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THE LINEAR SPACE OF RING CONFORMATIONS

BY

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ABSTRACT

The description of ring conformation in terms of a set of puckering coordinates relative to a mean plane is shown to be equivalent to the group theoretic definition of the conformation of a puckered ring in terms of out–of–plane displacements of a planar polygon. A description of the conformation of a general N–membered ring, based on crystallographic coordinates, is provided in terms of the one–dimensional displacement modes of the regular polygon of D_{Nh} symmetry. The set of puckered forms therefore represent a linear space. The out–of–plane displacement modes of the irreducible representations provide a natural basis set.

Two linearly independent modes equivalent to the two orthogonal modes of each two–dimensional representation, and a one–dimensional mode for an even–membered ring, form a (N–3)–dimensional basis. The linear coefficients are independent of the puckering amplitude and of the ring numbering scheme. The linear combination of primitive forms provides a simple algorithm to identify classical forms and a quantitative description of conformations, intermediate between the classical forms.

The one–dimensional model describes the conformation of large rings. Conformational analysis of nine–membered rings is completed by projection of the conformational space onto a three–dimensional surface defined by the puckering parameters. Intermediate forms are expressed as a linear combination of six primitive forms. The conformation of larger rings is characterized by the linear coefficients, interpreted graphically. A nomenclature for any symmetrical conformation is proposed.

DECLARATION

I declare that this dissertation is my own, unaided work, carried out under the supervision of Professor J. C. A. Boeyens. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.



D. G. Evans.

1 December 1988.

In Memory of my Father
Ivor Evans

PREFACE

My interest in ring conformations was initiated in the vacation of December 1986, as a student of Professor Boeyens. The conformational mapping of six– and seven–membered rings had been completed in 1980. Professor Boeyens' suggestion of extending the method to the more complex eight–membered rings led to their conformational characterization as part of my Honours project in the first half of 1987. Some of the problems encountered in this study prompted further investigation to a deeper understanding of conformational description. It is with gratitude that I acknowledge the collaboration with my supervisor, Professor Jan Boeyens, with whom it has been a pleasure to work. This project would never have materialized without his interest and encouragement over the past four years.

I have had the opportunity of presenting aspects of this work at a number of *conferences*, including a poster entitled "Conformations of eight–membered rings" at the Eleventh European Crystallographic Meeting in Vienna, Austria (August, 1988). The financial assistance of the University of the Witwatersrand and the Foundation for Research and Development is appreciated. I would also like to express my sincere thanks to:

The University of the Witwatersrand for the post of Junior Lecturer from December 1987– December 1988.

My colleagues of the Structural Chemistry Group for the useful discussions and Dr. Sue Dobson for access to her information on large macrocycles.

My mother, without whose encouragement and interest this would not have been possible.

My boyfriend, Noel Mack, for his assistance and unfailing patience. These ideas would never have developed without his support.

Mrs. S. Parker for typing the manuscripts for the journal articles, parts of which were used in this dissertation.

The Chemistry Department for the use of their equipment in the preparation of this dissertation.

The subject matter of this work has been submitted for publication in the journal Acta Crystallographica B. In particular Chapters 3, 4, and 5 have been submitted as articles entitled "Group theory of ring pucker", "Conformational analysis of ring pucker" and "*Mapping the conformation* of nine–membered rings" respectively. Chapter 2 is to be published as an article entitled "Mapping the conformation of eight–membered rings" in Acta Cryst. B *(1988)*.

CONTENTS

Chapter	Page
1. INTRODUCTION	1
2. CONFORMATIONAL MAPPING OF EIGHT-MEMBERED RINGS	
2.1. Introduction	5
2.2. Method of Study	5
2.3. *Results*	9
3. GROUP THEORY OF RING PUCKER	
3.1. Introduction	13
3.2. Mathematical Derivation	13
3.3. Discussion	18
4. THE LINEAR SPACE OF RING *CONFORMATIONS*	
4.1. Introduction	22
4.2. Description of Ring Pucker	23
4.3. Mathematical Formulation	28
4.4. Application of the Method	31
4.5. The Program CONFOR	33
4.6. Examples	35
4.7. Discussion	40

CONTENTS (CONT)

5. THE CONFORMATION OF NINE-MEMBERED RINGS

5.1. Introduction 42

5.2. Method of Study 42

5.3. Results and Discussion 50

5.4. Examples 59

6. CONFORMATIONAL SPACES OF LARGE RINGS

6.1. Introduction 63

6.2. Conformational Description 63

6.3. *Discussion* 69

7. SUMMARY 71

8. CONCLUSIONS 73

APPENDIX

1. Character Tables for the D_{Nh} Point *Groups* 77

2. Trigonometric Identities 79

3. Properties of the Linear Coefficients 81

4. The Program CONFOR

4.1. Program *Listing* 92

4.2. Sample Output File 105

5. Cartesian Coordinates of the Classical Forms 106

REFERENCES 108

LIST OF TABLES

Table	Page
3.1. Puckering analysis of the SC_8 boat form	20
4.1. Classical nomenclature of the primitive forms	26
4.2. The subroutines of CONFOR	34
4.3. Conformational analysis of five–membered rings	36
4.4. Conformational analysis of six–membered rings	38
5.1. Torsion angles of the classical forms of nine–membered rings	45
5.2. Puckering amplitudes of the classical forms of *nine–membered rings*	46
5.3. Endocyclic torsion angles of nitrogen and sulphur donor macrocycles	60
5.4. Puckering analysis of nitrogen and sulphur donor macrocycles	60
5.5. Linear coefficients of intermediate forms	61
6.1. Conformational analysis of twelve–membered rings	65

LIST OF FIGURES

Figure		Page
2.1.	The polar angle θ	6
2.2.	The torus defined by q_2, q_3, ϕ_2 and ϕ_3	6
2.3.	The conformational surface of eight–membered rings	7
2.4.	Two–dimensional projection of the surface	8
2.5.	The C–TC pseudorotational cycle	9
2.6.	*The B–BB / OC–TCC pseudorotational cycles*	10
2.7.	The BC–TBC pseudorotational cycles	11
4.1.	The primitive forms of small rings	27
4.2.	Structure of the program CONFOR	33
5.1.	Classical forms of nine–membered rings	43
5.2.	Geometrical interpretation of puckering parameters	47
5.3.	The complex surface for the mapping of nine–membered rings	48

LIST OF FIGURES (*CONT*)

5.4. A two–dimensional projection of the surface 49

5.5. The TBC–BC pseudorotational cycle 50

5.6. The TBB–BB pseudorotational cycle 51

5.7. The TCC–CC pseudorotational cycle 52

5.8. The TCB–CB pseudorotational cycle 53

5.9. The TB–B pseudorotational cycle 54

5.10. The TC–C pseudorotational cycle 55

5.11. The TCC''–CC'' pseudorotational cycle 56

5.12. The TBC''–BC'' pseudorotational cycle 57

5.13. Primitive forms of nine–membered rings 58

5.14. Nitrogen and sulphur donor macrocycles 59

6.1. The conformation of large macrocycles 66

6.2. Coefficient maps of 18–crown–6 complexes 68

1. INTRODUCTION

The conformation of a ring compound as a planar polygon, with a strain energy one-half the difference between the internal angle and 109.5°, was introduced by Baeyer (1885). The hypothesis that a ring compound could be constructed in a number of different puckered shapes, free of angle strain (Sachse, 1890), was verified by the existence of trans-decalin (Kückel, 1925), a compound predicted to be highly strained by the Baeyer theory.

It is now recognized that the nature and extent of puckering is a balance of two strain effects. In the smaller rings, the bond angles are usually constrained to be smaller than their open-chain values. The angles generally become smaller and the strain increases as the ring puckers. Torsional strain is greatest in the planar form, when all bonds are in eclipsed conformations. This strain is lowered by a puckering of the ring.

The conformation of small rings has since been the subject of several detailed studies (Hendrickson, 1961, 1964, 1967a,b; Flapper and Romers, 1975; Bocian, Pickett, Rounds and Strauss, 1975; Kilpatrick, Pitzer, and Spitzer, 1947). The characterization of the energetically preferred cycloalkanes and the analysis of the various modes of interconversion have been completed.

The concept of ring conformation has been extended to all explanatory levels of chemistry. Chemical reactivity, products of organic syntheses and the interaction of drugs with receptor sites can be rationalized using the concept of molecular shape. An unambiguous, accurate description and identification of ring conformation is therefore required.

Quantitative description of ring puckering is a non-trivial problem in three-dimensions, that requires *3N parameters for the* characterization of an N-membered ring. The set of Cartesian coordinates (x_j, y_j, z_j) for each ring atom j would be such a set, but with limited descriptive power due to the large number of parameters involved. *It was first shown by Kilpatrick,* Pitzer and Spitzer (1947) that the conformation of any puckered form of cyclopentane can be specified in terms of two parameters-- an amplitude and a phase angle. These parameters are derived from the out-of-plane displacements required to generate the puckered form from the planar polygon. Generalization of the concept to the larger rings was formulated by Pickett and others (Pickett and Strauss, 1970,1971; Bocian, Pickett, Rounds *and Strauss,* 1975; Strauss,1971).

Puckered forms of an N-membered ring are generated by the set of N *displacements perpendicular to a regular* polygon. This one-dimensional description is unique for the smaller rings ($N \leq 12$), and 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 not immediate. Early attempts (Adams, Geise, and Bartell, 1970; Geise, Adams, and Bartell, 1969) to define a general set of coordinates for five-membered rings required a number of approximations and were limited to a given degree of pucker.

A general definition of ring puckering coordinates for any type of cyclic *compound was given by Cremer* and Pople (1975a,b). The method defines a unique mean plane for a general monocyclic ring. The geometry of the puckering, relative to this mean plane, is described by a set of N-3

parameters, which are generalisations of the phase and amplitude of *cyclopentane* (Kilpatrick, Pitzer and Spitzer, 1947).

The method has been of practical importance in crystallography since the set of puckering parameters is calculated directly from the atomic coordinates. The conversion of these puckering parameters into a description of conformational type is not trivial. As a practical measure it is useful to map the conformation as a function of puckering parameters onto a surface in relation to the classical forms. Such a scheme requires the analysis of all possible canonical forms of the symmetrical conformations. The surface has been interpreted as a circle for five–membered rings (Altona and Sundaralingam, 1972), a sphere for six–membered rings (Boeyens, 1978) and a torus for seven–membered rings (Boessenkool and Boeyens, 1980). The method has been extended to the eight–membered rings (Evans and Boeyens, 1988), as reviewed in Chapter 2.

The Cremer and Pople (1975a) algorithm to calculate the mean plane and the puckering parameters has not been correlated directly with a physical model. A theoretical interpretation of the puckering coordinates is presented in Chapter 3. The one–to–one correspondence between the puckering parameters and the N–3 symmetry–adapted coordinates of Pickett and Strauss (1971) is demonstrated. The expressions for the ring puckering coordinates as out–of–plane displacement modes are derived from group theoretic representations to illustrate the general applicability of the model.

The calculated puckering parameters of any ring do not necessarily match those of the classical forms exactly. Where the match is close enough, a

symmetrical type is identified, but more often an intermediate form is indicated. In these cases, a quantitative expression for the deviation of an actual form from a symmetrical type has been proposed as the Euclidean distance between the points in (N–3)–dimensic. al space (Evans and Boeyens, 1988). This useful guide has no theoretical basis and is sensitive to the degree of pucker.

A better description of these intermediate forms is given in Chapter 4. The group theoretic model of Pickett and Strauss (1971) gives the set of ring conformations as a linear space. It is suggested that the normal modes of displacement be used as a basis for representing any conformation as a linear combination of a *few* simple puckered shapes in the correct relative proportions.

The assignment of conformational type of the larger rings ($N > 8$) is largely descriptive (Dale, 1973a,b; Boeyens and Dobson, 1987). In Chapters 5 and 6 the methods used in the conformational assignment of the smaller rings are extended to the medium–sized and large rings. The conversion of the puckering parameters of nine–membered rings into a description of the conformational type is achieved by mapping the classical forms onto a complex three–dimensional surface. A geometrical interpretation of the puckering parameters of larger rings in three–dimensional space is too complicated to be of any practical significance. The conformation of these rings is described by the set of coefficients in the linear expansion of basis forms.

2.CONFORMATIONAL MAPPING OF EIGHT–MEMBERED RINGS

2.1 INTRODUCTION

The conversion of puckering parameters into conformational type is achieved by mapping the set of conformations onto a three–dimensional surface. The use of these conformational maps in the field of the puckering parameters is limited by the number of puckering parameters to rings smaller than eight– or nine–membered rings. The analysis of eight–membered rings prompted the investigation of an accurate description of intermediate forms, and a brief review of the topic is thus appropriate.

2.2 METHOD OF STUDY

The Cremer and Pople (1975a) puckering parameters map a set of ten symmetrical conformations unto a three–dimensional surface. These classical forms comprise a set of symmetrical conformations not confined to the low energy cycloalkane forms of Hendrickson (1967a,b). Standard puckering analysis (Cremer and Pople, 1975a) yields three amplitudes (q_2, q_3, q_4) and two phase angles (ϕ_2, ϕ_3). The mapping represents the geometrical interpretation of five parameters in three–dimensional space.

To facilitate the geometric interpretation, the third amplitude is transformed to an angular coordinate, $0 \leq \theta \leq \pi$, such that

$$\cos\theta = \frac{q_4}{\sqrt{\sum_n q_n^2}} = \frac{q_4}{Q}, \text{ where } Q = \sqrt{\sum_n q_n^2}$$

The angular value θ is interpreted as the polar angle of the unit sphere, shown in Figure 2.1.

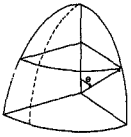


Figure 2.1 The polar angle θ

It is noted that for $q_m = 0$, the phase angle ϕ_m has no meaning. The four parameters q_2, q_3, ϕ_2, and ϕ_3 define a torus, shown in Figure 2.2.

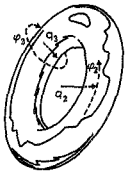


Figure 2.2 The torus defined by q_2, q_3, ϕ_2 and ϕ_3

A surface for the mapping of all possible conformations can be constructed by defining a unit sphere, with polar angle $0 \leq \theta \leq \pi$. At each value of θ, a torus is defined in terms of q_2, q_3, ϕ_2, and ϕ_3. The plane through the associated central track cuts the sphere at θ, as shown in Figure 2.3.

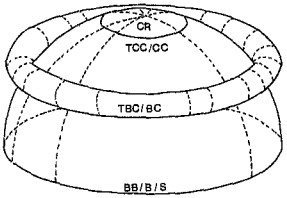


Figure 2.3 The conformational surface of eight-membered rings

A two-dimensional projection of this surface, shown in Figure 2.4, illustrates the various interconversion modes between the symmetrical forms. This representation, a projection of all tori along the surface of the sphere and with their radial axes along the $\phi_3 = 0$ circle, maps the BC–TBC forms uniquely. Overlap occurs at the positions X, Y and Z.

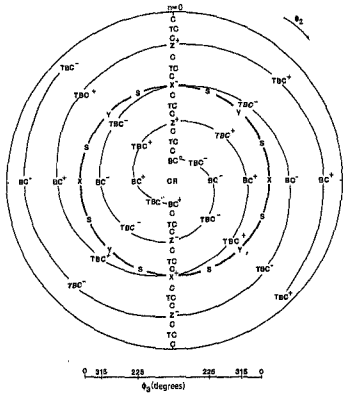


Figure 2.4 Two-dimensional projection of the surface. The + superscript refers to forms with $\theta<90°$ and the − superscript refers to forms with $\theta>90°$. $Y=(TCC^{s}, D)$; $X^{+}=(CC^{s}, BB, BC^{+})$; $X^{-}=(CC^{s}, BB, BC^{-})$; $Z^{+}=(TC, BC^{+})$ and $Z^{-}=(TC, BC^{-})$

2.3 RESULTS

This surface is a combination of the surfaces used in the analysis of six- (Boeyens, 1978) and seven- membered (Boessenkool and Boeyens, 1980) rings. The conformations of eight-membered rings are mapped onto a set of tori which lie at specific polar angles *on a sphere.*

The pseudorotational pathways outlined by Hendrickson (1967b) are examined in two-dimensional projection. *The C–TC cycle is shown in Figure* 2.5. The $\phi_2 - \theta$ polar projection in Figure 2.6 details the B–BB and the CC–TCC pseudorotational cycles. The BC–TBC cycles, shown in Figure 2.7, are polar projections of the tori lying at polar angles of 75° and 105°.

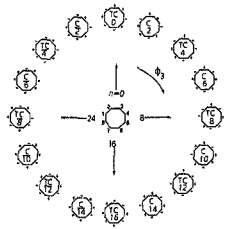


Figure 2.5 The C–TC pseudorotational cycle

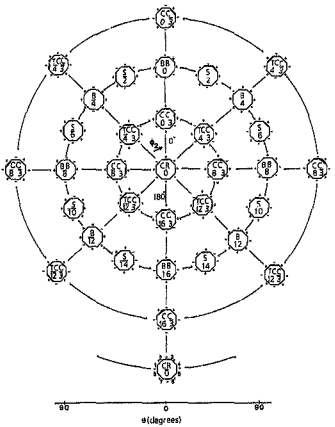


Figure 2.6 The BB–TBB / CC–TCC pseudorotational cycles. The bold side of the TCC symbol indicates a torsion angle of 56.2°. The bold side of the CC symbol indicates a torsion angle of 105°, with the point of the wedge adjacent to a torsion angle of −105°. The bold side of the S symbol indicates a torsion angle of 70°.

These projections indicate the gradual change in bond torsion angle, from maximum positive values, through zero, to negative values. In the BC–TBC cycle, the torsion angles change at regular intervals from positive to negative values. In each *CC–TCC cycle, the atoms remain in the same relative* position with respect to the mean plane. The pseudorotational cycle is described as a type of breathing mode where each torsion angle changes gradually in magnitude, but not in sign

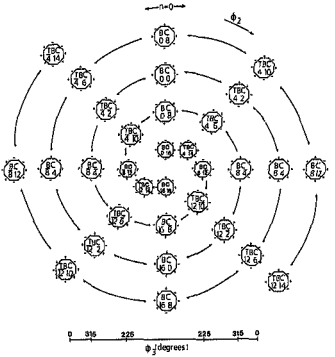


Figure 2.7 The BC–TBC pseudorotational cycles at $\theta = 75^\circ$ and 105°.

A unique nomenclature, based on angular value of each canonical conformation is proposed. Each conformation is unambiguously described by the integers h, k and l that specify the angular positions $\phi_2 = h\pi/16$, $\phi_3 = k\pi/16$ and $\theta = l\pi/16$ respectively. Positive indices are obtained by defining $\bar{h}$, $\bar{k} = 32-h$, k and $\bar{l} = 16-l$. All forms are uniquely distinguished by at most two indices.

An investigation of a number of heterocyclic rings, not represented exactly by classical forms, introduced an expression for the deviation of an actual conformation from a classical form in the neighbourhood. The deviation, ΔX, is defined as

$$\sqrt{\sum_i (x_i - x_i')^2}$$

where x_i represent actual puckering parameters, and x_i' are the puckering parameters of the classical form X.

3. GROUP THEORY OF RING PUCKER

3.1 INTRODUCTION

The group theoretic model (Pickett and Strauss, 1971) describes any puckered form of a cycloalkane ring as an out-of-plane displacement mode of the planar polygon. A conformation is characterized by N-3 symmetry-adapted coordinates. Given the coordinates of a general N-membered ring, the application of the model is not immediate. The characterization of a general monocyclic ring by N-3 puckering parameters (Cremer and Pople, 1975a), defined in terms of atomic displacements relative to a mean plane, is always possible. These puckering parameters have previously not been subjected to physical interpretation. The equivalence of the N-3 symmetry-adapted coordinates and the puckering parameters is now demonstrated. The expressions for ring puckering coordinates as out-of-plane displacement modes are derived directly from the group theoretical analysis.

