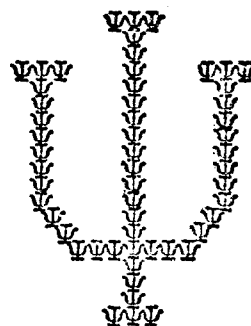


QCPE

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R I N G

A coordinate transformation program
for evaluating the degree and type
of puckering of a ring compound

b y

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Introduction

RING is a coordinate transformation program written to provide the quantitative data which aid the interpretation of ring conformations. These data are termed ring puckering coordinates for they describe the nonplanar character of a ring in a unique way: a set of puckering amplitudes q_m and phase angles ϕ_m determines the amount and type of puckering. A ring formed by N atoms has a total of $(N-3)$ puckering coordinates, i.e. the three-membered ring is always planar (q_1 and ϕ_1 are not defined), the four-membered ring has just one possible puckering mode described by the amplitude q_2 , the puckered five-membered ring conformations are characterized by the amplitude-phase pair (q_2, ϕ_2) , the six-membered ring forms are defined by the pair (q_2, ϕ_2) and an additional amplitude q_3 , etc. For odd-membered rings there are

$\frac{1}{2} (N-3)$ amplitude-phase pairs (q_m, ϕ_m) with

$m = 2, 3, \dots (N-1)/2.$

For even-membered rings there are

$\frac{1}{2} (N-4)$ amplitude-phase pairs (q_m, ϕ_m) with

$$m = 2, 3, \dots (N-2)/2$$

and an additional puckering amplitude $q_{(N/2)}$.

The N perpendicular displacements z_j ($j = 1, 2, \dots, N$) of a puckered ring from a reference plane, which is chosen as the mean ring plane, can be expressed in terms of the puckering coordinates q_m and ϕ_m :

$$z_j = \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_{m=2}^{\frac{1}{2}(N-1)} q_m \cos \left[\phi_m + 2m(j-1)/N \right] ; N \text{ is odd}$$

$$z_j = \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_{m=2}^{\frac{1}{2}(N-2)} q_m \cos \left[\phi_m + 2m(j-1)/N \right] + \left(\frac{1}{N}\right)^{\frac{1}{2}} q_{(N/2)} (-1)^{(j-1)} ; N \text{ is even}$$

The mean ring plane ($z=0$) is not identical with a least square plane found by minimization of $\sum z_j^2$. The displacements

z_j of a least square plane cannot generally be expressed in closed algebraic equations.

The mathematical procedure to determine the mean ring plane and to find the puckering coordinates has been described elsewhere.¹⁾ The interpretation of the puckering coordinates is straightforward. Each (q, ϕ) -pair with $q > 0$ and $0 \leq \phi \leq 2\pi$ corresponds to a conformation on a pseudorotation circuit of the N-membered ring in question. The single puckering amplitude $q_{(N/2)}$ for even-membered rings can take both positive and negative values, the latter of which correspond to conformations that can be thought of as the result of an inversion process of a form with positive $q_{(N/2)}$.

Every ring conformation is a point of a $(N-3)$ -dimensional hypersphere for $N \geq 7$, a point of a sphere for $N=6$, a point of a plane for $N=5$ or a point of a line for $N=4$.

Because of reasons of interpretation it turns out to be valuable to use the spherical ($N=6$) or hyperspherical ($N > 6$) coordinate set (Q, ϕ_m, θ_m) rather than the (q_m, ϕ_m) set.¹⁾ Therefore, the total puckering amplitude Q and the "polar angles" θ_m are also calculated by program *RING*.

If once a mean ring plane is determined the relative orientations of the ring substituent bonds with regard to this plane can be calculated. We have suggested²⁾ that those bonds which are close to perpendicular to the mean ring plane are called g-axial (g for geometrical) and those which are almost parallel to this plane g-equatorial. Bonds whose orientation is neither g-axial nor g-equatorial but intermediate are termed g-inclinal because

they are inclined with regard to the mean plane. Such a definition generalized the Barton-Hassel-Pitzer-Prelog terminology of the C-H bonds in cyclohexane³⁾ for all rings in a well-defined manner. It avoids those terms which are only useful for certain conformations of certain rings. Program *RING* evaluates the parameters α and β which give the orientation of substituent bond as illustrated by figure 1.

