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Dedicated to Prof. Bogdan C. Simionescu on the occasion of his 75th anniversary

RELATIONSHIP BETWEEN TETRAHEDRAL AND DIHEDRAL ON HYPERSPHERE COORDINATES

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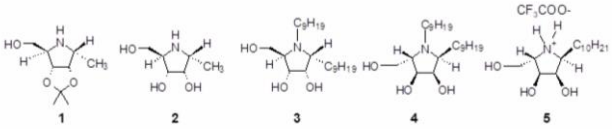
The wave character of the NMR data (chemical shift $\Delta\delta_{Cn}$[ppm] – vicinal coupling constant $^3J_{HH}$[Hz]) enable calculation the tandem dihedral-vicinal or tetrahedral-internal angles with 3-sphere approach. Golden ratio, invers of Fibonacci number, and manifold inversion torus to Dupin cyclide under 3-sphere units ensure the calculation of the tetrahedral angles of five membered ring in opposite with dihedral angles *sin versus tan* functions. The transformation from space/time to space under electric and magnetic rule gives dodecahedron and icosahedron values for calculation tetrahedral angles from polyhedron and hypersphere equations. Tetrahedral angles of five membered ring can be calculated from carbon chemical shift $\Delta\delta_{Cn}$[ppm] with Java Script program and hypersphere equations.



9a: $\varphi_{C1} = \cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$

9b: φ_{C2} or $\varphi_{C3} = \cos^{-1}\sin\{-[60 - (\tan^{-1}1/R_m)]/2\}$

9c: $\varphi_{C4} = \cos^{-1}\sin[-(\sin^{-1}1/R_m)/2]$

INTRODUCTION

Six dihedral angles with *cis, trans* stereochemistry can be placed on three concentric cones, *i.e.* three cones of a solid sphere, or two sets angles on 3-sphere approach[1], from the hypersphere S^3 in 4D to the Bloch sphere S^2 in 3D space[2] to circles in 2D[3]. 3-Sphere, a hypersphere in four dimensions (R^4) with Hopf fibration (R^{32} for eq. I, II with positive and negative sign, and R^{16} for eq. III, IV) useful for calculation of the dihedral angle from vicinal angle[4], angle result from vicinal coupling constant $^3J_{HH}$[Hz] and *vice versa*. The invers of the circles (III, IV) ensuring the calculation all the possible isomers with positive and negative sign[5].

Solid sphere: $\cos^2\theta = R_m$; $R_m = f(\delta_X, X = C, H)$.

3-Sphere approach:

cis, trans-ee: $\sin^{-1}\cos\phi = \theta_{HnHn+1}$, (I)

trans-aa: $\cos^{-1}\sin(-\phi) = \theta_{HnHn+1}$, (II)

cis, trans-ee: $\tan^{-1}\sin(-\phi) = Y$, (III)

cis, trans-ee: $\tan^{-1}(1 / \sin-\phi) = Y$, (IV)

cis, trans-ee: $\sin^{-1}\tan(-\phi) = Y$, (V)

where: $Y = \theta_{HnHn+1}$ – dihedral angle or $\theta_{n,n+1}$ – torsional angle.

Between 0 to 13.4[Hz] result *cis, trans-ee, gauche* and *trans-aa* dihedral angles θ_{HnHn+1}[deg] or torsional angles $\theta_{n,n+1}$[deg] from eq. A. *cis* $\phi = (2x^3J_{HH})^{1/2}$ or eq. B. *trans*$\phi = (^3J_{HH})^{1/2}$, as presented in Table 1[6].

Our aim in this paper is to demonstrate the relationship between the dihedral – vicinal and tetrahedral – internal angles of five membered ring with 3-sphere theory.

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Table 1

Dihedral θ_{HnHn+1}[deg] and torsional $\theta_{n,n+1}$[deg] angles which results from vicinal coupling constant $^3J_{HH}$[Hz] with eq. I, III, IV, V

Entry	Equations	θ_{HnHn+1} [deg]			$\theta_{n,n+1}$ [deg]	θ_{HnHn+1} [deg]	θ_{HnHn+1} [deg]
		Eq. A			Eq. B		
	$^3J_{HnHn+1}$[Hz]	*cis*	*trans-ee*	*gauche*	*cis / trans-aa*	*trans-ee*	*gauche*
1.	$\sin^{-1}\cos\phi$	2.8–6.1	0–2.5	2.6, 2.7 6.2	5.5–12.2	12.5–13.4	12.3, 12.4
2.	$\tan^{-1}\sin-\phi$	0.1–6.1	–	–	5.5–13.4	–	–
3.	$\sin^{-1}(1 / \tan-\phi)$	3.6–5.7 5.9, 6.0	5.8	3.5	7.1–11.4	6.8, 6.9 11.5, 11.6	7.0
4.	$\sin^{-1}(\tan-\phi)$	0.1–3.1 6.1	3.3, 3.4	3.2	5.5–6.3 11.8–13.4	6.5–6.7, 11.7	6.4

Dihedral and tetrahedral angles are expected from the trigonometric point of view to be in relationship *sin–tan* under manifold inversion and rhombic dodecahedron geometry, explored with chemical shift transformed from ppm in *J* / moli or gauss, electric *versus* magnetic, from space / time to space[6].

