

DISTANCES $I_{HnHn+1}[A^0]$ CALCULATED FROM 3-SPHERE DIHEDRAL ANGLES $\theta_{HnHn+1}[\text{deg}]$

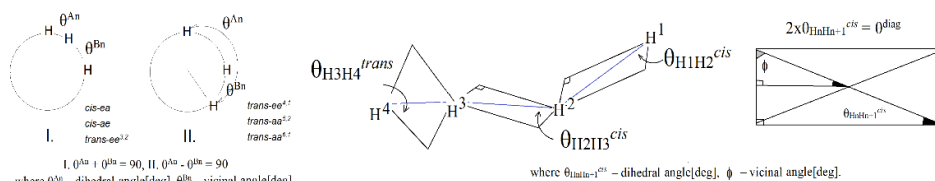
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Dihedral angles $\theta_{HnHn+1}[\text{deg}]$ calculated from NMR data with 3-Sphere approach, a method under Hopf fibration and Lie group theories, are angles in close relationship with vicinal angles $\phi[\text{deg}]$,

angles result from vicinal coupling constant ${}^3J_{HnHn+1}[\text{Hz}]$. The signs of dihedral angles calculated with algebraic equations are demonstrated with A2 root system Lie group. In attempt to find the best model for visualization of the phase angle of the pseudorotation $P[\text{deg}]$ the proton-proton distances $I_{HH}[A^0]$ between two atoms of carbon consecutives are calculated from 3-Sphere dihedral angles $\theta_{HnHn+1}[\text{deg}]$. The string resulting from four protons around five membered rings inscribed on rectangles geometry is expected to give information about conformational constrain. Two protons on two atoms of carbon and their images on mirror are in case of *cis* stereochemistry inscribed on rectangle geometry using dihedral angle $\theta_{HnHn+1}[\text{deg}]$ and vicinal angles $\phi[\text{deg}]$. In case of *trans-aa* and *trans-ee* stereochemistry are inscribed on rhombus geometry using dihedral angle with *trans-aa* stereochemistry and corresponding *cis* angle or both dihedral angles with *trans-ee* stereochemistry.



INTRODUCTION

3-Sphere theory, a hypersphere in 4D, was extensively analyzed from NMR data point of view. The wave character of NMR data unable calculation of the 3-Sphere dihedral angle $\theta_{HnHn+1}[\text{deg}]$ in close relationship with vicinal angle $\phi[\text{deg}]$, angle result from vicinal coupling constant ${}^3J_{HnHn+1}[\text{deg}]$. Hopf fibration and Lie group theories are used for demonstrating the relationship between the dihedral angle and vicinal angle.¹ Only from the vicinal constant coupling with torus and invers of torus equations can be calculated dihedral angles with right sign and stereochemistry,² but from chemical shift can be calculated dihedral angles in close relationship with

tetrahedral angles.³⁻⁵ Once the rule was established between dihedral and tetrahedral angles, tetrahedral angles can be predicted only from vicinal constant coupling, but result same value for two atoms of carbon from only one vicinal coupling constant ${}^3J_{HH}[\text{Hz}]$.⁵ Dihedral angles are calculated from carbon and/or proton chemical shift $\delta[\text{ppm}]$ using manifold equations: conic, Vilarceau circles,¹ rectangles,⁶ and six sets on two units or seven sets on one unit, with angles reassembles the equilateral triangle and covering all the *cis*, *trans-aa*, *trans-ee* stereochemistry. 3-Sphere dihedral angle $\theta_{HnHn+1}[\text{deg}]$ calculated from chemical shift $\delta[\text{ppm}]$ is an angle chose from unit with value almost equal with dihedral angle result from recorded vicinal coupling constant ${}^3J_{HnHn+1}[\text{Hz}]$.

