

Hopf Fibration on Relationship Between Dihedral Angle $\theta_{\text{HnHn+1}}$ [deg] and Vicinal Angle ϕ [deg], Angles Calculated from NMR Data with 3-Sphere Approach and Java Script

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Abstract: 3-Sphere theory, a hypersphere in four dimensions, is applied for calculation dihedral angles with the right stereochemistry and sign in D, -L ribitol series from proton and carbon chemical shift ($\Delta\delta_{\text{XnXn+1}}$ [ppm], X = H, C) and vicinal coupling constant ($^3J_{\text{HnHn+1}}$ [Hz]) with Java Script. A method in three steps, easy to calculate by hand or with Java Script program: 1. prediction of the dihedral angle only from $^3J_{\text{HnHn+1}}$ [Hz], 2. calculation the angle of set A with manifold equation (conic section, Villarceau circles) from chemical shift, 3. building of the seven sets unit or six sets units, from which is chose an angle almost equal with the predicted one having its stereochemistry and sign. Angles of set A and set B, relationships between vicinal angle and dihedral angle (X_0-X_{15}) are introduced instead of polar angle and azimuthal angle in spherical coordinates (eq. 1 versus eq. 3). Hopf coordinates, trigonometric equations, confirmed by algebraic equations are disclosed for all *cis*-ae/ea, *trans*-ee, *trans*-aa stereochemistry. Octonionic fibration $S^7 \rightarrow S^{15} \rightarrow S^8$ in R^{16} , with real fibration $S^0 \rightarrow S^1 \rightarrow S^1$ as unit, reassembles all possible stereochemistry gives by the HCCH fragment on two congruent disks, each centered on the perimeter of the other with equilateral triangles as vertices. Complex Hopf fibration in R^4 ensuring the calculation of the dihedral angle from vicinal angle and *vice versa*, demonstrating the relationships between sets A, B, C.

Keywords: 3-sphere, Hopf Fibration, Villarceau Circles, Dihedral Angle, Vicinal Angle, Vicinal Coupling Constant, Java Script

1. Introduction

In strict definition, dihedral angle [1] result from the geometric spatial representation of two protons on HCCH fragment and other two imaginary proton, an angle at the intersection of two plans. From the NMR data point of view, dihedral angle with *cis* or *trans* stereochemistry can be drawn on two congruent disks [2], each centered on the perimeter of the other, having equilateral triangles as vertices (Figure 1, I, II). Dihedral angle is in close relationship with the vicinal angle [3], angle results from the vicinal coupling constant $^3J_{\text{HH}}$ [Hz] (Figure 1): I. *cis*-ae, *cis*-ea, *trans*-ee^{3,2}; $\theta^{\text{An}} + \theta^{\text{Bn}} =$

90, II. *trans*-ee^{4,1}, *trans*-aa^{6,1}, *trans*-aa^{5,2}; $\theta^{\text{An}} - \theta^{\text{Bn}} = 90$. The trigonometric equations and algebraic equation [4], under 3-sphere and Lie group theories ensure a great correlation between the vicinal coupling constant and the dihedral angle with its corresponding sign and stereochemistry, using one set angles (dihedral angle - θ^{An} , vicinal angle - $\phi = f(\phi_{1A}/2, \phi_{2A})$, or two set angles (dihedral angle - θ^{An} , vicinal angle - θ^{Bn} , $n = 1-6$) under ± 60 [deg] rule. The vicinal angle result from angles of three sets angles [3], demonstrate using angular velocity representation in R^4 (Figure 1, III).

A method easy to calculate dihedral angles by hand or with Java Script [3] in three steps: 1. Prediction of the dihedral angle only from the vicinal coupling constant, a step which

gives the sign without any ambiguity [5]. 2. Manifold equations transformed the NMR data (the differences in chemical shift between two atoms of carbon and/or protons) in angle(s). 3. Construction of the unit with seven sets angles and the corresponding parallel unit. To the angle almost equal

with the predicted one, having the contribution of the chemical shift, is added the sign of the predicted one. The vicinal coupling constant can be calculated from the dihedral angle, a way for verification at list the sign and stereochemistry.

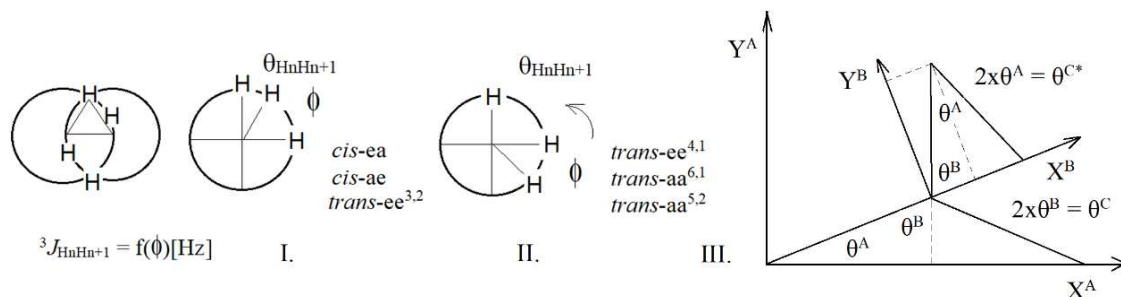


Figure 1. Dihedral angles with cis and trans stereochemistry on two intersecting circles: I. $\theta^{An} + \theta^{Bn} = 90$, II. $\theta^{An} - \theta^{Bn} = 90$, where θ^{An} – dihedral angle[deg], θ^{Bn} – vicinal angle[deg], III. Angular velocity ($\theta^C \neq \theta^{C*}$) in R^4 .

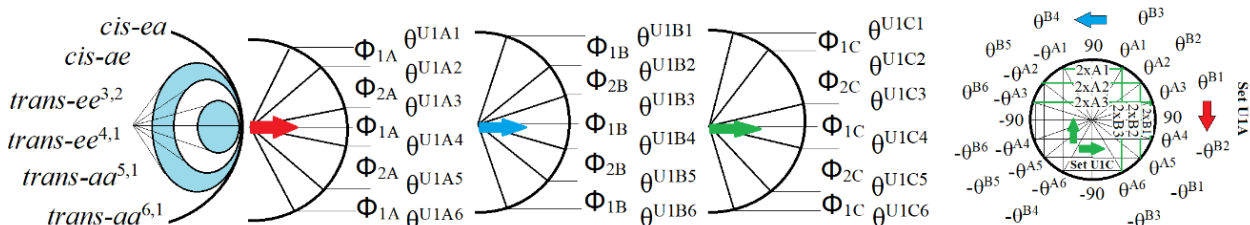


Figure 2. Dihedral angle and vicinal angle on three sets angles A, B, C of unit U1: $\theta^{U1A1} = \phi_{1A}/2$, $\theta^{U1B1} = \phi_{1B}/2$, $\theta^{U1C1} = \phi_{2A}$, $\theta^{U1C2} = \phi_{2B}$.

