

$= 0.0020$ (14) and $u_3 = -0.0006$ (15), $(\Delta/\sigma)_{\max} \leq 0.080$. The angle between the dipolar axis and the [100] direction is less than in phase I, being 3° . The centre of gravity stays near the crystalline axis and its distance to the origin has not changed. The residual factors are $R = 0.068$ and $wR = 0.042$ (instead of 0.075 and 0.102 respectively for the continuous cylindrical rotation model).

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Mapping the Conformation of Eight-Membered Rings

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Abstract

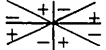
It is demonstrated how puckering parameters, calculated from atomic coordinates, map out the various symmetrical conformations of eight-membered rings onto the surface, defined by a set of tori on a unit sphere. The ten classical forms occur on right toroidal surfaces located at positions, fixed by characteristic values of a polar angle, on the sphere. The mapping represents the geometrical interpretation of five parameters in three-dimensional space. The surface projects as a two-dimensional presentation that can be interpreted directly. Some of the tori have minor radii of zero and contract into circles which represent simple pseudorotational cycles. When the major radius is zero a great circle, perpendicular to the equator of the unit sphere, is generated. A logical nomenclature to distinguish all settings of the possible conformations is proposed. There is one-to-one correspondence with all pseudorotational and interconversion pathways determined before by independent methods.

Introduction

The purpose of this work is to establish a direct procedure to obtain a consistent specification of the conformation of eight-membered cyclic fragments from crystallographic or Cartesian atomic coordinates. The conformation is to be specified in terms of a limited number of possible symmetrical forms, not necessarily the low-energy forms. External steric factors can conceivably freeze any flexible unit into a transitional conformation not normally accessible to the isolated entity. An identification scheme should therefore include all symmetrical forms, irrespective of steric strain.

The possible symmetry elements with respect to the mean plane through a puckered eight-membered ring include vertical axes and planes, and horizontal twofold axes. Possible vertical axes are C_4 , S_4 and C_2 . The full symmetry of possible forms should be consistent with the condition of chemical viability, to exclude arrangements with severely interpenetrating non-bonded atoms

Table 1. Ten symmetrical conformations of eight-membered rings, with the unique endocyclic torsion angles specified in clockwise sequence, starting from the left (or upper left) by reference to the conformational diagram, as defined by mirror planes or axes in the molecular plane; where appropriate, the nomenclature refers to a sequence of subunits with chair and boat-like conformations

(i)	Ring	Symbol	Symmetry	Conformation	Torsion angles (°)
(i)	Crown	Cr	D_{4d}		87.5
(ii)	Saddle	S	S_4	$= ++ =$ $++ =$	70.0, 30.0
(iii)	Boat-boat	BB	D_{2d}	$\pm + - =$ $- = + \pm$	52.5
(iv)	Boat	B	D_{2d}	$0 + 0 =$ $= + 0$	73.5
(v)	Twist-chair-chair	TCC	D_2	$+ - - +$ $+ - - +$ $+ - - +$	56.2, -82.4, 114.6
(vi)	Chair-chair	CC	C_{2v}	$\pm = \pm =$ $- + - +$	66.0, -105.2
(vii)	Chair	C	C_{2h}	$0 + 0 =$ $+ - + -$ $0 + 0 =$	119.9, -76.2
(viii)	Twist-chair	TC	C_{2h}	$+ - + -$ $+ - + -$	37.3, -109.3
(ix)	Twist-boat-chair	TBC	C_2	$+ - + + -$ $- + - + -$	88.0, -93.2, 51.9, 44.8, -115.6
(x)	Boat-chair	BC	C_s	$\pm \pm = \pm$ $- - + -$	65.0, 44.7, -102.2, 65.0

and implausible bond angles. Ten viable forms and their point groups are listed, roughly in order of decreasing symmetry, in Table 1.

Puckering modes, reflecting atomic displacements from the mean molecular plane, are commonly defined in terms of a 2π phase cycle which includes inversion. Equivalent forms of eight-membered rings in pseudo-rotational relationship are therefore separated by phase intervals of $\pi/8$. Since transitional forms occur at intermediate positions, symmetrical conformations alternate at intervals of $\pi/16$. This condition, rather than minimum energy, was preferred to fix the atomic coordinates of reference conformations at phase angles of $n\pi/16$. The final coordinates listed in Table 2 were derived by modification of the internal coordinates given by Hendrickson (1964, 1967), using constant bond lengths of 1.54 Å in the program *SHELX76* (Sheldrick, 1978). *ORTEP* plots of these canonical forms are shown in Fig. 1.

The initial definition of S_4 configurations in terms of the coordinates proposed by Hendrickson (1967) had to be modified in order to repeat at phase intervals of $\pi/16$. As eventually defined the strain energies of the S_4 ,

B and BB conformations were calculated, using the molecular-mechanics program and hydrocarbon force field due to Boyd (1968), as 26.0, 25.0 and 18.0 kJ mol⁻¹, respectively. These appear to be closer to the expected ratios than the relative strain energies, calculated by Hendrickson (1967) as 0.9:10.3:1.4. The conformation, defined by the torsion angles $\omega_1 = -\omega_3 = \omega_5 = -\omega_7 = 70^\circ$ and $\omega_2 = -\omega_4 = \omega_6 = -\omega_8 = 30^\circ$, is concluded to be the better description of the S_4 type.

