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Geometry of the Five-Membered Ring Mathematical Demonstration of the Pseudorotation Formulae

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Abstract. The geometrical relations between the 15 typical parameters (bond lengths and angles, torsion angles) of a five-membered ring are derived for any ring then for a regular one. It is demonstrated that for the case of the 20 symmetrical C_2 and C_S conformations, only geometrical considerations are needed to obtain the pseudorotation formulae for the torsion angles. However, the puckering intensity as well as the bond angle values cannot be expressed from geometrical constraints alone but would require energetical considerations.

Key words: Five-membered ring – Pseudorotation – Conformational analysis – Molecular geometry

Introduction

The five-membered rings are frequently encountered structures in molecules of biological interest: peptides with proline residue, nucleotides, penicillins, steroids . . . Their conformation and their motion have been extensively studied [1, 2] either experimentally by X-Rays, nuclear magnetic resonance, Infra-Red and Raman spectroscopy, electronic diffraction, or theoretically [3–7].

The conformation of this ring is usually represented by the pseudorotation concept [8–12] of which no mathematical demonstration has ever been given [10]. This concept involves that the torsion angle values χ_i satisfy the relations:

$$\chi_i = \chi_m \cos\,[P + (i - 1)\,\delta]$$

in which the variation of the phase angle P allows either to generate the different possible conformations or to localize the deformation in the case of a privileged conformation; the value of δ is $4\,\pi/5$, and χ_m is the puckering amplitude. This representation is very useful to determine the ring conformations in terms of

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only two parameters. The theoretical basis of this concept are energetical computer calculations but Lifson et al. [5] using significantly different potential functions, underlines the probably geometrical origin of the pseudorotational path for cyclopentane.

Recently, correlations have been suggested between conformation of the thiazolidine ring of penicillins and their antibacterial activity spectrum [13].

Within the scope of conformation-activity relationships, it is of importance, in order to improve the understanding of the ring conformations, to separate the geometrical and energetical involvements [1], the geometrical properties will be the same for any five-membered ring whereas the energetical ones will depend on the nature of the constituent atoms and on the substituents.

In this perspective, the geometrical relations for five-membered rings have been establish. In the case of the 20 symmetrical conformations C_2 and C_S, the pseudorotation relations are deduced for torsion angles, and hence appear to be free of any energetical consideration for a given puckering amplitude χ_m.

I. General Case, Non-Regular Ring

1. Number of Relations

Fifteen parameters take part in the description of a five-membered ring (cf. Fig. 1):

5 bond lengths l_i,
5 bond angles ϕ_i,
5 torsion angles χ_i.

The construction of such a ring requires the knowledge of only nine parameters; since starting from the A atom:

the B atom is positioned knowing l_1,
the C atom is positioned knowing l_2, ϕ_2,
the D atom is positioned knowing l_3, ϕ_3, χ_2,
the E atom is positioned knowing l_4, ϕ_4, χ_3.

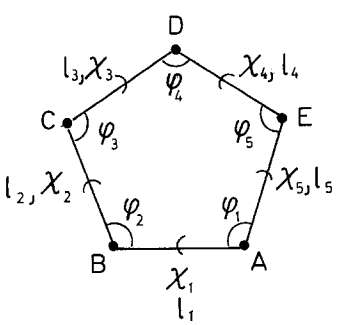

Fig. 1. Parameters taking part in the description of a five-membered ring

Among the 15 parameters characterizing the ring, nine are consequently independent and there are $15 - 9 = 6$ independent relations strictly geometrical, between the quantities l_i, ϕ_i, χ_i. Given their nature, these relations will be valid whatever the nature of the constituant atoms and whatever the substitutions which will be made on them.

These relations are established below in the general case of a non regular ring.