INPUT

The input consists of five parts which are explained in the following paragraphs.

1. Title card: FORMAT(20A4)

The comment chosen by the user to identify the particular run may be as long as 80 columns.

2. Option card: FORMAT(3I2)

N	Number of ring atoms (N is limited to $4 \leq N \leq 15$)
ICELL	= 0; the coordinates which will be read in are already cartesian coordinates. = 1; cell coordinates will be read in which have to be transformed to cartesian coordinates.
ISUB	= 0; only the coordinates of the N ring atoms will be read in. = 1; the coordinates of the ring substituents will follow those of the ring atoms. An additional card (see 4) is necessary to determine the number of substituent atoms. This number must not exceed (45-N).

= 2; the polar angles α and β which determine the orientation of a particular substituent bond will also be evaluated.

= 3; in addition, the angles α and β of the ring bonds will be calculated.

3. Cell card (only if ICELL=1): FORMAT(6F10.5)

The cell data a,b,c, α , β and γ (in this order) have to be read in. They are used for the transformation from crystallographic cell coordinates to cartesian coordinates.

4. Substituent card (only if ISUB \neq 0): FORMAT(15I2)

If ISUB is equal to 1 the total number of atoms not incorporated into the ring, i.e. the number of substituent atoms, has to be read in. If ISUB is greater than 1 only those atoms which are directly bonded to the ring will be considered in the program. For each of the N ring atoms an integer value of 0, 1 or 2 specifying the number of atoms directly bonded has to be read in.

5. Coordinate cards: FORMAT(3F10.5)

The final set of cards read in may consist of two subsets. The first subset of cards contains the (cell or cartesian) coordinates of the ring atoms, each atom one card with the X-, Y- and Z-values. The order of the cards corresponds to the numbering of the ring atoms. If ISUB is 1 the second subset contains the coordinate cards of all substituent atoms. For ISUB=2 or 3 all those

cards have to be eliminated from this subset which correspond to atoms not directly bonded to one of the ring atoms. Only up to 2 atoms, i.e. NSUB(I) = 0, 1 or 2, can be considered as directly bonded.

The first data deck can be followed by any number of further data decks. Termination is affected by \$\$ in the two first columns of a title card.

OUTPUT

Depending on the options chosen the user will get output in varying degrees. The initial output will consist of a header line giving the size of the ring and the identification of the run, the cell parameters if cell coordinates were read in and the input coordinates.

In the next part the transformed coordinates and the puckering coordinates are printed out. An additional line shows whether the two conditions

$$\sum_j^N z_j = 0 \quad \text{and} \quad \sum_m q_m^2 = \sum_j^N z_j^2$$

are fulfilled.

For ISUB = 2 (or 3) the third part of the output contains the polar angles α and β of the substituent bonds (and ring bonds). For each substituent it is shown whether it has to be named axial, equatorial or inclinal. The prefix t- indicates that the substituent is located on the top side, a b- that it is on the bottom side of the ring.

The last part of the output gives the internal ring angles, the dihedral angles of the ring and the distance matrix.

General Description of the Program

Program *RING* has been carefully written in standard FORTRAN which should run under most of the available compilers today. The present version has been tested on the Control Data FTN (FORTRAN extended) compiler. Further tests were carried out with FORTRAN compilers of a UNIVAC 1108, a SIEMENS 4004 and a XEROX SIGMA 5 system.

RING needs $15\,452_8$ words (= 6954_{10} words) of core. This amount of core can be easily reduced by overlaying the subroutines *READIN*, *TRANSF*, *PUCKER*, *SUBSTI* and *OUTPUT*.

The following is a brief description of the program and its subroutines.

PROGRAM RING: This is the main program which calls the first five of the following subroutines.

SUBROUTINE READIN: This is the input routine. The important parts of the input are immediately printed.