3.2 MATHEMATICAL DERIVATION

Following Pickett and 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. The 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 irreducible representations are readily found using the character tables, for N even and odd, presented in Appendix I.

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

$$\Gamma\,(\mathrm{N\ odd}) = E_2'' + E_3'' + \ldots + E''_{(N-1)/2}$$

The symbol (g:u) is taken as g for N/2 *odd and as* u *for* N/2 *even*. The symbol (u:g) reads u for N/2 odd and g for N/2 even. The translational (A_{2u}, or A_2'' for N odd) and the rotational (E_{1g}, or E_1'' for N odd) motions, which are of no conformational significance, are excluded.

For each irreducible representation, the out–of–plane coordinates of each ring atom, z_j, are written down 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

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

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

$z(\vartheta) = \rho_m \cos(m\vartheta - \phi_m)$, $m = 2,3, \ldots$,

limited to the out–of–plane displacements of the ring atoms only.

The out–of–plane displacements of a general conformation may be expressed *as a linear combination* of the out–of–plane displacements of the irreducible representations (Herzberg, 1945).

Thus for a general conformation

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

$$z_j = \sum_m \rho_m \cos(2\pi jm/N + \phi_m) \qquad (N \text{ odd})$$

The expression for each z_j is a linear sum over all possible m values. The normal modes are also mutually orthogonal and hence we can consider only one value of m without loss of generality.

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

Consider

$$\sum_j z_j \cos(2\pi jm/N) \quad (1)$$

and

$$\sum_j z_j \sin(2\pi jm/N) \quad (2)$$

Substituting the expression for z_j in these equations gives equation (1) as

$$\sum_j \rho_m \cos(2\pi jm/N + \phi_m) \cos(2\pi jm/N) \text{ or}$$
$$\sum_j \rho_m \cos\phi_m \cos^2(2\pi jm/N) - \sum_j \rho_m \sin\phi_m \cos(2\pi jm/N) \sin(2\pi jm/N)$$

and equation (2) as

$$\sum_j \rho_m \cos(2\pi jm/N + \phi_m) \sin(2\pi jm/N) \text{ or}$$
$$\sum_j \rho_m \cos\phi_m \cos(2\pi jm/N) \sin(2\pi jm/N) - \sum_j \rho_m \sin\phi_m \sin^2(2\pi jm/N)$$

$\sum_j \cos^2(2\pi jm/N)$, $\sum_j \sin^2(2\pi jm/N)$, 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.

Equation (1) therefore reduces to $\frac{N}{2}\rho_m \cos\phi_m$, and equation (2) reduces to $-\frac{N}{2}\rho_m \sin\phi_m$.

Hence

$$(N/2)\,\rho_m \cos\phi_m = \sum_j z_j \cos(2\pi jm/N) \qquad (3)$$

and

$$(N/2)\,\rho_m \sin\phi_m = -\sum_j z_j \sin(2\pi jm/N) \qquad (4)$$

$$\sum_j z_j^2 = \sum_j \rho_m^2 \cos^2(2\pi jm/N + \phi_m) = \frac{N}{2}\rho_m^2$$

The coordinates ρ_m may be normalized so that

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

Using the normalized coordinates, equations (3) and (4) become

$$\rho_m \cos\phi_m = \sqrt{2/N}\sum_j z_j \cos(2\pi jm/N)$$

$$\rho_m \sin\phi_m = -\sqrt{2/N}\sum_j z_j \sin(2\pi jm/N)$$

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:

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

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

These expressions are those given by Cremer and Pople (1975a) 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 $\rho_m = 0; \forall\, m = 2,3,4 \ldots (N/2) - 1$

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

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

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

But $$\sum_j z_j^2 = Q \sum_{j=1}^{N} (-1)^j z_j \qquad (6)$$

Equating expressions (5) and (6),

$$\frac{1}{N} \sum_j (-1)^j z_j = Q$$

Once again the value of Q *must be normalised:*

$$\sum_j z_j^2 = Q^2$$

Replacing Q by the normalized value gives

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

j must be replaced by (j–1) to correspond with the atomic numbering of the previous *expressions:*

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

Q is the same as the parameter $q_{N/2}$ of Cromer and Pople (1975a). Replacing ρ_m and Q with the normalized values yields *the expressions for* the out–of–plane displacements as defined by Cromer and Pople (1975a).

N even:

$$z_j = \sqrt{1/N}\,(-1)^{j-1} Q + \sqrt{2/N} \sum_m^{(N/2-1)} \rho_m \cos\left[2\pi m(j-1)/N + \phi_m\right], \quad m=2, \ldots$$

N odd:

$$z_j = \sqrt{2/N} \sum_m \rho_m \cos\left[2\pi m(j-1)/N + \phi_m\right], \quad m=2, \ldots (N-1)/2$$

3.3 DISCUSSION

Pickett and Strauss (1971) approached the conformational description of a ring on the basis of symmetry–allowed displacements normal to the plane of D_{Nh} polygons. Cremer and Pople (1975a) presented a method to reduce the pucker of actual rings to displacements from an idealized polygon in the mean ring plane -- the inverse operation. The two methods have now been shown to be consistent.

Any puckered shape is generated from the out–of–plane displacements of a regular polygon. The group theoretical analysis is based on infinitesimal *perpendicular displacements*. In conformational analysis this is an approximation since the puckered shape of a chemical ring compound may involve *finite perpendicular displacements* from the mean plane and hence motion of the atoms in the mean plane. The perpendicular displacements involved in generating the form are, however, *much larger* than the in–plane motions. The one–dimensional model is therefore quite adequate in describing the three–dimensional conformation *uniquely*.

The Cremer and Pople (1975a) analysis of a puckered ring *relies on the* definition of a unique mean plane. The equivalence of this method and the group theoretic model requires the planar polygon to be oriented with respect to the puckered mode so that this form may be envisaged as arising from only out–of–plane displacements of the flat ring. The out–of–plane displacements are therefore subjected to the special conditions that restrict overall translation and rotation of the polygon. These conditions, used by Cremer and Pople (1975a) to define the mean plane:

$\sum_j z_j = 0$, $\sum_j z_j \cos [2\pi(j-1)/N] = 0$ and $\sum_j z_j \sin [2\pi(j-1)/N]$, have now been shown 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. The Cremer and Pople (1975a) analysis of a general monocyclic ring, having all bond lengths and angles, is therefore in terms of the perpendicular displacements of a regular polygon. For moderate variations in bond length, as in most chemical structures, the conditions to fix the mean plane do not necessarily give zero angular momentum, but they do ensure that the projection of the ring onto the plane most closely resembles a regular polygon.

The theoretical basis of the Cremer and Pople ring puckering coordinates now provides insight 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, as demonstrated empirically (Boessenkool and Boeyens, 1980; Evans and Boeyens, 1988). The observed alternation of the symmetry elements C_2 and C_s along the pseudorotational pathways is also rationalized.

The *theoretical* derivation of the puckering coordinates has, however, shown the model to be a one–dimensional description of a three–dimensional phenomenon . Extension of group–theoretical arguments to the general N–membered ring must be exercised with caution.

As an example, consider the hypothetical heterocyclic six–membered ring:



with puckering coordinates as given in Table 3.1.

Table 3.1

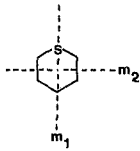
Cartesian and puckering coordinates of the SC_5 boat form

atom	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

$q_2 = 0.87$ Å $\quad q_3 = 0$ Å $\quad \phi_2 = 0°$

Its puckering parameters are the same as those of the *cyclohexane boat form*. The $\phi_2 = 0$ indicates a mirror plane through the sulphur atom, 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.

It has been shown that the total pucker of a ring results from a linear combination of *symmetry–adapted normal* modes. The displacement modes of the D_{Nh} point group therefore provide a natural basis set for conformational analysis, and the details of this scheme will be discussed in the following chapter.

4. THE LINEAR SPACE OF PUCKERED FORMS

4.1 INTRODUCTION

The group theoretical analysis of the normal modes of displacement of an *N–membered polygon provides the basis of a quantitative formulation of ring* pucker. The set of puckered forms of a ring constitute a linear space with the normal modes of displacement as a finite–dimensional basis.

The description of conformation in terms of the symmetry–adapted displacement coordinates is 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 the small rings (Boeyens, 1978; Boessenkool and Boeyens, 1980; Evans and Boeyens, 1988). The transformation from crystallographic coordinates to conformational type is achieved by mapping the general ring onto the appropriate surface as a function of the puckering parameters. Conformational type is then assigned on account of the proximity to a symmetrical form located on the surface. The assignment of conformational type of a form lying intermediate between two or more classical forms is expected to be largely descriptive. The conformation could be described as a linear combination of the symmetrical classical forms, with the share of the contributing forms estimated by their distance on the surface from the site of the cyclic fragment of interest. A quantitative expression for the deviation of an actual conformation from the symmetrical types in the neighbourhood has been proposed (Evans and Boeyens, 1988), but it is sensitive to the amplitude of pucker and has no

theoretical basis.

A description of the intermediate forms is now established from the group theoretical derivation of ring pucker. It is suggested that the normal modes of displacement, at different values of the Cremer and Pople (1975a) phase angle, and not the symmetrical classical forms, be used as a basis for representing any conformation as a linear combination of these basic forms.

4.2 DESCRIPTION OF RING PUCKER

The out-of-plane displacements of a general N-membered ring may be generated as a linear combination of the normal mode displacements (Pickett and Strauss, 1971; Section 3.2), represented by

$$\Gamma\,(\text{even}) = B_{2(u,g)} + \sum_m E_{m(g,u)}$$
$$\Gamma\,(\text{odd}) = \sum_m E^n_m$$

The $B_{2(u,g)}$ mode represents displacements

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

Each mode of this representation is a multiple of the form

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

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

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

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

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

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 and Pople (1975a) analysis, as shown in Chapter 3.

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

N even

$$z_j = \sqrt{1/N}\,(-1)^{j-1}\, q + \sqrt{2/N} \sum_m \rho_m \cos [\phi_m + (2\pi m/N)(j-1)]$$

N odd

$$z_j = \sqrt{2/N} \sum_m \rho_m \cos [\phi_m + (2\pi m/N)(j-1)]$$

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:

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

It has already been recognized, for six– and seven–membered rings, that the coefficients $\sqrt{2/N}\ \rho_m \cos\phi_m$, $\sqrt{2/N}\ \rho_m \sin\phi_m$ and $\sqrt{1/N}\ q$ carry the planar ring into the normal modes where

$$z_j \approx \begin{matrix}\cos \\ \sin\end{matrix}[(2\pi m/N)(j-1)],\ (-1)^{j-1} \text{ respectively,}$$

(Bodan, Pickett, Rounds and Strauss, 1975; Pickett and Strauss, 1970; Strauss, 1971). The Cremer and Pople (1975a) 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_2 representation for N even). These fundamental primitive forms and their relative out–of–plane atomic displacements for five– to eight–membered rings are described in Figure 4.1 and in Table 4.1.

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

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

is also a normal mode of the E_m representation (Herzberg, 1945). The equivalent forms at phase angles ϕ_m, have

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

Table 4.1

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 [a]
	E_3'' (sin–form)	twist–chair [a]
8	B_{2u}	crown
	E_{2u} (cos–form) / E_{2u} (sin–form)	boat–boat
	E_{3g} (cos–form) / E_{3g} (sin–form)	twist–chair

a – see Section 4.4

Consider the forms $^{1,4}B$, $^{6}T_2$ and $B_{2,5}$, in the nomenclature of the six-membered rings proposed by Bosyens (1976), with x_j given by :

$^{1,4}B$: cos [4π/6 (j–1)]

$^{6}T_2$: sin [4π/6 (j–1)]

$B_{2,5}$: cos 60° * $^{1,4}B$ – sin 60° * $^{6}T_2$

$^{1,4}B$ is equivalent to $B_{2,5}$, although they differ in phase angle, by 60°. The equivalent forms are themselves normal modes of the E_m representation and should form part of an 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.

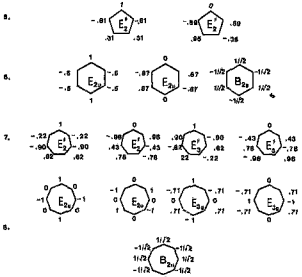


Figure 4.1 *The primitive forms of small rings*

4.3 MATHEMATICAL FORMULATION

The set of normal modes, whose z_j are given by

$\sqrt{1/2}\ (-1)^{j-1}$, cos $[(2\pi m/N)(j-1)]$, sin $[(2\pi m/N)(j-1)]$ are linearly independent, as shown in Appendix 3. These modes can therefore form a suitable basis for conformational type.

Group theoretical analysis shows that the forms equivalent to the cos–form and sin–form of each m have a constant difference in phase angle. Given any arbitrary ring, its ϕ_m value will lie between those of a "cos–type" form and a "sin–type" form.

The forms equivalent to the cos–form and the sin–form can be expressed as linear combinations of these forms using the Cremer–Pople (1975a) equations. Any arbitrary ring can also be expressed as a linear combination of the cos– and sin–forms using this equation.

The arbitrary ring lying at Q (N even), q_m, and ϕ_m, where m = 2, 3, ... N/2–1 (N even), or (N–1)/2 (N odd), is given by

$$z_j = \sqrt{2/N}\,[\,Q\,\sqrt{1/2}\,(-1)^{j-1} + \sum_m q_m \cos\phi_m \cos[(2\pi m/N)(j-1)] - \sum_m q_m \sin\phi_m \sin[(2\pi m/N)(j-1)]$$

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

The cos–type form is given by

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

The sin–type form is given by

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

These normal modes are linearly independent (Appendix 3.), and any arbitrary conformation may be expressed as a linear combination of the forms at a_m and b_m, over all values of 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

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

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

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

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

When N is even, there is a coefficient for the normal mode of the $B_{2(g:u)}$ representation. The displacements of the normal mode, z_j, are taken as $\sqrt{1/2}\,(-1)^{j-1}$, so that the linear coefficient corresponds with the normalised puckering amplitude Q. It is noted that, as above, the factor of $\sqrt{2/N}$ has been omitted since the coefficients are normalised in the final analysis. When the sign of Q is negative, the normal mode used in the linear combination is the mirror image of the form $z_j = \sqrt{1/2}\,(-1)^{j-1}$ i.e. $z_j = \sqrt{1/2}\,(-1)^j$. This ensures that the coefficient is equal in magnitude to Q, but greater than zero.

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

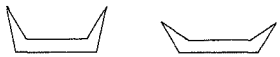
The cos–type and sin–type forms are always linearly independent, but they are only orthogonal when separated by 90 degrees in phase angle. The set of all possible ring conformations can be generated by a finite–dimensional basis. In all cases, (N–3) normal modes can be used as generating conformations. 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 comprise a reference set of ring conformations, called the primitive forms.

The coefficients in the linear expansion are independent of phase. The linear coefficients are thus always the same, irrespective of the ring numbering used, as illustrated in Appendix 3.

A description of ring conformation is really a description of molecular shape, and should therefore be independent of the degree 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, the rings shown below are both boat conformations that differ in puckering amplitude.



4.4 APPLICATION OF THE METHOD

The primitive forms in the linear expansion 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 the smaller rings. The symmetrical forms, or classical conformations in conventional use, take on certain characteristic values of the linear coefficients.

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

The primitive forms are often the traditional classical forms. For example, for six–membered rings, the cos–form is a boat and the sin–form is a twist conformation. The conformation of five– and six–membered rings 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 rings, different forms may assume the same coefficients. Since the phase angles of the primitive forms may differ, a unique description is given by

$$\chi = a(1) + \sum_m b_m (\phi_m) + c_m (\phi_m')$$

where the b_m and c_m are linear coefficients,

ϕ_m and ϕ_m', the phase angles of the primitive cos–form and sin–form respectively, are characterized by the integer k of $k\pi/2N$. a(1) occurs only for N even: (1) denotes the usual $B_{2(g:u)}$ 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 of the primitive forms will differ.

4.5 THE PROGRAM CONFOR

A FORTRAN 77 program, CONFOR, has been written to complete the description of the conformation of intermediate forms and to identify a ring as a classical form. It is included as a subroutine of PUCKER, a program that calculates the Cremer–Pople puckering parameters from atomic coordinates. The general structure of the program CONFOR is shown in Figure 4.2. CONFOR consists of a number of subroutines whose functions are given in Table 4.2.

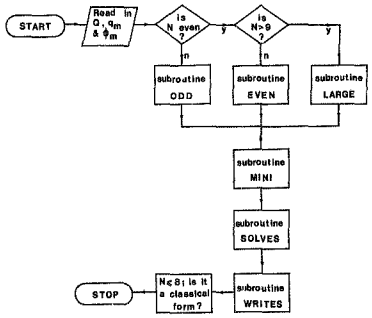


Figure 4.2 Structure of the program CONFOR

Table 4.2

The program CONFOR.

SUBROUTINE	FUNCTION
Large, Odd, Even	generates the phases of the primitive forms and determines if a ring is a classical form
Mini	finds the primitive forms closest in phase angle to the ring of interest
Solves	solves for the coefficients in the linear expansion
Writes	normalizes the coefficients to unity and writes these and the phase information to file

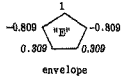
The phase angles of the primitive forms to be used as the basis are calculated. The linear coefficients are solved by the methods detailed in Section 4.3 and normalized to unity. The linear coefficients of the conventional classical forms of five-, six-, seven- and eight-membered rings have been determined, and are used to automate the identification of any ring as one of these forms.

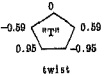
As noted the linear coefficients need not be unique. Results show that sets of similar coefficients with different phase angles are not likely for the classical *forms. The only such cases* are the forms of the S/TS and H/T pseudorotational cycles for seven–membered rings (Boessenkool and Boeyens, 1980). The program CONFOR calculates the sum of the moduli of the *difference in linear coefficients of any ring* and a symmetrical form. Below a certain threshold, the ring is identified as similar to one of the classical forms. For even smaller differences, the ring is taken as one of the classical forms, except in the case where there is more than one *m for which* $\rho_m \neq 0$ [BS, S, TS, T, H (seven–membered rings), Boessenkool and Boeyens, 1980; BC, TBC (eight–membered rings), Evans and Boeyens, 1988]. The phase angles are then checked against the phases of the classical forms, as *determined from the* two–dimensional projection of the relevant conformational surface. A listing of the program CONFOR and a sample output file is given in Appendix 4.1 and 4.2.

4.6 EXAMPLES

Five–membered rings

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





These are equivalent to the envelope and twist forms (Altona and Sundaralingam, 1972). A number of rings reported in the literature have been analyzed and the results given in Table 4.3.

Table 4.3

Conformational analysis of five-membered rings

Ring	Ref.	Q_2(Å)	ϕ_2(°)	a * ϕ(E) + b * ϕ(T)
1	c	.49	342.9	5(20) + 95(19)
2	c	.48	348.7	37(20) + 63(19)
3	d	.45	356.3	79(20) + 21(19)
4	e	.42	217.0	95(12) + 5(13)
5	f	.35	265.1	27(14) + 73(15)

a,b are given as percentages. ϕ is expressed as a multiple of $\pi/10$

c. Bosyens, Bull, Tuinman and van Rooyen (1973)

d. Ceccarelli, Ruble and Jeffrey (1980)

e. Gal, Feher, Tihanyi, Horvath , Jerkovich, Argay and Kalman (1980)

f. Cremer and Pople (1975a)

The 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.

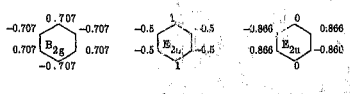
A description like this is more familiar to chemists than the puckering parameters or a linear combination of "Z" and "T" as :

ring 2 = 0.47 "Z" − 0.09 "T"

The method is also suitable for a description of heterocyclic rings. Ring 5, a *furanoid ring, is readily identified as a twist conformation with some* distortion to an envelope form.

Six–membered rings

The basis is three–dimensional, consisting of sixty-boat forms of



crown boat twist

A number of rings reported in the literature have been analyzed and the results given in Table 4.4.

