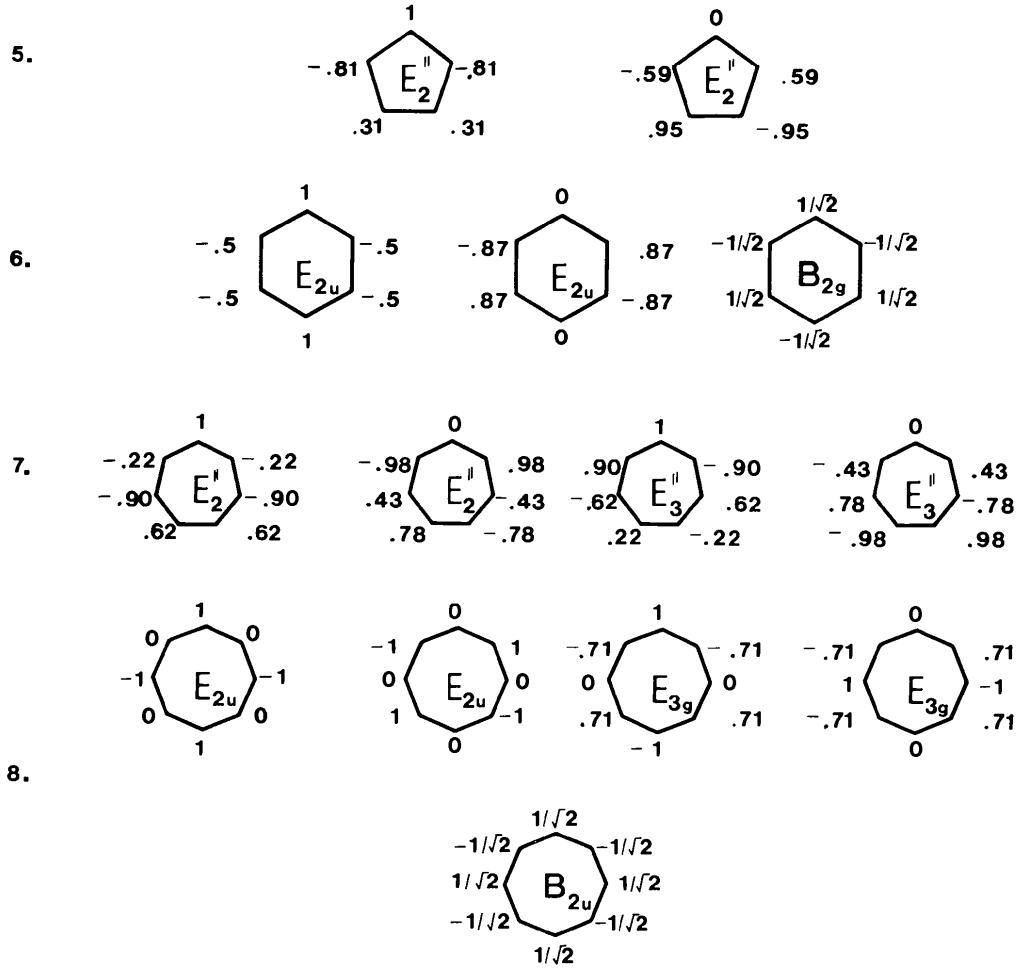


Fig. 1. Relative out-of-plane displacements for five- to eight-membered rings.

The forms equivalent to the cos form and the sin form can be expressed as linear combinations of these forms using the Cremer–Pople equations. Any arbitrary ring can also be expressed as a linear combination using this equation.

The arbitrary ring lying at A, q_m, φ_m is given by

$$z_j = (2/N)^{1/2}\{A(-1)^{j-1}/2^{1/2} + \sum_m q_m \cos\varphi_m \cos[(2\pi m/N)(j-1)] - \sum_m q_m \sin\varphi_m \sin[(2\pi m/N)(j-1)]\}.$$

For each mode, E_m, there is a cos form and a sin form lying closest to the ring at a_m and b_m phase angles.

These are also linear combinations of the Cremer & Pople normal modes.

'cos type'

$$z_j = \sum_m \cos a_m \cos[(2\pi m/N)(j-1)] - \sin a_m \sin[(2\pi m/N)(j-1)].$$

'sin type'

$$z_j = \sum_m \cos b_m \cos[(2\pi m/N)(j-1)] - \sin b_m \sin[(2\pi m/N)(j-1)].$$

Because the set of Cremer & Pople normal modes are linearly independent, the arbitrary conformation may be expressed as a linear combination of the forms at a_m and b_m.