The mapping of different conformations was achieved in terms of puckering parameters (Cremer & Pople, 1975) as described before for six- (Boeyens, 1978) and seven-membered rings (Boessenkool & Boeyens, 1980) and reviewed (Boeyens & Dobson, 1987) for medium-sized rings.

Method of study

A puckering analysis of each conformation was performed by computing the appropriate amplitudes and angles of pucker, consistent with the scheme of Cremer & Pople (1975), and based on the Cartesian

Table 2. Coordinates of the conformations of eight-membered rings

x	y	z	x	y	z
	BC			TCC	
-0.6713	-0.9829	-0.9770	-0.6747	0.5813	1.2564
-0.4597	-0.7450	-2.4950	-0.8174	-0.3811	2.4643
0.9944	-0.9017	-3.0115	0.5115	-1.0022	2.9680
1.7698	-2.1413	-2.4940	0.9953	-2.2455	2.1770
2.7963	-1.8771	-1.3617	2.3227	-2.0781	1.3924
2.2336	-1.3927	0.0000	2.2092	-1.4044	0.0000
1.5510	0.0000	0.0000	1.5510	0.0000	0.0000
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	TBC			TC	
-0.7283	-0.9468	1.1252	-0.6842	0.4475	-1.3234
-1.0904	-2.4000	0.7218	0.0174	0.0141	-2.6370
0.0198	-3.4618	0.9357	0.6549	-1.3998	-2.6329
0.9348	-3.7439	-0.2884	2.2059	-1.3925	-2.6305
1.6286	-2.4222	-0.9898	2.8859	-1.8497	-1.3136
2.2336	-1.3927	0.0000	2.1846	-1.4157	0.0000
1.5510	0.0000	0.0000	1.5510	0.0000	0.0000
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	S			C	
-0.7359	-0.5228	-1.4086	-0.7038	-1.3887	-0.0070
0.0547	-0.3281	-2.7287	-0.6974	-2.1260	-1.3715
1.3589	-1.1447	-2.9236	0.0105	-3.5060	-1.3676
1.4310	-2.5317	-2.2332	1.5615	-3.5018	-1.3639
1.5374	-2.5704	-0.6863	2.2619	-2.1179	-1.3645
2.2578	-1.3806	0.0000	2.2578	-1.3806	0.0000
1.5510	0.0000	0.0000	1.5510	0.0000	0.0000
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	Crown			BB	
-0.6814	-0.0694	1.4034	-0.7320	-0.8529	-1.0770
-0.9185	-1.4907	1.9774	-0.3620	-0.6310	-2.5660
0.2542	-2.1004	2.7890	1.1290	-0.7130	-2.9860
1.3171	-2.8771	1.9690	1.9380	-1.9680	-2.5660
2.4818	-2.0312	1.3915	1.913	-2.4100	-1.0790
2.2336	-1.3927	0.0000	2.290	-1.3610	0.0000
1.5510	0.0000	0.0000	1.5540	0.0040	0.0040
0.0000	0.0000	0.0000	0.0030	-0.0030	-0.0070
	CC			B	
-0.6577	0.3606	1.3650	-0.7298	-0.3984	1.3160
-0.4131	-0.6617	2.5055	0.1400	-0.7586	2.5485
1.0610	-0.7822	2.9727	0.8740	-2.1250	2.5474
1.7964	-2.0627	2.4982	0.6934	-3.0476	1.3138
2.8219	-1.8441	1.3553	1.4194	-2.6572	0.0000
2.2092	-1.4044	0.0000	2.2818	-1.3681	0.0000
1.5510	0.0000	0.0000	1.5510	0.0000	0.0000
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

coordinates of Table 2. In summary, the conformation of an n -membered ring is uniquely defined by its $n-3$ puckering parameters. The n atoms in a puckered ring are specified by Cartesian coordinates (x_j, y_j, z_j) or position vectors R_j , with the origin chosen at the geometrical centre, such that $\sum_{j=1}^n R_j = 0$, with the mean plane defined for the $\sum z_j = 0$, and the two additional conditions to avoid trivial rotation,

$$\sum z_j \cos 2\pi(j-1)/n = 0$$

$$\sum z_j \sin 2\pi(j-1)/n = 0.$$

Puckering coordinates of equivalent forms, related by pseudorotation, were obtained by consistent rotation of the atom numbers and inversion of the z_j puckering coordinates of each ring.

The standard puckering analysis yields three amplitudes (q_2, q_3, q_4) and two phase angles (φ_2, φ_3). These parameters can map a conformation onto a surface defined by five independent variables. For even-

membered rings the puckering coordinates are defined by

$$q_m \cos \varphi_m = \sqrt{(2/n)} \sum z_j \cos \{2\pi m(j-1)/n\}$$

$$q_m \sin \varphi_m = -\sqrt{(2/n)} \sum z_j \sin \{2\pi m(j-1)/n\},$$

where $m = 2, 3, \dots, (n/2-1)$, $q_m > 0$, $0 < \varphi_m < 2\pi$ and $q_{n/2} = 1/\sqrt{(n)} \sum (-1)^j z_j$, which may have either sign.