RESULTS

Rhombic polyhedron geometries (Eq. 1), rhombic dodecahedron with acute and obtuse angles drown inside of the sphere[7], five obtuse tetrahedral angles on five membered ring. The eqs. 2, 3 give the tetrahedral angle sp^3

$$\begin{aligned} &\textit{Acute angle}: \alpha = 2\tan^{-1}(1 / 1.618034), \\ &\textit{Obtuse angle}: \beta = 2\tan^{-1}(1.618034). \end{aligned} \quad (1)$$

$$\begin{aligned} \alpha &= 2\cot^{-1}(2^{1/2}) = 70.53 \text{ deg}, \\ \beta &= 2\tan^{-1}(2^{1/2}) = 109.47 \text{ deg}. \end{aligned} \quad (2)$$

Polyhedron unit, a set with three internal and three tetrahedral angles build with polyhedron equation, was used to demonstrated recently the relationship between tetrahedral angle and vicinal coupling constant[8], now our aim is to demonstrate the direct relationships between tetrahedral and dihedral angle exploring other mathematical equations.

$$\textit{Polyhedral}: \tan(\varphi/2) = 1/E^n = 2\sin(\gamma/2), \quad (3)$$

where: dihedral angle of polyhedral, $\varphi = D^D$ (116.56506 [deg] – dodecahedron) or D^I (138.189685 [deg] – icosahedron), E^n – energy [J / mol × 10^6]: n = 1, E = 1.618033952 dodecahedron – golden ratio, n = 2, E = $(1.618033952)^2$ isosahedron, φ – tetrahedral angle[deg], γ – internal angle [deg].

Once the polyhedral eq. 3 was replaced with rhombic polyhedron eq. 4[6] the tetrahedral angle – are calculated in opposite with dihedral angle as presented in Table 2.

$$\begin{aligned} \alpha &= a\times\sin^{-1}(1 / E^n) = \theta^1 \text{ [deg]}, \\ \beta &= a\times\tan^{-1}(1 / E^n) = \theta^2 \text{ [deg]}, \end{aligned} \quad (4)$$

where: a = ½, 2, 4, n = 1, ½, 2, θ^1, θ^2 = φ and / or ϕ[deg], $E = \delta_{Cn} \times \omega_C \times h \times N_A$[J / moli × 10^{-6}], δ_{Cn} – carbon chemical shift[ppm], ω_L – Larmor frequency[MHz], h = 6.626070080 × 10^{-34}[J×s], N_A = 6.023 × 10^{23}[mol^{-1}].

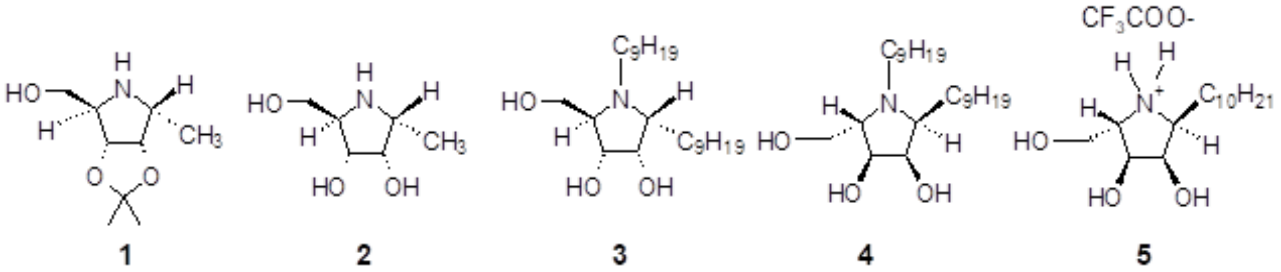


Fig. 1 – Five membered ring iminocyclitols with α-D-ribitol (**1**-**3**) and β-L-ribitol (**4**, **5**) stereochemistry.