2. Method and Its Mathematic Theories

2.1. 3-Sphere Approach

Six dihedral angles with cis-, trans-stereochemistry, angles of set A, can be inscribed on three concentric cons with two characteristics angles ϕ_{1A} and ϕ_{2A} (Figure 2), angles of set B. 3-Sphere theory, a hypersphere in 4-dimension space, and Lie group theory comprise on one circle: three set angles, from north to south set A, from east to west set B, and set C with

three angles from set A and three from set B multiplied by two (Figure 2). Totally 36 angles θ^{Nn} on one circle, where $n = 1-6$, $N = A, B, C$, with positive and negative angles. Four sets angles on two units (U and S) ensures the calculation of the dihedral angles for cis-, trans- stereochemistry with trigonometric equations, in agreement with differential topology (Figure 3, I). In fact, six set angles on two parallel units (U and S) as demonstrated with vicinal angles [3] for cis-, trans-stereochemistry, two Veen diagram (Figure 3), six circles on two units.

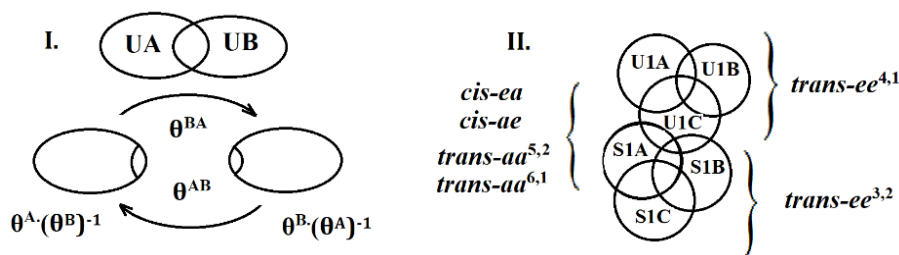


Figure 3. I. Two manifold charts and their transition map: $^3J_{HH} = 3.1$ [Hz], $51x(1/39) = 1.30769 = 1/0.76470 = 39x(1/51)$. II. Three set angles on two Veen diagram - six circles on two units.

2.2. Hopf Coordinates

Trigonometric equations between two sets angles are obtained from Euler tessellation, analog to Hopf coordinates [2b, 6], embedded S^3 in C^2 (θ, ϕ_1, ϕ_2). Relationships between sets A, B, C can be demonstrated with quaternions (H),

Euler's analog equation. Quaternions are points on R^4 , and for any point P in S^3 the preimage $s.h^{-1}(P)$ is a circle in S^2 . [7] A circle of latitude gives a torus (T^2 in R^3), more circles of latitude give tori. [8]

In the light of dihedral angle - vicinal coupling constant relationship, under Hopf model [2b, 6] results the eq. 1 or 2 (equation as set of coordinates):

$$X_0 = \cos\phi\sin\theta, X_1 = \sin\phi\sin\theta \quad (1)$$

$$X_2 = \cos\theta\sin\phi, X_3 = \sin\theta\sin\phi \quad (2)$$

with $\phi = f(\phi_1/2, \phi_2)$ - vicinal angle[deg], θ - dihedral angle[deg];

$$X_0 = \cos\theta^{Bn}\sin\left(\frac{\theta^{Cn}}{2}\right), X_1 = \sin\theta^{Bn}\sin\left(\frac{\theta^{Cn*}}{2}\right) \quad (3)$$

$$X_3 = \sin\theta^{An}\sin\left(\frac{\theta^{Cn}}{2}\right), \text{ instead of } X_3 = \cos\theta^{An}\sin\left(\frac{\theta^{Cn}}{2}\right) \quad (4)$$

with $\theta^{Bn} = \theta^{U1Cn*}/2$, $\theta^{An} = \theta^{Cn}/2$, $n = 1-6$; θ^{Bn} - angle of set B, θ^{An} - angle of set A, θ^{Cn} - angle of set C, $\theta^{Cn*} \neq \theta^{Cn}$:

$$\begin{aligned} X &= a\sin\theta\cos\phi \\ Y &= b\sin\theta\sin\phi \\ Z &= c\cos\phi \end{aligned} \quad (5)$$

where θ - polar angle[deg], ϕ - azimuthal angle[deg].

In this paper are introduced angles of set A and set B, relationships between vicinal angle ϕ and dihedral angle θ , or vice versa (X_0-X_{15} , eq. 1: $\phi = \theta^{Bn}$, eq. 2: $\theta = \theta^{An}$), instead

of polar angle and azimuthal angle in spherical coordinates (eq. 5), or coordinates for a right circular conic surface [9, 2c], or Euler angles [2d]. Hopf fibration [10-12] describe 3-sphere in terms of circles and ordinary sphere. Four dimensions (R^4)[13], relationships between sets A and B, complex Hopf fibration $S^1 \rightarrow S^3 \rightarrow S^2$, a way to calculate with eq. 1 angle A from angle B (θ from ϕ), or with eq. 2 angle B from angle A (ϕ from θ). R^{16} from the *cis/trans* stereochemistry point of view, octonionic Hopf fibration $S^7 \rightarrow S^{15} \rightarrow S^8$, quaternionic multiplication $S^3 \rightarrow S^7 \rightarrow S^4$, with real fibration $S^0 \rightarrow S^1 \rightarrow S^1$ as generalized 3-sphere Hopf fibration (eq. 6: X_0-X_{15}), a way to calculate angle in one direction. Two set equations in R^{16} results for *cis*, *trans* stereochemistry with positive and negative angles, because the generalized R^4 octonionic Hopf fibration gives R^{32} , and unfortunately the sphere S^{31} don't fiber [2b] over S^{16} with fiber S^{15} . The Blakers-Massey element [14] $\pi_6 S^3 \rightarrow S^6$ depends on two quaternions with their extension to the octonions through $\pi_{14}(S^7)$ and exotic diffeomorphism of S^{14} . In other word, two set equations in R^{16} , for each the Hopf fibration 3-spheres on S^{4n-1} parallel to one another [10].