In principal, it is possible to map the five parameters in two dimensions by first reducing the number of amplitudes through the introduction of a third angular variable, $0 < \theta < \pi$, such that

$$\cos \theta = q_4 / (\sum_m q_m^2)^{1/2} = q_4 / Q,$$

as shown in Fig. 2.

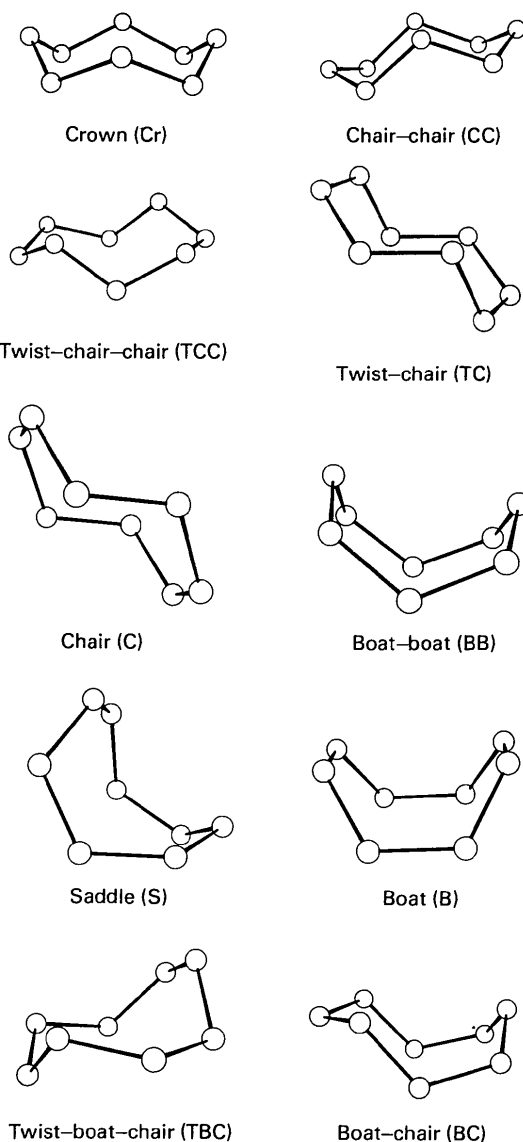


Fig. 1. ORTEP plots of the canonical forms.

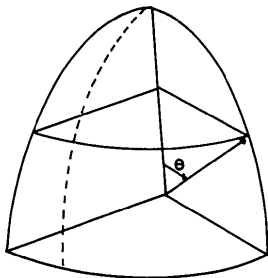
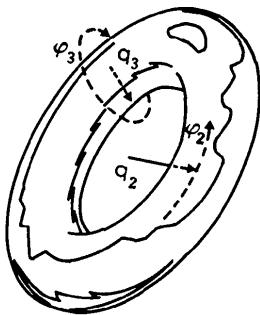
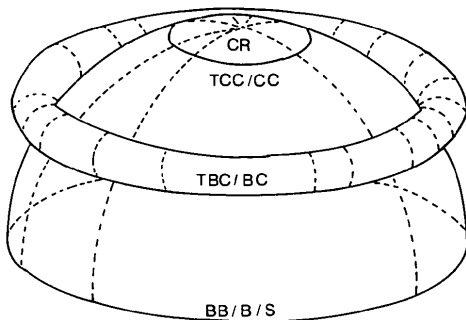
Fig. 2. The polar angle θ .Fig. 3. The torus defined by q_2 , q_3 , ϕ_2 and ϕ_3 .

Fig. 4. The three-dimensional surface for simultaneous mapping of all possible conformations.

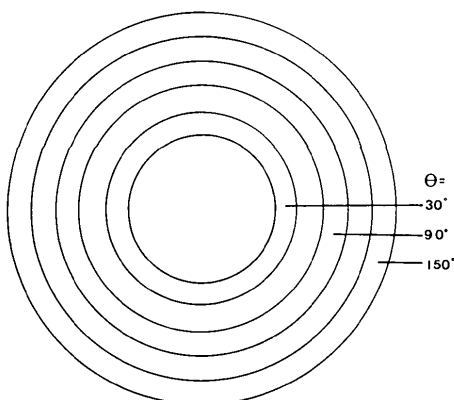
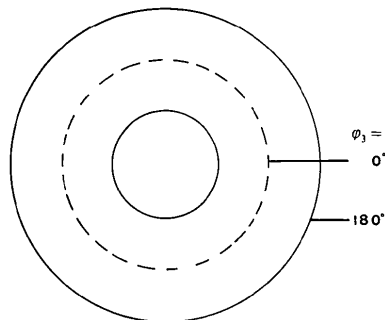
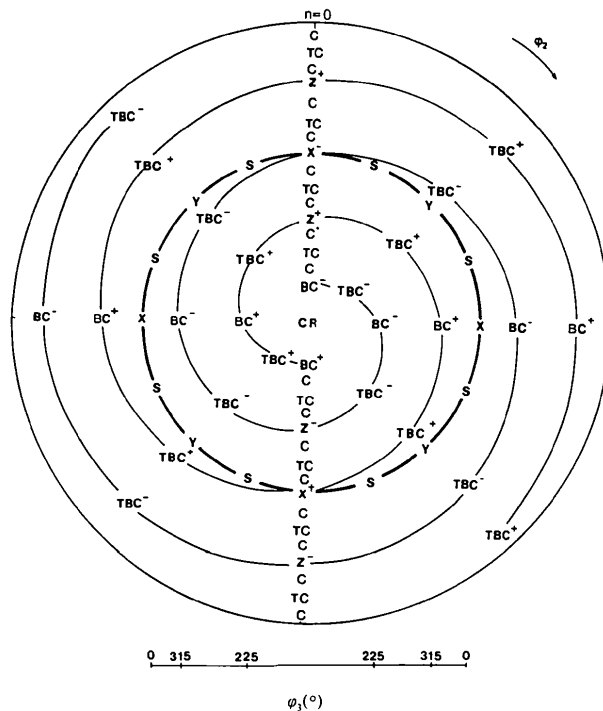