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As defined in organic chemistry, dihedral angle is an angle at intersection of two planes having positive or negative sign (Fig. 1),

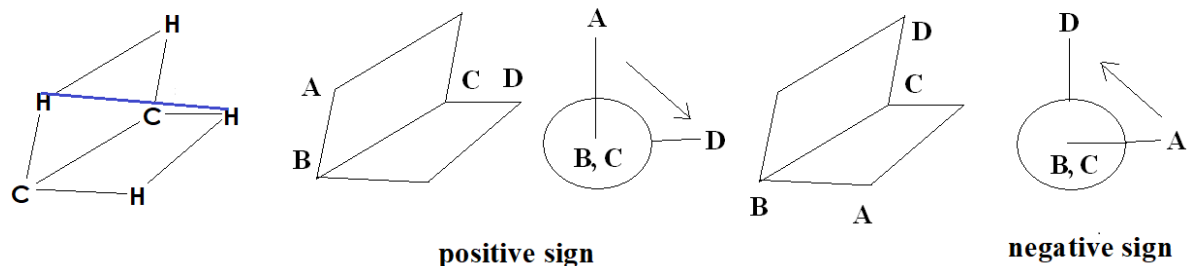


Fig. 1– Dihedral angles at intersection of two planes.

Relative to classical representation (Fig. 1), hypersphere method for calculation dihedral angles places it on two intersecting circles (Figs. 2, 3), generalized on one circle for all stereochemistry.¹ The translation from 4D to 2D, from hypersphere to torus, giving two intersecting circles. Considering two halves of circles with six angles on each, namely set A and set B, can be established trigonometric and algebraic relationship.¹ for all *cis*, *trans-ee*, *aa* stereochemistry. For example, for a

calculated usually with Karplus equations without information about the sign, but established with varies methods.

vicinal constant coupling of 4.1[Hz] results a dihedral angle of 22.18[deg] in set A and a vicinal angle of 67.81[deg] in set B (Fig. 3). Trigonometric equation ensuring the sign of the dihedral angle in close relationship with vicinal constant coupling.¹ In contradiction to Karplus angles, 3-Sphere angles are between *cis* – *trans* stereochemistry in relationship of 180 and 120[deg],⁷ instead of 120[deg] for all stereochemistry as state for polynomial equations.

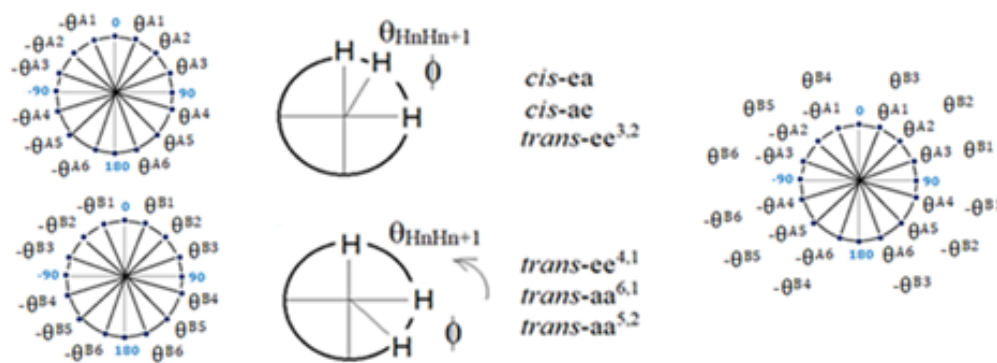


Fig. 2 – 3-Sphere dihedral $\theta_{HnHn+1} = \theta^{An}$ [deg] and vicinal $\phi = \theta^{Bn}$ [deg] angles with *cis* and *trans* stereochemistry on circles: I. $\theta^{An} + \theta^{Bn} = 90$ [deg]; II. $\theta^{An} - \theta^{Bn} = 90$ [deg].