2. *Relation Between the Sines of Torsion Angles*

Given the sum of the triple scalar products:

$$S = (\mathbf{AB}, \mathbf{BC}, \mathbf{CD}) + (\mathbf{BC}, \mathbf{CD}, \mathbf{DE}) + (\mathbf{CD}, \mathbf{DE}, \mathbf{EA}) + (\mathbf{DE}, \mathbf{EA}, \mathbf{AB})$$

Grouping the products two by two leads to:

$$S = (\mathbf{AB} + \mathbf{DE}, \mathbf{BC}, \mathbf{CD}) + (\mathbf{DE}, \mathbf{EA}, \mathbf{CD} + \mathbf{AB})$$

Taking into account:

the closing relations of the type: $\mathbf{AB} = \mathbf{AE} + \mathbf{ED} + \mathbf{DC} + \mathbf{CB}$,

the fact that a triple scalar product containing two identical vectors is zero,

the sum S becomes:

$$S = (\mathbf{AE} + \mathbf{ED} + \mathbf{DC} + \mathbf{CB} + \mathbf{DE}, \mathbf{BC}, \mathbf{CD}) + (\mathbf{DE}, \mathbf{EA}, \mathbf{CD} + \mathbf{AE} + \mathbf{ED} + \mathbf{DC} + \mathbf{CB})$$

$$S = (\mathbf{AE}, \mathbf{BC}, \mathbf{CD}) + (\mathbf{DE}, \mathbf{EA}, \mathbf{CB}) = (\mathbf{CD} + \mathbf{DE}, \mathbf{EA}, \mathbf{CB})$$
$$= -(\mathbf{CE}, \mathbf{EA}, \mathbf{BC})$$
$$= -(\mathbf{CB} + \mathbf{BA} + \mathbf{AE}, \mathbf{EA}, \mathbf{BC})$$
$$= -(\mathbf{EA}, \mathbf{AB}, \mathbf{BC}).$$

Therefore:

$$S = (\mathbf{AB}, \mathbf{BC}, \mathbf{CD}) + (\mathbf{BC}, \mathbf{CD}, \mathbf{DE}) + (\mathbf{CD}, \mathbf{DE}, \mathbf{EA}) + (\mathbf{DE}, \mathbf{EA}, \mathbf{AB})$$
$$= -(\mathbf{EA}, \mathbf{AB}, \mathbf{BC}).$$

As $(\mathbf{AB}, \mathbf{BC}, \mathbf{CD}) = AB \times BC \times CD \times \sin \chi$, (cf. Appendix 1)

the latter relation leads to:

$$\boxed{\Sigma_i \, l_{i-1} \, l_i \, l_{i+1} \sin \chi_i = 0} \quad . \tag{1}$$

Hence *there exists a relation between the bond lengths* l_i *and torsion angles* χ_i, *independent of the bond angles* ϕ_i.

3. Relations System Between the Cosines of Torsion Angles

The cosine of a dihedral angle is (cf. Appendix 1):

$$\cos\chi = \frac{\alpha - l^2\,\mathbf{AB}\cdot\mathbf{CD}}{\gamma} \tag{2}$$

in which: $\alpha = (\mathbf{AB}\cdot\mathbf{BC})\,(\mathbf{CD}\cdot\mathbf{BC})$

$l = BC$

$$\gamma = \sqrt{[|\mathbf{AB}|^2|\mathbf{BC}|^2 - (\mathbf{AB}\cdot\mathbf{BC})^2]\,[|\mathbf{CD}|^2|\mathbf{BC}|^2 - (\mathbf{CD}\cdot\mathbf{BC})^2]}\,.$$

Using the notations of Fig. 1:

$$\cos\chi_2 = \frac{\alpha_2 - l_2^2\,\mathbf{AB}\cdot\mathbf{CD}}{\gamma_2} \qquad \text{where: } \begin{cases}\alpha_2 = l_1\,l_2^2\,l_3\cos\phi_2\cos\phi_3\\ \gamma_2 = l_1\,l_2^2\,l_3\sin\phi_2\sin\phi_3\end{cases}.$$

Using the closing relation: $\mathbf{CD} = \mathbf{CB} + \mathbf{BA} + \mathbf{AE} + \mathbf{ED}$ and multiplying scalarely both sides by $\mathbf{AB}$:

$$\mathbf{AB}\cdot\mathbf{CD} = l_1\,l_2\cos\phi_2 - l_1^2 + l_1\,l_5\cos\phi_1 + \mathbf{AB}\cdot\mathbf{ED}.$$