Suppose the coefficients of the 'cos-type' and 'sin-type' forms are c_m and d_m for each m. Then, denoting the Cremer–Pople normal modes as X_m, Y_m for each m, we have

$$\sum_m q_m \cos\varphi_m X_m - q_m \sin\varphi_m Y_m = \sum c_m(\cos a_m X_m - \sin a_m Y_m) + d_m(\cos b_m X_m - \sin b_m Y_m).$$

Since X_m, Y_m are linearly independent, we can solve for c_m and d_m as follows:

$$c_m = \frac{q_m(-\cos\varphi_m \sin b_m + \sin\varphi_m \cos b_m)}{\sin a_m \cos b_m - \cos a_m \sin b_m}$$

$$d_m = \frac{q_m(\cos\varphi_m \sin a_m - \sin\varphi_m \cos a_m)}{\sin a_m \cos b_m - \cos a_m \sin b_m}.$$

When N is even, there is a coefficient for the normal mode of the B_{2u} representation. This coefficient is q. Where $q < 0$, the normal mode used in the linear combination is the mirror image of the form $z_j = (-1)^{j-1}/2^{1/2}$, *i.e.* $z_j = (-1)^j/2^{1/2}$. This ensures that the coefficient is equal in magnitude to q but greater than zero.

Table 1. *Classical nomenclature of the primitive forms*

N	Primitive form	Classical nomenclature
5	E_2'' (cos form)	Envelope
	E_2'' (sin form)	Twist
6	B_{2g}	Chair
	E_{2u} (cos form)	Boat
	E_{2u} (sin form)	Twist-boat
7	E_2'' (cos form)	Boat
	E_2'' (sin form)	Twist-boat
	E_3'' (cos form)	Chair*
	E_3'' (sin form)	Twist-chair*
8	B_{2u}	Crown
	E_{2u} (cos form)	Boat-boat
	E_{2u} (sin form)	
	E_{3g} (cos form)	Twist chair
	E_{3g} (sin form)	

*See text.

In fact, choosing the phase angles of the cos form and sin form, so that the phase angle of the general ring lies between them, ensures that the coefficients in the linear expansion are always positive.

It is shown in the Appendix that these cos-type and sin-type forms are always linearly independent for each m. They are not orthogonal. The set of all possible ring conformations can be generated by a finite-dimensional basis. In all cases, $(N-3)$ normal modes can be used as generating conformations. These groups of $(N-3)$ normal modes are always linearly independent. The set of all equivalent cos forms and sin forms therefore form an extended basis, which consists of a number of overlapping subsets, or sub-bases, each with $N-3$ linearly independent forms. Which subset is used as a basis depends on the phase angles of the ring under investigation.

The elements of this extended basis generate a reference set of ring conformations, called the primitive forms.

The coefficients in the linear expansion are independent of phase. The linear coefficients are always the same, irrespective of the ring numbering used. This is illustrated in the Appendix.

A description of ring conformation is really a description of molecular shape. It should therefore be independent of the extent of pucker. The overall molecular shape can be generated by adding together the primitive forms in the correct proportions. The same molecular shape is obtained provided the coefficients are in the same ratio. The linear coefficients are therefore normalized to unity. The method can now be applied to any ring type, irrespective of the puckering amplitude. For example, these are both

boat conformations, but differ in puckering amplitude.

Application of the method

Every conformation can be expressed as a linear combination of primitive forms. The linear coefficients are independent of atomic numbering and extent of pucker. The primitive forms are relatively simple conformations of either C_s or C_2 symmetry, and are easily interpreted as boat-like, chair-like and their twisted counterparts for smaller rings. The symmetrical forms, or classical conformations in conventional use, take on certain characteristic values of the linear coefficients.

It is important to realize that information on the phase angle is lost in the coefficients. The linear coefficients are not unique. A description of the ring in terms of linear coefficients is only unique if the phases of the cos and sin forms are reported. This is only true when there is more than one m value with $\rho_m \neq 0$.

The primitive forms are often the traditional classical forms, *e.g.* for six-membered rings, the cos form is a boat and the sin form a twist conformation. For five- and six-membered rings a conformation may therefore be reported as the linear combination of two or three classical forms respectively. The cos form of a seven-membered ring where $m = 3$ takes the form of a chair. This is not the chair form of Hendrickson (1967). It is suggested that this chair (a combination of a primitive boat and a primitive chair) be denoted by the symbol H (half-chair) and its pseudorotation partner as T (twist-half-chair). For rings larger than six-membered, the linear coefficients are not unique. Different forms may assume the same coefficients. Since the phase angles of the primitive forms differ, a unique description requires three terms, like

$$\chi = a(1) + \sum_m b_m(\varphi_m) + c_m(\varphi_m),$$

where the b_m and c_m are coefficients in the linear sum; φ_m are the phase angles of the primitive forms, characterized by the integer k of $k\pi/2N$. $a(1)$ only occurs for N even: (1) denotes the usual B_{2u} mode and (-1) its mirror image.