SUBROUTINE TRANSF: If the input coordinates are cell coordinates *TRANSF* transforms them to cartesian coordinates.

- SUBROUTINE PUCKER: This subroutine does the actual work. The mean ring plane and the corresponding coordinate system is found. The puckering coordinates of the ring are evaluated.
- SUBROUTINE SUBSTI: This subroutine calculates the polar angles α and β of substituent and ring bonds.
- SUBROUTINE OUTPUT: This is the printing routine which gives all the calculated information (see output description). It calls the following subroutines:
- SUBROUTINE DISTAN: In this routine the distance matrix is evaluated.
- SUBROUTINE ANGLE: This routine calculates and prints the internal ring angles.
- SUBROUTINE DIHEDL: The dihedral angles of the ring are calculated and printed.
- SUBROUTINE OUTMAT: This is a matrix printing routine used to output the distance matrix.

References

- (1) D. Cremer and J.A. Pople, J.Amer.Chem.Soc., 97, 1358 (1975)
- (2) D. Cremer to be submitted.
- (3) D.H.R. Barton, O.Hassel, K.S. Pitzer, V.Prelong, Science, 119, 49 (1953); Nature, 172, 1096 (1953)

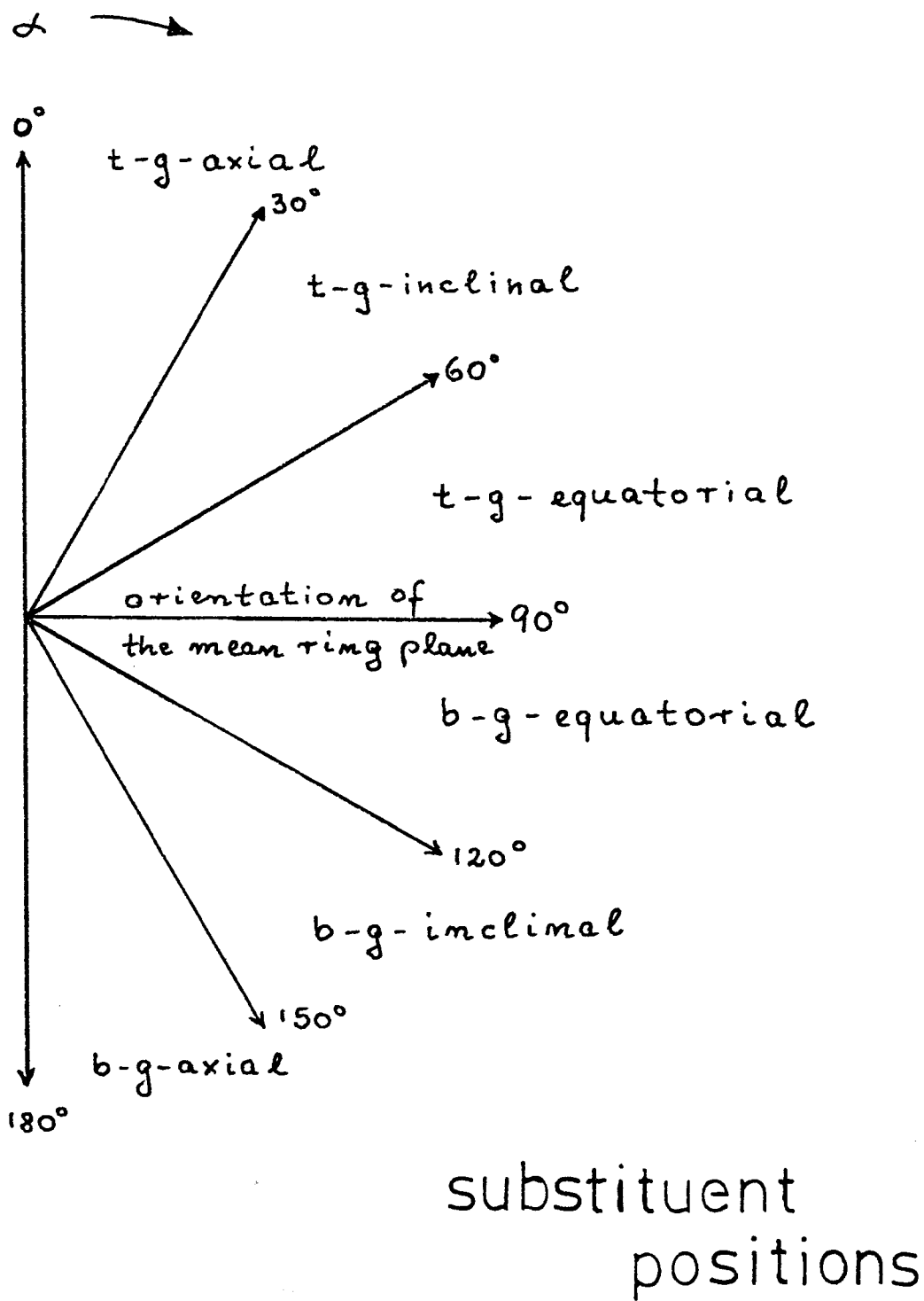


FIGURE 1

Output of sample 1

5 MEMBERED RING: SUCROSE, FURANOID RING, BROWN AND LEVY, ACTA CRYSTALLOGR., SECT.B, 29, 790

CELL DATA : A = 10.8633 B = 8.7050 C = 7.7585 ALPHA = 90.0000 BETA = 102.9450 GAMMA = 90.0000