Replacing the scalar products by their expression given by Eq. (2), we get:

$$\boxed{A_2\cos\chi_2 + A_5\cos\chi_5 = B_5} \tag{3}$$

where: $A_2 = -\dfrac{\gamma_2}{l_2^2} = -\,l_1\,l_3\sin\phi_2\sin\phi_3$

$$A_5 = -\frac{\gamma_5}{l_5^2} = -\,l_4\,l_1\sin\phi_5\sin\phi_1$$

and $\quad B_5 = -\dfrac{\alpha_5}{l_5^2} - \dfrac{\alpha_2}{l_2^2} + l_1\,l_2\cos\phi_2 + l_1\,l_5\cos\phi_1 - l_1^2\,.$

$$B_5 = -\,l_1\,l_3\cos\phi_2\cos\phi_3 - l_4\,l_1\cos\phi_5\cos\phi_1 + l_1\,l_2\cos\phi_2 + l_1\,l_5\cos\phi_1 - l_1^2\,.$$

The Eq. (3) demonstrated for the two dihedral angles χ_5 and χ_2, is also true for any pair $(\chi_i,\ \chi_{i+2})$, giving thus rise to a system of five equations:

$$\boxed{A_i\cos\chi_i + A_{i+2}\cos\chi_{i+2} = B_i} \tag{4}$$

which allow to express the torsion angle cosines in terms of bond lengths and angles: by a linear combination of the previous system's equations, we get:

$$2 A_1 \cos \chi_1 = B_1 - B_2 - B_3 + B_4 + B_5$$

Hence:
$$\boxed{\cos \chi_1 = \frac{2 (l_1 - l_2 \cos \phi_2) (l_1 - l_5 \cos \phi_1) + 2 l_3 l_4 \cos \phi_4 - (l_1^2 - l_2^2 + l_3^2 + l_4^2 - l_5^2)}{2 l_2 l_5 \sin \phi_1 \sin \phi_2}} \quad . \tag{5}$$

The formulae giving $\cos \chi_2$, $\cos \chi_3$ . . . are obtained from Eq. (5) by circular permutation on the indices i.

It is then obvious that:

– a torsion angle depends on the five bond lengths l_i but only on three bond angles: the two adjacent and the opposite one to the considered bond (cf. Fig. 1).

II. Small Deformations of a Regular Ring

In practice, given the size of the energetical variations involved:
– the bond lengths can be considered invariable,
– the bond angles are close to the planar ring one's ($\phi = 3\pi/5$),
– the torsion angle values are such that the expansion of the trigonometrical functions can be restricted to the second term:

$$\chi_i < 50° \rightarrow \cos \chi_i \sim 1 - \chi_i^2/2 \; .$$

In this paragraph, we shall restrict ourselves to rings assimilable to a regular one ($l_i = 1$).

The above general relations become simpler:
Eq. (1) becomes:

$$l^3 \Sigma_i \sin \chi_i = 0$$

hence: $\boxed{\Sigma_i \sin \chi_i = 0}$ (6)

and if the χ_i are small enough: $\Sigma_i \chi_i = 0$ (7)

Eq. (5) become:

$$\boxed{\cos \chi_1 = \frac{2 (1 - \cos \phi_2) (1 - \cos \phi_1) + 2 \cos \phi_4 - 1}{2 \sin \phi_1 \sin \phi_2}} \quad . \tag{8}$$

These relations were given by Dunitz [14] in the case of the symmetrical C_2 and C_s conformations of a regular ring.