This nomenclature is unique if reported in order of increasing m. The linear coefficients give an indication of the relative contributions of each primitive form, and will be the same irrespective of atomic numbering, although the phase angles will differ.

A computer program, *CONFOR*, has been written in Fortran to generate the phase angles of the primitive forms. It calculates the phases of the primitive forms to be used in the linear combination. The linear coefficients are solved and normalized. The linear coefficients of all the accepted classical forms (of five-, six-, seven- and eight-membered rings) have been determined. As noted these linear coefficients need not be unique. Results show that a set of similar coefficients but different phase angles is not likely for the classical forms. The only such cases are the forms of the *S/TS* and *H/T* pseudorotational cycles for seven-membered rings. The program calculates the sum of the modulus of the difference in linear coefficients of any ring and a symmetrical form. Below a certain threshold, the ring is taken as one of these classical forms, except in the case where there is more than one m for which $\rho_m \neq 0$. The phase angles are then checked against those of the classical forms [*BS, H, TS, T*(7-*M*): Boessenkool & Boeyens (1980); *BC, TBC* (8-*M*): Evans & Boeyens (1988)]. The program completes the description of the conformation of intermediate forms and identifies a ring if it is a classical form.

The general structure of the program is given in Fig. 2 and Table 2. Details will be published elsewhere, but interested readers are welcome to approach the authors for advance copies.

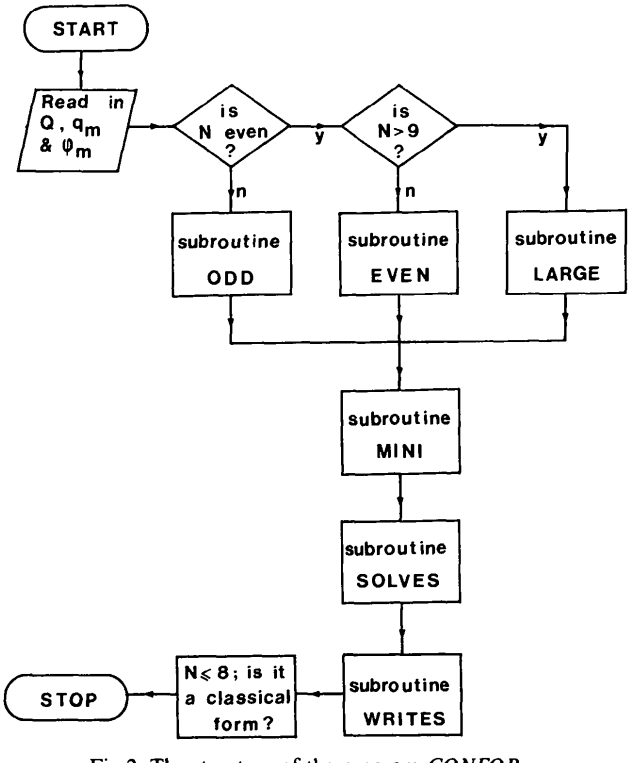


Fig 2. The structure of the program *CONFOR*.

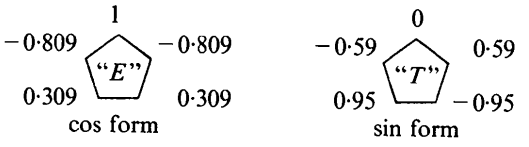
Table 2. *The program CONFOR*

Subroutine	Function
LARGE, ODD, EVEN	Generates the primitive forms
MINI	Finds the primitive forms closest in phase angle
SOLVES	Solves for the coefficients in the linear expansion
WRITES	Normalizes the coefficients to unity and writes these and the phase information to file

Examples

Five-membered rings

The basis is two-dimensional, consisting of the equivalent forms



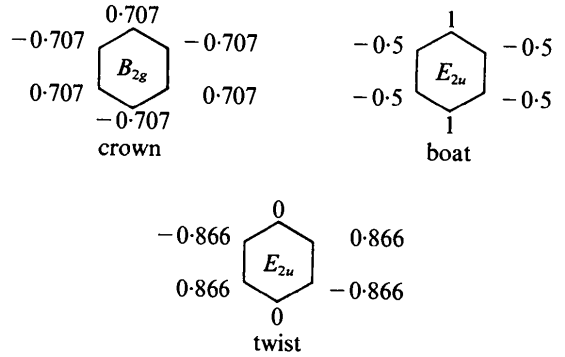
These are equivalent to the envelope and twist forms (Altona & Sundaralingam, 1972). A number of rings reported in the literature have been analysed and the results are given in Table 3.