Table 4.4

Conformational analysis of six–membered rings

Ring	Ref.	Q_2 (Å)	Q_3 (Å)	ϕ_2 (°)	a(±1)	b ϕ(B)	c ϕ(T)
1	d	0.05	0.55	183.7	92(+1)	7(12)	1(14)
2	e	0.29	0.24	47.0	45(+1)	31(4)	24(2)
3	f	0.41	–.22	196.0	34(–1)	31(12)	35(14)

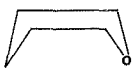
a, b, and c are given as percentages. ϕ is a multiple of $\pi/12$

d. Cremer and Pople (1975a)

e. Gal, Feher, Tihanyi, Horvat, ...rkovich, Argay and Kalman (1980)

f. *Boeyens (1978)*

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



is estimated to a 10 percent contribution *from the primitive boat at* $\phi_2 = \pi$, a conclusion easily reached from an examination of the linear coefficients.

Ring (2), a cyclohexene with a much smaller amplitude of pucker, is readily described in terms of the linear coefficients. Ring (3) has been described as midway between the forms H, E and S. The conformation found here is intermediate between a boat, a 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. These forms are not linearly independent, and an unambiguous definition of the number of mixed forms to include *in the linear expansion is not possible.*

Seven– and eight–membered rings can be expanded in terms of a four– or five–dimensional basis. For example, the ring described by

q_2 , ϕ_2 = 1.05 Å , 0.4°

q_3 , ϕ_3 = 0.58 Å , 0.9°

q_4 = –0.32 Å

as

$\chi = 0.163(-1) + 0.335(0) + 0(6) + 0.291(0) + 0(4)$,

a boat–chair form, is in agreement with previous conformational assignments (Evans and Boeyens, 1988).

4.7 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 mutually orthogonal cos– and sin–forms of each E_m representation, and one of the two possible equivalent modes of $B_{2(g:u)}$ can be combined in varying relative proportions to give any puckered shape, from a few simple forms.

It is noted from Figure 4.1 that the cos–type and sin–type forms for m = 2,3 in eight–membered rings are equivalent. The sin–form is a primitive phase of the cos–form. In a case like this, the linear expansion is not unique for all phases. The coefficients of the cos–form and sin–form are interchangeable, as shown in Appendix 3.

In general, if two rings are compared to see whether they are of the same conformational type it is advisable to ensure, by relative rotation if necessary, that the phases of lowest index (m=2) have matching values. The equivalence of the ring conformations 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)–dimensional subspace has been interpreted (Petit, Dillen and Geise, 1983) to imply that conformational analysis requires *a priori* definition of standard conformations *for each class of chemical compound.*

This seems to invalidate the procedure of mapping conformations to normalized surfaces without taking the amplitude of pucker into account. However, as noted by Cromer (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. This does not lead to an ambiguous description for any given ring, since a specific projected shape can be obtained at only one value of the total puckering amplitude if the bond lengths and angles remain fixed.

The method proposed here is independent of absolute molecular geometry or chemical identity. The conformation depends only on the relative contributions from the group theoretic modes of displacement. Any puckered six-membered ring with 100 percent contribution from the E_{2g} mode has, by definition, 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 the E_{2u} and the B_{2g} representations. The amount of pucker cannot affect this ratio. Even heterocyclic rings, with irregular molecular geometry, can assume a chair shape, at $\phi_2 = \theta = 0$. The fact that the ring does not display D_{3d} symmetry in three dimensions is not important. The shape factor of interest, the ring puckering, is one-dimensional and consists of a contribution from the B_{2g} mode only.

5. THE CONFORMATION OF NINE–MEMBERED RINGS

5.1 INTRODUCTION

The various modes of interconversion of nine–membered rings have been suggested and a few of the low energy cycloalkane conformations structurally characterized (Hendrickson, 1964; 1967b). The symmetrical forms along these pathways are now identified and mapped as a function of puckering parameters onto a three–dimensional surface, in a general scheme to convert atomic coordinates into conformational type. The conformation of nine–membered rings as a linear expansion of six basis forms is presented as an alternative description of ring pucker based on the linear coefficients.

5.2 METHOD OF STUDY

The set of symmetrical conformations of nine–membered rings need not be limited to the low energy cycloalkane conformations. Steric factors and crystal packing forces can force a ring to adopt a conformation other than those of the isolated entity. Sixteen conformations, some based on molecular models, have been identified. These include the six conformations detailed by Hendrickson (1964). These forms are not representative of a particular chemical system, but their bond lengths and angles are within the limits of chemical viability, and exclude arrangements with interpenetrating non–bonded atoms. Pairs of forms, with C_2 and C_s symmetry, having the same ratio of the puckering amplitudes, formally constitute pseudorotational pathways (Boessenkool and Boeyens, 1980; Evans and Boeyens, 1988). It is noted that in the cycloalkanes, where the C_s forms are of high energy, these

pathways are not low energy interconversion modes and hence are not pseudorotational cycles in the sense described by Dale (1973b). The classical nomenclature of the C_s forms is derived from the shapes of the forms in projection. Their pseudorotational partners are described as twist forms. Torsion angles of the classical forms are given in Table 5.1 and the forms are illustrated in Figure 5.1. Cartesian coordinates are given in Appendix 5.

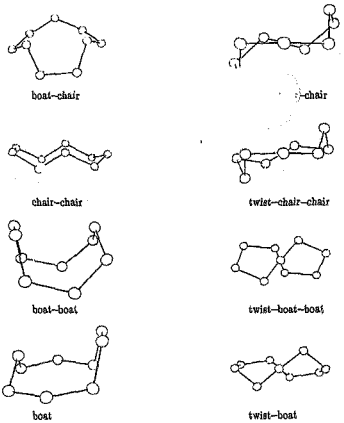
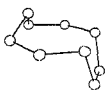
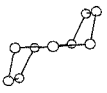


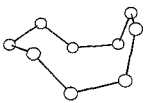
Figure 5.1 Classical forms of nine–membered rings



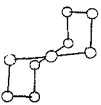
chair



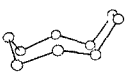
twist–chair



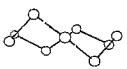
chair–boat



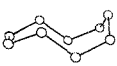
twist–chair–boat



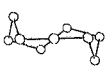
chair–chair "



twist–chair–chair "



boat–chair "



twist–boat–chair "

Figure 5.1 (cont.) Classical forms of nine–membered rings

Table 5.1

Torsion angles (in degrees) of the classical forms. The symmetry element (C_2 or C_s) passes through the first atom.

nomen-clature	symm-etry	ω_1	ω_2	ω_3	ω_4	ω_5
BC	C_{3v}	−114	0	114	−114	0
TBC	D_3	−57	130	−57	−57	130
CC	C_s	−69	108	−139	83	0
TCC	C_2	−54	126	−115	80	−77
C	C_s	121	−30	−80	117	0
TC	C_2	−70	100	0	−88	125
B	C_s	−121	39	−80	117	0
TB	C_2	−70	108	−43	72	−143
BB	C_s	67	46	−10	−83	0
TBB	C_2	80	−70	−10	−34	155
CB	C_s	80	−108	0	90	0
TCB	C_2	−72	79	44	−105	93
BC"	C_s	65	51	−140	82	0
TBC"	C_2	−43	124	−88	−28	117
CC"	C_s	−98	72	−134	117	0
TCC"	C_2	−62	120	−84	91	−124

There are six Cremer and Pople (1975a) puckering parameters for a nine–membered ring – three amplitude and phase angle pairs, (q_m, ϕ_m); m=2, 3, 4. The puckering amplitudes of the classical forms are given in Table 5.2. As noted for eight–membered rings (Evans and Boeyens, 1988), when $q_m=0$, ϕ_m has no meaning.

Table 5.2

Puckering amplitudes (in Å) of the classical forms

RING	q_2	q_3	q_4
BC	0.00	1.25	0.00
TBC	0.00	1.24	0.00
CC	0.00	0.53	0.87
TCC	0.00	0.53	0.87
C	0.54	1.19	0.22
TC	0.68	1.04	0.30
B	1.35	0.39	0.58
TB	1.25	0.36	0.53
BB	2.15	0.00	0.00
TBB	2.05	0.00	0.00
CB	1.64	0.67	0.43
TCB	1.29	0.82	0.45
BC"	0.61	1.09	0.25
TBC"	0.64	1.14	0.24
CC"	0.85	0.40	0.87
TCC"	0.90	0.43	0.93

The geometrical interpretation of the six parameters is shown in Figure 5.2.

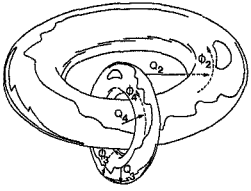


Figure 5.2 Geometrical interpretation of the puckering parameters

This definition may be interpreted as mapping the forms onto

- a series of tori lying at positions determined by q_2 and ϕ_2 on a major torus.
- a tube, helically coiled about a torus defined by $_{2}$, ϕ_2, q_4 and ϕ_4. q_3 and ϕ_3 define a point on this tube.

The former interpretation is the logical extension of the eight-membered rings mapped onto a series of tori located on a sphere, whereas the latter interpretation has the advantage of mapping the forms onto a continuous tube, shown in Figure 5.3.

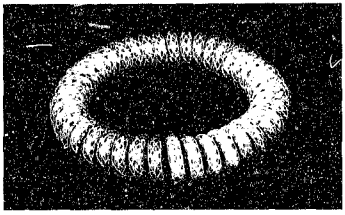


Figure 5.3 The complex surface for the mapping of nine–membered rings

A two–dimensional projection of either surface is achieved by projecting all forms onto $\phi_2 = 0$. The forms then map onto a torus given by q_3, q_4, ϕ_3 and ϕ_4. A polar projection of this composite torus at $\phi_2 = 0$, with the radial axis along the $\phi_3 = 0$ circle, is shown in Figure 5.4. Pseudorotational cycles appear as spirals. In three dimensions these may be visualized as helices on a minor torus stretched around the major torus, or as a helix wound around a tube, coiled in space. Overlap of the forms occurs at all positions S, S', T and T'. The BB–TBB cycle is illustrated as the circle J–K, where ϕ_4 is replaced by ϕ_2, to avoid projection of all forms to a point. The subscripts indicate the atom through which the symmetry element passes.

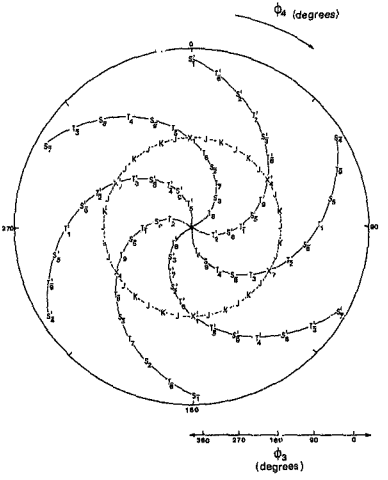


Figure 5.4 A two-dimensional projection of the surface. S=(CC, CC", BC", B), S'=(CB, C), T=(TCC, TCC", TBC", TB), T'=(TCB, TC), K=BB, J=TBB.

5.3 RESULTS AND DISCUSSION

The *TBC–BC* and *TBB–BB* pseudorotational cycles map onto mutually perpendicular circles, and are shown in Figures 5.5 and 5.6.

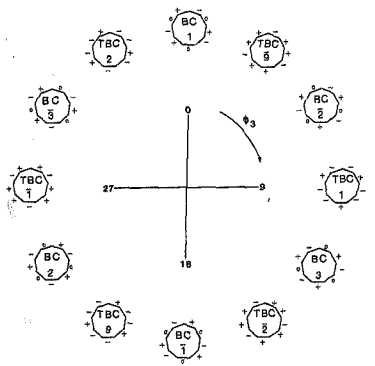


Figure 5.5 The TBC–BC pseudorotational cycle

The CC and TCC forms map onto a torus given by q_3, q_4, ϕ_3 and ϕ_4. A polar projection of this surface is shown in Figure 5.7.

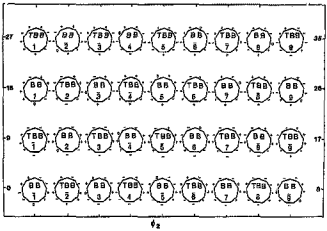


Figure 5.6 The TBB–BB pseudorotational cycle. The circle is represented linearly for clarity.

All other pseudorotational cycles map onto the complex surface and are best viewed as two-dimensional projections in Figures 5.8–5.12. The least confusing projection is onto the surface given by $\tilde{q}_4 = 0$. A projection of the resulting torus, defined by q_2, q_3, ϕ_2 and ϕ_3, is taken at fixed amplitudes with the phases along the Cartesian axes. The angular values are denoted by the integer k of $k\pi/18$.

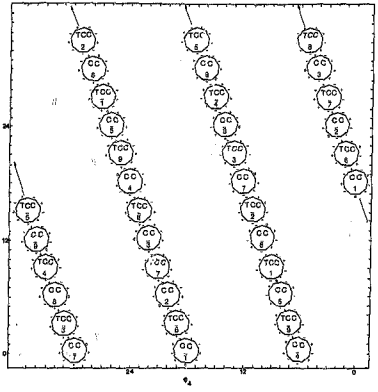


Figure 5.7 The TCC–CC pseudorotational cycle

In all these illustrations, the atomic numbering starts at the top of each polygon and proceeds clockwise. The signs of the endocyclic torsion angles are indicated. In Figures 5.8–5.12, the form with $\phi_4 = 0$ *is indicated. The* value of ϕ_4 increases in steps of $\pi/16$ along each *pseudorotational cycle.*

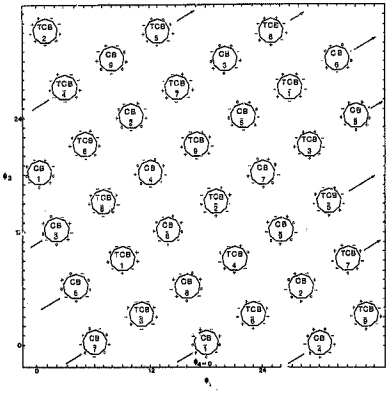


Figure 5.2 The TCB--CB pseudorotational cycle

The angular positions of all symmetrical forms can be expressed as integral multiples of $\pi/18$. Enantiomeric forms lie at angular positions

$$\phi'_m = \phi_m + \pi$$

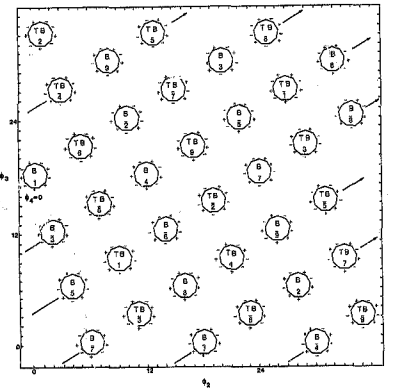


Figure 5.2 The TE–B pseudorotational cycle

Each classical form X is represented as Xn, where n is the number of the atom through which the symmetry element (C_2 or C_s) passes. The mirror image is denoted $\overline{Xn}$, as for seven–membered rings (Boessenkool and Boeyens, 1980).

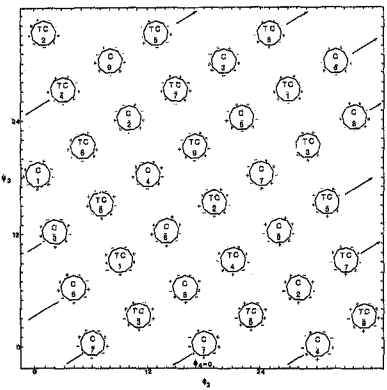


Figure 5.10 The TC–C pseudorotational cycle

The endocyclic torsion–angle change along all pseudorotational pathways takes place gradually, decreasing in positive value to negative values, often through zero.

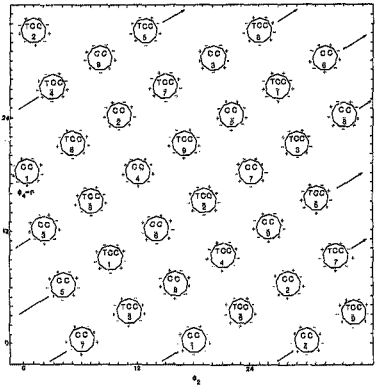


Figure 5.11 The TCC"–CC" pseudorotational cycle

There is a progression of the symmetry element through an atom to a symmetry element through an adjacent bond in all the pseudorotational cycles except in the BB–TBB cycle, where a symmetry element through an atom progresses to a symmetry element through an adjacent atom, as observed in the B–TB cycle of seven–membered rings (Boessenkool and Boeyens, 1980).

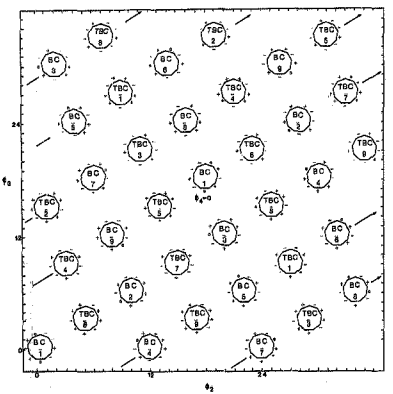


Figure 5.12 The TBC"–BC" pseudorotational cycle

A quantitative description of an intermediate form in terms of the conformational surface is clearly not possible. In this case, a mixed form is expressed as a linear combination of primitive forms, as detailed in the previous chapter. A nine-membered ring is a linear combination of six *primitive forms*, illustrated in *Figure 5.13*.

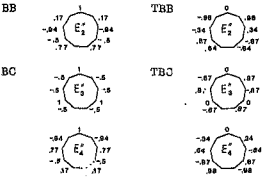


Figure 5.13 Primitive forms of nine–membered rings

The E_4'' representations do not correspond with any classical forms. These primitive forms require bond lengths significantly different from those in common chemical rings. The remaining twelve classical forms are linear combinations of the six basis forms in specific relative proportions. An identification procedure to establish these forms, based on the values of their linear coefficients and phase angles, has been included in ODD, a subroutine of the program CONF (Appendix 4.1). The procedure is entirely analogous to the methods used for the smaller rings (Section 4.5).

The relative contributions from each E_m'' representation, and hence the shape of the puckered ring, depend only on the ratios of the q_m values. The conformations of the nine–membered rings can therefore be mapped onto a normalized surface, independent of ring type and extent of puckering, to avoid a definition of classical forms for each chemical class of rings (Evans, Boeyens and Geise, 1983).

5.4 EXAMPLES

Conformational analyses, reviewed by Boeyens and Dobson (1987), show that most nitrogen and sulphur donor macrocycles adopt either a [333] or a [234] conformation in terms of the Dale (1973a,b) formalism. The results of a puckering analysis of a number of nine-membered macrocycles, characterized in Figure 5.14 and Table 5.3, are given in Table 5.4.



(a)
(Setzer, Ogle, Wilson,and Glass, 1983)



(b)
(Glass, Wilson, and Setzer, 1980)



(c)
(Zompa, and Margulis 1978)



(d)
(Hart, Boeyens ,Michael and Hancock, 1983)



(e)
(Boeyens, Dobson and Hancock, 1985)



(f)
(Dobson, 1986)

Figure 5.14 Nitrogen and sulphur donor macrocycles

Table 5.3

Endocyclic torsion angles (in degrees) of nitrogen and sulphur donor macrocycles

	(a)	(b)	(c)	(d)	(e)	(f)
ω_1	59	−131	134	−55	−116	−117
ω_2	54	58	−45	−49	50	50
ω_3	−131	55	−71	144	75	75
ω_4	59	−131	134	−74	−85	−94
ω_5	56	59	−44	−43	−44	−31
ω_6	−132	55	−70	136	150	141
ω_7	57	−131	133	−72	−67	−75
ω_8	56	59	−46	−51	−38	−36
ω_9	−132	55	−71	120	98	98

Table 5.4

Puckering analysis of nitrogen and sulphur donor macrocycles

RING	q_2 (Å)	ϕ_2 (°)	q_3 (Å)	ϕ_3 (°)	q_4 (Å)	ϕ_4 (°)
a	0.01	11	1.60	157	0.01	180
b	0.00	18	1.59	23	0.00	46
c	0.02	275	1.25	206	0.01	258
d	0.09	337	1.36	335	0.11	352
e	0.60	148	1.20	354	0.38	20
f	0.51	156	1.20	356	0.36	16

On the basis of Figure 5.5, the structures (a)–(d) are described as twist–boat–chair forms with some distortion to the boat–chair forms. Structures (e) and (f) cannot be correlated with any classical forms on the basis of the q_m and ϕ_m values. These intermediate forms are best described as a linear combination, as shown in Table 5.5. The linear coefficients also quantify the distortion of the rings (a)–(d) from the TBC form.