$$\begin{aligned} X_0 &= \cos\theta^{U1B3}\sin\theta^{U1A6}, X_1 = \sin\theta^{U1B3}\sin\left(\frac{\theta^{U1C5}}{2}\right), \phi_{aa6,1} = \theta^{U1B3}, \theta_{HH} = \theta^{U1A6}, \left(\frac{\theta^{U1C5}}{2}\right) = \theta^{U1B3}: \text{trans-aa}^{6,1}, \\ X_2 &= \cos\theta^{U1B2}\sin\theta^{U1A5}, X_3 = \sin\theta^{U1B2}\sin\left(\frac{\theta^{U1C4}}{2}\right), \phi_{aa5,2} = \theta^{U1B2}, \theta_{HH} = \theta^{U1A5}, \left(\frac{\theta^{U1C4}}{2}\right) = \theta^{U1B2}: \text{trans-aa}^{5,2}, \\ X_4 &= \cos\theta^{U1B1}\sin\theta^{U1A4}, X_5 = \sin\theta^{U1B1}\sin\left(\frac{\theta^{U1C1}}{2}\right), \phi_{ee4,1} = \theta^{U1B1}, \theta_{HH} = \theta^{U1A4}, \left(\frac{\theta^{U1C1}}{2}\right) = \theta^{U1B1}: \text{trans-ee}^{4,1}, \\ X_6 &= \cos\theta^{U1B1}\sin\theta^{U1A3}, X_7 = \sin\theta^{U1B1}\sin\left(\frac{\theta^{U1C1}}{2}\right), \phi_{ee4,1} = \theta^{U1B1}, \theta_{HH} = \theta^{U1A3}, \left(\frac{\theta^{U1C1}}{2}\right) = \theta^{U1B1}: \text{trans-ee}^{3,2}, \\ X_8 &= \sin\theta^{S1B1}\cos\theta^{S1A3}, X_9 = \sin\theta^{S1B1}\sin\left(\frac{\theta^{S1C1}}{2}\right), \phi_{ee3,2}^{U1B} = \theta^{S1B1}, \theta_{HH} = \theta^{S1A3}, \left(\frac{\theta^{S1C1}}{2}\right) = \theta^{S1B1}: \text{trans-ee}^{3,2}, \\ X_{10} &= \sin\theta^{S1B1}\cos\theta^{S1A4}, X_{11} = \sin\theta^{S1B1}\sin\left(\frac{\theta^{S1C1}}{2}\right), \phi_{ee3,2}^{U1B} = \theta^{S1B1}, \theta_{HH} = \theta^{S1A4}, \left(\frac{\theta^{S1C1}}{2}\right) = \theta^{S1B1}: \text{trans-ee}^{4,1}, \\ X_{12} &= \cos\theta^{U1B3}\sin\theta^{U1A1}, X_{13} = \sin\theta^{U1B3}\sin\left(\frac{\theta^{U1C5}}{2}\right), \phi_{aa1,6} = \theta^{U1B3}, \theta_{HH} = \theta^{U1A1}, \left(\frac{\theta^{U1C5}}{2}\right) = \theta^{U1B3}: \text{cis-ae/ea}^{1,6}, \\ X_{14} &= \cos\theta^{U1B2}\sin\theta^{U1A2}, X_{15} = \sin\theta^{U1B2}\sin\left(\frac{\theta^{U1C4}}{2}\right), \phi_{ae2,5} = \theta^{U1B2}, \theta_{HH} = \theta^{U1A2}, \left(\frac{\theta^{U1C4}}{2}\right) = \theta^{U1B2}: \text{cis-ae/ea}^{2,5}. \end{aligned} \quad (6)$$

Dihedral angles with positive sign or negative in east or west side of the hypersphere are in R^{16} admitting the coordinates X_6, X_7 and X_{10}, X_{11} for *trans-ee* stereochemistry in units U and S, otherwise are in R^{12} in strict application rule.

The trigonometric eq. 7 ensure a perfect relationship between angles of set A and B for positive and negative angles with *cis*- and *trans*-stereochemistry in relationship of 180[deg], but with equal ϕ_N for *trans-ee*^{3,2} and *trans-ee*^{4,1} stereochemistry.

$$\cos^{-1} \sin \theta^{UmNn} = \phi_N \quad (7)$$

$$\begin{aligned} \text{cis/trans-aa}^{6,1}: \quad \phi_{aa6,1} &= 60 + \frac{\phi_{1A}}{2} = \theta^{B3} \\ \theta^{B3} &= 60 + \theta^{B1} = \theta^{C1} + \theta^{C2} + \theta^{B1} \end{aligned} \quad (8)$$

where $m = 1$ to infinite, $n = 1-6$, $N = A, B, C$; if $\theta^{UmNn} = \theta^{U1An}$, $\phi_N = \theta^{Bn}$, with $n = 3, 2, 1$ for θ^{U1An} positive, and $n = 4, 5, 6$ for θ^{U1An} negative.

2.3. Algebraic Equations

Algebraic equations can be expressed relative to angle $\phi = f(\phi_1/2, \phi_2)$ of the set A, set containing also the required dihedral angle, or relative to angles θ of set B ($\phi = f(\theta^{Bn})$) or C ($\phi = f(\theta^{Cn}, \theta^{Bn})$), in close relationships with set A.

Algebraic equations 8-10 for positive dihedral angles with *cis*-, *trans*-stereochemistry:

$$\begin{aligned} \text{cis/trans} - aa^{5,2}: \quad \phi_{aa^{5,2}} &= \phi_{2A} + \frac{\phi_{1A}}{2} = \theta^{B2} \\ \theta^{B2} &= \theta^{A2} + \frac{\theta^{B1}}{2} = \theta^{C2} + \theta^{B1} \end{aligned} \quad (9)$$

$$\text{cis/trans} - aa^{3,2}: \phi_{ee^{3,2}} = \frac{\phi_{1A}}{2} = \theta^{B1}, \quad (10)$$

Algebraic equations 11-13 for negative dihedral angles with *cis*-, *trans*-stereochemistry:

$$\text{cis/trans} - aa^{6,1}: \phi_{aa^{6,1}} = 120 - \frac{\phi_{1A}}{2} = 120 - \theta^{B1}, \quad (11)$$

$$\text{cis/trans} - aa^{5,2}: \phi_{aa^{5,2}} = 120 + \frac{\phi_{1A}}{2} = 120 + \theta^{B1}, \quad (12)$$

$$\text{cis/trans} - ee^{4,1}: \phi_{ee^{4,1}} = 120 + \phi_{2A} + \frac{\phi_{1A}}{2} = 120 + \theta^{B2} + \theta^{B1}. \quad (13)$$