Ring 1 is best described as a twist form according to the program *CONFOR*. These results demonstrate the ease of interpretation of this method. Ring 2 is a twist conformation showing distortion to an envelope form. The method gives an exact value for the degree of this distortion. A description like this is more familiar to chemists than the puckering parameters or a linear combination of "*E*" and "*T*", *viz*

$$\text{ring 2} = 0{\cdot}47\text{"}E\text{"} - 0{\cdot}09\text{"}T\text{"}.$$

Six-membered rings

The basis is three-dimensional, consisting of equivalent forms:



A number of rings reported in the literature have been analysed and the results are given in Table 4.

Table 3. *Analysis of five-membered rings*

a, *b* are given as percentages. φ is expressed as a multiple of $\pi/2N$.

Ring	Ref.	Q_2	φ_2	$a\varphi(E) + b\varphi(T)$
1	(*a*)	0·49	342·90	5 (20) + 95 (19)
2	(*a*)	0·48	348·7	37 (20) + 63 (19)
3	(*b*)	0·45	356·30	79 (20) + 21 (19)
4	(*c*)	0·422	217·0	95 (12) + 5 (13)
5	(*d*)	0·353	265·10	27 (14) + 73 (15)

References: (*a*) Boeyens, Bull, Tuinman & Van Rooyen (1979); (*b*) Ceccarelli, Ruble & Jeffrey (1980); (*c*) Gal, Feher, Tihanyi, Horvath, Jerkovich, Argay & Kálmán (1980); (*d*) Cremer & Pople (1975).

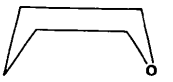
Table 4. *Analysis of six-membered rings*

Linear combination of the three primitive forms.

Ring	Ref.	Q_2	Q_3	φ_2	$a(\pm 1)$	$b\varphi(B)$	$c\varphi(T)$
1	(*a*)	0·05	0·554	183·7	92 (+1)	7 (12)	1 (14)
2	(*b*)	0·286	0·244	47·0	45 (1)	31 (4)	24 (2)
3	(*c*)	0·406	−0·216	196·0	34 (−1)	21 (12)	35 (14)

References: (*a*) Cremer & Pople (1975); (*b*) Gal, Feher, Tihanyi, Horvath, Jerkovich, Argay & Kálmán (1980); (*c*) Boeyens (1978).

The pyranoid ring (1) is shown by program *CONFOR* to be much like a crown form. The distortion towards the form



is estimated as a 10% contribution from the primitive boat at $\varphi_2 = \pi$, a conclusion easily reached from an examination of the linear coefficients. Ring 2 is a cyclohexene. Although the extent of pucker is much less, the linear coefficients give a readily interpretable description of ring conformation. Ring 3 has been described as midway between *H*, *E* and *S*. The conformation found here is intermediate between a boat, twist and a chair form. These two assignments are not contradictory. The *E*, *H* and *S* forms are themselves mixtures of the chair, boat and twist forms. The ring conformation could be expressed as a linear combination of the *E*, *H* and *S* forms since *E*, *H* and S forms can be expressed as a linear combination of the independent forms. In other words, any conformation can be expressed as a linear combination of these mixed forms, but such a scheme would be complicated. Not much additional information is gained in using these classical forms. These are also not linearly independent.

Discussion

The normal displacement modes of a planar *N*-membered regular polygon serve as a basis for the conformation of a puckered *N*-membered ring. Two linearly independent modes, equivalent to the mutu-

ally orthogonal cosine and sine forms of each E_m representation and one of the two possible equivalent modes of B_{2u} can be combined to match the puckering parameters of any conformation. Any analysis incorporates an appropriate subset of $N-3$ linearly independent, though not necessarily orthogonal, elements, chosen from an extended basis set, to define the closest primitive forms in the vicinity of the unknown conformation. The conformation is reduced to a linear combination of these primitive forms, resulting in a unique quantitative symbolic description, in terms of simple familiar shapes. This approach is superior to the graphical procedures in common use since the quantitative nature of numerical puckering analysis is preserved.

It is noted from Fig. 1 that the cos-type and sin-type forms for $m = 2$, 3 in eight-membered rings are equivalent. The sin form is like a primitive phase for the cos form. In a case like this the linear expansion is not unique for all phases. The coefficients of the cos form and the sin form are interchangeable (see Appendix). If two rings are therefore compared to see whether they are of the same conformational type it is advisable to ensure, in the first instance, by relative rotation if necessary, that the phases of lowest index ($m = 2$) have matching values. The identity of the rings can then be considered established only if the calculated phases correspond for all m.