3-Sphere is a hypersphere in 4D, n + 1 Euclidean space, n-manifold with hypersphere – sphere – Hopf fibration coordinates. A toroidal circle giving a torus, more toroidal circles giving tori. A torus has four

characteristics circles: toroidal, poloidal, Villarceau circles. At intersection of a torus with a bitangent plane occurs two intersecting sphere or two intersecting circles, Villarceau circles[9]. Dihedral angle calculated from the NMR data, chemical shift or vicinal coupling constant, is an angle at intersection of two disks, in close relationship with vicinal angle, angle result from vicinal coupling constant [1] or manifold angle result from chemical shift under unit rule. On two intersecting circles with positive and negative angles, with *cis* and *trans* stereochemistry, can be found a dihedral angle on circle A (set A) and the vicinal angle on second circle B (set B). That must be mentioned on sets A and B are considered only the positive angles, the sign of the calculated angle resulting from the trigonometric equations I–IV.

Table 2

Tetrahedral angle φ[deg] and dihedral angle θ_{HH}[deg] calculated from carbon chemical shift δ[ppm] with rhombic polyhedron eq. 4

Entry	$^3J_{HH}$ [Hz]	δ_{Cn}[a] [ppm]	E [J / moli × 10^6]	$1 / E^n$ [π]	Φ[deg] $^3J_{HH}$[Hz]	θ_{HnHn+1} [deg]	φ[b][deg] eq. 4
1.	**1**-H_1H_2: 4.1	55.8	1.67021	n = 2 n = 1	68.993, 4.15 118.179, 5.43	21.00^S –28.238^T	109.721^T 106.442^S
2.	**1**-H_2H_3: 5.4	83.5	2.49932	n = 1 / 2	115.368, 5.37	–25.36^T	101.524^S
3.	**1**-H_2H_3: 5.4	84.3	2.52322	n = 1 / 2	115.62, 5.37	–25.62^T	101.968^S
4.	**1**-H_3H_4: 0	65.9	1.97252	n = 1 / 2	0.798, 0.446	89.201^S	109.097^T
6.	**2**-H_1H_2: 3.1	57.4	1.71810	n = 2	39.603, 3.14	50.39^S	108.714^T
7.	**2**-H_2H_3: 3.9	71.5	2.14014	n = 1	62.143, 3.94	27.856^S	102.522^T
8.	**2**-H_2H_3: 3.9	71.7	2.14613	n = 1	62.227, 3.94	27.77^S	102.491^T
9.	**2**-H_3H_4: 8.8	66.8	1.99946	n = 1 / 2	78.748, 8.8	168.74^S	109.463^T
11.	**3**-H_1H_2: 4.8	63.7	1.90667	n = 1 / 2	92.80, 4.81	–2.805^S	108.175^T
12.	**3**-H_2H_3: 5.2	72.5	2.17007	n = 1	109.758, 5.23	–19.758^S	102.370^T
13.	**3**-H_2H_3: 5.2	74.0	2.21497	n = 1 n = 1 / 2	107.352, 5.18 106.948, 5.17	–17.352 –16.94^T	102.148 101.553^C
14.	**3**-H_3H_4: 0	69.3	2.07429	n = 1 / 2	2.052, 0.716	–87.947^S	107.386^T
15.	**4**-H_1H_2: 4.8	68.4	2.04735	n = 1 / 2	91.325, 4.77	–1.325^S	107.474^T
16.	**4**-H_2H_3: 5.2	71.1	2.12817	n = 1 / 2	107.214, 5.17	–17.214^T	101.681^S
17.	**4**-H_2H_3: 5.2	72.7	2.17606	n = 1 / 2	107.066, 5.17	–17.066^T	101.830^C
18.	**4**-H_3H_4: 0	70.9	2.12218	n = 1 / 2	86.699, 0.908	86.699^S	107.233^T
19.	**5**-H_1H_2: 2.8	63.3	1.8946	n = 2	31.131, 2.78	58.868^T	106.174^S
20.	**5**-H_2H_3: 3.6	72.1	2.1581	n = 2	51.059, 3.57	38.941^T	102.398^S
21.	**5**-H_2H_3: 3.6	73.4	2.1970	n = 2	50.978, 3.56	39.148^T	101.956^S
22.	**5**-H_3H_4: 8.8	63.9	1.9126	n = 1 / 2	78.422, 8.85	168.422^S	108.260^T

a. δ[ppm] ^{13}C-NMR, 75MHz, ^{1}H-NMR 400 MHz: **1**, **3**, **4**-$CDCl_3$, **2**-D_2O, **5**-CD_3OD; b. **1**-C_4 106.36^{TUS}, **2**-C_1 106.781^{CUS}, **2**-C_4 107.63^{TU}, **3**-C_1 107.73^{TUS}, **3**-C_4 106.02^{CU}, **4**-C_1 106.98^{CUS}, **4**-C_4 106.65^{CU}, **5**-C_4 106.308^{CU}[deg].