The algebraic eq. 14 don't fit into the trigonometric eq. 7, equation unable to discriminate between *trans-ee*^{4,1} and *trans-ee*^{3,2} stereochemistry around the 90[deg].

$$\text{cis/trans} - ee^{3,2}: \phi_{ee^{3,2}}^{U1A} = \phi_2^{U1A} - (\phi_1^{U1A}/2). \quad (14)$$

Analog to torus inversion to Dupin Cyclide [15, 16], the hypersphere trigonometric eq. 15 don't discriminated between angles with *trans-ee* stereochemistry. Positive vicinal coupling constant around 0[deg] result from a negative vicinal angle ϕ [deg] only under CAD rule: $(-x)^{1/2} = +/x$. The eq. 16 is compatible with eq. 7 for all stereochemistry excepting the sign of *trans-aa* stereochemistry.

The shadows of sets U1An and U1Bn, sets S1An and S1Bn (Table 1), having one angle θ^{S1N1} (N = A, B) of unit S1 equal with the algebraic angle $\phi_{ee^{3,2}}^{U1A}$ of unit U1 (eq. 14), make the difference between *trans-ee*^{4,1} and *trans-ee*^{3,2} stereochemistry through eq. 18. For both, positive and negative algebraic for *trans-ee*^{3,2} stereochemistry (eq. 14) the

calculated angle θ^{S1B3} will be positive (Eq. 18). The eq. 19 for negative algebraic angle gives an angle with *trans-ee*^{4,1} stereochemistry in unit S1, and for positive algebraic angle result an angle with *trans-ee*^{3,2} stereochemistry, *trans-ee*^{3,1} as results from Hopf coordinates (X_6, X_8).

$$\begin{aligned} \sin^{-1}\left(\frac{1}{\tan-\phi}\right) &= \theta_{\text{HnHn}+1} \\ \sin^{-1}\left(\frac{1}{\tan(+/-)\theta^{A3}}\right) &= +/\theta^{B1} \\ \sin^{-1}\left(\frac{1}{\tan(+/-)\theta^{A4}}\right) &= -/+ \theta^{B1} \end{aligned} \quad (15)$$

$$\begin{aligned} \tan^{-1}\left(\frac{1}{\tan-\phi}\right) &= \theta_{\text{HnHn}+1} \\ \tan^{-1}\left(\frac{1}{\tan(+/-)\theta^{A3}}\right) &= +/\theta^{B1} \\ \tan^{-1}\left(\frac{1}{\tan(+/-)\theta^{A4}}\right) &= -/+ \theta^{B1} \end{aligned} \quad (16)$$

$$\tan^{-1}(\sin - \phi) = \theta_{\text{HnHn}+1} \quad (17)$$

Table 1. Venn diagrams. Three sets U1A, U1B, U1C with corresponding parallel sets S1A, S1B, S1C; data from Table 2, Entry 3: *trans*-3,2 H₃H₄ (1).

Entry	θ^{U1An} [deg]	θ^{U1Bn} [deg]	θ^{U1Cn} [deg]	Entry	θ^{S1An} [deg]	θ^{S1Bn} [deg]	θ^{S1Cn} [deg]
1	19.65860	10.34139	20.68796	2	28.97580	1.02419	2.04839
	40.34139	49.65601	39.31203		31.02419	58.97580	57.95160
	79.65860	70.34398	80.68796		88.97580	61.02419	62.04839
	100.34139	109.65601	99.31203		91.02419	118.97580	117.9516
	139.65860	130.34398	140.68796		148.97580	121.02419	122.04839
	160.34139	169.65601	159.31203		151.02419	178.97580	177.95160
ϕ_2	39.31720	20.68796	41.37593	ϕ_2	57.95160	2.04839	4.09678
$\phi_1/2$	10.34139	19.65601	9.31203	$\phi_1/2$	1.02419	28.97580	27.95160

$$\sin^{-1}(\cos\phi^{\text{vic}}) = \theta_{\text{HnHn}+1}^{\text{cis or trans-ee}} \quad (18)$$

if $\phi^{\text{vic}} = (+/-)\phi_{U1A}/2$, $[(+/-) = + \text{ or } -]$; $\theta_{\text{HnHn}+1}^{\text{trans-ee}^{4,1}} = 180 - \theta_{\text{HnHn}+1}^{\text{trans-ee}^{3,2}}$, preferably $(+/-)\theta_{\text{HnHn}+1}^{S1A1}$, $\theta_{\text{HnHn}+1}^{\text{trans-ee}} = \theta^{S1B3}$,

$$\cos^{-1}(\sin - \phi^{\text{vic}}) = \theta_{\text{HnHn}+1}^{\text{trans-aa}} \quad (19)$$

if $\phi^{\text{vic}} = \theta^{S1A1}$, $\theta_{\text{HnHn}+1}^{\text{trans-ee}} = \theta^{S1B4}$, $\theta^{S1A1} = \phi_2^{U1A} - \phi_1^{U1A}/2$, where: ϕ^{vic} - vicinal angle[deg], θ^{S1B3} - *trans-ee*^{3,2} dihedral angle[deg], θ^{S1B4} - *trans-ee*^{4,1} dihedral angle[deg].

Considering the unit SM (M = 1 to infinite), a unit parallel with unit UM, totally in agreement with eq. 18 for *trans-ee*^{3,2} stereochemistry, only the positive algebraic angle must be considered, since negative or positive dihedral angles have

different vicinal coupling constants: *i.e.* *trans-ee*^{3,2} 87.34[deg] with $^3J_{\text{HH}}$ 0.815[Hz] and *trans-aa*^{6,1} -87.34[deg] with $^3J_{\text{HH}}$ 6.65[Hz] (eq. 7).

Otherwise, D-, L- ribitol series have equal vicinal coupling constant and smaller carbon chemical shift differences, and *trans-aa*^{6,1} H₃H₄ is negative for D ribitol and positive for L ribitol, as demonstrated with molecular models [17], and positive in both cases as result from trigonometric eq. 19, *i.e.* *trans-aa*^{6,1} 167.44[deg] with $^3J_{\text{HH}}$ 8.8[Hz] and *trans-aa*^{6,1} -167.44[deg] with $^3J_{\text{HH}}$ 10.1[Hz]. Negative sign result from eq. 15 (-167.12[deg]), but with a difference of 0.02[Hz], 0.313[deg], since from eq. 17 result *trans-aa*^{5,2} stereochemistry (-135.69[deg]).