Table 5.5

The linear coefficients of intermediate forms. The phase angles of the basis forms, denoted as k of $k\pi/18$, are given in parenthesis.

RING	PRIMITIVE FORM					
	E_2''		E_3''		E_4''	
	cos–form	*sin*–form	*cos*–form	*sin*–form	*cos*–form	*sin*–form
a	.00	.00	.25(18)	.75(15)	.00	.00
b	.00	.00	.22(0)	.78(3)	.00	.00
c	.00	.00	.13(18)	.86(21)	.00	.00
d	.04(34)	.02(33)	.15(36)	.73(33)	.01(36)	.05(35)
e	.05(14)	.23(15)	.44(36)	.11(33)	.17(2)	.00
f	.14(16)	.11(15)	.51(36)	.07(33)	.10(2)	.07(1)

The results show that the conformations of rings (a)–(d) are similar, and this form can be correlated with the [333] conformation of the Dale (1973a) formalism. The 9–ane–N_3 macrocycle (ring c) shows a smaller distortion to the BC form. The 9–ane–N_2S of the Ni^{II} complex shows a slight distortion from a form on the BC–TBC cycle. The similar conformations of (e) and (f) can be correlated with the [234] conformation of the Dale (1973a) formalism.

These results corroborate previous observations (Boeyens and Dobson, 1987; Dobson, 1986) :

9–ane–N_3, 9–ane–S_3 and 9–ane–N_2S when complexed with Ni^{II} adopt a similar conformation along the BC–TBC pseudorotational cycle. When 9–ane–N_2S is complexed with Cu^{II}, a different intermediate conformation is energetically preferred.

6. CONFORMATIONAL SPACES OF LARGE RINGS

6.1 INTRODUCTION

Methods to assign the conformation of the large macrocyclic compounds are largely descriptive (Dale, 1973a,b). The characterization of a ring conformation by the set of endocyclic torsion angles is not readily interpreted (Goldberg, 1980). Conformation is, however, an important concept in macrocyclic chemistry (Boeyens and Dobson, 1987). A projection of the conformational space of large rings onto a three-dimensional surface using the puckering parameters would require an extensive set of symmetrical forms and a geometrical interpretation of at least seven parameters. The conformation of a large ring is now described as a linear combination of N–3 basis forms. The linear coefficients of eighteen-membered rings are interpreted graphically. A nomenclature based on the linear coefficients is proposed. This semi-quantitative method is compared with the Dale (1973a,b) nomenclature.

6.2 CONFORMATIONAL DESCRIPTION

The description of all rings having less than eighteen ring atoms, as a linear combination of basis forms, is possible from an analysis of the primitive forms. The phase angles of all the canonical forms of these primitive forms have been derived group theoretically, from the symmetry of the forms. All the canonical conformations are included in the program CONFOR, in the subroutines ODD and LARGE (Appendix 4.1).

A complete one-dimensional description of ring pucker is obtained from the set of N-3 coefficients of the primitive forms and the phase information. For an eighteen-membered ring this may require a set of fifteen linear coefficient and phase angle pairs. A simplification of this quantitative scheme is necessary, albeit at the expense of information.

A conformation may be specified by the linear coefficients only. The linear coefficients of any given series of ring structures can then be subjected to statistical procedures including, say, a cluster analysis. The problems associated with ignoring the phase information (Section 4.4) can be minimised by a comparison of the phases in the final stages of analysis.

The method of a linear expansion is greatly simplified in the special case of a symmetrical ring, where many of the coefficients reduce to zero. In the smaller rings, the coefficients are reported as pairs of the coefficients of the E_m representation, in order of increasing m (Section 4.4). In the large rings, where there are a number of basis forms, the coefficients of zero are omitted. An unambiguous nomenclature is established by denoting the crown form by the letter A (N even only). The cos- and sin-forms of the E_2 representation are denoted by B and B' respectively. All other pairs of the E_m representation are similarly denoted by letters, in alphabetic progression as m increases. The coefficients, which are multiplied by ten and estimated to the nearest integer, are given as subscripts.

A pair of symmetrical twelve-membered rings (Boeyens and Dobson, 1967), detailed in Table 6.1, illustrate these general principles.

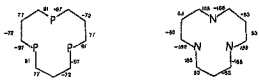


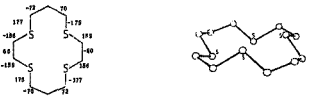
Table 6.1

Conformational analysis of twelve–membered macrocycles

	12–ane–P_3	12–ane–N_3
$q_2(Å)$; $\phi_2(°)$	*0.00* ; 332	0.00 ; 324
$q_3(Å)$; $\phi_3(°)$	2.26 ; 2	0.14 ; 0
$q_4(Å)$; $\phi_4(°)$	0.00 ; 230	0.00 ; 162
$q_5(Å)$; $\phi_5(°)$	0.00 ; 353	0.00 ; 181
$q_6(Å)$	0.11	–0.84
Nomenclature Dale(1973a,b)	A_1C_2	A_2C_1
Nomenclature	$[444]_3$	$[444]_3$

The Dale (1973a,b) nomenclature in both cases is $[444]_3$, despite a difference in the magnitude of the torsion angles. The differences in the out–of–plane *puckering* of the two rings is clearly illustrated by the nomenclature proposed here. The nomenclature in terms of the crown form and the E_2 representation has the advantage of *indicating a three–fold* axis, as predicted by group theory (Pickett and Strauss, 1971).

The general utility of the model is illustrated in Figure 6.1.



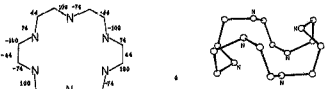
fourteen–membered (Davis, White and Belford, 1975)

$$\chi = A_6C_3C_1' \ (S_2)$$



sixteen–membered (Smith, Ekstrand and Raymond, 1978)

$$\chi = B_8F_2 \ (C_2)$$

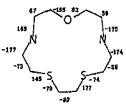


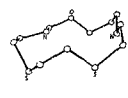
eighteen–membered (Yoshikawa, Toriumi, Ito, and Yamatera, 1982)

$$\chi = A_1C_4C_5' \ (S_6)$$

Figure 6.1 The conformation of large macrocycles. The symmetry element is indicated in parenthesis.

The various symmetry elements ensure that a number of the coefficients are zero. The method is appropriate for large even-membered macrocycles, where at least one element of symmetry is generally observed (Boeyens and Dobson, 1987). This is not so for large odd-membered rings, where the lack of symmetry gives a large number of non-trivial coefficients. For example, 15-ane-N_2OS_2 (Louis, Pélissard and Weiss, 1976),





is described as $B_2^1C_1D_1E_3E_1^1F_2$

A large number of non-zero coefficients may be subjected to graphical interpretation. This method is used in the study of the complexes of 18-crown-6 with alkali metal cations. The conformations of these complexes have been used to model the transport mechanism for metal ions across biological membranes, exhibited by antibiotics like nonactin and valinomycin (Dobler and Phizackerley, 1974; Dunitz, Dobler, Seiler, and Phizackerley, 1974; Dunitz and Seiler, 1974; Seiler, Dobler and Dunitz, 1974). The percentage contribution of each primitive form is plotted as a bar graph in Figure 6.2.

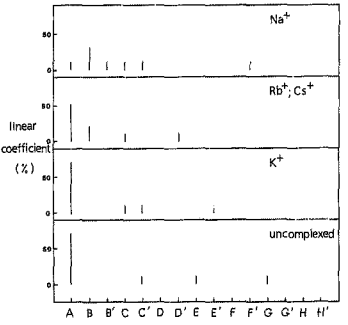


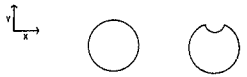
Figure 6.2 Coefficient maps of 18–crown–6 complexes

The coefficient maps of the uncomplexed ligand and the potassium complex are similar, although this does not necessarily imply three–dimensional congruence (Section 6.3). The coefficient maps of the rubidium and caesium complexes are identical and show a decrease in the contribution from the primitive crown. The conformation of the sodium complex is irregular.

This is consistent with the structural findings of Dunitz and others. A distortion from the free ligand conformation is expected in complexes where the cation is either too large (Rb^+, Cs^+) or too small (Na^+) for the ligand "equilibrium cavity". A justification of the ligand selectivity for the potassium ion based on this limited data is not possible, but the general utility of the method is evident.

6.3 DISCUSSION

The methods used to describe the conformation of small rings have the general limitation of increasing complexity as ring size increases. The *one-dimensional model reduces the number of parameters* necessary for conformational assignment, but not without a few approximations. The conformation of a small ring can be specified uniquely by the out-of-plane coordinates alone. For large rings ($N \geq 16$), a set of out-of-plane displacements may be obtained from different in-plane shapes (Pickett and Strauss, 1971):



It is no longer strictly true that the out-of-plane displacements are much larger than the in-plane displacements. An unambiguous description holds for most conformations, but the model must be interpreted and applied carefully.

The Dale (1973a,b) nomenclature is based on the signs of the endocyclic torsion angles. It is a description of the shape of the ring as projected onto the Cremer and Pople (1975a) mean plane, and is thus perpendicular to the description in terms of out–of–plane displacements. Both afford a description of the shape of a projected ring, but only the out–of–plane displacement model conforms to the accepted notion of ring puckering. Rings which do not have the same symmetry may be equivalent in the Dale formalism. The semi–quantitative method proposed here reflects a symmetry element in the linear coefficients, but the nomenclature is concise only if some symmetry is present. The analysis in terms of the linear coefficients affords a description of the conformation of all rings in terms of one model.

7. SUMMARY

A general definition of the Cremer and Pople puckering parameters has been derived from a group theoretical analysis of the out–of–plane displacements of a planar polygon (Pickett and Strauss, 1971). The conditions required to fix the unique Cremer–Pople mean plane have been shown to be natural consequences of the group theory. The conformation of a general N–membered ring relative to this mean plane is therefore correlated with the out–of–plane displacement modes of a regular polygon. The theoretical basis of the Cremer–Pople method has provided insight into the relationship between the puckering parameters and symmetry type and into the interpretation of this one–dimensional model.

It has been shown group theoretically that the set of puckered forms of an N–membered ring is a linear space. The normal out–of–plane displacement *modes provide a natural basis set for* the analysis of complex conformations. Two linearly independent modes equivalent to the cos– and sin–forms of each E_m representation, and one of *the two possible modes* of the B_2 representation for N even only, are superimposed to generate any puckered shape. These forms are part of an extended *basis set, consisting of* overlapping subsets, each with N–3 linearly independent elements. The linear coefficients of these primitive forms are independent of *the extent of* pucker and of the ring numbering scheme. The method has provided a simple algorithm to identify the classical forms. Any intermediate form is a linear combination of a few simple shapes, weighted according to the linear coefficients. In contrast to the graphical procedures, the method proposed here preserves the quantitative nature of the puckering parameters.

The conformational analysis of nine–membered rings in terms of the one–dimensional model has been completed. Sixteen symmetrical conformations have been proposed and characterized. The nine–membered rings are the largest rings for which a projection of the conformational space onto a three–dimensional surface via the puckering parameters is of any practical importance. The various pseudorotational cycles map as simple paths on the complex surface. Classical forms are identified from the two–dimensional projections of the surface. Intermediate forms are best described as a linear combination of six primitive forms.

The conformation of a large ring has been described as a linear combination of basis forms. The linear coefficients provide a basis for the comparison of ring conformations, although ultimately the phase information of the primitive forms must also be examined. The derived nomenclature is concise for the case of a symmetrical ring, where many linear coefficients are zero. The method has been applied to the general case, where many non–zero coefficients are interpreted graphically.

A description of conformation should be concise and accurate. The one–dimensional model is a compromise of these two requirements. Future work should involve a detailed study of the applications of this method including, for example, investigations on the relationship between preferred conformation and biological activity of ring compounds. The possibility of another model, involving fewer approximations, cannot be discounted. This does not, however, seem likely at this stage of the development of conformational analysis in terms of the accepted views of molecular structure.

8. CONCLUSIONS

The concept of the conformation of a ring compound can be invoked to rationalise a variety of chemical phenomena, not explained by electronic effects. A simple procedure to describe and compare conformations of cyclic compounds in different environments is therefore of importance to the practical chemist. A set of quantitative parameters characterizing a ring conformation is essential to establish the relationship between observed chemical behaviour and molecular shape. The work presented here provides the basis for the characterization of any ring compound.

The conformation of any N–membered ring may be envisaged as arising from the out–of–plane displacements of the planar polygon. A group theoretical analysis in terms of this model shows that any conformation can be expressed as a linear combination of $(N-3)$ mutually orthogonal displacement modes. This set consists of orthogonal pairs of doubly–degenerate displacement modes, and includes a non–degenerate mode for even–membered rings. A number of forms, equivalent in shape to the two orthogonal modes of each degenerate pair, are characterised by group theoretically defined "phase angles". A pair of forms from each degenerate mode, chosen to correspond most closely with the ring of interest, and the non–degenerate mode (or its mirror image) are superimposed to generate any puckered shape.

The (N–3) displacement modes and their equivalent forms are the most basic shapes that cannot be decomposed into simpler shapes, and they are referred to as PRIMITIVE FORMS.

Every conformation can therefore be expressed as a combination of (N–3) of these simple primitive shapes in the correct relative proportions.

The primitive forms often take on shapes familiar to the practical chemist. For example, any six–membered ring

$\chi =$ A  + B  + C  .

(chair) (boat) (twist–boat)

The coefficients A, B, and C give the relative contributions of each primitive form. The values are independent of the ring numbering scheme or chemical identity of the ring, and can be used to characterize any conformation. A unique description of ring conformation is obtained from the coefficients and the phase angles of the primitive forms.

These coefficients form the basis of a concise nomenclature, useful for large rings. The pair of forms of each degenerate mode, E_m (m=2, 3 ...), are denoted by the letters X and X', starting with B and B' and progressing alphabetically as m increases. The non–degenerate mode of even–membered rings is denoted by A. The coefficients, which are multiplied by a factor of ten and rounded to the nearest integer, appear as subscripts.

For example, the six–membered ring described as:

$\chi =$ 0.90  + 0.10  ,

can be identified as $\chi = A_9 B_1$.

A Fortran 77 program, CONFOR, has been written to convert atomic coordinates of any ring into a description of conformational type as a combination of primitive forms. The input requires only the number of ring atoms and the atomic coordinates. The primitive forms closest to the ring of interest are determined. The algorithm, obtained from the group theoretical analysis, is used to calculate the coefficients of each primitive form. The output provides the investigator with a set of coefficients and phase angles of the contributing primitive forms. CONFOR provides a quantitative expansion of any conformation into a linear sum of simple shapes.

The well–known classical forms (boat, chair, etc.) take on certain characteristic values of the coefficients and phase angles of the primitive forms. A comparison of these values provides a simple algorithm, used by CONFOR, to identify any ring as a traditional classical form.

The group theoretical analysis of ring conformation, which is of practical importance to the experimentalist, offers a number of advantages:

- Conformational analysis of cyclic compounds is simplified. A description is readily obtained from atomic coordinates using the program CONFOR.
- Identification of the classical forms is fully automated and thus provides an unambiguous assignment and an indication of any slight distortion from the classical forms.
- The description is suitable for low symmetry conformations and it provides a nomenclature of all rings.

- The coefficients provide a set of quantitative parameters on which statistical analyses of a series of compounds can be based.
- A complex shape is expressed as a sum of simple shapes. The puckered shape of any ring is readily visualized in terms of the superposition of a few familiar shapes.

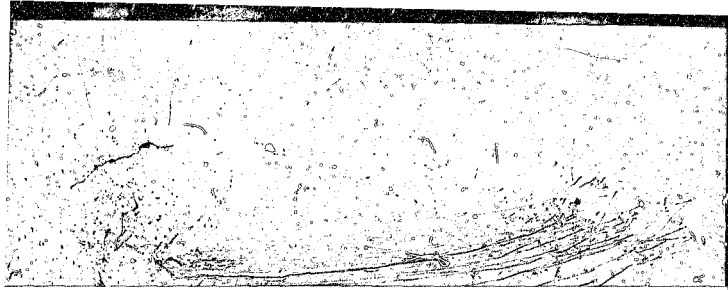
APPENDIX 1

CHARACTER TABLES FOR THE D_{Nh} POINT GROUPS

(Adapted from Wilson, Decius and Cross (1955) and Pickett and Strauss (1971))

$D_{Nh}(N \text{ odd})$

D_{Nh}	E	$2S_N(2t-1)/2$	$2C_N{}^t$	$2S_N(2t-3)/2$	...	σ_h	C_2	
A_1'	1	1	1	1	...	1	1	1
A_2'	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	z
E_1'	2	$2\cos(\pi/N)$	$2\cos(2\pi/N)$	$2\cos(3\pi/N)$	...	-2	0	R_x, R_y
E_2'	2	$2\cos(2\pi/N)$	$2\cos(4\pi/N)$	$2\cos(6\pi/N)$	...	2	0	x^2-y^2, xy
...					...			
$E_{(N-1)/2}'$	2	$2\cos[(N-1)\pi/N]$	$2\cos[2(N-1)\pi/N]$	$2\cos[3(N-1)\pi/N]$	...	-2	0	0
$E_{(N-1)/2}''$	2	$-2\cos[(N-1)\pi/N]$	$2\cos[2(N-1)\pi/N]$	$-2\cos[3(N-1)\pi/N]$	...	2	0	0
...					...			
E_1''	2	$-2\cos(\pi/N)$	$2\cos(2\pi/N)$	$-2\cos(3\pi/N)$	...	2	0	T_{xz}, T_{yz}



D_{Nh} (N even)

D_{Nh}	E	$2C_N$	$2C_N^2$	...	$C_N N/2 nC_2$	$N/2C_2'$	$N/2C_2''$	i	$2S_N N/2-1$	$2S_N N/2-3$	...	σ_h	$N/2\sigma_d$	$N/2\sigma_v$	
A_{1g}	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	R_z
B_{1g}	1	−1	1	...	$(-1)^{N/2}$	1	−1	1	−1	1	...	$(-1)^{N/2}$	1	−1	
B_{2g}	1	−1	1	...	$(-1)^{N/2}$	−1	1	1	−1	1	...	$(-1)^{N/2}$	−1	1	
E_{1g}	2	$2\cos(\frac{2\pi}{N})$	$2\cos(\frac{4\pi}{N}*1)$	...	−2	0	0	2	$2\cos(\frac{2\pi}{N})$	$2\cos(\frac{2\pi}{N}*2)$	...	−2	0	0	$R_{x,y}$
⋮															
E_{Nk}	2	$2\cos(\frac{2\pi}{N}*k)$	$2\cos(\frac{4\pi}{N}*2k)$	...	$2(-1)^k$	0	0	2	$2\cos(\frac{2\pi}{N}*k)$	$2\cos(\frac{2\pi}{N}*2k)$	...	$2(-1)^k$	0	0	
⋮															
$E_{((N/2)-1)g}$	2	$-2\cos(\frac{2\pi}{N})$	$2\cos(\frac{4\pi}{N}*2)$	...	$2(-1)^{(N/2-1)}$	0	0	2	$-2\cos(\frac{2\pi}{N})$	$2\cos(\frac{2\pi}{N}*2)$	...	$2(-1)^{(N/2-1)}$	0	0	
A_{1u}	1	1	1	...	1	1	1	−1	−1	−1	...	−1	−1	−1	
A_{2u}	1	1	1	...	1	−1	−1	−1	−1	−1	...	−1	1	1	T_z
B_{1u}	1	−1	1	...	$(-1)^{N/2}$	1	−1	−1	1	−1	...	$(-1)^{N/2+1}$	−1	1	
B_{2u}	1	−1	1	...	$(-1)^{N/2}$	−1	1	−1	1	−1	...	$(-1)^{N/2+1}$	1	−1	
E_{1u}	2	$2\cos(\frac{2\pi}{N})$	$2\cos(\frac{4\pi}{N}*2)$	...	−2	0	0	−2	$-2\cos(\frac{2\pi}{N})$	$-2\cos(\frac{2\pi}{N}*2)$	...	2	0	0	$T_{x,y}$
⋮															
E_{Nk}	2	$2\cos(\frac{2\pi}{N}*k)$	$2\cos(\frac{4\pi}{N}*2k)$	...	$2(-1)^k$	0	0	−2	$-2\cos(\frac{2\pi}{N}*k)$	$-2\cos(\frac{2\pi}{N}*2k)$	...	$2(-1)^{k+1}$	0	0	
⋮															
$E_{((N/2)-1)u}$	2	$-2\cos(\frac{2\pi}{N})$	$2\cos(\frac{4\pi}{N}*2)$	...	$2(-1)^{(N/2-1)}$	0	0	−2	$2\cos(\frac{2\pi}{N})$	$-2\cos(\frac{2\pi}{N}*2)$	...	$2(-1)^{N/2}$	0	0	

Note: When ($N/2$) is even, the columns under $N/2\ \sigma_v$ and $N/2\ \sigma_d$ are inverted.