The definition of conformation in terms of perpendicular displacements only contracts the model from $3N$ Cartesian coordinates to $N-3$ parameters. This projection from $3N-6$ conformational space to an $N-3$ subspace has been interpreted (Petit, Dillen & Geise, 1983) to imply that conformational analysis requires a prior definition of standard conformations in addition to the puckering parameters. This seems to invalidate the procedure of mapping conformations to normalized surfaces without taking the amplitude of pucker into account. However, as noted by Cremer (1984), perpendicular displacements relate to one-dimensional shape functions, by definition independent of the amplitude of pucker. It is this shape, rather than the extent of distortion from planarity, that should be equated with the notion of conformation.

The method is independent of absolute molecular geometry or chemical identity. The conformation only depends on the relative contributions from the group-theoretic modes of displacement. Any puckered six-membered ring with 100% contribution from the B_{2u} mode has a chair conformation. Any six-membered boat has the shape arising from the cos mode of E_{2u} atomic displacements only. The envelope form is a 59:41 combination of an E_{2u} and the B_{2u} representations. The amount of pucker cannot affect this ratio. Even heterocyclic rings with irregular molecular geometry can assume a chair shape, at $\varphi = \theta = 0$. The fact that the ring does not display D_{3d} symmetry in three dimensions is irrelevant, since the shape factor of interest is strictly one-dimensional.

APPENDIX

Characteristics of the linear coeffiecients

1. *Linear independence of the Cremer–Pople normal modes*

Owing to the nature of the primitive forms for each m, $\cos[2\pi m(j-1)/N]$, $\sin[2\pi m(j-1)/N]$, they are mutually orthogonal. That is,

$$\sum z_{\cos,j} z_{\sin,j} = 0.$$

In order for the set of these forms over all m to be a suitable basis, they should be linearly independent. By the fact that these forms are normal modes of different symmetry types, they are linearly independent.

Proof: To prove linear independence, we first show that the normal modes are orthogonal. That is

$$\sum z_j^\alpha z_j^\beta = 0, \ \alpha,\beta \text{ normal modes.}$$

For N even, consider

$$\sum_{j=1}^{N} \cos[\pi(j-1)]\cos[(2\pi m/N)(j-1)].$$

With the identities

$$\cos(A+B) = \cos A\cos B - \sin A\sin B$$

$$\cos(A-B) = \cos A\cos B + \sin A\sin B,$$

this is equivalent to

$$\tfrac{1}{2}\left\{\sum_{j=1}^{N}\cos[(\pi + 2\pi m/N)(j-1)] + \sum_{j=1}^{N}\cos[(\pi - 2\pi m/N)(j-1)]\right\}.$$

Using the lemma given in a previous paper (Boeyens & Evans, 1989), this reduces to zero, since $\sin(N\pi/2 + m\pi) = 0$ if N is even.

Similarly,

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

Therefore, $\cos[\pi(j-1)]$ or $(-1)^{j-1}$ is orthogonal to any linear combination of $a\cos[(2\pi m/N)(j-1)] + b\sin[(2\pi m/N)(j-1)]$, as required.

For N even or odd, we need

$$\cos[(2\pi/N)(j-1)M_1],\ \sin[(2\pi/N)(j-1)M_1],$$
$$\cos[(2\pi/N)(j-1)M_2],\ \sin[(2\pi/N)(j-1)M_2],$$

are orthogonal.

(a) $$\sum_j \cos[(2\pi/N)(j-1)M_1]\cos[(2\pi/N)(j-1)M_2]$$
$$= \tfrac{1}{2}\sum_j \cos[(2\pi/N)(j-1)(M_1+M_2)]$$
$$+ \tfrac{1}{2}\sum_j \cos[(2\pi/N)(j-1)(M_1-M_2)]$$
$$= 0.$$

(b) $$\sum_j \sin[(2\pi/N)(j-1)M_1]\sin[(2\pi/N)(j-1)M_2]$$
$$= -\tfrac{1}{2}\sum_j \cos[(2\pi/N)(j-1)(M_1+M_2)]$$
$$+ \tfrac{1}{2}\sum_j \cos[(2\pi/N)(j-1)(M_1-M_2)]$$
$$= 0.$$

(c) $$\sum_j \sin[(2\pi/N)(j-1)M_1]\cos[(2\pi/N)(j-1)M_2]$$
$$= \sum_j \cos[(2\pi/N)(j-1)M_1$$
$$- \pi/2]\cos[(2\pi/N)(j-1)M_2]$$
$$= \tfrac{1}{2}\sum_j \cos[-\pi/2 + (2\pi/N)(j-1)(M_1+M_2)]$$
$$+ \tfrac{1}{2}\sum_j \cos[-\pi/2 + (2\pi/N)(j-1)(M_1-M_2)]$$
$$= 0.$$

(d) $$\sum_j \sin[(2\pi/N)(j-1)M_2]\cos[(2\pi/N)(j-1)M_1] = 0.$$

(By analogy with c.)