Fig. 5. A polar projection showing concentric tori.

Table 3. Characteristic puckering amplitudes (q_m) and polar angles (θ) of the ten idealized symmetrical conformations

Ring	q_2 (Å)	q_3 (Å)	q_4 (Å)	θ (°)
CR	0	0	± 0.87	0,180
S	1.63	0	0	90
BB	1.54	0	0	90
B	1.64	0	0	90
TCC	0.46	0	± 0.80	30,150
CC	0.46	0	± 0.80	30,150
C	0	0.96	0	90
TC	0	0.96	0	90
TBC	0.67	0.82	0.28	75,105
BC	1.07	0.61	0.33	75,105

Fig. 6. A projection of all the tori with their radial axes along the $\phi_3 = 0$ circle.Fig. 7. The positions of all symmetrical conformations in two-dimensional projection. The + superscript refers to forms where θ is less than 90° and the - superscript refers to forms where θ is greater than 90° . $Y = (TCC^\pm, B)$, $X^+ = (CC^\pm, BB, BC^+)$, $X^- = (CC^\pm, BB, BC^-)$, $Z^+ = (TC, BC^+)$ and $Z^- = (TC, BC^-)$.

The puckering amplitudes and derived θ for the symmetrical forms are listed in Table 3. It is noted that for $q_m = 0$ the parameter φ_m has no meaning. Apart from the boat-chair forms, therefore, all other conformations can be mapped by angular coordinates θ and $\varphi_{2,3}$ on the surface of a sphere of radius $q_{2,3}$. To accommodate the exceptional forms would require definition of a suitable surface with two extra parameters, centred on the sphere at $\theta = 75^\circ$ and 105° . This defines a torus, as shown in Fig. 3. It is noted that for the chair forms (C and TC) the second, major radius of the torus contracts to zero and the resulting great circle lies on a meridian and not along the equator.

By analogy with the previous argument, a surface for simultaneous mapping of all possible conformations

can now be constructed. Define an arbitrary unit sphere, normalized to Q , with polar angle $0 \leq \theta \leq \pi$. At each value of θ , define a torus in terms of the parameters q_2, q_3, φ_2 and φ_3 , so that θ defines the plane through the central track of the associated torus, shown in Fig. 4. In this representation the radius q_2 has no operational meaning and is tied to θ . The radius q_3 can be chosen for convenience and so as to avoid confusing overlap.

The composite surface can now be viewed in projection. A standard polar projection would separate the tori at different θ positions as shown in Fig. 5. Alternatively, a projection along the surface of the sphere would place all tori at the same position, with their radial axes along the $\varphi_3 = 0$ circle, shown in Fig. 6.