2.4. Prediction of the Vicinal Angle

The vicinal coupling constant can be predicted from the vicinal angle ϕ with eq. 20, and the vicinal angle from the vicinal coupling constant eq. 21, 22.

$$^3J_{HH} = (\phi)^{1/2}/m, \text{ trans } m = 1, \text{ cis } m = 2, \quad (20)$$

$$\phi = (2x^3 J_{HH}^{\text{cis}})^2 - \text{cis and trans-ee stereochemistry}, \quad (21)$$

$$\phi = ({}^3J_{HH}^{\text{trans}})^2 - \text{trans-aa stereochemistry}, \quad (22)$$

where: $\phi = f(\phi_1/2, \phi_2)$ – the vicinal angle.

Dihedral angles are predicted [5] only from vicinal coupling constants with eq. 21, 22: the eq. 21 is used for *cis* and *trans-ee* stereochemistry and the eq. 22 for *trans-aa* stereochemistry. Negative dihedral angles are between 4.8 and 8[Hz] for *cis/trans-ee* stereochemistry (eq. 18), and between 9.4 and 9.9[Hz] for *trans-aa* stereochemistry (eq. 19, Step123SkewVillar.html – Figure 5). With the eq. 18 from the negative or positive vicinal angle result *trans-ee*^{3,2}

stereochemistry, and with eq. 19 from negative vicinal angle result *trans-ee*^{4,1} stereochemistry. Under manifold (R_m) value and unit rule all the angles are positive, in case of the algebraic angle with *trans-ee*^{3,2} stereochemistry the difference between the ϕ_2 and $\phi_1/2$ has sometimes negative sign, but will be ignored, and take in consideration the transformation from U1 to S1 with positive sign (eq. 14).

3. Results and Discussion

In table 2 are presented the dihedral angles and the corresponding vicinal coupling constants of iminocyclitols [18] 1-3 with α -D-ribitol and 4, 5 with β -L-ribitol stereochemistry (Figure 4) calculated from the NMR data, the differences between two atoms of carbon ($\Delta\delta_{CnCn+1}$) or protons ($\Delta\delta_{HnHn+1}$) chemical shift, transformed from ppm in gauss, under conic section rule (θ_{HnHn+1}^A [deg]) and conic section approach (θ_{HnHn+1}^A [deg]). In table 3 are calculated angles with noncoplanar Villarcieu circles. [3]

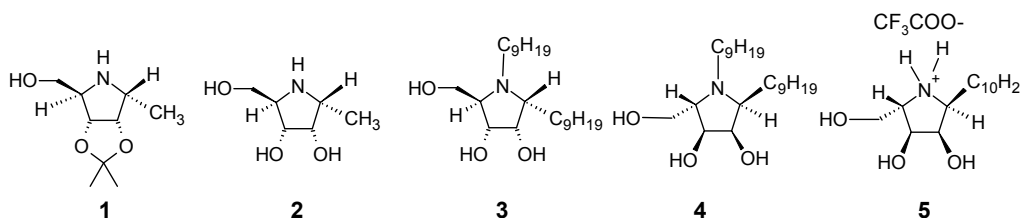


Figure 4. Iminocyclitols with D-ribitol 1-3 and L-ribitol 4, 5 stereochemistry.

3.1. Prediction of the Dihedral Angle

In step 1 are predicted [5] only from vicinal coupling constants the vicinal angles with *cis*- and *trans*-stereochemistry (eq. 21, 22), then the dihedral angles. The Java Script programs for calculation of the dihedral angles used eq. 18 [5] for *cis* and *trans-ee* stereochemistry and eq. 19 [3] for *trans-aa* stereochemistry. Knowledge about the approximated values of the dihedral angle and its sign from the first step easiest the step 3. Between a huge number of angles under six sets angles on two units' rule, or on units with seven sets angles can be chose one with values almost equal with the predicted one.

3.2. Calculation of the Angle of Set A with Manifold Equations

In step 2[19] are calculated angles of set A and B from the

differences between two atoms of carbon chemical shift δ_{CnCn+1} [ppm], or two protons δ_{HnHn+1} [ppm], with the manifold equations ($\sin^{-1}R_m = \theta^{An}$, $n = 1-6$): conic section ($R_m = f(\Delta\delta_{XnXn+1}$, $X = C, H$)), and skew circles – non coplanar Villarcieu circles ($R_m = f(\Delta\delta_{HnHn+1}/\Delta\delta_{CnCn+1})$).

Conic section [3]: one angle of set A can be calculated with *sin* function (eq. 23) from the differences between two consecutive atoms of carbon or two protons with Java Script program Step123CONIC.html.

The hypersphere trigonometric eq. 7 results from Euler tessellation of the spherical coordinates eq. 23.

$$\sin\theta^{An} = R_m = \cos\theta^{Bn} \quad (23)$$

with $\cos^{-1}R_m = 90 \pm \theta^{An} = \theta^{Bn}$, or $\sin\theta_{HnHn+1} = R_m$, $\cos^{-1}R_m = \phi$, resulting eq. 7: $\cos^{-1}\sin\theta_{HnHn+1} = \phi$, where: θ^{An} , θ^{Bn} – angles of set A and B[deg], θ_{HnHn+1} – dihedral angle, ϕ – vicinal angle[deg].

Table 2. Dihedral angles θ_{HnHn+1} [deg] calculates with 3-sphere approach and conic section or conic section approach.