We now show orthogonality $\Rightarrow$ linear independence.

Suppose the z_i of the modes α, β, ..., ξ are given as $z_i^{(\alpha)}$, ..., $z_i^{(\xi)}$. Suppose these modes are not linearly independent. Then

$$\alpha' z_i^{(\alpha)} + \ldots + \xi' z_i^{(\xi)} = 0 \,\forall i$$
$$\Rightarrow \exists \text{ at least two coefficients} \neq 0$$
$$(\text{since } z_i \neq 0 \,\forall i).$$

At least one of the modes, say α, is a linear combination of at least one other mode β:

$$z_i^{(\alpha)} = \gamma z_i^{(\beta)} + \sum_\delta \pi_\delta z_i^{(\delta)}.$$

Now α and β are orthogonal

$$\sum_i z_i^{(\alpha)} z_i^{(\beta)} = \sum_i z_i^{(\beta)}(\gamma z_i^{(\beta)} + \sum_\delta \pi_\delta z_i^{(\delta)})$$
$$= \gamma \sum_i z_i^{(\beta)} z_i^{(\beta)} + \sum_i \left(\sum_\delta \pi_\delta z_i^{(\delta)} z_i^{(\alpha)} \right)$$
$$= \gamma \sum_i z_i^{(\beta)} z_i^{(\beta)}.$$

But

$$\gamma \sum_i z_i^{(\beta)} z_i^{(\beta)} \neq 0 \ \left(\text{since } \sum_i z_i^{(\beta)^2} = 0 \Rightarrow z_i = 0 \ \forall i\right).$$

But α,β are orthogonal and hence $\sum_i z_i^{(\alpha)} z_i^{(\beta)} = 0$. This is a contradiction. The modes are therefore linearly independent.

Hence, for N even

$$A(-1)^j + \sum_m a_m\{\cos[2\pi m(j-1)/N]\}$$
$$+ b_m\{\sin[2\pi m(j-1)/N]\} = 0, \quad \forall j$$
$$\Rightarrow A, a_m, b_m = 0, \quad \forall m;$$

and for N odd

$$\sum_m a_m\{\cos[2\pi m(j-1)/N]\}$$
$$+ b_m\{\sin[2\pi m(j-1)/N]\} = 0, \quad \forall j$$
$$\Rightarrow a_m, b_m = 0, \quad \forall_m.$$

This is used in solving the equations for a linear combination of primitive forms.

2. *The primitive forms are linearly independent*

Each primitive form is a linear combination of the normal modes (which are linearly independent).

Consider a cos and sin form at φ_m and $\varphi_m + \kappa$, respectively. The coefficients of a form at φ''_m in the linear expansion in terms of $\cos[(2\pi m/N)(j-1)]$ and $\sin[(2\pi m/N)(j-1)]$ are $\cos\varphi''$ and $-\sin\varphi''$, respectively.

Let

$$\sum_m c_m\{\cos\varphi_m \cos[(2\pi m/N)(j-1)]$$
$$- \sin\varphi_m \sin[(2\pi m/N)(j-1)]\}$$
$$+ d_m\{\cos(\varphi_m + \kappa)\cos[(2\pi m/N)(j-1)]$$
$$- \sin(\varphi_m + \kappa)\sin[(2\pi m/N)(j-1)]\}$$
$$= 0.$$

Since $\cos[(2\pi m/N)(j-1)]$ and $\sin[(2\pi m/N)(j-1)]$ are linearly independent and the pairs in m are linearly independent, we have

$$c_m \cos\varphi_m + d_m \cos\varphi_m \cos\kappa - d_m \sin\varphi_m \sin\kappa = 0$$

and

$$c_m\sin\varphi_m + d_m\sin\varphi_m\cos\kappa + d_m\cos\varphi_m\sin\kappa = 0$$

for all m. Hence,

$$\sin\varphi_m(c_m\cos\varphi_m + d_m\cos\varphi_m\cos\kappa - d_m\sin\varphi_m\sin\kappa) = 0$$

$$\cos\varphi_m(c_m\sin\varphi_m + d_m\sin\varphi_m\cos\kappa + d_m\cos\varphi_m\sin\kappa) = 0$$

for all m. This gives:

$d_m\sin\kappa = 0$

or $d_m = 0$ unless $\kappa = 0$ or π, which it does not,

and $c_m\cos\varphi_m = 0$,

$c_m\sin\varphi_m = 0 \Rightarrow c_m = 0$.