Let us expand as limited power series the geometrical formulae in proximity to the value $\phi_i = 3\pi/5$ corresponding to the regular ring; i.e., let $\phi_i = \phi + \varepsilon_i$

($\phi = 108°$ and $\varepsilon_i < 10°$) and let us replace $\cos \phi_i$ by $(\cos \phi - \varepsilon_i \sin \phi)$ and $\sin \phi_i$ by $(\sin \phi + \varepsilon_i \cos \phi)$ we get from the exact Eq. (8) the approximate expression:

$$2 \cos \chi_1 = \frac{2\,(1 + \cos^2 \phi - 2 \cos \phi) + (2 \cos \phi - 1) + (1 - \cos \phi)\,(\varepsilon_1 + \varepsilon_2) \sin \phi - 2\,\varepsilon_4 \sin \phi}{\sin^2 \phi \left[1 + \dfrac{\cos \phi}{\sin \phi}\,(\varepsilon_1 + \varepsilon_2)\right]}.$$

If $\quad A = \dfrac{1 + 2 \cos^2 \phi - 2 \cos \phi}{\sin^2 \phi}$

$$2 \cos \chi_1 = A + (\varepsilon_1 + \varepsilon_2) \left[\frac{2\,(1 - \cos \phi)}{\sin \phi} - A \frac{\cos \phi}{\sin \phi}\right] - 2 \frac{\varepsilon_4}{\sin \phi}.$$

With $\phi = \dfrac{3\pi}{5}$, $A = 2$ and $2 \cos \phi - 1 = 2 \cos 2\phi$ (cf. Appendix 2)

Hence $$\boxed{\cos \chi_1 = 1 - 2(\varepsilon_1 + \varepsilon_2) \frac{\cos\ 2\phi}{\sin \phi} - \frac{\varepsilon_4}{\sin \phi}} \quad . \tag{9}$$

When $\cos \chi_1 \sim 1 - \chi_1^2/2$,

$$\boxed{\chi_1^2 \sin \phi = 4(\varepsilon_1 + \varepsilon_2) \cos 2\phi + 2\varepsilon_4} \quad . \tag{10}$$

Summing the two last relations on every torsion angle, we obtain:

$$\boxed{\Sigma_i \cos \chi_i = 5 - 4 \sin 2\phi\, \Sigma_i\, \varepsilon_i} \tag{11}$$

and: $$\boxed{\Sigma_i\, \chi_i^2 = 8 \sin 2\phi\, \Sigma_i\, \varepsilon_i = 8 \sin 2\phi\, \Sigma_i\, (\phi_i - \phi)} \tag{12}$$

i.e.: *the sum of the torsion angle squares is proportional to the sum of the differences between the actual bond angle values and the value corresponding to the planar ring.*

Moreover *the coefficient of proportionnality* $8 \sin 2\phi$ *being* < 0, *the sum* $\Sigma_i\, \varepsilon_i = \Sigma_i\, (\phi_i - \phi)$ *is always negative or zero* ($\Sigma_i\, \phi_i \leqslant 3\,\pi$).

Bond angle values: $\phi_i = \phi + \varepsilon_i$.

The Eqs. (9) or (10) of $\cos \chi_i$ or χ_i^2 in terms of ε_i's lead to a system of five equations of five unknowns ε_i. If we try to inverse this system in order to get the expressions of the ε_i's in terms of the χ_i's, we find that the matrix determinant of the ε_i's coefficients is:

$$| A | = (a^2 - a - 1)\,(2\,a^3 - 3\,a^2 - a + 1) \text{ with}$$
$$a = (1 - 2 \cos \phi) = -\,2 \cos 2\,\phi\ .$$

Taking into account the trigonometric identities given in Appendix 2, $a^2 - a - 1 = 0$ and $2a^3 - 3a^2 - a + 1 = 0$.

The A determinant being zero, the values of ε_i are indeterminate.

Given the five bond angles ϕ_i, the five torsion angles χ_i are completely determined. Conversely, given the five torsion angles, the five bond angles cannot be determined from goemetrical considerations.

III. Symmetrical Conformations

Only two relations are needed to retain the ring symmetry properties:

$$\text{i.e., } \begin{cases} \varepsilon_1 = \varepsilon_2 \\ \varepsilon_3 = \varepsilon_5 \end{cases} \text{ which involve [cf. Eq. (10)]: and } \begin{cases} \chi_2^2 = \chi_5^2 \\ \chi_3^2 = \chi_4^2 \end{cases}$$

1. C_S Symmetry

In the case of the C_S symmetry, $\chi_2 = \chi_5$ and $\chi_3 = -\chi_4$ (cf. Fig. 2).