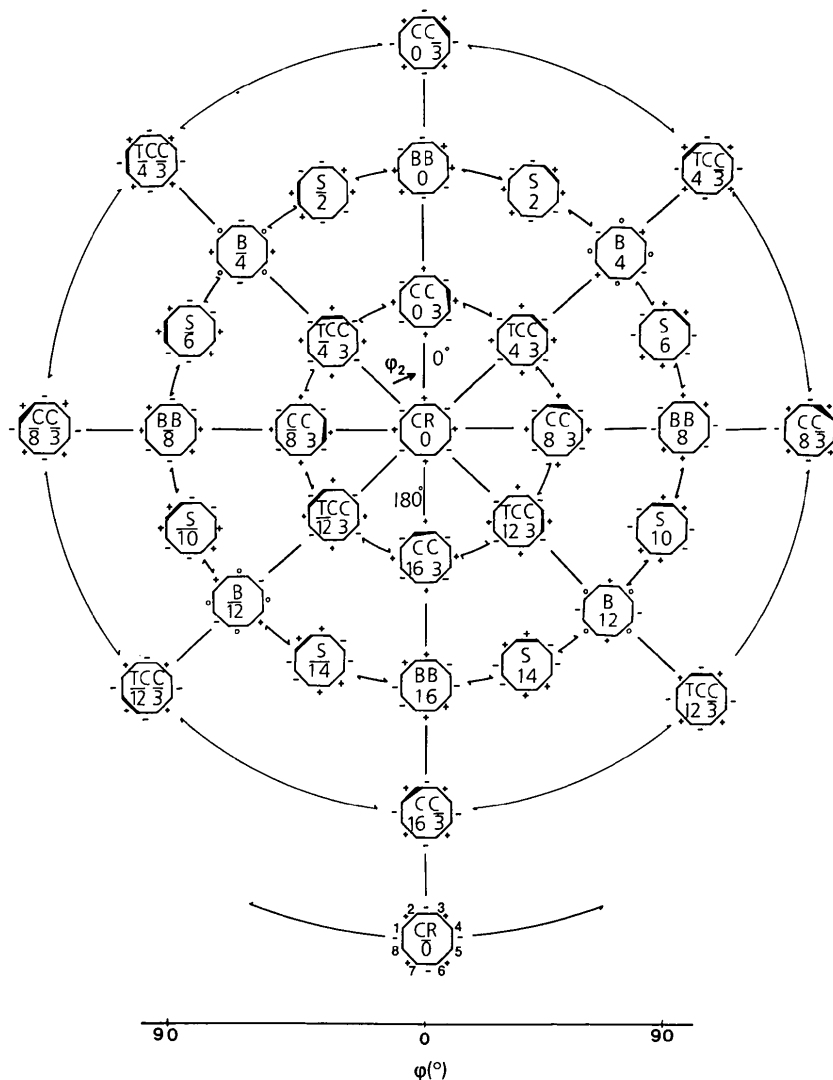


Fig. 8. Pseudorotational cycles of the B-BB, CC-TCC and crown forms. The magnitudes of the torsion angles are given uniquely by the sequence of signs for the B, BB and crown forms. The bold sides of the TCC symbols indicate a torsion angle of magnitude 56.2° about that bond. The bold wedges of the CC symbols indicate a torsion angle of 105° . The point of the wedge lies adjacent to the torsion angle of -105° . The bold side of the S symbol indicates a torsion angle of 70° .

This was found to be the least confusing representation. The positions of all symmetrical conformations in this mode of projection are shown in Fig. 7.

The conformations that map onto toroidal surfaces are uniquely resolved, but not those appearing along limiting circles. Overlap occurs at the positions marked *X*, *Y* or *Z*. The coincident forms are in all cases uniquely distinguished by different θ values. The phase angle φ_3 is measured radially from the zero circle, *X*–*Y*–*S*.

It is of interest to note that the surface described here is a combination of the surfaces used in the analysis of six- and seven-membered-ring conformations (Boeyens, 1978; Boessenkool & Boeyens, 1980). Instead of mapping conformations onto a sphere as for six-membered rings, or onto a torus as for seven-membered rings, the conformations of eight-membered rings are mapped onto tori which lie at specific polar angles on a sphere.

Results and discussion

The interrelationships between all conformational types are summarized by Fig. 7, but to appreciate better the detailed characteristics of each conformational family these should be examined in separate projections. The φ_2 – θ polar projection shown in Fig. 8 shows the relationship of the pseudorotational cycles B–BB and CC–TCC to each other and to the crown form. The saddle forms are interspersed between boat and boat–boat forms, but since it has no symmetry element in the mean plane it is not formally part of the pseudorotational process although physically it represents an intermediate form, as illustrated in Fig. 9. The TC–C pseudorotational cycle defined by φ_3 at $\theta = 90^\circ$ is shown in Fig. 10. The BC–TBC family that maps onto the tori at $\theta = 75$ and 105° is projected as a function of φ_2 and φ_3 in Fig. 11.

The nomenclature introduced by Figs. 9 to 11 is based on the integers that specify the angular positions of the canonical conformations: $\varphi_2 = h\pi/16$; $\varphi_3 = k\pi/16$ and $\theta = l\pi/16$. The latter has only positive values, $0 \leq l \leq 16$, but for the φ indices, $|h, k| \leq 16$. Positive values for all indices are obtained by defining $\bar{h}, \bar{k} = 32 - h, k$. Most forms are uniquely distinguished by no more than two indices and the complete set of conformations is made up of CR(*l*), S(*h*), BB(*h*), B(*h*), TCC(*h, l*), CC(*h, l*), C(*k*), TC(*k*), TBC(*h, k*), BC(*h, k*). Enantiomeric forms occur at

$$\varphi'_2 = \varphi_2 + \pi = \varphi_2(h + 16)$$

$$\varphi'_3 = \varphi_3(k + 16)$$

$$\theta' = \pi - \theta = \theta(16 - l)$$

The torsion angle at any given bond fluctuates gradually from a maximum (positive) value, through zero to a minimum (negative) value, along a pseudo-

rotational pathway. In the BC/TBC cycle however, there is no well defined symmetrical form with zero torsion angles and these flip, at regular intervals, from positive to negative values and back. In the CC/TCC cycle, the atoms remain in the same relative position with respect to the mean plane and axial substituents never take up equatorial positions (Hendrickson, 1967). The pseudorotational cycle therefore defines a type of breathing mode, where a CC form distorts towards TCC without flipping atoms through the mean plane.