Therefore the primitive forms are linearly independent.

3. *The coefficients in the linear expansion are independent of phase angle*

Since the normal modes of E_m are linearly independent, the equations for the linear coefficients may be solved in groups of m. The expressions for a ring at $\varphi_m = R$, with primitive forms at phase angles A and B, are

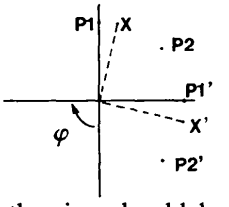
$$XA(M) = \frac{-Q\cos R\sin B + Q\sin R\cos B}{\sin A\cos B - \cos A\sin B}$$

(coefficient of cos form)

$$XB(M) = \frac{Q\cos R\sin A - Q\sin R\cos A}{\sin A\cos B - \cos A\sin B}$$

(coefficient of sin form).

Any equivalent primitive forms are generated by C_n or S_n operations: $\varphi' \rightarrow \varphi' + (2\pi m/N)$. Any ring will thus have equivalent forms (a different ring numbering) at $\varphi'_m + (2\pi m/N)$ (Pickett & Strauss, 1971).



A description of the ring should be independent of the ring numbering chosen; *i.e.* the linear coefficients should be equal in both these cases. This can be shown to be the case.

Consider the ring at $\varphi_m = R$, with the closest primitive forms at phase angles of A and B. An equivalent phase thus lies at $\varphi_m + 2\pi m/N$. Let $(2\pi m/N) = \alpha$. Then for this equivalent phase

$$\varphi \text{ (cos form)} = A + \alpha$$

$$\varphi \text{ (sin form)} = B + \alpha$$

$$\varphi \text{ (ring)} = R + \alpha.$$

The coefficients are given by XA' and XB'.

$$XA' = \frac{-\cos(R+\alpha)\sin(B+\alpha) + \sin(R+\alpha)\cos(B+\alpha)}{\sin(A+\alpha)\cos(B+\alpha) - \cos(A+\alpha)\sin(B+\alpha)}.$$

The numerator reduces to $-\cos R\sin B + \sin R\cos B$. The denominator becomes $\cos B\sin A - \cos A\sin B$. The numerator in the XB' expression is

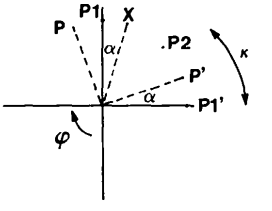
$$(\cos R\cos\alpha - \sin R\sin\alpha)(\sin A\cos\alpha + \cos A\sin\alpha)$$
$$- (\sin R\cos\alpha + \cos R\sin\alpha)(\cos A\cos\alpha - \sin A\sin\alpha)$$
$$= \cos R\sin A - \sin R\cos A.$$

XA', XB' are therefore the same as those given for the ring at R, even though the primitive forms are different.

If a form has neither C_2 nor σ_v symmetry, the enantiomeric form will not be generated by C_n or S_n operations. Thus the phase angle of $\varphi + (2m\pi/N)[+(\pi)]$ will not generate this form. It can only be generated by C_2 though atom 1 followed by σ_h. This implies (Pickett & Strauss, 1971)

$$\varphi \rightarrow -\varphi + \pi + \pi \equiv -\varphi.$$

Thus if a form lies at φ, the enantiomer lies at $-\varphi$. It must be shown that the coefficients of enantiomers are the same, since the enantiomer may be generated by a different atomic numbering.



P' is generated from P by rotation of 2κ, since the spacings of the primitive forms are 2κ. We now show P' and X have the same linear coefficients. Since P' and P are related by a C_n operation these have the same coefficients.