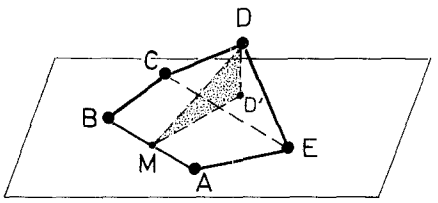

Fig. 2. C_S conformation. The four atoms A, B, C, E are coplanar and D is out of this plane

The Eq. (6) $\Sigma_i \sin \chi_i = 0$ then leads to: $\sin \chi_1 = 0$, hence to $\chi_1 = 0$, which in turn involves [cf. Eq. (10)]:

$$\boxed{\varepsilon_4 = -4\,\varepsilon_1 \cos 2\phi} \quad . \tag{13}$$

There remains only two geometrically independent variables: ε_1 and ε_3. The Eq. (10) giving the torsion angles in terms of bond angles become:

$$\begin{cases} \chi_1^2 = 0 \\ \chi_2^2 \sin \phi = \chi_5^2 \sin \phi = 4\,\varepsilon_1 \cos 2\phi + 4\,\varepsilon_3 \cos \phi \\ \chi_3^2 \sin 2\phi = \chi_4^2 \sin 2\phi = 8\,\varepsilon_1 \cos^2 2\phi + 2\,\varepsilon_3 \,. \end{cases} \tag{14}$$

If we choose another couple of independent variables, namely ε_1 and $\varepsilon_T = \Sigma_i \varepsilon_i$, the ε_1's coefficient cancels due to the identities of Appendix 2. Hence, *the torsion angles depend only on a single parameter ε_T.*

$$\boxed{\begin{cases} \chi_1^2 = 0 \\ \chi_2^2 \sin \phi = \chi_5^2 \sin \phi = 2\,\varepsilon_T \cos \phi \\ \chi_3^2 \sin \phi = \chi_4^2 \sin \phi = 2\,\varepsilon_T \cos 2\phi \end{cases}} \quad . \tag{15}$$

This parameter $\varepsilon_T = \Sigma_i \varepsilon_i$ represents the distorsion amplitude. Hence, in a C_S conformation:

– *For a given distorsion amplitude* ε_T, *the torsion angles* χ_i *are completely determined but the bond angles* ϕ_i *are not.*

– *Whatever the distorsion amplitude* ε_T, *the ratios:* χ_2/χ_3, χ_5/χ_4, $\varepsilon_1/\varepsilon_4$ *are constant:*

$$(\chi_2/\chi_3)^2 = (\chi_5/\chi_4)^2 = 4\,(\varepsilon_1/\varepsilon_4)^2 = 4\cos^2\phi$$
$$(\varepsilon_4/\varepsilon_1 = 1 + \sqrt{5}).$$

If we state:

$$\varepsilon_T = \chi_m^2 \sin^2\phi \sin 2\phi\,. \tag{16}$$

The Eq. (15) giving χ_i^2 become:

$$\boxed{\begin{aligned}\chi_1^2 &= 0\\ \chi_2^2 = \chi_5^2 &= \chi_m^2 \sin^2 2\phi\\ \chi_3^2 = \chi_4^2 &= \chi_m^2 \sin^2\phi\end{aligned}}\,. \tag{17}$$

2. C_2 *Symmetry*

In the case of the C_2 symmetry, $\chi_2 = \chi_5$ and $\chi_3 = \chi_4$ (cf. Fig. 3).