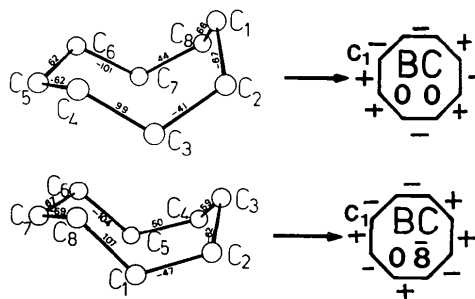
To ensure unique nomenclature for specific conformations an unambiguous numbering scheme is required. The simplest scheme (Boeyens, 1978) is to number the ring atoms in clockwise progression starting from a suitable unique atom, unless a standard chemical numbering scheme exists.

Application

Eleven eight-membered rings from crystallographic studies in the literature were analysed using the methods described here. The calculated puckering parameters, in each case, were used to map the data onto the conformational surface. Calculated θ parameters were used first to identify the appropriate projection, and conformations were then derived by matching the relevant phase angles φ_2 and/or φ_3 . Calculated puckering amplitudes were used as a final check on the assignment. The puckering parameters are listed in Table 4, in the same sequence as discussed below.

- (i) *cis*-Cyclooctane-1,5-diol
- (ii) Cyclooctane-1,5-dione (Miller & McPhail, 1979)

The thermodynamically preferred boat–chair conformation is reported for both rings. This assignment is confirmed by the puckering analysis, as shown diagrammatically below.



- (iii) Dichloro(5-methyl-1-thia-5-azacyclooctane)-palladium(II) (Hirschon, Musker, Olmstead & Dallas, 1981)

The authors concluded 'TACO (the ring) acts as a bidentate ligand by coordinating to the palladium atom through both nitrogen and sulphur atoms and adopting

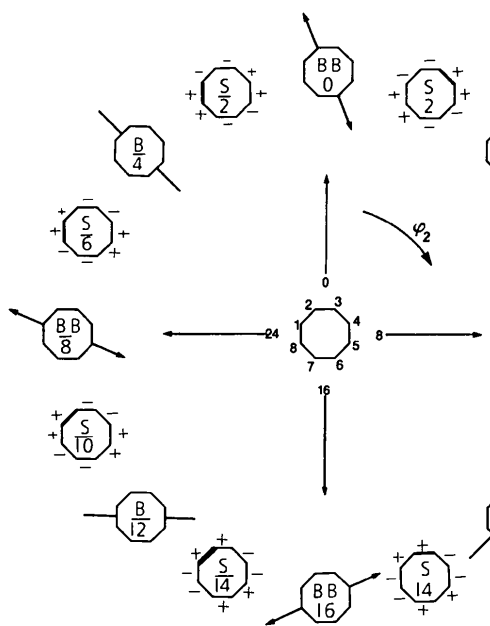


Fig. 9. Passage of the symmetry elements in the B-BB itinerary.

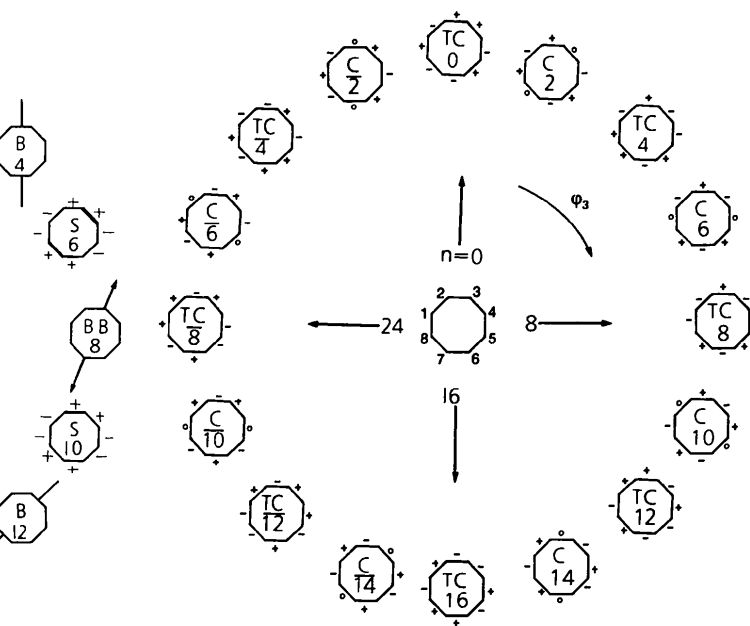


Fig. 10. The TC-C pseudorotational cycle.