EXPERIMENTAL COORDINATES

1	.2121	.0945	.3157
2	.1245	.1926	.3690
3	.0072	.1908	.2149
4	.0648	.1665	.0548
5	.1764	.0613	.1286

TRANSFORMED COORDINATES

(CARTESIAN SYSTEM, ORIGIN = GEOMETRICAL CENTER OF THE RING, XY-PLANE = MEAN RINGPLANE, ATOM 1 LIES IN YZ-PLANE)

1	0.0000	1.2111	-.0187
2	1.1625	.4348	.1458
3	.7427	-1.0015	-.2171
4	-.7224	-1.0309	.2056
5	-1.1829	.3865	-.1155

PUCKERING COORDINATES

Q(2) = .353 PHI(2) = 265.19

CAPITAL Q = .353

SUM OF Z-COORDINATES = .0000 SUM OF Z*Z = .1243 SUM OF Q(H)*Q(H) = .1243

BOND ANGLES

ANGLE 5 1 2 = 111.66

ANGLE 4 5 1 = 105.62

CALCULATED DIHEDRAL ANGLES

DIHEDRAL ANGLE 5 1 2 3 = 14.65
 DIHEDRAL ANGLE 1 2 3 4 = -31.17
 DIHEDRAL ANGLE 2 3 4 5 = 35.04
 DIHEDRAL ANGLE 3 4 5 1 = -27.26
 DIHEDRAL ANGLE 4 5 1 2 = 8.06

DISTANCE MATRIX

	1	2	3	4	5
1	0.0000				
2	1.4076	0.0000			
3	2.3424	1.5398	0.0000		
4	2.3662	2.3884	1.5252	0.0000	
5	1.4452	2.3604	2.3759	1.5245	0.0000

Output of sample 2

6 MEMBERED RING: SUCROSE (NEUTRON DIFFRACTION) BROWN ET AL.

CELL DATA : A = 10.6633 B = 8.7050 C = 7.7585 ALPHA = 90.0000 BETA = 102.9450 GAMMA = 90.0000

EXPERIMENTAL COORDINATES

1	.3772	.3988	.3686
2	.2996	.3579	.4849
3	.3125	.4747	.6360
4	.2854	.6367	.5645
5	.3740	.6709	.4420
6	.3592	.5511	.2953
7	.1714	.3463	.3917
8	.3347	.2451	.5388
9	.3080	.7477	.7028
10	.3488	.8141	.3563
11	.4575	.5708	.1846
12	.2638	.5613	.2093