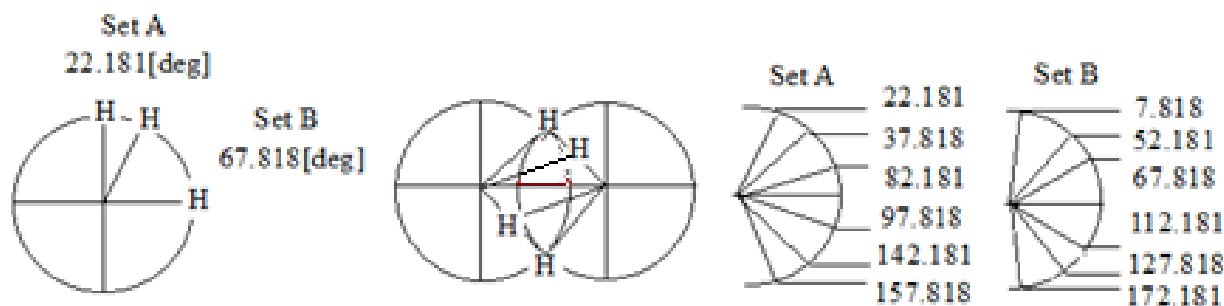
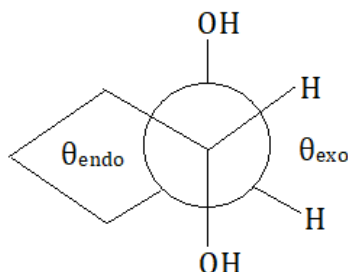


Fig. 3 – Dihedral θ_{HnHn+1} 22.16[deg] and vicinal ϕ 67.818[deg] angles on two sets angles for a vicinal coupling constant of 4.1[Hz].

Conformational analysis play an important role in determination of the structure of ADN,⁸ exactly determination of the phase angle of pseudorotation $P[\text{deg}]$ and angle of deviation from planarity $\theta_m[\text{deg}]$, geometrical angles defined by Altona.⁹

The endocyclic torsional angles (Fig. 4) are calculated with PSEUROT program¹⁰ from exocyclic torsional angles calculated from polynomial equations: Karplus,¹¹ Haasnoot,¹² Pacher,¹³ Diez,^{14,15} Lowary.¹⁶



$$\theta_{\text{exo}} = A + B\theta_{\text{endo}}$$

cis: $A=1, B=0$, *trans:* $A=1, B=120$

Fig. 4 – Exocyclic and endocyclic torsional angles.

3-Sphere approach as demonstrated⁴ with trigonometric equation and confirmed by Lie algebra used exocyclic torsional angles with right sign and stereochemistry, usfully for simulation of the conformation¹⁷ and configuration¹⁸ on molecular models.

RESULTS AND DISCUSSION

Under 3-Sphere theory dihedral angles calculated from NMR data can be drawn on two congruent disks in close relationships with its

corresponding vicinal angles calculated from vicinal coupling constant ${}^3J_{\text{HnHn+1}}[\text{Hz}]$.¹ The angular velocity and manifold chart¹ on their transition map demonstrate the relationships between dihedral $\theta_{\text{HnHn+1}}[\text{deg}]$ and vicinal $\phi[\text{deg}]$ angles on two units of six sets angles. Hopf fibration ensuring relationship between two angles on two sets angles, dihedral and vicinal angles, under R^2 : real fibration $S^0 \rightarrow S^1 \rightarrow S^1$, and twelve angles on two units with four sets angles under R^{16} quaternionic multiplication $S^3 \rightarrow S^7 \rightarrow S^4$ leading to octonionic fibration $S^7 \rightarrow S^{15} \rightarrow S^8$, for all *cis*-, *trans-ee*-, *-aa* stereochemistry.

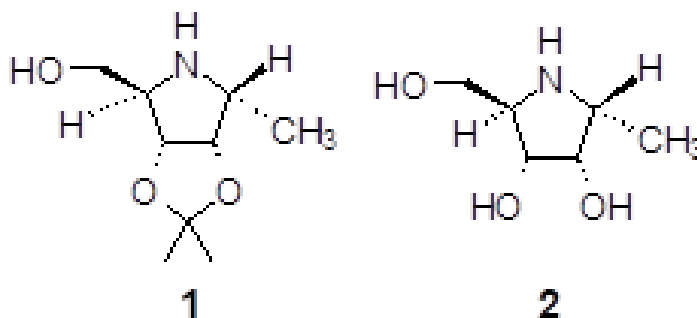


Fig. 5 – Iminocyclitols with C₁-methyl- α -D-ribitol stereochemistry.