APPENDIX 2

TRIGONOMETRIC IDENTITIES

It is required that

$$\sum_{j=1}^{N} \cos(4\pi jm/N) = 0 \quad \text{and} \quad \sum_{j=1}^{N} \sin(4\pi jm/N) = 0$$

According to Dur d Robson (1959),

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

and

$$\sum_{n=0}^{n-1} \sin(\alpha + n\beta) = \frac{\sin(\alpha + (n-1)/2\beta)\ \sin(n\beta/2)}{\sin(\beta/2)}$$

Hence

$$\begin{aligned}\sum_{j=1}^{N} \cos(4\pi jm/N) &= \cos(4\pi m/N) + \ \ldots\ + \cos(4\pi m) \\ &= \cos(4\pi m/N) + \ldots\ + \cos(4\pi m(N-1)/N) + \cos(0) \\ &= \cos[(N-1)/2\ (4\pi m/N)]\ \sin(2\pi m)\ /\ \sin(2\pi m/N) \\ &= 0\end{aligned}$$

and

$$\begin{aligned}\sum_{j=1}^{N} \sin(4\pi jm/N) &= \sin(4\pi jm/N) + \ \ldots\ + \sin(4\pi m) \\ &= \sin(0) + \ \ldots\ + \sin(4\pi m\ (N-1)/N) \\ &= \sin[(N-1)/2\ (4\pi m/N)]\ \sin(2\pi m)\ /\sin(2\pi m/N) \\ &= 0\end{aligned}$$

(These expressions hold if $\sin(2\pi m/N) \neq 0$

$m = 2,3, \ \ldots \ (N-1)/2$, N odd

$m = 2,3 \ \ldots \ (N/2)-1$, N even

However

$$\sin(2\pi(m/N)) = 0$$

$$\Rightarrow \quad 2m/N = K, \ K \in \mathbb{N}$$

$$\Rightarrow \quad N|2m$$

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

APPENDIX 3

CHARACTERISTICS OF THE LINEAR COEFFICIENTS

1. Linear independence of the Cremer–Pople normal modes

Due 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, $\Sigma z_{\cos,j} z_{\sin,j} = 0$

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

$\Sigma z_j^{\alpha} z_j^{\beta} = 0$, α,β normal modes

For N even, consider

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

Using 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

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

Using the identity given in Appendix 2, this reduces to zero, since $\sin(N\pi/2 + m\pi) = 0$ if N is even.

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

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

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

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

and $\sin[(2\pi/N)(j-1)M_2]$ are orthogonal

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

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

$= 0$

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

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

$= 0$

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

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

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

$\frac{1}{2}\sum_j \cos[-\pi/2 + (2\pi/N)(j-1)(M_1-M_2)]$

$= 0$

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_j of the modes $\alpha, \beta, \ldots \xi$ are given as

$z_j^{(\alpha)}, \ldots z_j^{(\xi)}$

Suppose these modes are not linearly independent

Then

$$\alpha z_j^{(\alpha)} + \ldots \xi z_j^{(\xi)} = 0 \quad \forall j$$

$\Rightarrow$ $\exists$ at least two coefficients $\neq 0$

(since $z_j \neq 0 \ \forall j$)

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

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

But

$$\gamma \sum_i z_i^{(\beta)} z_i^{(\beta)} \neq 0 \text{ , (since } \sum_i z_i^{(\beta)2} = 0 \implies z_i = 0 \ \forall \ i \text{)}$$

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

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

and for N odd

$$\sum_m a_m [\cos(2\pi m(j-1)/N)] + b_m [\sin(2\pi m(j-1)/N)] = 0, \forall j$$
$$\implies a_m, b_m = 0, \forall m$$

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 $\phi_m + \kappa$ respectively.
The coefficients of a form at ϕ_m^u in the linear expansion in terms of $\cos[(2\pi m/N)(j-1)]$ and $\sin[2\pi m/N)(j-1)]$ are $\cos \phi^u$ and $-\sin \phi^u$ respectively.

Let

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

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

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

and

$$c_m \sin \phi_m + d_m \sin \phi_m \cos \kappa + d_m \cos \phi_m \sin \kappa = 0 \text{ , for all m.}$$

Hence

$$\sin \phi_m * (c_m \cos \phi_m + d_m \cos \phi_m \cos \kappa - d_m \sin \phi_m \sin \kappa) = 0$$
$$\cos \phi_m * (c_m \sin \phi_m + d_m \sin \phi_m \cos \kappa + d_n \cos \phi_m \sin \kappa) = 0 \text{ ,}$$
for all m.

This gives: $d_m \sin \kappa = 0$

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

and $c_m \cos \phi_m = 0$

$c_m \sin \phi_m = 0 \Rightarrow c_m = 0$

Therefore the primitive forms are linearly independent.

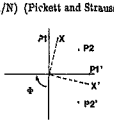
3. The linear coefficients are independent of the atomic numbering scheme

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 $\phi_m = R$, with primitive forms at phase angles A and B, are:

$$XA(M) = \frac{-\ Q \cos R \sin B + Q \sin R \cos B}{\sin A \cos B - \cos A \sin B} \quad \text{(coefficient of cos-form)}$$

$$XB(M) = \frac{Q \cos R \sin A - Q \sin R \cos A}{\sin A \cos B - \cos A \sin B} \quad \text{(coefficient of sin-form)}$$

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



A description of the ring should be independent of the ring numbering chosen;

This gives: $d_m \sin \kappa = 0$

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

and $c_m \cos \phi_m = 0$

$c_m \sin \phi_m = 0 \Rightarrow c_m = 0$

Therefore the primitive forms are linearly independent.

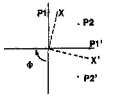
3. The linear coefficients are independent of the atomic numbering scheme

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 $\phi_m = R$, with primitive forms at phase angles A and B, are:

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Any equivalent primitive forms are generated by C_n or S_n operations: $\phi' = \phi' + (2\pi m/N)$. Any ring will thus have equivalent forms (a different ring numbering) at $\phi_m' + (2\pi m/N)$ (Pickett and 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 $\phi_m = R$, *with the closest* primitive forms at phase angles of A and B. An equivalent phase thus lies at $\phi_m + 2\pi m/N$.
Let $(2\pi m/N) = \alpha$ Then for this equivalent phase

ϕ (cosform) $= A + \alpha$
ϕ (sinform) $= B + \alpha$
ϕ (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:

$-\cos R \sin B \cos^2\alpha + \sin R \sin B \sin\alpha\cos\alpha - \cos B \cos R \sin\alpha$
$\cos\alpha + \cos B \sin R \sin^2\alpha + \sin R \cos B \cos^2\alpha + \cos R \cos B \sin\alpha$
$\cos\alpha - \sin B \sin\alpha \cos\alpha \sin R - \cos R \sin B \sin^2\alpha$
$= -\cos R \sin B + \sin R \cos B$

The denominator becomes

$\sin A \cos B \cos^2\alpha - \sin A \sin B \cos\alpha \sin\alpha + \cos A \cos B \sin\alpha \cos\alpha - \cos A$
$\sin B \sin^2\alpha + \cos B \sin A \sin^2\alpha - \cos A \sin B \cos^2\alpha - \cos A \cos B \cos\alpha$
$\sin\alpha + \sin A \sin B \cos\alpha \sin\alpha$
$= \cos B \sin A - \cos A \sin B$

The numerator in the XB' expression is

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

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

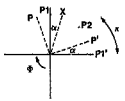
$= \cos R \sin A - \sin R \cos A$

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 $\phi + (2m\pi/N)(+\pi)$ will not generate this form. It can only be generated by C_2 though atom 1 followed by σ_h. This implies (Pickett and Strauss,1971)

$\phi + -\phi + \pi + \pi = -\phi$

Thus if a form lies at ϕ, the enantiomer lies at $-\phi$. 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:

$-\sin^2 A \sin \kappa \cos 2\kappa + \cos^2 A \sin 2\kappa \cos \kappa + \sin^2 A \cos \kappa \sin 2\kappa - \cos^2 A \sin \kappa \cos 2\kappa$

$= -\sin \kappa \cos 2\kappa + \sin 2\kappa \cos \kappa$

$= \sin \kappa$

The numerator reduces to

$-\sin A \cos A \cos \kappa \cos \alpha \cos 2\kappa - \sin^2 A \cos \kappa \sin \alpha \cos 2\kappa + \sin^2 A \cos \kappa \cos \alpha \sin 2\kappa - \sin A \cos A \cos \kappa \sin \alpha \sin 2\kappa - \cos^2 A \sin \kappa \cos \alpha \cos 2\kappa - \cos A \sin A \sin \kappa \sin \alpha \cos 2\kappa + \cos A \sin A \sin \kappa \cos \alpha \sin 2\kappa - \cos^2 A \sin \kappa \sin \alpha \sin 2\kappa + \cos A \sin A \cos \kappa \cos \alpha \cos 2\kappa - \cos^2 A \cos \kappa \sin \alpha + \cos^2 A \cos \kappa \cos \alpha \sin 2\kappa + \cos A \sin A \cos \kappa \sin \alpha \sin 2\kappa - \sin^2 A \sin \kappa \cos \alpha \cos 2\kappa + \cos A \sin A \sin \kappa \sin \alpha \cos 2\kappa - \cos A \sin A \sin \kappa \cos \alpha \sin 2\kappa - \sin^2 A \sin \kappa \sin \alpha \sin 2\kappa$

$= -\cos \kappa \cos 2\kappa \sin \alpha + \cos \kappa \sin 2\kappa \cos \alpha$

$-\sin \kappa \cos 2\kappa \cos \alpha - \sin \kappa \sin 2\kappa \sin \alpha$

$= \sin \alpha [-\cos \kappa (\cos^2 \kappa - \sin^2 \kappa) - 2 \sin^2 \kappa \cos \kappa]$

$+ \cos \alpha [2 \cos^2 \kappa \sin \kappa - \sin \kappa (\cos^2 \kappa - \sin^2 \kappa)]$

$= -\sin \alpha \cos \kappa + \cos \alpha \sin \kappa$

XB

The numerator of the forms:

$$P^1: \quad XB = \cos(A + 2\kappa - \alpha)\sin(A + 2\kappa) - \sin(A + 2\kappa - \alpha)\cos(A + 2\kappa)$$

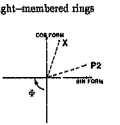
$$X: \quad XB = \cos(A + \alpha)\sin(A + 2\kappa) - \sin(A + \alpha)\cos(A + 2\kappa)$$
$$= -\sin\alpha$$

The expression for P^1 becomes:

$$\sin A \cos A \cos\alpha \cos^2 2\kappa + \sin^2 A \cos^2 2\kappa \sin\alpha$$
$$- \sin^2 A \cos 2\kappa \sin 2\kappa \cos\alpha + \cos A \sin A \cos 2\kappa \sin 2\kappa \sin\alpha$$
$$+ \cos^2 A \sin 2\kappa \cos 2\kappa \cos\alpha + \cos A \sin A \sin 2\kappa \cos 2\kappa \sin\alpha$$
$$- \cos A \sin A \sin^2 2\kappa \cos\alpha + \cos^2 A \sin^2 2\kappa \sin\alpha$$
$$- \cos A \sin A \cos^2 2\kappa \cos\alpha + \cos^2 A \cos^2 2\kappa \sin\alpha$$
$$- \cos^2 A \cos 2\kappa \sin 2\kappa \cos\alpha - \cos A \sin A \cos 2\kappa \sin 2\kappa \sin\alpha$$
$$+ \sin^2 A \sin 2\kappa \cos 2\kappa \cos\alpha - \sin A \cos A \sin 2\kappa \cos 2\kappa \sin\alpha$$
$$+ \sin A \cos A \sin^2 2\kappa \cos\alpha + \sin^2 A \sin^2 2\kappa \sin\alpha$$
$$= \sin\alpha$$

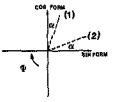
The coefficients of enantiomers are therefore the same

4. Two primitive forms (cos–form and sin–form) differ in phase only
   e.g. 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).

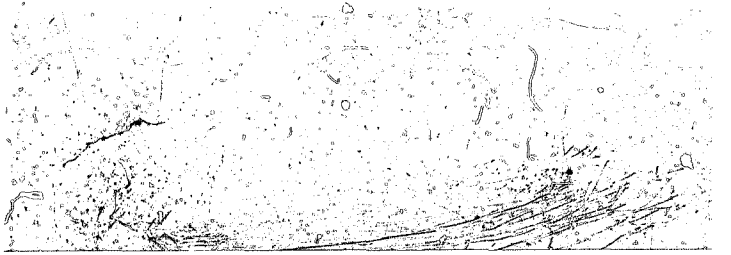
APPENDIX 4

THE PROGRAM CONFOR

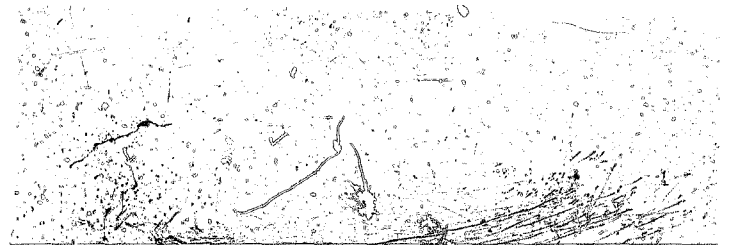
4.1 Program Listing

```
      SUBROUTINE CONFOR(Q,PHI,AAI,NN)
C
C
C     ***************************************************************
C     THIS PROGRAM EXPRESSES ANY CONFORMATION AS A LINEAR COMBINATION
C     OF PRIMITIVE FORMS- AS DEFINED BY THE CREMER-POPLE EQUATIONS.
C     THE PROGRAM IS ONLY FOR 10 -MEMBERED RINGS OR LESS.
C     ***************************************************************
C
      DIMENSION Q(20),PHI(20),XA(20),XB(20),XAA(20),XAB(20)
      M=(NN-1)/2
      WRITE(2,111)
      WRITE(2,109)
      WRITE(2,502)
      WRITE(2,103)(M,Q(M),PHI(M),M=2,M)
C
C     ***************************************************
C     DISTINGUISH BETWEEN ODD AND EVEN MEMBERED RINGS
C     ***************************************************
C
      IF(NN/2.GT.M)THEN
      IC=NN/2
      Q(IC)=AAI
      WRITE(2,104)IC,Q(IC)
      R=Q(IC)
      IF(NN.LE.8)CALL EVEN(Q,PHI,M,NN,R)
      IF(NN.GT.8)CALL LARGE(Q,PHI,M,NN,R)
      ELSE
      CALL ODD(Q,PHI,M,NN)
      ENDIF

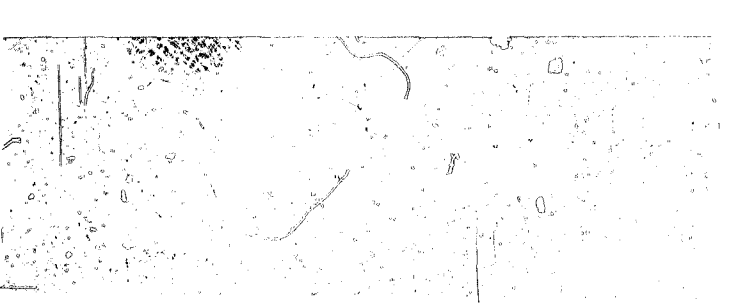
  111 FORMAT(///,5X,'CONFORMATIONAL ANALYSIS')
  102 FORMAT(6X,I2,4X,F8.3,4X,F7.2)
  109 FORMAT(//,5X,'PUCKERING PARAMETERS')
  104 FORMAT(//,5X,'Q(',I1,')=',F6.3)
  502 FORMAT(//,4X,'M',4X,'Q(M)',7X,'PHI(M)')
      RETURN
      END
      SUBROUTINE MIN1(K,XK,KM,WB,PHI)
C
C     ***************************************************
C     THIS SUBROUTINE FINDS THE PHI VALUES OF THE PRIMITIVE FORMS
C     CLOSEST TO THE RING
C     ***************************************************
C
      REAL KK(50),KM
      TH=360
      DO 1000 I=1,M
      T=ABS((KK(I)*180)/(2*WB))-PHI)
      IF(T.LT.TH)GO TO 1010
      GOTO 1000
 1010 TH=T
      KM=KK(I)
 1000 CONTINUE
      RETURN
      END
      SUBROUTINE SOLVE(Q,KMIN,LMIN,M,WB,PHI,XA,XB)
C
C     ***************************************************
C     THIS FINDS THE COEFFICIENTS IN THE LINEAR REGRESSION
C     ***************************************************
C
      DIMENSION Q(20),PHI(20),XA(20),XB(20),A(20),B(20),H(20),HH(20)
      REAL KMIN(50),LMIN(50)
```