Entry	H_nH_{n+1}	$^3J_{HH}^{\text{exp}}$ [Hz] ^a	θ^{pred} [deg] R_m^j [π] ^b	R_{mc} [π] ^b	θ_{HnHn+1} , $^3J_{HH}^{\text{calc}}$ [Hz]	A	θ_{HnHn+1}^A [deg]	R_{ml} [π] ^b	$\theta_{HnHn+1}^{\text{calc}}$, $^3J_{HH}^{\text{calc}}$ [Hz]	A	θ_{HnHn+1}^A [deg]
1.	1-H ₁ H ₂	4.1	22.76 0.386	0.7759	ea ^{6,1} : 20.88 ^{U1B1} , 4.15	0.498	25.372	0.0529	ea ^{6,1} : 22.02 ^{SU1C1} , 4.12	7.300	22.176
2.	1-H ₂ H ₃	5.4	-26.639 -0.448	0.0224	ae ^{6,1} : -28.71 ^{S1B1} , 5.44	-20.0	-25.692	0.0041	ae ^{6,1} : -29.76 ^{S1B1} , 5.47	-108.4	-25.69
3.	1-H ₃ H ₄	0 (d H ₃)	90, 1	0.5154	ee ^{3,2} : -88.97 ^{S1A3} , 0.506	1.94	89.81	0.0435	ee ^{3,2} : -87.50 ^{S1B3} , 0.79 ee ^{3,2} : -88.75 ^{S1E3} , 0.55	22.93	87.325
4.	2-H ₁ H ₂	3.1	51.55	0.3949	ae ^{5,2} : 50.209 ^{US1B2} , 3.15 ^c	1.98	46.13	0.0169	ae ^{5,2} : 49.67 ^{U1B2} , 3.17	46.31	45.87

Entry	H_nH_{n+1}	$^3J_{HH}^{exp}$ [Hz] ^a	θ_{HnHn+1}^{pred} [deg] R_m^j [°]	R_{mC} [°] ^b	$\theta_{HnHn+1}, ^3J_{HH}^{calc}$ [Hz]	A	θ_{HnHn+1}^A [deg]	R_{mH} [°] ^b	$\theta_{HnHn+1}^{calc}, ^3J_{HH}^{calc}$ [Hz]	A	θ_{HnHn+1}^A [deg]
5.	2-H ₂ H ₃	3.9	0.793 29.15 0.487	0.0056	ae ^{5,2} : 51.736 ^{U2F2} , 3.09 ea ^{6,1} : 29.67 ^{S1B1} , 3.88	86.97	27.91	0.0037	ea ^{6,1} : 29.78 ^{S1B1} , 3.87	129.6	27.91
6.	2-H ₃ H ₄	8.8	167.43 0.217	0.1375	aa ^{6,1} : -168.9 ^{SU1F6} , 8.87 ^c	1.58	167.51	0.0255	aa ^{6,1} : -169.51 ^{SU1B6} , 8.9 ^c	8.508	167.54
7.	3-H ₁ H ₂	4.8	-2.159 -0.0376	0.2464	ea ^{6,1} : -7.13 ^{U1D1} , 4.92 -2.918 ^{U2SC1} , 4.81 ^c	-0.15	-2.181	0.0342	ea ^{6,1} : -1.96 ^{S1A1} , 4.79	-1.101	-2.159
8.	3-H ₂ H ₃	5.2	-18.15 -0.3116	0.0420	ae ^{6,1} : -16.204 ^{S1G1} , 5.15 -19.197 ^{U1B1} , 5.22	-7.41	-17.86	0.0037	ae ^{6,1} : -15.107 ^{S1G1} , 5.12 -19.928 ^{U1B1} , 5.22	-82.93	-17.85
9.	3-H ₃ H ₄	0 (t H ₃)	90, 1	0.1316	ee ^{3,2} : - 86.34 ^{S1E3} , 0.95 ^c	7.59	87.47	0.0462	ee ^{3,2} : - 87.35 ^{S1B3} , 0.81 ^c	21.99	88.25
10.	4-H ₁ H ₂	4.8	-2.16 -0.0375	0.0756	ea ^{6,1} : -2.168 ^{S1D1} , 4.8	-0.498	-2.161	0.0345	ea ^{6,1} : -1.981 ^{S1A1} , 4.79	-1.089	-2.159
11.	4-H ₂ H ₃	5.2	-18.159 -0.3116	0.0448	ae ^{6,1} : -16.28 ^{S1G1} , 5.15 -19.14 ^{U1A1} , 5.22	-6.956	-17.863	0.0030	ae ^{6,1} : -15.08 ^{U1G1} , 5.12 -19.94 ^{U1A1} , 5.22	-103.6	-17.857
12.	4-H ₃ H ₄	0 bs (0.1)	90, 1 90.04	0.05042	ee ^{3,2} : 87.10 ^{S1B3} , 0.85	19.83	87.31	0.0454	ee ^{3,2} : 87.39 ^{S1B3} , 0.807	21.99	87.312
13.	5-H ₁ H ₂	2.8	58.63 0.8539	0.22969	ae ^{5,2} : 56.55 ^{U2B2} , 2.89 58.27 ^{U2F2} , 2.81	3.717	49.366	0.0233	ae ^{5,2} : 58.66 ^{S1A2} , 2.79	36.64	48.93
14.	5-H ₂ H ₃	3.6	38.159 0.6178	0.03641	ea ^{5,2} : 38.34 ^{S3B2} , 3.59 38.608 ^{U1C2} , 3.58	16.96	35.408	0.0033	ea ^{5,2} : 37.03 ^{S5B2} , 3.63 ea ^{5,2} : 39.85 ^{U1C2} , 3.54	182.654	35.4008
15.	5-H ₃ H ₄	8.8	167.43 0.2174	0.28291	aa ^{6,1} : 166.434 ^{U1B6} , 8.74 169.30 ^{S1B6} , 8.9	0.795	166.93	0.0266	aa ^{6,1} : 165.764 ^{S1F6} , 8.70 169.49 ^{U1B6} , 8.9	8.429	167.109

a. δ_C , δ_H [ppm], 1H 400MHz, ^{13}C 75MHz: 1-CDCl₃, 2-D₂O, 3-CDCl₃, 4-CDCl₃, δ_H 5-CDCl₃, δ_C 5-CD₃OD [18], b. $R_m = \Delta\delta_{Cn+1}X\omega_CX4/(6.7/6.28) \times 10^7 = \Delta\delta_{Cn+1}X\omega_CX4 \times 10^{-3}/(6.7/6.28) \times 10^4$ [1/T] = $\Delta\delta_{Cn+1}X\omega_CX4 \times 10^{-3}/10.71$ [gauss], $\Delta\delta$ – the differences in chemical shift between two consecutive atoms of carbons [ppm], ω_L – Larmor frequency [MHz], γ – gyromagnetic ratio; ^{13}C NMR: $\omega_C = 75$ [MHz], $\gamma = 10.71$ [MHzxT⁻¹] = 6.7 [10⁷xradxT⁻¹xs⁻¹], (6.7 [10⁷xradxT⁻¹xs⁻¹]/6.28 ~ 10.6668x10⁶ ~ 10.668 [MHzxT⁻¹]); $\omega_H = 400$ [MHz], $\gamma = 42.57$ [MHzxT⁻¹] = 26.75 [10⁷xradxT⁻¹xs⁻¹], c. D series rule. Note: Entry 4: US1B2 – transformation from U1 to U1 with S rule; Entry 6: SU1D6 – transformation S1 to U1 from the seven sets unit U1S1U1; Entry 7: U2SC1 – transformation U1 to S1 with U rule.