In Table 1 are presented algebraic and trigonometric equations for isopropylidene protected iminocyclitol **1** and deprotected iminocyclitol **2** with C₁-methyl- α -D-ribitol stereochemistry (Fig. 5). With algebraic equations¹ are calculated the vicinal angles

for all stereochemistry from $\phi_1/2$ and ϕ_2 , angles results from differences between θ^2 and θ^1 or 90 and θ^3 , and θ^3 and θ^2 , totally in agreement with trigonometric equations, but the corresponding sign can be analyzed only with A2 root system – Lie group (Fig. 6).

Table 1

Dihedral angles calculated from vicinal coupling constant for iminocyclitols **1**, **2**.

Entry	$^3J_{\text{HH}}[\text{Hz}]^a$	$\phi[\text{deg}]$	$\theta_{\text{HnHn+1}}[\text{deg}]$	$\theta_{\text{HnHn+1}}$	ϕ
1.	4.1	67.24	22.76	$\sin^{-1}(\cos\phi)$	<i>cis</i> - <i>ea</i> ^{1,6} : $60 + \phi_1/2$
2.	5.4	116.64	-26.64	$\sin^{-1}(\cos\phi)$	<i>cis</i> - <i>ae</i> ^{1,6} : $120 - \phi_1/2$
3.	0.5	1.02	-88.97 -91.02	$\sin^{-1}(\cos\phi)$ $\sin^{-1}(\tan-\phi)^b$	<i>trans</i> - <i>ee</i> ^{3,2} : $120 + \phi_2 + \phi_1/2$ <i>trans</i> - <i>ee</i> ^{1,4} : $\phi_1/2$
4.	3.1	38.44	51.56 -51.56 -52.53	$\sin^{-1}(\cos\phi)$ $\sin^{-1}(\cos\phi)$ $\sin^{-1}(\tan-\phi)$	<i>cis</i> - <i>ae</i> ^{2,3} : $\phi_2 + \phi_1/2$ <i>cis</i> - <i>ae</i> ^{2,3} : $120 - \phi_1/2$ <i>cis</i> - <i>ae</i> ^{2,3} : $\phi_2 + \phi_1/2$
5.	3.9	60.84	29.15	$\sin^{-1}(\cos\phi)$	<i>cis</i> - <i>ea</i> ^{1,6} : $60 + \phi_1/2$
6.	8.8	77.44	-167.44 -12.56	$\sin^{-1}(1/\tan-\phi)$ $\sin^{-1}(\cos\phi)^c$	<i>trans</i> - <i>aa</i> ^{6,1} : $60 + \phi_1/2$ <i>cis</i> - <i>ae</i> ^{1,6} : $120 - \phi_1/2$

a. NMR data from *Org. Lett.* **2006**, 8, 3465; ^1H 400[MHz], ^{13}C 75[MHz], entry 1–3: comp. **1** CDCl_3 , entry 4–6: comp. **2** D_2O ; b. $\theta_{\text{H}_3\text{H}_4} = \sin^{-1}(\tan-\phi) - 90$; c. $\theta_{\text{H}_3\text{H}_4} = -180 + \sin^{-1}(\cos\phi)$.