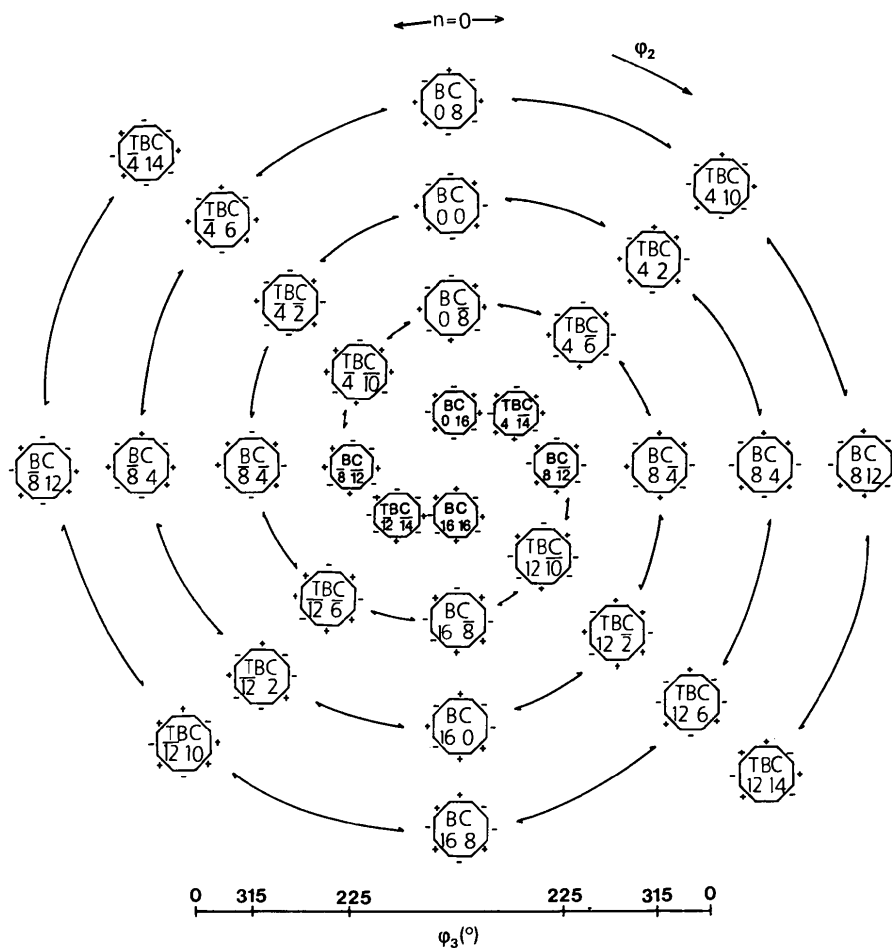
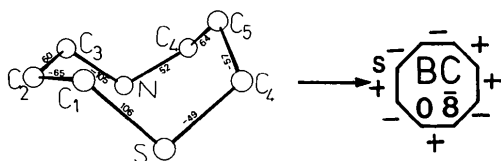


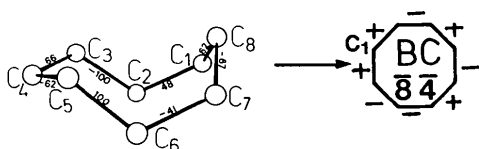
Fig. 11. A projection of the tori at $\theta = 75$ and 105° showing the BC-TBC pseudorotational cycles.

a boat-chair conformation'. This is supported by puckering analysis.



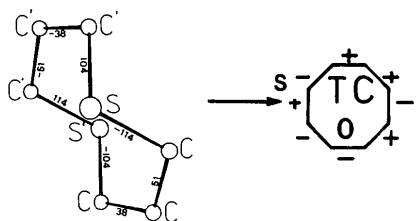
(iv) *trans*-1,4-Dichlorocyclooctane (Egmond & Romers, 1969)

The puckering analysis agrees with the 'boat-chair' assignment.



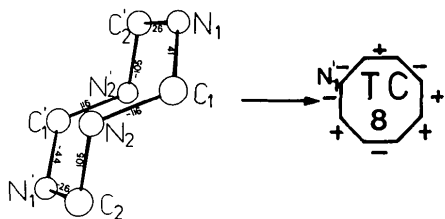
(v) 1,5-Dithiacyclooctane-3,7-dione bis(ethylene acetal) (Olmstead & Musker, 1981)

It was found that 'the compound must lie on a centre of inversion. Molecular models show that there are many dissimilar conformations that preserve the centre of symmetry'. Puckering analysis indicates the twist-chair conformation, TC0.



(vi) 1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (Santoro, Choi & Abel, 1975)

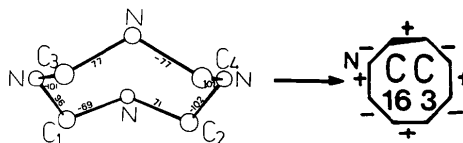
The conformation was described as twist-chair and confirmed by the puckering analysis.



(vii) δ -HMX (Cobbledick & Small, 1974)

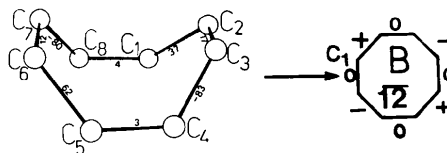
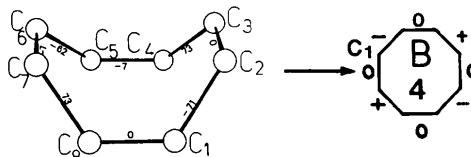
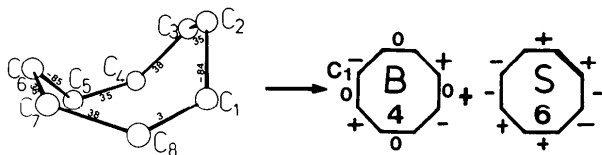
The conformation was described by the observation that 'the four carbon atoms of the eight-membered ring are coplanar'. The puckering analysis indicates a

conformation between the crown and CC 16 3 forms, at $\theta = 15^\circ$.