Table 3. Dihedral angles (θ_{HnHn+1} [deg]) calculated with 3-sphere approach and non-coplanar Villarceau circles.

Entry	H_nH_{n+1}	$^3J_{HH}^{exp}$ [Hz] ^a	R_m^c	An ^d [deg]	$\theta_{HnHn+1}^{calc}, ^3J_{HH}^{calc}$ [Hz]
1.	1-H ₁ H ₂	4.1	0.2714	15.747	ea ^{6,1} : 22.12 ^{U1E1} , 4.11
2.	1-H ₂ H ₃	5.4	0.7333	47.166	ae ^{6,1} : -25.66 ^{U1C1} , 5.37
3.	1-H ₃ H ₄	0 (d H ₃)	0.3362	19.647	ee ^{3,2} : -88.94 ^{S1A3} , 0.51 ^b ee ^{3,2} : -89.47 ^{S1G3} , 0.36 ^b
4.	2-H ₁ H ₂	3.1	0.1702	9.8011	ae ^{5,2} : 50.19 ^{U1A2} , 3.15 ea ^{6,1} : 26.01 ^{U1G1} , 3.99
5.	2-H ₂ H ₃	3.9	2.6666 ^c	2.6666	ea ^{6,1} : 28.09 ^{U2C1} , 3.93
6.	2-H ₃ H ₄	8.8	0.7401	47.743	aa ^{6,1} : -167.74 ^{U1A6} , 8.8 ^b ea ^{6,1} : -3.47 ^{S1B1} , 4.83
7.	3-H ₁ H ₂	4.8	0.5515	33.468	ea ^{6,1} : -1.735 ^{S1F1} , 4.78
8.	3-H ₂ H ₃	5.2	0.3555	20.824	ae ^{6,1} : -18.34 ^{U1C1} , 5.2
9.	3-H ₃ H ₄	0 (t H ₃)	1.3957 ^c	1.3957	ee ^{3,2} : - 88.47 ^{S1B3} , 0.61 ^b ee ^{3,2} : - 89.23 ^{S1G3} , 0.43 ^b
10.	4-H ₁ H ₂	4.8	1.8172 ^c	1.8172	ea ^{6,1} : -1.692 ^{S1F1} , 4.69
11.	4-H ₂ H ₃	5.2	0.2666	15.466	ae ^{6,1} : -15.46 ^{U1A1} , 5.13
12.	4-H ₃ H ₄	0 (bs H ₃)	3.6076 ^c	3.6076	ee ^{3,2} : 86.39 ^{S1B3} , 0.94
13.	5-H ₁ H ₂	2.8	0.27719	16.0926	ee ^{4,1} : 92.19 ^{U1C4} , 0.73
14.	5-H ₂ H ₃	3.6	0.4032	23.781	ae ^{5,2} : 56.89 ^{U1F2} , 2.87
15.	5-H ₃ H ₄	8.8	0.3692	21.666	ea ^{5,2} : 38.33 ^{U1A2} , 3.59
15.	5-H ₃ H ₄	8.8	0.3374	21.0192	aa ^{6,1} : 167.43 ^{U1S1C6} , 8.79

a. δ_C , δ_H [ppm], 1H 400MHz, ^{13}C 75MHz: 1-CDCl₃, 2-D₂O, 3- CDCl₃, 4- CDCl₃, δ_H 5- CDCl₃, δ_C 5-CD₃OD [18], b. sign in accord with D-series rule, c. manifold equations: $R_m = (\omega_H \cdot \Delta\delta_{HnHn+1} [Hz] / \omega_C \cdot \Delta\delta_{Cn+1} [Hz])$, d. An[deg] result from sin function as angle of set A, e. value higher as 0.999 are considered angles (the inverse function), then seven set angles are calculated with Java script program Step3sevesets.html.

Conic section approach [3]: the influence of the chemical shift on the dihedral angles was point out with the conic section approach (eq. 24, Table 2, A, θ_{HnHn+1}^A), where the differences between C_nC_{n+1} or H_nH_{n+1} curve of iminocyclitols 1-5 with D and L-stereochemistry made impossible the obtain a generalized equation, and the unit rule remain the key of the method (Step123CONIC.html). Dihedral angles θ_{HnHn+1}^A are around the expected values excepting few cases

(Table 2). Remarkably, for *trans-ee*^{3,2} stereochemistry result angles of set A in relationship with the dihedral angle from set B, and for *trans-aa*^{6,1} stereochemistry the corresponding *cis* angle.

Villarceau circles [20, 21]: two circles of the torus, results by cutting a torus oblique through the center. The angle at the intersection of the non-coplanar circles (skew circles) are calculated with eq. 25 (Step123SkewVillar.html – Figure 5).

where: $\theta_{\text{HnHn+1}}^{\text{pred}}$ – predicted dihedral angle from vicinal coupling constant, θ^{An} – calculated angle with conic section[deg], $R_m = f(\Delta\delta_{\text{CnCn+1}}$ or $\Delta\delta_{\text{HnHn+1}})$ [radians].

$$R_m = \sin\left(\frac{\omega_H * \Delta\delta_{HnHn+1}}{\omega_C * \Delta\delta_{CnCn+1}}\right) \quad (25)$$

with: $\Delta\delta_{\text{HnHn+1}}$ - the differences between two protons, $\Delta\delta_{\text{CnCn+1}}$ - the differences between two atoms of carbon [ppm], ω_L - Larmor frequency [MHz]: L = H - proton, C - carbon.

$$\begin{aligned} \theta_{HnHn+1}^{calc} &= A x \theta^{An} \\ \text{with } A &= \frac{\sin \theta_{HnHn+1}^{pred}}{\sin \theta^{An}} \\ \theta^{An} &= \sin^{-1} R_m \end{aligned} \quad (24)$$

[illegible]

Figure 5. Java Script program Step123SkewVillar.html.