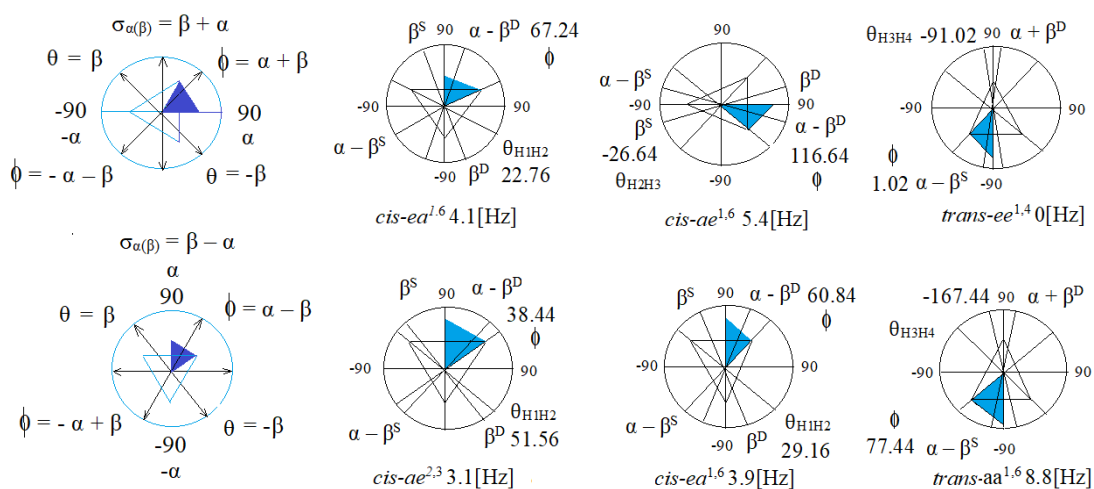


Fig. 6 – Dihedral angles calculated from vicinal coupling constant $^3J_{\text{HnHn+1}}[\text{Hz}]$ place on A2 root system Lie group.

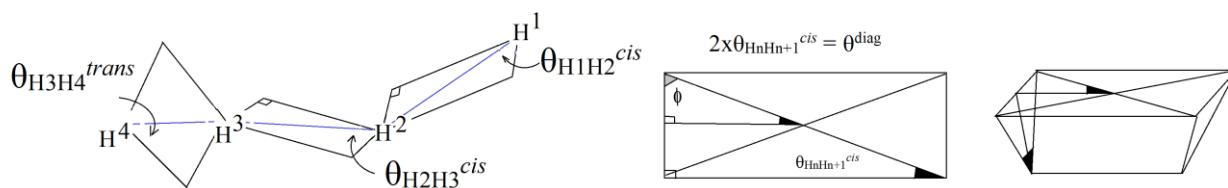


Fig. 7 – Dihedral angles with *cis* and *trans* stereochemistry on rectangle and rhombus geometries.

Table 2

Distances $l_{\text{HH}}[\text{Å}^0]$ calculated from dihedral angles $\theta_{\text{HnHn+1}}$ and vicinal angles $\phi[\text{deg}]$

Entry	$^3J_{\text{HH}}[\text{Hz}]$	$\phi[\text{deg}]$	$\theta_{\text{HnHn+1}}[\text{deg}]$	l_1 or $d_1[\text{Å}^0]$	l_2 or $d_2[\text{Å}^0]$	$l_{\text{HH}}[\text{Å}^0]$
1.	4.1	67.24	<i>cis</i> - <i>ea</i> : 22.76	0.976524	1.507636	2.48416
2.	5.4	116.64	<i>cis</i> - <i>ae</i> : -26.64	1.051294	1.484328	2.53562
3.	0.5	1.02	<i>trans</i> - <i>ee</i> : -88.49	2.628584	2.652087	2.62858
4.	3.1	38.44	<i>cis</i> - <i>ae</i> : -51.56	1.389480	1.23790	2.62738
5.	3.9	60.84	<i>cis</i> - <i>ea</i> : 29.15	1.095911	1.467213	2.56312
6.	8.8	77.44	<i>trans</i> - <i>aa</i> : -167.44	1.038516	3.121157	1.03851

l_1 – calculated from $\phi[\text{deg}]$, l_2 – calculated from $\theta_{\text{HnHn+1}}[\text{deg}]$, $l_{\text{H}_1\text{H}_1}^{\text{trans}}[\text{Å}^0] = d_1$.

In case of *cis* stereochemistry, two protons on two atoms of carbon and their images on mirror can be inscribed on rectangle (Fig. 7) using dihedral $\theta_{\text{HnHn+1}}[\text{deg}]$ and vicinal angles $\phi[\text{deg}]$ on the diagonal drawn between the real protons: $\theta_{\text{HnHn+1}} + \phi = 90[\text{deg}]$.

In case of *trans-aa* and *trans-ee* stereochemistry, two protons and their images on mirror are inscribed on rhombus geometry; using dihedral angle with *trans-aa* stereochemistry and corresponding *cis* angle or both dihedral angles with *trans-ee* stereochemistry.

As observation, the dihedral angle $\theta_{\text{HnHn+1}}[\text{deg}]$, angle at intersection of two planes along the two atoms of carbon is half of the diagonal angle of rectangle $\theta_{\text{diag}}/2[\text{deg}]$.