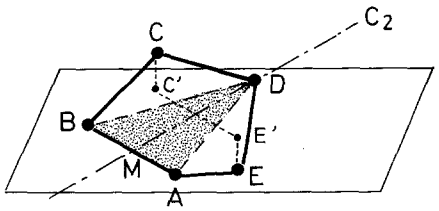

Fig. 3. C_2 conformation. C_2 is a symmetry axis; the two atoms C and E are located on both sides of the plane ABD

The Eq. (6) $\Sigma_i \sin\chi_i = 0$ leads to:

$$\sin\chi_1 = -2\,(\sin\chi_2 + \sin\chi_3)\,.$$

As was done for the C_S symmetry, for $\chi_1 = \chi_m$ the following angles are obtained:

$$\boxed{\begin{aligned}\chi_1^2 &= \chi_m^2\\ \chi_2^2 = \chi_5^2 &= \chi_m^2 \cos^2 2\phi\\ \chi_3^2 = \chi_4^2 &= \chi_m^2 \cos^2\phi\end{aligned}}\,. \tag{18}$$

Hence, for a C_2 conformation – *the distorsion amplitude* χ_m *(or* ε_T*) is sufficient to determine the torsion angle values but not the bond angles*
– *Whatever the distorsion amplitude may be, the ratios* χ_2/χ_3, χ_5/χ_4, are constant:

$$(\chi_2/\chi_3)^2 = (\chi_5/\chi_4)^2 = (\cos 2\,\phi/\cos\phi)^2.$$

In addition: $8\,\varepsilon_1 \cos 2\,\phi + 2\,\varepsilon_4 = \chi_m^2 \sin\phi$
or: $\varepsilon_T/\sqrt{5} = \varepsilon_1\,(1+\sqrt{5})/2 - \varepsilon_4/2$.

3. *Pseudorotation Formulae*

The pseudorotation concept describes the torsion angles by the formula:

$$\chi_i = \chi_m \cos\,[P + (i-1)\,\delta]\,.$$

P is called the phase angle and the value of δ is $4\pi/5$.

We go and prove that this parametrisation is right for the two C_S and C_2 conformation types, for strictly geometrical grounds (so far as the used approximations permit it).

Taking into account the identities given in Appendix 2, we may write the Eq. (17):

C_S *conformation*	C_2 *conformation*
$\chi_1^2 = 0$	χ_m^2
$\chi_2^2 = \chi_5^2 = \chi_m^2 \sin^2\delta$	$\chi_m^2 \cos^2\delta$
$\chi_3^2 = \chi_4^2 = \chi_m^2 \sin^2 2\delta$	$\chi_m^2 \cos^2 2\delta$

Now, as:
$\sin^2 2\delta = \sin^2 3\,\delta$, $\sin^2\delta = \sin^2 4\delta$,
$\cos^2 2\delta = \cos^2 3\delta$, $\cos^2\delta = \cos^2 4\delta$,

the previous relations can be condensed into:
for C_S conformation: $\chi_i^2 = \chi_m^2 \sin^2\,(i-1)\,\delta$
for C_2 conformation: $\chi_i^2 = \chi_m^2 \cos^2\,(i-1)\,\delta$.
We take the positive determinations (the negative ones give the mirror solution) and thus:

$\chi_i = \chi_m \cos\,[P + (i-1)\,\delta]$
with $P = \pi/2$ for the C_S conformation
and $P = 0$ for the C_2 conformation .

These P values (0 and $\pi/2$) have been determined in the case of symmetrical conformations where the χ_1 angle is set equal to χ_m or 0.

When $\chi_2, \chi_3, \chi_4, \chi_5$, are successively equal to χ_m or 0, the corresponding phase angle values are:

$P = -\delta, -2\delta, -3\delta, -4\delta$, for the C_2 symmetry and
$P = \pi/2 - \delta, \pi/2 - 2\delta, \pi/2 - 3\delta, \pi/2 - 4\delta$ for the C_S symmetry.

In both cases, by setting $P' = \pi - P$, we get the mirror conformations. Finally, the P values corresponding to the symmetrical conformations are:

for C_2 symmetry: $P = \pm 2n\pi/10$ with $n = 0$ to 5,
for C_S symmetry: $P = \pm (2n - 1)\pi/10$ with $n = 0$ to 5,

that is: 10 C_2 and 10 C_S conformations.

4. *Bond Angle Values*

If, from the equations system (Eq. 14), we try to determine ε_1 and ε_3 in terms of torsion angles, we see that the determinant of the coefficients is zero: thus the ε_i's, and therefore the ϕ_i's are undetermined.