3.3. Building of Unit with Seven Sets (U or S) or Units with Six Sets Angles (U, S)

In step 3 are builds seven set units on two units, U1 and S1 (Figure 6), totally 14 sets angles – three pair of six set angles. If from the manifold equation result the unit U1 or S1 can be easy identified: values around 69-70[deg] occurs in unit U1 and the gauche angle of 60[deg] on unit S1. The

transformation from unit S1 to unit U1 can be realized with eq. 26 (Step3SUtransf.html – Figure 7), and from U1 to S1 with *trans-ee*^{3,2} algebraic eq. 14 of unit U1 (Step3UStansf.html – Figure 8). The unit U1 result from angles of set A and set B in relationships of +/-60[deg], the half ϕ_1^A and ϕ_2^A of set A are angles of set B and C, the first angles of sets A and B are angle ϕ_2 of sets D and F. Half ϕ_1 of sets A, D and F are first angles of sets B, E and G.

$$\phi_{1U1B} = \left(\frac{60 - \theta^{S1B1}}{1.5} \right), \text{ with } \theta^{U1A1} = \left(\frac{\phi_{1U1B}}{2} \right) \quad (26)$$

where: θ^{S1B1} – first angle of set B - unit S1 in relationship of 60[deg] with a gauche angle[deg] from set A – unit S1, θ^{U1A1} – first angle of the unit U1.

The experimental data reveal that, sometimes the seven sets unit (A, B, C - D, E, A - F, G, B) has two pairs of three set angles U and one S (Table 2, entry 6), or two S and one U. In the first preliminary communication [4] was considered the method of increasing the number of units through set C the best way for calculation all the angles with values almost equals with the predicted one. At this moment, as result from tables 2, 3, from first unit is choose one pair of three set angles and calculate (if is necessary) the parallel pair of three sets angles, totally six sets angles on two units having all stereochemistry. The Java Script program [3] ensure the calculation of the first unit with seven set angles, unit from which is take the angle required for calculation the unit S or U, in function of the stereochemistry. Thus, the shadow (the parallel unit) is the unit S for unit U, or the unit U for unit S. For a vicinal coupling constant of 3.6[Hz] the corresponding

dihedral angle was found on unit S3 or S5, as calculated from carbon or proton chemical shift, and after transformation from S1 to U1 in set C and set B of unit U1 (Table 2, entry 14). All the angles are on unit U1 or S1, only for a vicinal coupling constant of 2.8[Hz] (Table 2, entry 13) was extracted from unit U2.

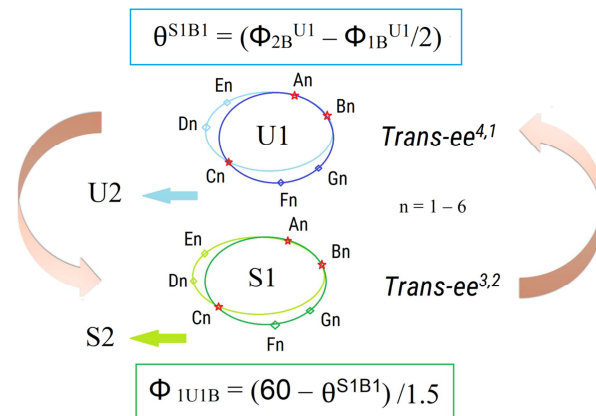


Figure 6. Seven set units. The transformation $U1$ to $S1$ and $S1$ to $U1$.

[illegible]

Figure 7. Java Script program Step3SUtransf.html.

Sometimes, seven set unit (Step3sevensets.html) can be preferred, in function of the interval 60 - 65[deg], instead of six sets angles. The calculation of the dihedral angle with the non-coplanar Villarceau circles approach gives the best results (Table 3), but in absences of enough NMR data all the methods are useful. The vicinal coupling constant $^3J_{\text{HH}}[\text{Hz}]$ can be calculated from dihedral angle $\theta_{\text{HnHn+1}}^{\text{calc}}[\text{deg}]$ extracted in step 3 with Java Script program Step4vicinalcoupling.html, or by hand with eq. 7, 8.

The program Step123SkewVillar.html presented in Figure 5 has three main steps: 1. *Prediction*: the vicinal coupling constant $^3J_{\text{HH}}[\text{Hz}]$ for *cis*, *trans-ee* or *trans-aa* stereochemistry will be introduced in the explorer prompt windows (Script Prompt) resulting one of the vicinal angles Bcd, BTed, BTd = ϕ and one of the predicted angles Acd (*cis*), ATed (*trans-ee*^{3,2}), ATed (*trans-ee*^{4,1}), ATd (*trans-aa*) = $\theta_{\text{HnHn+1}}^{\text{pred}}$. 2. *Manifold*: from the carbon and proton chemical shift $\delta[\text{ppm}]$ and Larmor frequency $\omega_L[\text{Hz}]$ introduced in Script Prompt results the value R[radians] (or in deg for $R > 1$) and one angle of set A, angle Ad[deg] using the manifold eq. 12, the non-coplanar Villarceau circles. 3. *Seven sets unit*: the program itself with angle An[deg] build seven set angles unit (U1 or S1, N1 > or < 5[deg], N = A, B, C, D, E, F, G). The angle with value almost equal with the predicted one is the required dihedral angle, otherwise the dihedral angle will be found in unit U or S with programs Step3SUtransf.html (Figure 7) and Step3Utransf.html (Figure 8) as presented in subheading 3.3. Thus, from the seven sets angles will be chose one pair of three set angles, and with first angle of first set will be made the transformation U to S or S to U.

4. Conclusion

The hypersphere trigonometric eq. 4, confirmed by algebraic eq. 5, enable the calculation of the dihedral angle from chemical shift (carbon and/or proton) and vicinal coupling constant. The advantages of the 3-sphere approach [19]: the right stereochemistry with corresponding sign results from a perfect mathematic symmetry, gives by nature itself (the universe shape), with applications on conformation [16, 22] and configuration [23] of iminocyclitols [24]. A method for calculation of the dihedral angles from NMR data by hand with right stereochemistry and sign, or with Java Script programs [25, 26]: 1. *Non-coplanar Villarceau circles*: Prog1: Step123SkewVillar.html, 2. *Conic section and conic section approach*: Prog2: Step123CONIC.html, 3. *Building of seven and six sets angles*: 3a. Prog3: Step3sevensets.html, 3b. Prog4: Step3Utransf.html, 3c. Prog5: Step3SUtransf.html, 3d. Prog6: Transee32.html. *Calculation of the vicinal coupling constant* from the calculated dihedral angle: Prog7: Step4vicinalcoupling.html. Information about the Java script programs can be obtained from cmitan@yahoo.com, the programs can be used with Notepad++.

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