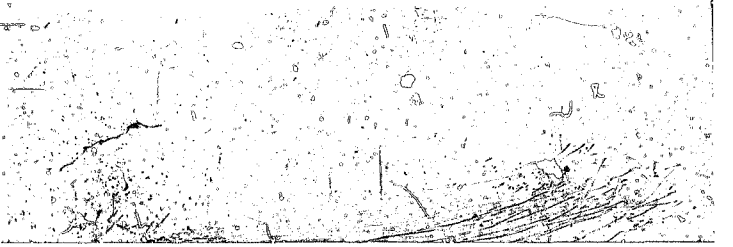


```
C
C     THE EQUATIONS IN THE LINEAR COMBINATION ARE NOW SOLVED
  150 PI=3.14159265
      DO 161 N=2,N
      A(N)=(EXIN(N)*PI)/(2*WR))
      C(N)=((EXIN(N)*PI)/(2*WR))
      M(N)=(SIN(A(N)))*(COS(B(N)))-(COS(A(N)))*(SIN(B(N)))
C     THE COEFFICIENTS IN THE REGRESSION ARE NOW SOLVED
      FACT=0.0174533
      RHI(N)=RHI(N)*(FACT)
      XA(N)=(1/M(N))*((-D(N))*(COS(RHI(N)))*(SIN(M(N)))+Q(N)*(SIN(RHI(N
     &))*(COS(B(N))))
      XB(N)=(1/M(N))*(Q(N)*(COS(RHI(N)))*(SIN(A(N)))-D(N)*(SIN(ARZ(N)))*
     &(COS(B(N))))
  201 CONTINUE
      RETURN
      END
      SUBROUTINE WRITES(N,XA,XB,Y,EXIN,LEIN,XIA,XIB,YY)
C
C     ***************************************************
C     THIS NORMALIZES COEFFICIENTS AND WRITES THEM TO FILE
C     ***************************************************
C
      DIMENSION XA(20),XB(20),XYA(20),XIB(20)
      REAL EXIN(50),LEIN(50)
      TOTL=0
      DO 250 N=2,N
      TOTL=TOTL+XA(N)+XB(N)
  250 CONTINUE
      TOTL=TOTL+Y
      WRITE(2,110)
      WRITE(2,504)
      WRITE(2,105)(N,XA(N),XB(N),N=2,N)
      WRITE(2,111)
      WRITE(2,505)
      WRITE(2,506)
      WRITE(2,507)
      DO 508 N=2,N
      XIA(N)=XA(N)/(TOTL)
      XIB(N)=XB(N)/TOTL)
      WRITE(2,106)N,XIA(N),EXIN(N)
      WRITE(2,107)XIB(N),LEIN(N)
  180 CONTINUE
      YY=Y/(TOTL)
  105 FORMAT(5X,I3,6X,F8.3,6X,F8.3)
  106 FORMAT(5X,I2,8X,F8.3,8X,F4.1)
  107 FORMAT(15X,F8.3,8X,F4.1)
  110 FORMAT(//,5X,'COEFFICIENTS OF PRIMITIVE FORMS')
  111 FORMAT(//,5X,'NORMALIZED COEFFICIENTS')
  504 FORMAT(//,6X,'N',7X,'COSFORM',5X,'SINFORM')
  505 FORMAT(//,6X,'N',5X,'COEFFICIENT',3X,'ANGULAR VALUE')
  506 FORMAT(12X,'OF PRIMITIVE',2X,'OF PRIMITIVE')
  507 FORMAT(12X,'FORM',11X,'FORM')
      RETURN
      END
      SUBROUTINE KVEM(Q,PHI,W,HH,H)
C
C     ***********************************************
C     THIS GENERATES THE PRIMITIVE FORMS FOR 6 AND 8
C     REVERSED RINGS
C     ***********************************************
C
      DIMENSION Q(20),PHI(20),RA(20),XB(20),EXA(20),EXB(20),YY(6),YY2(6
     &),XY(4),WT(15),WT2(15),WT3(15),WT4(15),XXX(15),XXX(15),Z(6),QXA
     &(6)
      REAL E(50),L(50),EXIN(50),LEIN(50)
```

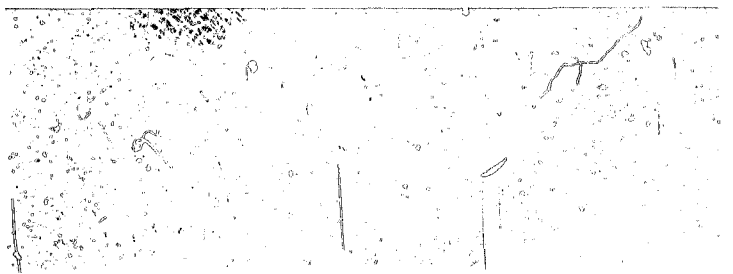


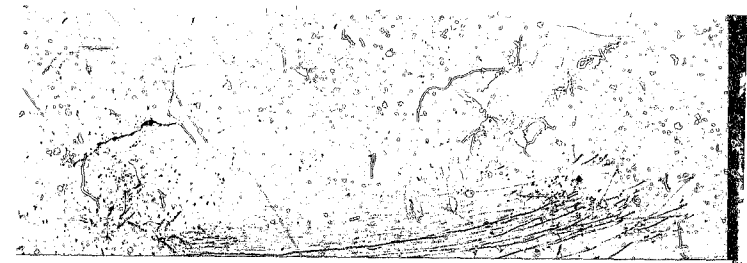
```
      CHARACTER NAME(6),NAME1(18)*3
C
C     ***************************************************
C     THIS FINDS THE CROWN FORM CLOSEST TO THE RING
C     ***************************************************
C
      IF (N.LE.0)THEN
      AA=-1.0
      RL=LE
      AA=1.0
      ENDIF
      P=ABS(R)
C
C     ***************************************************************
C     THIS DETERMINES THE ANGULAR VALUES OF PRIMITIVE FORMS OF 6-E RINGS
C     ***************************************************************
C
      IF(RS.EQ.6)THEN
      DO 86 N=2,N
      DO 85 I=1,7
      K(I)=64*(I-1)
      L(I)=64*(7-I)+2
   85 CONTINUE
      NY=7
      CALL NIM1(NX,K,KNIM(N),NB,PHI,IA,IB)
      CALL NIM1(NX,L,LNIM(N),NB,PHI(N))
   86 CONTINUE
      CALL SOLVE(Q,KNIM,LNIM,N,NB,PHI,IA,IB)
      CALL WRITE6(K,IA,IB,Y,KNIM,LNIM,IBA,IBB,YY)
      WRITE(2,100)NB/2,YY,AA
C
C     ***************************************************
C     THIS FINDS OUT IF TWO 6-E RING IS A CLASSICAL FORM
C
      DATA FOR 6-N CLASSICAL FORMS
C     ***************************************************
C
      DATA NAME /'B','T','C','E','S','H'/
      DATA TF1  /1.0,0.0,0.0,0.0,0.586,0.0,0.0/
      DATA TF2  /0.0,1.0,0.0,0.0,0.0,0.707,0.551/
      DATA TF3  /0.0,0.0,1.0,0.414,0.293,0.449/
      DO 7000 I=1,6
      YIX=ABS(TF1(I)-YYA(2))+ABS(TF2(I)-XYB(2))+ABS(TF3(I)-YY)
      IF(YIX.LE.0.2.AND.YIX.GT.0.1)WRITE(2,7031)NAME(I)
      IF(YIX.LE.0.1)WRITE(2,7030)NAME(I)
 7000 CONTINUE
 7030 FORMAT(/,5X,'WARNING:THIS IS A',A4,'  FORM')
 7031 FORMAT(/,5X,'WARNING:THIS IS VERY SIMILAR TO A ',A4,' FORM')
C
C     ***************************************************
C     THE PRIMITIVE FORMS OF EIGHT MEMBERED RINGS
C     ***************************************************
C
      RL=LE
      DO 141 N=2,N
C
C     ***************************************************************
C     PRIMITIVE FORMS ARE AT DIFFERENT PHI VALUES FOR N=2 AND 3
C     ***************************************************************
C
   90 IF(N.EQ.2)THEN
      DO 120 I=1,3
      K(I)=64*(I-1)
      L(I)=64*(3-I)+8
  120 CONTINUE
      NY=3
      CALL NIM1(NY,K,KNIM(N),NB,PHI(N))
```



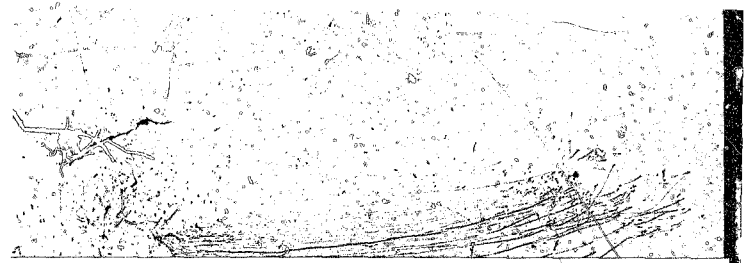


```
      CALL MINI(Nf,L,LMIN(3),NR,PHI(N))
      ELSE
      DO 140 I=1,5
      K(I)=6*(I-1)
      L(I)=6*(I-1)+4
  140 CONTINUE
      NI=5
      CALL MINI(N1,K,KMIN(N),NR,PHI(N))
      CALL MINI(N1,L,LMIN(N),NR,PHI(N))
      ENDIF
  141 CONTINUE
      CALL SORTE(Q,KMIN,LMIN,N,NR,PHI,EA,EB)
      CALL WRITE3(N,KA,KB,V,KMIN,LMIN,KKB,KKB,VV)
      WRITE(2,106)NR/2,VV,AA
C
C     THIS FINDS OUT IF A 6-N RING IS A CLASSICAL FORM
C
C     ***********************************************
C     DATA FOR CLASSICAL FORMS
C     ***********************************************
C
      DATA NAMES /'EB ','EB ','C2 ','TC ','TC ','C ','S ','S ',
     &'C2 ','C2 ','TCC','TCC','BC ','BC ','TBC'/
      DATA UP1 /1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.707,0.293,0.293,0.0,0.0,0.294
     &,0.530,0.0,4.229/
      DATA UP2 /0.0,1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.293,0.707,0.0,0.0,0.353,0.254
     &,0.0,0.530,0.229/
      DATA UP3 /0.0,0.0,0.0,0.0,1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.249,0
     &.0,0.213/
      DATA UP4 /0.0,0.0,0.0,0.0,0.0,1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.2
     &49,0.213/
      DATA UP5 /0.0,0.0,1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.648,0.648,0.533,0
     &.172,0.172,0.116/
      Do 7500 I=1,15
      YIX(I)= ABS(XIA(2)-UP1(I))+ ABS(XIB(2)-UP2(I))+ ABS(XIA(3)-UP3(I)
     &)+ ABS(XIB(3)-UP4(I)) + ABS(YY-UP5(I))
 7500 CONTINUE
      DO 7501 I=1,12
      IF(YIX(I).LE.0.2.AND.YIX(I).GT.0.1)WRITE(2,7514)NAMEX(I)
      IF(YIX(I).LE.0.1)WRITE(2,7513)NAMEX(I)
 7501 CONTINUE
      DO 9669 I=2,N
      NI=ABS(PHI(I)-360)
      IX(NI.LT.5)YH5A(1)=360-PHI(I)
 9669 CONTINUE
      IF(YIX(13).LE.0.2.OR.YIX(14).LE.0.2)THEN
      DO 3014 I=1,5
      ANG=(6*100*(I-1))/16
      ANGA=100+(6*100*(I-1))/16
      ANGL=100 + (4*)  *(I-1))/16
      ELA= ABS(PHI(2)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)ELA= ABS(PHI(2)+360-ANG)
      IF(ANG.GE.720)ELA= ABS(PHI(2)+720-ANG)
      ELA= ABS(PHI(2)-ANGA)
      IF(ANGA.GE.360.AND.ANGA.LT.720)ELA= ABS(PHI(2)+360-ANGA)
      IF(ANGA.GE.720)ELA= ABS(PHI(2)+720-ANGA)
      ELA= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360)ELA= ABS(PHI(3)+360-ANGL)
      Ch..)=ELA=ELA
      QXA(2)=ELA=ELA
 3014 CONTINUE
      QXX=10.03
      QXXA=10.03
      DO 3030 J=..5
      IF(QX(J).LE.10.AND.AA.EQ.1.0)QXX=QX(J)
      IF(QXA(J).LE.10.AND.AA.EQ.1.0)QXXA=QXA(J)
```

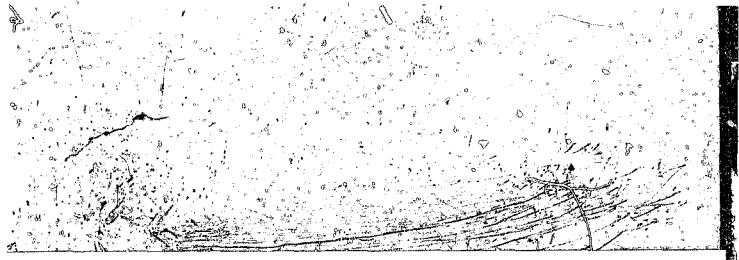





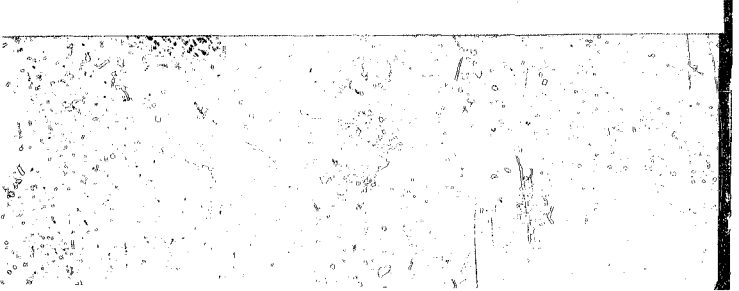
```
3000 CONTINUE
     IF(QEX.LT.10.AND.YZX(13).LE.0.1.OR.QEX.LE.10.AND.YZX(14).LE.0.1
    &)THEN
     WRITE(2,7013)NAMEX(13)
     IF(QEX3.LE.10.AND.YZX(13).GT.0.1.OR.QEX3.LE.10.AND.YZX(14).
    &GT.0.1)THEN
     WRITE(2,7014)NAMEX(13)
     ENDIF(YZX(15).LE.0.2)THEN
     DO 3002 J=1,2
     ANG= (4*180)/16 +(8*180*(2-1))/16
     ANG2=180- 4*180/16 + (8*180*(2-1))/16
     ANG3=180 + 2*180/16 + (4*180*(2-1))/16
     BL= ABS(PHI(2)-ANG)
     IF(ANG.GE.360.AND.ANG.LT.720)BL= ABS(PHI(2)+360-ANG)
     IF(ANG.GE.720)BL= ABS(PHI(2)+720-ANG)
     BLA= ABS(PHI(2)-ANG2)
     IF(ANG2.GE.360.AND.ANG2.LE.720)BLA= ABS(PHI(2)+360-ANG2)
     IF(ANG2.GE.720)BLA= ABS(PHI(2)+720-ANG2)
     BLA= ABS(PHI(3)-ANG3)
     IF(ANG3.GE.360)BLA= ABS(PHI(3)+360-ANG3)
     QX(2)=BL+BLA
     QX3(2)=BLA+BLL
3002 CONTINUE
     QXX=10.00
     QX3=10.00
     DO 3005 J=1,2
     IF(QX(2).LE.10.AND.AA.EQ.-1.0)QXX=QX(2)
     IF(QX3(2).LE.10.AND.AA.EQ.1.0)QXX=QX3(2)
3005 CONTINUE
     IF(QEX.LE.10.AND.YZX(15).LE.0.1)WRITE(2,7013)NAMEX(15)
     IF(QEX.LE.10.AND.YZX(15).GT.0.1)WRITE(2,7014)
    &NAMEX(15)
     IF(QEX3.LE.10.AND.YZX(15).LE.0.1)WRITE(2,7013)NAMEX(15)
     IF(QEX.LE.10.AND.YZX(15).GT.0.1)WRITE(2,7014)NAMEX(15)
     ELSE
     CONTINUE
     ENDIF
7013 FORMAT(' 5',
    &' 15 6',A4,'  FORM')
7014 FORMAT('
    &  ',A4,' FORM')
7051 END
     SUBROUTINE GGA(Q,PHI,W,NE)
C
C
C     * * *
```

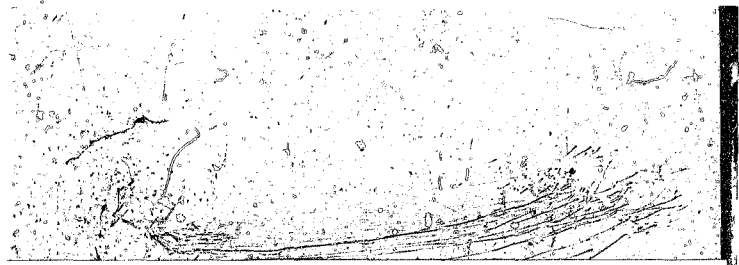


```
      L(I)=10*(I-1)+5
 4031 CONTINUE
      CALL MINI(NUM,K,KMIN(N),NR,PHI(N))
      CALL MINI(NUM,L,LMIN(N),NR,PHI(N))
      KL=SIGN(NR,KP).15.AND.M.EQ.3.OR.NR.EQ.15.AND.M.EQ.4)THEN
      NUM=11
      DO 4033 I=1,11
      K(I)=4*(I-1)
      L(I)=4*(I-1)+3
 4033 CONTINUE
      CALL MINI(NUM,K,KMIN(N),NR,PHI(N))
      CALL MINI(NUM,L,LMIN(N),NR,PHI(N))
      KL=2
      DO 40 I=1,NUM
      K(I)=2*(I-1)
      L(I)=2*(I-1)+1
   40 CONTINUE
      CALL MINI(NUM,K,KMIN(N),NR,PHI(N))
      CALL MINI(NUM,L,LMIN(N),NR,PHI(N))
      ENDIF
   45 CONTINUE
      V=0
      CALL SOLVE(Q,KMIN,LMIN,M,NR,PHI,XA,XB)
      CALL WRITES(M,XA,XB,V,KMIN,LMIN,XIA,XIB,VT)
C
C     ***************************************************
C     THIS DETERMINES IF A NINE IS A CLASSICAL FORM
C     ***************************************************
C
      IF(NB.GT.9)GO TO 4994
      IF(NB.EQ.5)THEN
C
C     ****************************
C     DATA FOR 5-N CLASSICAL FORMS
C     ****************************
C
      DATA NAME /'E','T'/
      DATA SF1 /1.0,0.0/
      DATA SF2 /0.0,1.0/
      DO 9900 I=1,2
      YZ = ABS(XF1(1)-XIA(2))*ABS(SF2(1)-XIB(2))
      IF(YZ.LE.0.1)WRITE(2,9200)NAME(I)
      IF(YZ.GT.0.1.AND.YZ.LE.0.2)WRITE(2,9201)NAME(I)
 9900 CONTINUE
 9200 FORMAT(/,5X,'WARNING;THIS IS A',A4,'  FORM')
 9201 FORMAT(/,5X,'WARNING;THIS IS VERY SIMILAR TO A',A4,' FORM')
      ENDIF
C
C     ****************************
C     DATA FOR 7-N CLASSICAL FORMS
C     ****************************
C
      DATA NF/NR /'S ','TS','C ','TC','SS','S ','TS','S ','T '/
      DATA XF1 /1.00,0.0,0.0,0.0,0.783,0.1,0.0,0.1,417,0.0/
      DATA XF2 /0.0,1.0,0.0,0.0,0.0,0.0,0.0,0.444,0.0,0.48/
      DATA XF3 /0.0,0.0,1.0,0.0,0.0,217,0.0,0.0,0.583,0.0/
      DATA XF4 /0.0,0.0,0.0,1.0,0.0,0.0,0.0,0.555,0.0,0.54/
      DO 4999 I=1,9
      YZX(I)= ABS(XIA(2)-XF1(I))+ ABS(XIB(2)-XF2(I))+ ABS(XIA(3)-XF3(I))
     &+ABS(XIB(5)-XF4(I))
 4008 CONTINUE
      DO 9669 I=2,M
      EX=ABS(PHI(I)-360)
      IF(EX.LT.5)PHI(I)=360-PHI(I)
 9669 CONTINUE
      IF (YZX(5).LE.0.2)THEN
```