TRANSFORMED COORDINATES

(CARTESIAN SYSTEM, ORIGIN = GEOMETRICAL CENTER OF THE RING, XY-PLANE = MEAN RINGPLANE, ATOM 1 LIES IN YZ-PLANE)

1	.0000	1.3839	.1976
2	1.1997	.7624	-.2106
3	1.2356	-.7040	.2393
4	.0110	-1.4564	-.2550
5	-1.2300	-.7208	.2420
6	-1.2164	.7350	-.2133
7	1.3498	.8496	-1.6219
8	2.0018	1.3240	.2935
9	-.0286	-2.7852	.2548
10	-2.4243	-1.2748	-.2627

PUCKERING COORDINATES

Q(2) = .050 PHI(2) = 183.06 THETA(2) = 5.13
 Q(3) = .554
 CAPITAL Q = .557

SUM OF Z-COORDINATES = .0000 SUM OF Z*Z = .3098 SUM OF Q(N)*Q(M) = .3098

POSITIONS OF THE RING SUBSTITUENTS

BONDS AT RING ATOM 2

POLAR ANGLES OF EXTERNAL BOND 2 - 7 : ALPHA = 173.0 BETA = 2.3

ATOM 7 IS IN A B-G-AXIAL POSITION

POLAR ANGLES OF EXTERNAL BOND 2 - 8 : ALPHA = 62.8 BETA = 357.4

ATOM 8 IS IN A T-G-EQUATORIAL POSITION

BONDS AT RING ATOM 4

POLAR ANGLES OF EXTERNAL BOND 4 - 9 : ALPHA = 69.0 BETA = 2.1

ATOM 9 IS IN A T-G-EQUATORIAL POSITION

BONDS AT RING ATOM 5

POLAR ANGLES OF EXTERNAL BOND 5 - 10 : ALPHA = 111.0 BETA = 5.5

ATOM 10 IS IN A B-G-EQUATORIAL POSITION

BONDS AT RING ATOM 6

POLAR ANGLES OF EXTERNAL BOND 6 - 11 : ALPHA = 65.9 BETA = 4.1

ATOM 11 IS IN A T-G-EQUATORIAL POSITION

POLAR ANGLES OF EXTERNAL BOND 6 - 12 : ALPHA = 175.1 BETA = 348.5

ATOM 12 IS IN A B-G-AXIAL POSITION

BOND ANGLES

ANGLE 6 1 2 = 115.94

ANGLE 1 2 3 = 110.85

ANGLE 2 3 4 = 111.03

ANGLE 5 6 1 = 110.66

CALCULATED DIHEDRAL ANGLES

DIHEDRAL ANGLE 6 1 2 3 = -54.90
 DIHEDRAL ANGLE 1 2 3 4 = 54.98
 DIHEDRAL ANGLE 2 3 4 5 = -56.02
 DIHEDRAL ANGLE 3 4 5 6 = 56.29
 DIHEDRAL ANGLE 4 5 6 1 = -54.91
 DIHEDRAL ANGLE 5 6 1 2 = 55.16

DISTANCE MATRIX

	1	2	3	4	5	6	7	8	9	10
1	0.0000									
2	1.4115	0.0000								
3	2.4265	1.5343	0.0000							
4	2.8762	2.5175	1.5198	0.0000						
5	2.4382	2.8824	2.4656	1.5258	0.0000					
6	1.4386	2.4162	2.8788	2.5120	1.5254	0.0000				
7	2.3277	1.4219	2.4271	2.9964	3.5490	2.9296	0.0000			
8	2.0050	1.1014	2.1686	3.4634	3.8248	3.3107	2.0782	0.0000		
9	4.1696	3.7830	2.4351	1.4238	2.3886	3.7446	4.3167	4.5837	0.0000	
10	3.6278	4.1582	3.7386	2.4427	1.4105	2.3457	4.5397	5.1632	2.8795	0.0000
11	2.3664	3.6875	4.2333	3.8708	2.5266	1.5229	4.2776	4.3606	4.9094	2.8915
12	2.0890	2.7360	3.3201	2.7912	2.1528	1.1033	2.6736	3.7179	4.0865	2.5543

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