Conclusion

In a five-membered ring in which the bond lengths are nearly identical, the bond angles ϕ_i little deviate from the plane ring value $\phi = 108°$, and the torsion angles stay lower than 50°, we have derived the following geometrical relations:

$\Sigma_i \sin \chi_i = 0$
$\Sigma_i \chi_i^2 = 8 \sin 2\phi \; \Sigma_i \varepsilon_i$ with $\varepsilon_i = \phi_i - \phi$
$\chi_i^2 \sin \phi = 4 (\varepsilon_i + \varepsilon_{i+1}) \cos 2\phi + 2\varepsilon_{i+3}$.

Moreover for symmetrical conformations, by setting:

$\varepsilon_T = \Sigma_i \varepsilon_i \; (= \chi_m^2 \sin^2 \phi \sin 2\phi)$:

for C_S *symmetry*.

$\varepsilon_4 = -4\varepsilon_1 \cos 2\phi$
$\chi_1^2 = 0, \; \chi_2^2 = \chi_5^2 = \chi_m^2 \sin^2 2\phi, \; \chi_3^2 = \chi_4^2 = \chi_m^2 \sin^2 \phi$

for C_2 *symmetry*.

$2\varepsilon_4 = -8\varepsilon_1 \cos 2\phi + \chi_m^2 \sin \phi$
$\chi_1^2 = \chi_m^2, \; \chi_2^2 = \chi_5^2 = \chi_m^2 \cos^2 2\phi, \; \chi_3^2 = \chi_4^2 = \chi_m^2 \cos^2 \phi$

which can be condensed into the pseudorotation formulae:

$$\chi_i = \chi_m \cos [P + (i - 1)\,\delta] \text{ with } \delta = 4\,\pi/5 \text{ and } P = k\pi/10\,.$$

(Wherever the angles lie outside trigonometrical functions, they are expressed in radians.)

Thus, in a five-membered ring assimilable to a regular one with little deformations, for a fixed puckering amplitude, the pseudorotation formulae for the torsion angles are shown to be, in the case of the 20 symmetrical conformations C_2 and C_S, the expression of the only geometrical properties.

On the basis of the above geometrical formulae, we shall consider in a forthcoming paper [15] the effect of added energetical constraints which allows to get expression for the puckering amplitude as also for the bond angles, and to define the pathway between two symmetrical conformations.

Appendix 1

Vectorial Expressions of the Dihedral Angle Cosine and Sine

Let four points A, B, C, D be no coplamar and let χ be the dihedral angle of the two planes containing on the one hand the vectors **AB** and **BC** and on the other hand **BC** and **CD** (cf. Fig. 4)

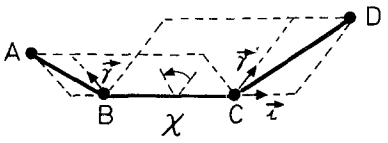

Fig. 4. Dihedral angle χ

1. Expression of cos χ

Let **i** be the unit vector supported by **BC**, and let **j** and **j′** be the unit vectors perpendicular to **i**, located in the planes ABC and BCD respectively.

$$\cos\chi = \mathbf{j} \cdot \mathbf{j}'$$

$$\mathbf{AB} \cdot \mathbf{CD} = (a\mathbf{i} + b\mathbf{j}) \cdot (c\mathbf{i} + d\mathbf{j}') = ac + bd\cos\chi\,.$$

Hence $$\cos\chi = \frac{\mathbf{AB} \cdot \mathbf{CD} - ac}{bd}\,.$$

Let us write the components a, b, c, d of the vectors **AB** and **CD** from the vectorial expressions:

$$a = \mathbf{AB} \cdot \mathbf{i} = \frac{\mathbf{AB} \cdot \mathbf{BC}}{BC}$$

$$c = \mathbf{CD} \cdot \mathbf{i} = \frac{\mathbf{CD} \cdot \mathbf{BC}}{BC}$$

b is such as $a^2 + b^2 = |\mathbf{AB}|^2$ Hence $b = \pm \sqrt{|\mathbf{AB}|^2 - a^2}$

d is such as $c^2 + d^2 = |\mathbf{CD}|^2$ and $d = \pm \sqrt{|\mathbf{CD}|^2 - c^2}$