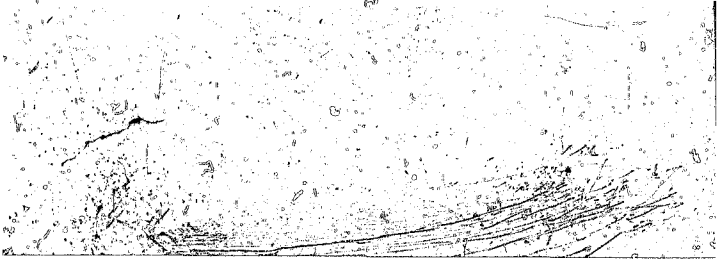


```
      DO 4041 J=1,14
      ANGA=180+(6*180*(J-1))/14
      ANGL=(2*180*(J-1))/14
      HLA= ABS(PHI(2)-ANGA)
      IF(ANGA.GE.360.AND.ANGA.LT.720)HLA= ABS(PHI(2)+360-ANGA)
      IF(ANGA.GE.720.AND.ANGA.LT.1080)HLA= ABS(PHI(2)+720-ANGA)
      IF(ANGA.GE.1080)HLA= ABS(PHI(2)+1080-ANGA)
      HLL= ABS(PHI(3)-ANGL)
      QX(J)=HLA+HLL
4041  CONTINUE
      QIX=10.03
      DO 4944 J=1,14
      IF(QX(J).LE.10)QXX=QX(J)
4944  CONTINUE
      IF(QXX.LE.10.AND.YZZ(5).LE.0.1)WRITE(2,4091)
      IF(QXX.LE.10.AND.YZZ(5).GT.0.1)WRITE(2,4092)
      ELSEIF(YZZ(6).LE.0.2.OR.YZZ(6).LE.0.2)THEN
4026  DO 4021 J=1,14
      ANG=(6*180*(J-1))/14
      ANGA=180+(6*6   *(J-1))/14
      ANGL=(2*180*(J-   ,/14
      HL= ABS(PHI(2)-ANG)
      IF(ANG.GE.360.AND.ANG.LE.720)HL= ABS(PHI(2)+360-ANG)
      IF(ANG.GE.720)HL= ABS(PHI(2)+720-ANG)
      HLA= ABS(PHI(2)-ANGA)
      IF(ANGA.GE.360.AND.ANGA.LT.720)HLA= ABS(PHI(2)+360-ANGA)
      IF(ANGA.GE.720.AND.ANGA.LT.1080)HLA+ ABS(PHI(2)+720-ANGA)
      IF(ANGA.GE.1080)HLA= ABS(PHI(2)+1080-ANGA)
      HLL= ABS(PHI(3)-ANGL)
      QX(J)=HL+HLA
      QYA(J)=HLA+HLL
4021  CONTINUE
      QIX=10.63
      QIXA=10.03
      DO 4998 J=1,14
      IF(QX(J).LE.10)QXX=QX(J)
      IF(QXA(J).LE.10)QIXA=QXA(J)
4998  CONTINUE
      IF(QXX.LE.10.AND.YZZ(6).LE.0.1)WRITE(2,4071)
      IF(QXX.LE.10.AND.YZZ(6).GT.0.1.AND.YZZ(6).LE.0.2)WRITE(2,4072)
      IF(QIXA.LE.10.AND.YZZ(6).LE.0.1)WRITE(2,4061)
      IF(QIXA.LE.10.AND.YZZ(6).GT.0.1.AND.YZZ(6).LE.0.2)WRITE(2,4062)
      GO TO 5001
      ELSEIF(YZZ(7).LE.0.2.OR.YZZ(9).LE.0.2)THEN
      DO 5005 J=1,14
      ANGH=(3*180)/14 + ((6*180*(J-1))/14)
      ANGHA=180+((3*180)/14) + ((6*180*(J-1))/14)
      ANGLH= (180/14) + ((2*180*(J-1))/14)
      HH= ABS(PHI(2)-ANGH)
      IF(ANGH.GE.360.AND.ANGH.LT.720)HH= ABS(PHI(2)+360-ANGH)
      IF(ANGH.GE.720)HH= ABS(PHI(2)+720-ANGH)
      HHA= ABS(PHI(2)-ANGHA)
      IF(ANGHA.GE.360.AND.ANGHA.LT.720)HHA= ABS(PHI(2)+360-ANGHA)
      IF(ANGHA.GE.720.AND.ANGHA.LT.1080)HHA= ABS(PHI(2)+720-ANGHA)
      IF(ANGHA.GE.1080)HHA= ABS(PHI(2)+1080-ANGHA)
      HHH= ABS(PHI(3)-ANGLH)
      QY(J)= HH + HHH
      QYA(J)= HHA + HHH
5005  CONTINUE
      QYX=10.03
      QYXA=10.03
      DO 4999 J=1,14
      IF(QY(J).LE.10)QYX= QY(J)
      IF(QYA(J).LE.10)QYXA= QYA(J)
4999  CONTINUE
      IF(QYY.LE.10.AND.YYZ(7).LE.0.1)WRITE(2,5010)
```

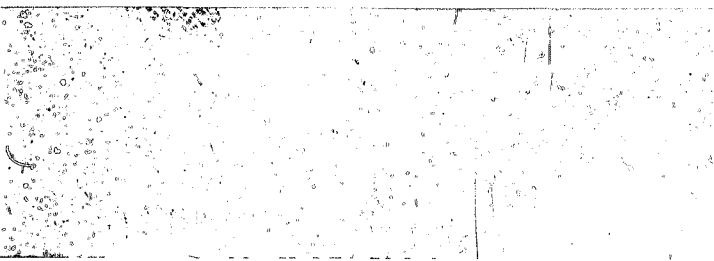



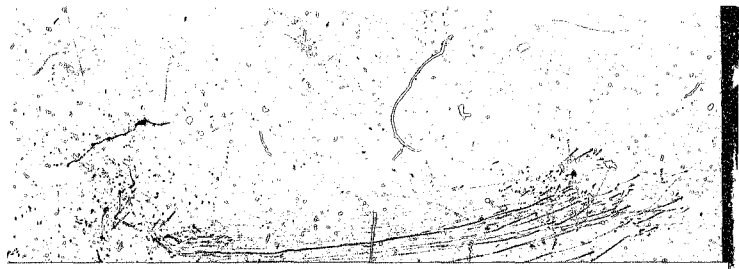


```
      IF(QTY.LE.10.AND.YIX(7).GT.0.1.AND.YIX(7).LE.0.2)WRITE(2,5011)
      IF(QTYA.LE.10.AND.YIX(9).LE.0.1)WRITE(2,5012)
      IF(QTYA.LE.10.AND.YIX(9).GT.0.1.AND.YIX(9).LE.0.2)WRITE(2,5013)
      ELSE
      DO 4919 I=1,5
      IF(YIX(1).LE.0.1)WRITE(2,4992)NAMEX(I)
      IF(YIX(1).GT.0.1.AND.YIX(1).LE.0.2)WRITE(2,4983)NAMEX(I)
4919 CONTINUE
      ENDIF
4971 FORMAT(/,5X,'WARNING:THIS IS A S FORM')
4972 FORMAT(/,5X,'WARNING:THIS IS VERY SIMILAR TO A S FORM')
4981 FORMAT(/,5X,'WARNING:THIS IS AN H FORM')
4982 FORMAT(/,5X,'WARNING:THIS IS VERY SIMILAR TO A H FORM')
4991 FORMAT(/,5X,'WARNING:THIS IS AN HS FORM')
4992 FORMAT(/,5X,'WARNING:THIS IS VERY SIMILAR TO A HS FORM')
5010 FORMAT(/,5X,'WARNING:THIS IS A TS FORM')
5011 FORMAT(/,5X,'WARNING:THIS IS VERY SIMILAR TO A TS FORM')
5012 FORMAT(/,5X,'WARNING:THIS IS A T FORM')
5013 FORMAT(/,5X,'WARNING:THIS IS VERY SIMILAR TO A T FORM')
4983 FORMAT(/,5X,'WARNING:THIS IS A',A4,' FORM')
4993 FORMAT(/,5X,'WARNING:THIS IS VERY SIMILAR TO A ',A4,' FORM')
      ELSE
C     ************************
C     DATA FOR 9-E CLASSICAL FORMS
C     ************************
C
      DATA NAMX /'HS','HHS','HC ','TSC','CC','TCC','HC'','TSC'','S','CC
     A'','TS','TCC'','C','CS','TC','TCS'/
      DATA IX1  /1.00,0.0,0.0,0.0
```



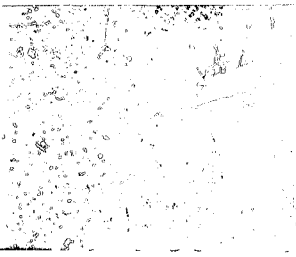
```
      DO 5112 I=1,18
      ANG=100+ 3*100/18*(6*1E0*(I-1))/18
      ANGL=100/18*(3*100*(I-1))/18
      RL= ABS(PHI(I)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)RL= ABS(PHI(3)+360-ANG)
      IF(ANG.GE.720.AND.ANG.LT.1080)RL= ABS(PHI(3)+720-ANG)
      IF(ANG.GE.1080)RL= ABS(PHI(3)+1080-ANG)
      RLL= ABS(PHI(4)-ANGL)
      QX(I)=RL*RLL
5112  CONTINUE
      QXS=10.
      DO 5997 I=1,18
      IF(QX(I).LE.10)QXS=QX(I)
5997  CONTINUE
      IF(QXS.LE.10.AND.YIX(6).GT.0.1)WRITE(2,7016)NAME(6)
      IF(QXS.LE.10.AND.YIX(6).LE.0.1)WRITE(2,7011)NAME(6)
C
      READ(2Y2(7),LE.0.2.OR.YIX(9).LE.0.2.OR.YIX(10).LE.0.2.OR.YIX(15)
     &.LE.0.2.OR.YIX(14).LE.0.2)THEN
      DO 5113 I=1,18
      ANG= 180 + (10*180*(I-1))/18
      ANGL=180 + (6*180*(I-1))/18
      ANGH= (2*1E (I-1))/18
      RL= ABS(PHI(I)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)RL= ABS(PHI(2)+360-ANG)
      IF(ANG.GE.720.AND.ANG.LT.1080)RL= ABS(PHI(2)+720-ANG)
      IF(ANG.GE.1080.AND.ANG.LT.1440)RL= ABS(PHI(2)+1080-ANG)
      IF(ANG.GE.1440.AND.ANG.LT.1800)RL= ABS(PHI(2)+1440-ANG)
      IF(ANG.GE.1800)RL= ABS(PHI(2)+1800-ANG)
      RLL= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)RLL= ABS(PHI(3)+360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LT.1080)RLL= ABS(PHI(3)+720-ANGL)
      IF(ANGL.GE.1080)RLL= ABS(PHI(3)+1080-ANGL)
      RLH= ABS(PHI(4)-ANGH)
      IF(ANGH.GE.360)RLH= ABS(PHI(4)+360-ANGH)
      QX(I)=RL*RLL*RLH
5113  CONTINUE
      QXS=15.03
      DO 5996 I=1,18
      IF(QX(I).LE.15)QXS=QX(I)
5996  CONTINUE
      IF(QXS.LE.15.AND.YIX(7).GT.0.1)WRITE(2,7010)NAME(7)
      IF(QXS.LE.15.AND.YIX(7).LE.0.1)WRITE(2,7011)NAME(7)
      DO 5115 I=1,18
      ANG= (10*180*(I-1))/18
      ANGL=180+(6*180*(I-1))/18
      ANGH=(2*180*(I-1))/18
      RL= ABS(PHI(I)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)RL= ABS(PHI(2)+360-ANG)
      IF(ANG.GE.720.AND.ANG.LT.1080)RL= ABS(PHI(2)+720-ANG)
      IF(ANG.GE.1080.AND.ANG.LT.1440)RL= ABS(PHI(2)+1080-ANG)
      IF(ANG.GE.1440.AND.ANG.LT.1800)RL= ABS(PHI(2)+1440-ANG)
      IF(ANG.GE.1800)RL= ABS(PHI(2)+1800-ANG)
      RLL= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)RLL= ABS(PHI(3)+360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LT.1080)RLL= ABS(PHI(3)+720-ANGL)
      IF(ANGL.GE.1080)RLL= ABS(PHI(3)+1080-ANGL)
      RLH= ABS(PHI(4)-ANGH)
      IF(ANGH.GE.360)RLH= ABS(PHI(4)+360-ANGH)
      QX(I)=RL*RLL*RLH
5115  CONTINUE
      QXS1=15.03
      DO 5994 I=1,18
      IF(QX1(I),LE.15)QXS1=QX1(I)
5994  CONTINUE
      IF(QXS1.LE.15.AND.YIX(9).GT.0.1.AND.YIX(9).LE.0.2)WRITE(2,7010)NAM
```

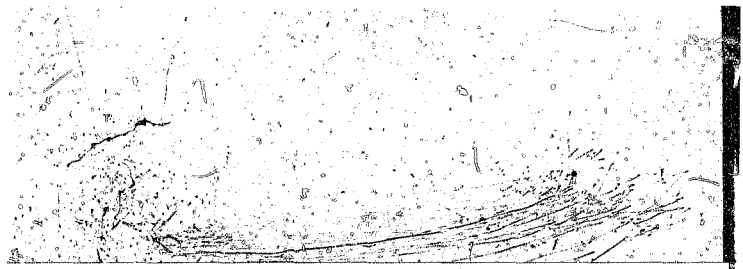





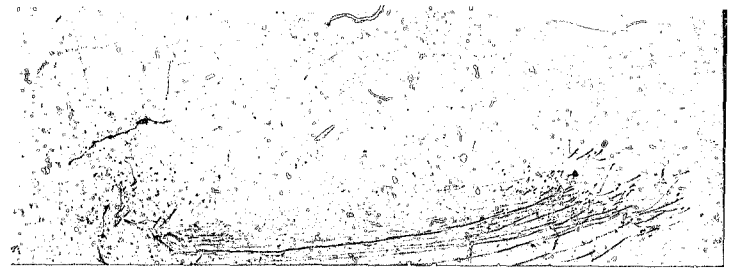
```
     &R(9)
      IF(QX1).LE.15.AND.YIX(9).LE.0.1)WRITE(2,7011)MANK(9)
      IF((QX11.GE.15.AND.YIX(10).GT.0.1.AND.YIX(10).LE.0.2)WRITE(2,7010)M
     &ANK(10)
      IF((QX11.LE.15.AND.YIX(10).LE.0.1)WRITE(2,7011)MANK(10)
C
      DO 5117 I=1,16
      ANG= 180+(10*180*(I-1))/10
      ANGL=(4*180*(I-1))/10
      ANGR=(2*180*(3-1))/10
      RL= ABS(PHI(3)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)RL= ABS(PHI(3)+360-ANG)
      IF(ANG.GE.720.AND.ANG.LT.1080)RL= ABS(PHI(3)+720-ANG)
      IF(ANG.GE.1080.AND.ANG.LT.1440)RL= ABS(PHI(3)+1080-ANG)
      IF(ANG.GE.1440.AND.ANG.LT.1800)RL= ABS(PHI(3)+1440-ANG)
      IF(ANG.GE.1800)RL= ABS(PHI(3)+1800-ANG)
      RLA= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)RLA= ABS(PHI(3)+360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LT.1080)RLA= ABS(PHI(3)+720-ANGL)
      IF(ANGL.GE.1080)RLA= ABS(PHI(3)+1080-ANGL)
      RLR= ABS(PHI(3)-ANGR)
      IF(ANGR.GE.360)RLR= ABS(PHI(3)+360-ANGR)
      QX(3)=RL+RLA+RLR
5117  CONTINUE
      QXI=15.03
      DO 5992 I=1,16
      IF(QX(3).LE.15)QXI=QX(3)
5992  CONTINUE
      IF(QX12.LE.15.AND.YIX(15).GT.0.1.AND.YIX(13).LE.0.2)WRITE(2,7015)M
     &ANK(12)
      IF(QX12.LE.15.AND.YIX(15).LE.0.1)WRITE(2,7011)MANK(15)
      IF(QX12.LE.15.AND.YIX(14).GT.0.1.AND.YIX(14).LE.0.2)WRITE(2,7010)M
     &ANK(14)
```

```
     2F(QXF?.LE.15.AND.YIX(14).LE.0.1)WRITE(2,7011)MANK(14)
     F.LE.F(YIX(8).LE.0.2.OR.YIX(11).LE.0.2.OR.YIX(12).LE.0.2.OR.YIX(15
     4).LE.0.2.OR.YIX(16).LE.0.2)THEN
      DO 5114 I=1,16
      ANG= 180 + 5*180/10+(10*180*(I-1))/10
      ANGL= 180 + 3*180/10+(4*180*(I-1))/10
      ANGR=180/10+ (2*180*(3-1))/10
      RL= ABS(PHI(2)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)RL= ABS(PHI(2)+360-ANG)
      IF(ANG.GE.720.AND.ANG.LT.1080)RL= ABS(PHI(2)+720-ANG)
      IF(ANG.GE.1080.AND.ANG.LT.1440)RL= ABS(PHI(2)+1080-ANG)
      IF(ANG.GE.1440.AND.ANG.LT.1800)RL= ABS(PHI(2)+1440-ANG)
      IF(ANG.GE.1800)RL= ABS(PHI(2)+1800-ANG)
      RLA= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)RLA= ABS(PHI(3)+360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LT.1080)RLA= ABS(PHI(3)+720-ANGL)
      IF(ANGL.GE.1080)RLA= ABS(PHI(3)+1080-ANGL)
      RLR= ABS(PHI(4)-ANGR)
      IF(ANGR.GE.360)RLR= ABS(PHI(4)+360-ANGR)
      QX(3)=RL+RLA+RLR
5114  CONTINUE
      QXI=15.03
      DO 5995 I=1,16
      IF(QX(3).LE.15)QXI=QX(3)
5995  CONTINUE
      IF(QX1.LE.15.AND.YIX(8).GT.0.1)WRITE(2,7010)MANK(8)
      IF(QXI.LE.15.AND.YIX(8).LE.0.1)WRITE(2,7011)MANK(8)
      DO 5114 I=1,16
      ANG= 5*180/10+(10*180*(I-1))/10
      ANGL=180+ 3*180/10+(4*180*(I-1))/10
      ANGR=180/10+(2*180*(3-1))/10
      RL= ABS(PHI(2)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)RL= ABS(PHI(2)+360-ANG)
```

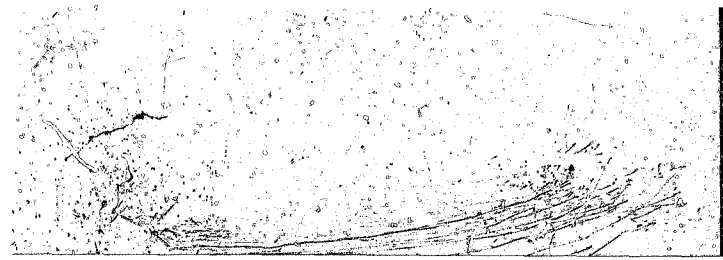


```
      GK(9)
      IF(PIX1.LE.15.AND.YIX(9).LE.0.1)WRITE(2,7011)MARK(9)
      IF(QX11.LE.15.AND.YIX(10).GT.0.1.AND.YIX(10).LE.0.2)WRITE(2,7010)M
     &ARK(10)
      IF(YIX1.LE.13.AND.YIX(10).LE.0.1)WRITE(2,7011)MARK(10)
C
      DO 9117 J=1,16
      ANG= 180+(10*10)*(J-11)/10
      ANGL=(6*180*(J-11)/18
      A=SQR(1.0*180*(J-11))/18
      BL= ABS(PHI(2)-ANG)
      IF(ANG.GE.360.AND.ANG.LE.720)BL= ABS(PHI(3)+360-ANG)
      IF(ANG.GE.720.AND.ANG.LE.1080)BL= ABS(PHI(2)+720-ANG)
      IF(ANG.GE.1080.AND.ANG.LE.1440)BL= ABS(PHI(2)+1080-ANG)
      IF(ANG.GE.1440.AND.ANG.LE.1800)BL= ABS(PHI(2)+1440-ANG)
      IF(ANG.GE.1800)BL= ABS(PHI(2)+1080-ANG)
      BLA= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)BLA= ABS(PHI(3)+360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LE.1080)BLA= ABS(PHI(3)+720-ANGL)
      IF(ANGL.GE.1080)BLA= ABS(PHI(3)+1080-ANGL)
      BLM= ABS(PHI(4)-ANGM)
      IF(ANGM.GE.360)BLM= ABS(PHI(4)+360-ANGM)
      QX2(J)=BL+BLL+BLA+BLM
9117  CONTINUE
      QXX=16.02
      DO 9992 J=1,16
      IF(QX2(J).LE.15)QXX2=QX2(J)
9992  CONTINUE
      IF(QXX2.LE.15.AND.YIX(13).GT.0.1.AND.YIX(13).LE.0.3)WRITE(2,7010)M
     &ARK(13)
      IF(QXX2.LE.15.AND.YIX(13).LE.0.1)WRITE(2,7011)MARK(13)
      IF(QXX2.LE.15.AND.YIX(14).GT.0.1.AND.YIX(14).LE.0.3)WRITE(2,7010)M
     &ARK(14)
      IF(QXX2.LE.15.AND.YIX(14).LE.0.1)WRITE(2,7011)MARK(14)
      ELSEIF(YIX(8).LE.0.2.OR.YIX(11).LE.0.2.OR.YIX(12).LE.0.2.OR.YIX(15
     &).LE.0.2.OR.YIX(16).LE.0.2)THEN
      DO 5114 J=1,16
      ANG= 180 + 6*180/10*(10*180*(J-1))/18
      ANGL= 180 + 3*180/10+(6*180*(J-1))/18
      ANGM=^^     ^^180*(J-11)/18
      BL=                    .LT.720)BL= ABS(PHI(2)+360-ANG)
                             .LT.1080)BL= ABS(PHI(2)+720-ANG)
                             .ANG.LT.1440)BL= ABS(PHI(2)+1080-ANG)
      IF(ANG.                .ANG.LE.1800)BL= ABS(PHI(2)+1440-ANG)
      IF(ANG.GE.1800)BL= ABS(PHI(2)+1080-ANG)
      BLA= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)BLA= ABS(PHI(3)+360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LE.1080)BLA= ABS(PHI(3)+720-ANGL)
      IF(ANGL.GE.1080)BLA= ABS(PHI(3)+1080-ANGL)
      BLM= ABS(PHI(4)-ANGM)
      IF(ANGM.GE.360)BLM= ABS(PHI(4)+360-ANGM)
      QX(J)=BL+BLL+BLA+BLM
5114  CONTINUE
      QXX=15.02
      DO 5995 J=1,16
      IF(QX(J).LE.15)QXX=QX(J)
5995  CONTINUE
      IF(QXX.LE.15.AND.YIX(8).GT.0.1)WRITE(2,7010)MARK(8)
      IF(QXX.LE.15.AND.YIX(8).LE.0.1)WRITE(2,7011)MARK(8)
      DO 8116 J=1,16
      ANG= 9*180/10+(10*180*(J-1))/18
      ANGL=180+ 3*180/10+(6*180*(J-1))/18
      ANGM=180/18+(2*180*(J-11))/18
      BL= ABS(PHI(2)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)BL= ABS(PHI(2)+360-ANG)
```