The form X

$$XA = \frac{-\cos(A+\alpha)\sin(A+\kappa) + \sin(A+\alpha)\cos(A+\kappa)}{\sin A(\cos A\cos\kappa - \sin A\sin\kappa) - \cos A(\sin A\cos\kappa + \sin\kappa\cos A)}$$
$$= \frac{\sin\alpha\cos\kappa - \sin\kappa\cos\alpha}{-\sin\kappa}$$

The form P'

$$XA = \frac{-\cos(A+2\kappa-\alpha)\sin(A+\kappa) + \sin(A+2\kappa-\alpha)\cos(A+\kappa)}{\sin(A+2\kappa)\cos(A+\kappa) - \cos(A+2\kappa)\sin(A+\kappa)}.$$

This denominator becomes $\sin\kappa$. The numerator reduces to

$$-\cos\kappa\cos2\kappa\sin\alpha + \cos\kappa\sin2\kappa\cos\alpha - \sin\kappa\cos2\kappa\cos\alpha$$
$$- \sin\kappa\sin2\kappa\sin\alpha = -\sin\alpha\cos\kappa + \cos\alpha\sin\kappa.$$

XB. The numerator of the forms:

$$P': \quad XB = \cos(A + 2\kappa - \alpha)\sin(A + 2\kappa) - \sin(A + 2\kappa - \alpha)\cos(A + 2\kappa)$$

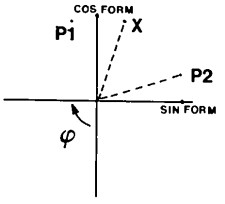
$$X: \quad XB = \cos(A + \alpha)\sin(A + 2\kappa) - \sin(A + \alpha)\cos(A + 2\kappa) = -\sin\alpha$$

The expression for P' becomes $\sin\alpha$.

The coefficients of enantiomers are therefore the same.

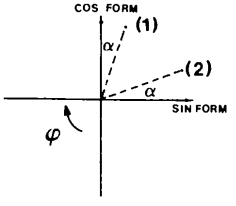
4. *Two primitive forms (cos form and sin form) differ in phase only*

For example, primitive forms of eight-membered rings.



Consider the case where an equivalent form of the primitive cos form is the primitive sin form. An equivalent form of X will therefore lie at $P2$. The coefficients of $P2$ and X will not be the same, but the coefficients of each cos and sin form will be reversed. The forms X and $P2$ are equivalent simply because the cos form and sin form are different phases of the same form.

To show that the coefficients are inverted, consider the forms (1) and (2)



with the φ_m of the cos and sin forms as A and B, respectively.

$$XA(1) = \frac{-\cos(A + \alpha)\sin B + \sin(A + \alpha)\cos B}{\sin A\cos B - \cos A\sin B}.$$

The numerator is given by

$$-\cos A\cos\alpha\sin B + \sin A\sin\alpha\sin B + \sin A\cos\alpha\cos B + \cos A\cos B\sin\alpha.$$

$$XB(2) = \frac{\cos(B - \alpha)\sin A - \sin(B - \alpha)\cos A}{\sin A\cos B - \cos A\sin B}.$$

The numerator is given by

$$\cos B\cos\alpha\sin A + \sin B\sin A\sin\alpha - \sin B\cos\alpha\cos A + \cos B\sin\alpha\cos A.$$

$XA(2)$ is similarly equal to $XB(1)$.

References

ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

BOCIAN, D. F., PICKETT, H. M., ROUNDS, T. C. & STRAUSS, H. L. (1975). *J. Am. Chem. Soc.* **97**, 687–695.

BOESSENKOOL, I. K. & BOEYENS, J. C. A. (1980). *J. Cryst. Mol. Struct.* **10**, 11–18.

BOEYENS, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.

BOEYENS, J. C. A., BULL, J. R., TUINMAN, A. & VAN ROOYEN, P. H. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 1279–1287.

BOEYENS, J. C. A. & EVANS, D. G. (1989). *Acta Cryst* **B45**, 577–581.

CECCARELLI, C., RUBLE, J. R. & JEFFREY, G. A. (1980). *Acta Cryst.* **B36**, 861–865.

CREMER, D. (1984). *Acta Cryst.* **B40**, 498–500.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

EVANS, D. G. & BOEYENS, J. C. A. (1988). *Acta Cryst.* **B44**, 663–671.

GAL, M., FEHER, O., TIHANYI, E., HORVATH, G., JERKOVICH, G., ARGAY, G. & KÁLMAN, A. (1980). *Tetrahedron Lett.* **21**, 1567–1570.

HENDRICKSON, J. B. (1961). *J. Am. Chem. Soc.* **83**, 4537–4547.

HENDRICKSON, J. B. (1964). *J. Am. Chem. Soc.* **86**, 4854–4866.

HENDRICKSON, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7036–7046, 7047–7061.

PETIT, G. H., DILLEN, J. & GEISE, H. J. (1983). *Acta Cryst.* **B39**, 648–651.

PICKETT, H. M. & STRAUSS, H. L. (1970). *J. Am. Chem. Soc.* **92**, 7281–7284.

PICKETT, H. M. & STRAUSS, H. L. (1971). *J. Chem. Phys.* **55**, 324–334.

STRAUSS, H. L. (1971). *J. Chem. Educ.* **48**, 221–223.