The algebraical signs of b and d, therefore of bd, depend on the choosen orientations for the $\mathbf{j}$ and $\mathbf{j}'$ vectors. According to the bd sign, we shall obtain cos χ or cos $(\pi - \chi)$. If we take the IUPAC conventions [16], for which $\chi = 0$ when the atoms A and D are in cis position, then cos $\chi = 1$ and the vectors $\mathbf{j}$ and $\mathbf{j}'$ are colinear. The componants of **AB** and **CD** along $\mathbf{j}$ (or $\mathbf{j}'$) have then opposite signs and we must choose $bd < 0$.

therefore $bd = -\sqrt{(|\mathbf{AB}|^2 - a^2)\,(|\mathbf{CD}|^2 - c^2)}$

hence the final expression for cos χ:

$$\boxed{\cos\chi = \frac{(\mathbf{AB} \cdot \mathbf{BC})\,(\mathbf{CD} \cdot \mathbf{BC}) - |\mathbf{BC}|^2\,\mathbf{AB} \cdot \mathbf{CD}}{\sqrt{[|\mathbf{AB}|^2|\mathbf{BC}|^2 - (\mathbf{AB} \cdot \mathbf{BC})^2]\,[|\mathbf{CD}|^2|\mathbf{BC}|^2 - (\mathbf{CD} \cdot \mathbf{BC})^2]}}} \,.$$

2. Expression for sin χ.

The χ angle between the two planes ABC and BCD is equal to the angle between the two perpendiculars to every one.

The perpendiculars to the ABC and BCD planes are given by the unit vectors:

$$\frac{\mathbf{AB} \wedge \mathbf{BC}}{(AB)\,(BC)} \text{ and } \frac{\mathbf{BC} \wedge \mathbf{CD}}{(BC)\,(CD)} \text{ respectively.}$$

The vector product of these two vectors perpendicular to BC give sin χ) and is supported by **BC**:

$$\sin\chi \frac{\mathbf{BC}}{BC} = \left(\frac{\mathbf{AB} \wedge \mathbf{BC}}{(AB)\,(BC)}\right) \wedge \left(\frac{\mathbf{BC} \wedge \mathbf{CD}}{(BC)\,(CD)}\right) = \frac{(\mathbf{AB}, \mathbf{BC}, \mathbf{CD}) \cdot \mathbf{BC}}{(AB)\,(BC)^2\,(CD)} \,.$$

Hence: $$\boxed{\sin\chi = \frac{(\mathbf{AB}, \mathbf{BC}, \mathbf{CD})}{(AB)\,(BC)\,(CD)}} \,.$$

Here also, the IUPAC conventions are satisfied: $\sin \chi$ is > 0, therefore χ is > 0 when looking along the bond, the far end rotated clockwise relative to the near end.

Appendix 2

Used Trigonometrical Identities

Given the particular values of the ϕ and δ angles, ($3\,\pi/5$ and $4\,\pi/5$), there are, for these angles, some remarkable trigonometrical identities. A partial list of these identities is given hereunder:

$$\sin 2\delta = -\sin \phi \qquad \sin \delta = -\sin 2\phi$$
$$\cos 2\delta = -\cos \phi \qquad \cos \delta = \cos 2\phi$$
$$\sin 2\phi = \sin 4\delta \qquad \sin 2\delta = -\sin 4\phi$$
$$4 \cos \phi \cos 2\phi = 1 \qquad 4 \cos^2 2\phi + 2 \cos 2\phi = 1$$
$$2 \cos 2\phi + 1 = 2 \cos \phi \qquad 4 \cos^2 \phi - 2 \cos \phi = 1$$
$$4 \sin \phi \sin 2\phi = 4 \cos \phi - 1 \qquad 8 \cos^3 \phi - 4 \cos \phi = 1$$
$$4 \cos \delta = -1 - \sqrt{5} \qquad 4 \sin \phi \sin 2\phi = -\sqrt{5}$$
$$4 \cos 2\delta = -1 + \sqrt{5}$$

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