(viii), (ix) *cis-cis* Cyclooctadiene complexes of CuCl and RhCl, respectively (Boeyens, Denner, Orchard, Rencken & Rose, 1986)

It was stated that 'both types of coordination require a boat-like conformation of *cc*-COD. It is interesting to note that the boat conformation occurs in the rhodium complex and the twist-boat conformation in the copper complex'. Puckering analysis substantiates the former conclusion and the two independent rings of the rhodium complex have enantiomeric boat conformations B4 and B12. The conformation of the ring in the copper complex is intermediate between boat and saddle forms.



(x) Ni(DACO)₂(ClO₄)₂·2H₂O (Boeyens, Fox & Hancock, 1984)

It is stated that previous workers 'had found a planar eight-membered ring folded along the 1,5-axis. Re-interpretation of the X-ray data revealed molecular disorder and the above structure, was suggested. This conformation is in agreement with other DACO complexes...'. Puckering analysis now confirms this as a reasonable conformation.

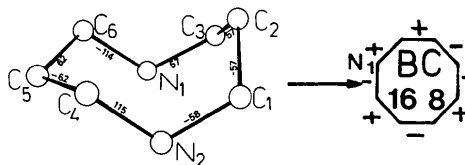
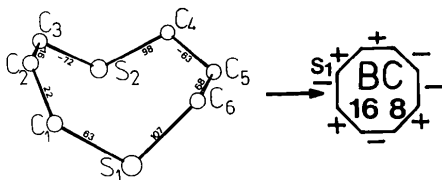


Table 4. *Puckering parameters of some eight-membered rings from the literature, according to the atomic numbering and compound identification in the text.*

Compound	q_2 (Å)	q_3 (Å)	θ (°)	φ_2 (°)	φ_3 (°)
(i)	1.05	0.58	105	0	1
(ii)	0.95	0.62	73	358	269
(iii)	1.05	0.59	75	360	293
(iv)	1.09	0.57	105	268	313
(v)	0.0	1.23	90	326	3
(vi)	0.0	0.86	90	84	86
(vii)	0.22	0.05	15	178	206
(viii)	1.30	0.0	83	59	210
(ix)a	1.49	0.0	90	45	27
(ix)b	1.51	0.0	88	221	73

(xi) *Bis(1,5-dithiacyclooctane)nickel(II) chloride* (Hill & Hope, 1974)

This dithioether ligand is analogous to DACO (x). The authors stated that 'the ligand molecule assumes a boatlike conformation. The disorder features associated with C(2) indicate that the ligand adopts both chair-boat and double-chair conformations, the C(2) can assume two different positions'. The large anisotropic vibrations, however, suggest additional disorder and reinterpretation of the data by the method of Boeyens, Fox & Hancock (1984) may be necessary to establish the exact conformation. An approximate puckering analysis was calculated from averaged fractional coordinates confirming the unlikely conformation identified before (BC 16,8 \leftrightarrow CC 16,3).



Conclusion

Only by rare coincidence could one expect calculated puckering parameters to match any of the classical symmetrical conformations exactly. In many cases the match is close enough to identify a related symmetrical type unambiguously, but more often an intermediate configuration is indicated. In these important cases it would be convenient to represent the actual conformation as a linear combination of canonical forms. Alternatively this could be done more simply in terms of parameters that measure the deviation of an actual form from symmetrical types in the neighbourhood. This is conveniently defined as

$$\Delta X = [\sum (x_i - x'_i)^2]^{1/2},$$

where the x_i represent actual puckering parameters and x'_i are the puckering parameters for the fully symmetrical canonical form, X . This expression is related to

the parameter proposed by Miller & McPhail (1979) to quantify deviations from full symmetry.

Each set of puckering parameters consists of q_2 , q_3 , φ_2 , φ_3 and θ , with all angular parameters measured in radians. The formula does not provide an absolute index which is valid for general forms. It should be used only to compare the relative weights of related contributing forms, since the elements in the expression are not vectorial measures on the hypersurface. It is noted that ΔX , being sensitive to degree of pucker (Δq_i), is not to be interpreted in terms of conformations only.

Despite the limitations, ΔX is a useful guide in the description of intermediate forms. Applied to the previous examples where intermediate configurations were inferred, one calculates deviations for compounds (vii), (viii) and (xi) of

$$\text{(vii): } \Delta(\text{CC}) = 0.64, \Delta(\text{CR}) = 0.34$$

$$\text{(viii): } \Delta(\text{S}) = 0.37, \Delta(\text{B}) = 0.43$$

$$\text{(xi): } \Delta(\text{BC}) = 0.44, \Delta(\text{CC}) = 0.97.$$

This identifies the respective dominant forms as 65% CR, 54% S and 69% BC.

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