The distances $l_{\text{HnHn+1}} [A^0]$ between two protons on two atom consecutives of carbon can be calculated from dihedral $\theta_{\text{HnHn+1}}[\text{deg}]$ and vicinal angles $\phi[\text{deg}]$ as presented in Table 2 with Eq. 1–3.

The distances $l_{\text{H}_1\text{H}_1^i} [A^0]$ between proton H_1 and its mirror image H_1^i can be calculated from dihedral angle (Fig. 7) with rectangle approach (Eq. 4): $2 \times \theta_{\text{HnHn+1}} = \theta_{\text{diag}}[\text{deg}]$ and $l_{\text{H}_1\text{H}_1^i} [A^0] = l_2$ or from intersection of two planes, in case of *cis* stereochemistry, relative to *trans* stereochemistry with all $l_{\text{H}_1\text{H}_1^i} [A^0]$ distances calculated from $90[\text{deg}]$.

Rectangle geometry for *cis-ae* or *-ea*: $\theta_{\text{HnHn+1}} + \phi = 90[\text{deg}]$

$$\begin{aligned} l_{\text{HnHn+1}} &= (l_1 + l_2): l_1 = 1.57 \times \cos^{1/2} \phi [A^0], \\ l_2 &= 1.57 \times \cos^{1/2} \theta_{\text{HnHn+1}} [A^0] \end{aligned} \quad (1)$$

where: ϕ vicinal and $\theta_{\text{HnHn+1}}$ dihedral angle [deg].

Rhombus geometry for *trans-ee* or *-aa*:

$$l_{\text{HnHn+1}} = d_1 = 2 \times 1.57 \times \cos^{1/2} (\theta_{\text{HnHn+1}}^{A_n/2}) [A^0], \quad (2)$$

$$d_2 = 2 \times 1.57 \times \cos^{1/2} (\theta_{\text{HnHn+1}}^{A_n/2}) [A^0] \quad (3)$$

where:

$\theta_{\text{HnHn+1}}^{A_n}$: $\theta_{\text{HnHn+1}}^{A_3}$ and $\theta_{\text{HnHn+1}}^{A_4}$ – dihedral angles with *trans-ee* stereochemistry on set A;

$\theta_{\text{HnHn+1}}^{A_6}$ and $\theta_{\text{HnHn+1}}^{A_1}$ – dihedral angles with *trans-aa* and corresponding *cis* stereochemistry on set A.

Bond lengths $l_{\text{H}_1\text{H}_1^i} [A^0]$ between H_1 and H_1^i :

$$l_{\text{H}_1\text{H}_1^i} [A^0] = l_2 = 1.57 \times \cos^{1/2} (\theta_{\text{HnHn+1}}) \quad (4)$$

where $\theta_{\text{HnHn+1}}$ – dihedral angle [deg] for *cis* stereochemistry, in case of *trans* stereochemistry is equal with $90[\text{deg}]$.

Three rectangles on four atoms of carbon results from three vicinal coupling constant ${}^3J_{\text{HnHn+1}}[\text{Hz}]$, a string around four protons result from diagonals of rectangle and rhombus geometries ensuring the conformation of five membered ring. Alternatively, every atom of carbon can be inscribed on circle. Newman projection models are used on Macintosh

SEWIT J,¹⁹ MestRE-J,²⁰ or MatLab program with graphical interface (GUI),²¹ programs based on dihedral angles calculated from polynomial Karplus, Haasnoot and Diez equations and corresponding torsional angles.

CONCLUSIONS

Under wave theory, 3-sphere dihedral angles $\theta_{\text{HnHn+1}}[\text{deg}]$ can be calculated from trigonometric and algebraic equations with right sign and stereochemistry. 3-Sphere dihedral angles are usefully for conformational,^{17,4} and configurational analysis,¹⁸ calculation of tetrahedral angles $\varphi_{\text{Cn}}[\text{deg}]$,³⁻⁵ carbon-carbon bond lengths $l_{\text{CC}}[A^0]$,^{5,22} proton – proton distances $l_{\text{HH}}[A^0]$.

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