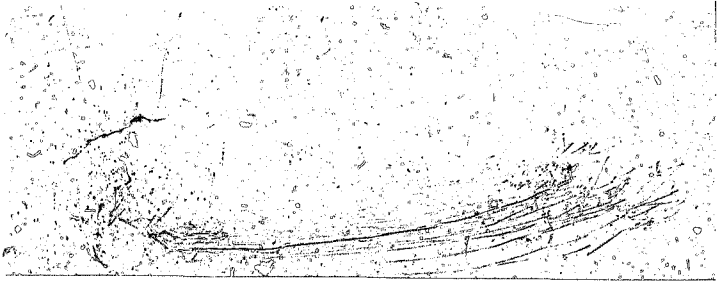


```
      IF(ANG.GE.720.AND.ANG.LT.1080)BL= ABS(PHI(2)*720-ANG)
      IF(ANG.GE.1080.AND.ANG.LT.1440)BL= ABS(PHI(2)*1080-ANG)
      IF(ANG.GE.1440.AND.ANG.LT.1800)BL= ABS(PHI(2)*1440-ANG)
      IF(ANG.GE.1800)BL= ABS(PHI(2)*1800-ANG)
      BLA= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)BLA= ABS(PHI(3)*360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LT.1080)BLA= ABS(PHI(3)*720-ANGL)
      IF(ANGL.GE.1080)BLA= ABS(PHI(3)*1080-ANGL)
      BLH= ABS(PHI(4)-ANGH)
      IF(ANGH.GE.360)BLH= ABS(PHI(4)*360-ANGH)
      QIX3(2)=BL*BLA*BLH
5110  CONTINUE
      pIX3=15.93
      DO 5993 J=1,15
      IF(QIX3(3).LT.15)QIX3=QIX3(J)
5993  CONTINUE
      IF(QIX3.LE.15.AND.YIX(11).GT.0.1.AND.YIX(11).LE.0.2)WRITE(2,7010)N
     &ANK(11)
      IF(QIX3.LE.15.AND.YIX(11).LE.0.1)WRITE(2,7011)BANK(11)
      IF(QIX3.LE.15.AND.YIX(12).GT.0.1.AND.YIX(12).LE.0.2)WRITE(2,7010)N
     &ANK(12)
      IF(QIX3.LE.15.AND.YIX(12).LE.0.2)WRITE(2,7011)BANK(12)
      DO 5115 J=1,15
      ANG= 5*180/10+180*(5*180*(J-1))/15
      ANGL= 5*180/10+(5*180*(J-1))/10
      ANGH=180/10+(2*180*(J-1))/15
      BL= ABS(PHI(2)-ANG)
      IF(ANG.GE.360.AND.ANG.LT.720)BL= ABS(PHI(2)*360-ANG)
      IF(ANG.GE.720.AND.ANG.LT.1080)BL= ABS(PHI(2)*720-ANG)
      IF(ANG.GE.1080.AND.ANG.LE.1440)BL= ABS(PHI(2)*1080-ANG)
      IF(ANG.GE.1440.AND.ANG.LT.1800)BL= ABS(PHI(2)*1440-ANG)
      IF(ANG.GE.1800)BL= ABS(PHI(2)*1800-ANG)
      BLA= ABS(PHI(3)-ANGL)
      IF(ANGL.GE.360.AND.ANGL.LT.720)BLA= ABS(PHI(3)*360-ANGL)
      IF(ANGL.GE.720.AND.ANGL.LE.1080)BLA= ABS(PHI(3)*720-ANGL)
      IF(ANGL.GE.1080)BLA= ABS(PHI(3)*1080-ANGL)
      BLH= ABS(PHI(4)-ANGH)
      IF(ANGH.GE.360)BLH= ABS(PHI(4)*360-ANGH)
      QIX(3)=BL*BLA*BLH
5115  CONTINUE
      QIX4=15.93
      DO 5991 J=1,15
      IF(QIX4(J).LE.15)QIX4=QIX4(J)
5991  CONTINUE
      IF(QIX4.LE.15.AND.YIX(15).GT.0.1.AND.YIX(15).LE.0.2)WRITE(2,7010)N
     &ANK(15)
      IF(QIX4.LE.15.AND.YIX(15).LE.0.1)WRITE(2,7011)BANK(15)
      IF(QIX4.LE.15.AND.YIX(16).GT.0.1.AND.YIX(16).LE.0.2)WRITE(2,7010)N
     &ANK(16)
      IF(QIX4.LE.15.AND.YIX(16).LE.0.1)WRITE(2,7011)BANK(16)
      ELSE
      DO 8000 I=1,4
      IF(YIX(I).LE.0.2.AND.YIX(I).GT.0.1)WRITE(2,7010)*ANK(I)
      IF(YIX(I).LE.0.1)WRITE(2,7011)BANK(I)
8000  CONTINUE
      ENDIF
70;\ FORMAT(/,55,'WARNING:THIS IS A ',A4,' FORM')
7010 FORMAT(/,55,'WARNING:THIS IS VERY SIMILAR TO A ',A4,' FORM')
8001 ENDIF
4994 RETURN
      END
      SUBROUTINE LARGE(Q,PHI,N,NB,B)

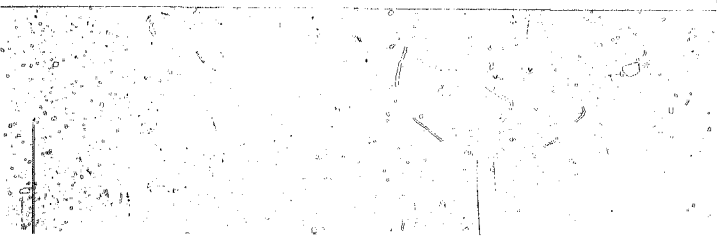
C     ***********************************************************
C     THIS SUBROUTINE FINDS THE PERIPITYE FORMS OF EVEN RINGS
C     WITH MORE THAN 16 RING ATOMS
```



```
C     ***************************************************************
      DIMENSION Q(20),MXE(20),AA(20),EN(20),XIA(20),XID(20)
      REAL B(50),L(50),KMIN(50),LMIN(50)
C
      IF (N.LE.0)THEN
      AA=-1.0
      ELSE
      AA=1.0
      ENDIF
      V=ABS(N)
C
      IF(NN.EQ.10)THEN
      DO 284 M=2,N
      DO 285 I=1,11
      B(I)=4*(I-1)
      L(I)=4*(I-1)+2
285   CONTINUE
      MIN=11
      CALL MINI(KMIN,M,KMIN(M),MS,PHI(K))
      CALL MINI(KLM,L,LMIN(M),MS,PHI(M))
284   CONTINUE
      CALL SOLVE(Q,KMIN,LMIN,M,MS,PHI,XA,IB)
      CALL WRITES(W,XA,IB,P,KMIN,LMIN,XIA,XID,VV)
      WRITE(3,118)MS/2,VV,AA
118   FORMAT(5X,I2,8X,F9.3,6X,F4.1)
      ELSEIF(NN.EQ.12)THEN
      DO 296 M=2,N
      IF(M.EQ.3)THEN
      DO 308 I=1,3
      K(I)=2*(I-1)
      L(I)=2*(I-1)+12
308   CONTINUE
      MIN=3
      ELSE
      DO  295 I=1,13
      K(I)=4*(I-1)
      L(I)=2*(I-1)+4
295   CONTINUE
      MIN=13
      ENDIF
      CALL MINI(MIX,K,KMIN(M),MS,PHI(K))
      CALL MINI(MIX,L,LMIN(M),MS,PHI(M))
296   CONTINUE
      CALL SOLPE(Q,KMIN,LMIN,M,MS,PHI,XA,IB)
      CALL WRITES(W,XA,IB,P,KMIN,LMIN,XIA,XID,VV)
      WRITE(2,117)MS/2,VV,AA
117   FORMAT(5X,I2,6X,F9.3,6X,F4.1)
      ELSEIF(NN.EQ.14)THEN
      DO 302 M=2,N
      DO 301 I=1,15
      K(I)=2*(I-1)
      L(I)=2*(I-1)+2
303   CONTINUE
      MIN=15
      CALL MINI(MIC,K,KMIN(M),MS,PHI(K))
      CALL MINI(MIC,L,LMIN(M),MS,PHI(M))
302   CONTINUE
      CALL SOLVE(Q,KMIN,LMIN,M,MS,PHI,XA,IB)
      CALL WRITES(W,XA,IB,P,KMIN,LMIN,XIA,XID,VV)
      WRITE(3,111)MS/2,VV,AA
111   FORMAT(5X,I2,6X,F9.3,6X,F4.1)
      ELSEIF(NN.EQ.16)THEN
      DO 309 M=2,N
      IF(M.EQ.2.OR.M.EQ.6)THEN
      DO 393 I=1,5
      K(I)=16*(I-1)
```



```
      L(I)=16*(I-1)+8
  393 CONTINUE
      NEC=6
      ESCHIP(N.EQ.4)THEN
      DO 373 I=1,3
      K(I)=32*(I-1)
      L(I)=32*(I-1)+16
  373 CONTINUE
      NEC=3
      ELSE
      DO 383 I=1,9
      K(I)=8*(I-1)
      L(I)=8*(I-1)+6
  383 CONTINUE
      NEC=9
      ENDIF
      CALL MINI(NEC,K,KMIN(N),NB,PHI(N))
      CALL MINI(NEC,L,LMIN(N),NB,PHI(N))
  309 CONTINUE
      CALL SOLVE(Q,KMIN,LMIN,N,NB,PHI,XA,XB)
      CALL WRITES(6,XA,XB,Y,KMIN,LMIN,XXA,XXB,VV)
      WRITE(2,151)NR/2,VV,AA
  151 FORMAT(5X,I2,5X,F8.3,5X,F4.1)
      ELSE
      DO 569 N=2,N
      IF(N.EQ.3.OR.N.EQ.4)THEN
      DO 593 I=1,7
      K(I)=12*(I-1)
      L(I)=12*(I-1)+6
  593 CONTINUE
      NEC=7
      ELSE
      DO 573 I=1,19
      K(I)=4*(I-1)
      L(I)=4*(I-1)+2
  573 CONTINUE
      NEC=19
      ENDIF
      CALL MINI(NEC,K,KMIN(N),NB,PHI(N))
      CALL MINI(NEC,L,LMIN(N),NB,PHI(N))
  509 CONTINUE
      CALL SOLVE(Q,KMIN,LMIN,N,NB,PHI,XA,XB)
      CALL WRITES(N,XA,XB,Y,KMIN,LMIN,XXA,XXB,VV)
      WRITE(2,551)NR/2,VV,AA
  551 FORMAT(5X,I2,5X,F8.3,5X,F4.1)
      ENDIF
      RETURN
      END
```

4.2 Sample Output File

CONFORMATIONAL ANALYSIS OF
AN ILLUSTRATIVE EXAMPLE
8 MEMBERED RING

PUCKERING PARAMETERS

M	Q(M)	PHI(M)
2	1.250	5.00
3	.000	90.00

Q(4)= .000

COEFFICIENTS OF PRIMITIVE FORMS

M	COSFORM	SINFORM
2	1.245	.109
3	.000	.000

NORMALISED COEFFICIENTS

M	COEFFICIENT OF PRIMITIVE FORM	ANGULAR VALUE OF PRIMITIVE FORM
2	.920 [a]	0.0 [b]
	.080	8.0
3	.000	8.0
	.000	4.0
4	.000	−1.0

WARNING : THIS IS VERY SIMILAR TO A BB FORM

a– the coefficients for each m refer to the cos– and sin–forms respectively

b– the phase angles are expressed as k of kπ/2N

APPENDIX 5

CARTESIAN COORDINATES OF THE CLASSICAL FORMS

x	y	z	x	y	z
	BC			22C	
0.0000	1.5071	0.5937	-0.0000	2.2860	0.0197
1.2471	1.4268	-0.2920	1.2245	1.3889	0.8045
2.0434	0.2823	-0.2940	1.8046	0.3652	-0.3864
1.3868	-0.7955	0.5862	1.2179	-1.0998	-0.4076
0.7709	-1.9181	-0.2937	0.5969	-1.7458	0.8012
-0.7801	-1.9127	-0.2914	-0.5911	-1.7516	-0.4959
-1.3080	-0.7885	0.5878	-1.2087	-1.1071	0.8084
-2.0424	0.2934	-0.2928	-1.8071	0.3616	0.4656
-1.2567	1.4317	-0.2998	-1.2310	1.3806	-0.5213
	BC'			TBC"	
0.0000	1.5444	-0.6867	-0.0000	2.2852	0.0013
1.3199	1.7364	0.1004	1.2637	1.3869	-0.2239
1.5876	0.2984	0.6167	1.7072	0.0560	0.6222
1.4605	-0.8375	-0.6317	1.9239	-1.1026	-0.3785
0.7048	-2.1452	0.6572	0.5305	-1.7884	-0.5580
-0.7442	-2.1326	0.6894	-0.5362	-1.7888	0.5983
-1.4557	-0.8523	-0.4298	-1.9236	-1.1023	0.3706
-1.5904	0.2844	0.6160	-1.7073	0.0580	-0.6226
-1.3405	1.7241	0.0969	-1.1640	1.3853	0.2228
	CC			TCC	
0.0000	2.3785	-1.1692	0.0000	1.5299	-0.3670
1.3145	1.6721	0.2885	1.4228	1.0575	-0.8049
1.6135	0.3142	-0.4287	1.7234	0.3561	0.3535
1.4527	-0.9465	0.4619	1.5380	-0.5399	-0.4648
0.7543	-2.1767	-0.2073	0.6606	-2.8882	0.3649
-0.7566	-2.1915	-0.2051	-0.8130	-1.0993	-0.1641
-1.4430	-0.9748	0.4536	-1.7784	0.0434	0.1800
-1.6271	0.2909	-0.4288	-1.5746	0.3967	-0.3624
-1.3535	1.6458	0.2956	-0.8647	1.4095	0.4400
	CC'			TCC"	
0.6400	1.8080	0.6200	0.0000	2.1760	0.0000
1.5280	1.6560	-0.2180	1.1280	1.8000	0.7400
1.7560	0.2000	0.8320	1.9100	0.4400	-0.3100
1.0040	-1.0000	-0.8960	1.1560	-1.6000	0.9150
0.7600	-2.1000	0.4727	0.5700	-1.7400	-0.8250
-0.7600	-2.1000	0.4727	-0.5700	-1.7400	0.8250
-1.0000	-1.0080	-0.8960	-1.1560	-1.6000	-0.9150
-1.7560	0.2080	0.8320	-1.9100	0.4400	0.3100
-1.5280	1.6560	-0.2180	-1.1280	1.8000	-0.7400

x	y	z	x	y	z
	CB			TCB	
-0.7778	0.3462	1.5127	0.0000	2.0000	-0.2195
-0.7542	-0.9407	2.3752	1.0162	1.1410	0.0880
0.5554	-1.2212	3.1403	2.0917	0.4678	0.5200
1.4280	-2.3923	2.6105	1.6271	-0.8175	-0.7675
0.0642	-3.1581	1.2921	0.7544	-1.7920	0.1589
1.2634	-3.6185	3.0057	-0.7544	-1.7920	-0.1589
2.2234	-1.9927	0.6000	-1.6271	-0.8175	0.7675
1.5510	0.0000	0.0000	-2.0917	0.4673	-0.5200
0.0000	0.0000	0.0000	-1.0162	1.1418	-0.8585
	HB			TCB	
-0.6744	-1.2927	0.3740	-0.0000	1.6690	0.5240
-0.1576	-2.5181	-0.5242	0.7621	0.7805	-0.9815
-0.4334	-2.5043	-2.0504	2.0872	0.3038	-0.3315
0.3143	-1.4208	-2.0694	1.7631	-0.7052	0.5805
1.0341	-1.2895	-2.5999	0.2558	-1.0656	0.6403
2.3840	-2.0792	-1.3827	-0.2036	-1.0949	-0.6400
2.2234	-1.2927	0.0000	-1.7289	-0.8213	-0.8617
1.5510	0.0000	0.0000	-2.1144	0.1727	0.3240
0.0000	0.0000	0.0000	-0.8210	0.7464	0.9602
	S			TB	
-0.8496	-1.0963	-0.9536	-0.0000	1.9849	0.0012
-1.4928	-2.0749	-0.1845	1.0246	1.1349	-0.8149
-0.9944	-3.0411	-0.2651	2.0461	0.5139	0.1040
0.5882	-3.4298	-0.1646	1.9295	-1.4317	0.2968
1.2447	-3.3182	-1.8136	0.5142	-1.4520	0.4770
2.1438	-2.0014	-1.4197	-0.4440	-1.4889	-0.4778
2.1348	-1.4369	0.0000	-1.8890	-1.1439	-0.2969
1.5510	0.0000	0.0000	-2.0588	0.3942	-0.1069
0.0000	0.0000	0.0000	-1.1038	1.0787	0.8160
	C			TC	
-0.5618	-1.2198	0.6993	-0.0000	2.0625	0.5914
-1.4932	-2.0784	-0.1991	1.1409	1.2008	0.6852
-0.9896	-3.5392	-0.3595	2.1213	0.6814	-0.2257
0.5532	-3.5856	-0.2046	1.8944	-1.0433	-0.3900
1.2694	-3.3681	-1.5481	0.7686	-1.6663	0.3550
2.1717	-2.8520	-1.4233	-0.6797	-1.6977	-0.3524
2.1348	-1.4369	0.0000	-1.8827	-1.0695	0.3905
1.5510	0.0000	0.0000	-2.1319	0.4511	0.2219
0.0000	0.0000	0.0000	-1.1629	1.2413	-0.4598

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