Tetrahedral angles (Table 3) are calculated from carbon chemical shift with eqs. 5a–b, two trigonometric equations[6]: a. Dupin cyclide to torus, b. torus inversion to Dupin cyclide. From two calculated tetrahedral angles is chose one with the expected values for the position on the ring, or as verification test one in opposite with the corresponding dihedral angle. Tetrahedral angles calculated for every stereochemistry with eqs. 5c–f from vicinal angles ϕ and other angles in close relationship are presented in last column of Table 3.

$$\cos^{-1}\sin - Z / 2 = \varphi_{Cn} \quad (5)$$

$$\sin^{-1}1 / R_{mCn} = \theta^{C1An,}, \sin^{-1}(\tan - \theta^{T1An}) = Z, \quad (5a)$$

$$\tan^{-1}1 / R_{mCn} = \theta^{T1An}, \tan^{-1}\sin - \theta^{C1An} = Z, \quad (5b)$$

$$\text{cis}^{5,2}: Z = \phi_{1A} / 2 = \phi_{2B} / 2 = \theta^{B1}, Z = \phi / 2, \quad (5c)$$

$$\text{cis}^{6,1}: Z = \phi - X, X = 30, 60 \text{ for / or } \theta^3, \theta^4, \quad (5d)$$

$$C_2, C_3: Z = [60 - (\theta^{S4} - 90)] / 1.5, \quad (5c,d)$$

$$\textit{trans-aa}^{6,1}: Z = \phi - 60, \quad (5e)$$

$$\textit{trans-ee}^{3,2}: C_1, C_4: Z = [60 - (\theta^{S4} - 90)] / 1.5, \quad (5f)$$

where: $R_m = \Delta\delta_C \times \omega_L \times 4 \times 10^{-3} / \gamma$ [gauss], ω_L – Larmor frequency [MHz], δ – chemical shifts [ppm], γ – gyromagnetic ratio: ^{13}C NMR: γ = 10.71[MHz ×

T^{-1}] = 6.7[10^7 × rad × T^{-1} × s^{-1}], ^{1}H NMR: γ = 42.57[MHz × T^{-1}] = 26.75[10^7 × rad × T^{-1} × s^{-1}], ϕ – vicinal angle (algebraic angle) [deg], θ – angle of set A or B [deg].

Table 3

Tetrahedral angle φ[deg] and dihedral angle θ_{HH}[deg] calculated from carbon chemical shift with 3-sphere approach eq. 5a–f

Entry	$^3J_{HH}$[a] [Hz]	θ_{HH}[b] [deg]	δ_{Cn}[a] [ppm]	R_m[c] [π]	θ_{HH} [deg]	φ^{5a-b} [deg]	Hypersphere equations	φ^{5c-f} [deg]
1.	**1**-H_1H_2: 4.1	22.76	55.8	1.5630	20.22^S	106.30^T	φ_{C1}= $\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	106.74^e
2.	**1**-H_2H_3: 5.4	-26.64	83.5	2.3389	-25.31^S	101.57^T	φ_{C2}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	101.56^f
3.	**1**-H_2H_3: 5.4		84.3	2.3613	-25.05^S	101.47^T	φ_{C3}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	101.44
4.	**1**-H_3H_4: 0	89.96	65.9	1.8459	-88.44^T	106.40^S	φ_{C4}=$\cos^{-1}\sin[-(\sin^{-1}1/R_m)/2]$	106.40^g
5.	**2**-H_1H_2: 3.1	51.56	57.4	1.6078	51.54^S	105.93^T 107.31^d	φ_{C1} =$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	107.31
6.	**2**-H_2H_3:3.9	29.16	71.5	1.9953	29.922^S	103.30^T 101.12^d	φ_{C2}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	100.12
7.	**2**-H_2H_3:3.9		71.7	2.0084	29.861^S	103.23^T 101.17^d	φ_{C3}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	101.17
8.	**2**-H_3H_4: 8.8	168.74	66.8	1.8711	169.2^d 168.7^d	106.15^S 105.93^T	φ_{C4}=$\cos^{-1}\sin[-(\sin^{-1}1/R_m)/2]$ φ_{C4}=$\cos^{-1}\sin\{-[60 - (\tan^{-1}1/R_m)]/2\}$	106.15^h
9.	**3**-H_1H_2: 4.8	-2.159	63.7	1.7843	-2.928^T	107.04^S	φ_{C1}=$\cos^{-1}\sin[-(\sin^{-1}1/R_m)/2]$	107.04
10.	**3**-H_2H_3:5.2	-18.16	72.5	2.0308	-18.73^{Td}	103.11^T *101.26*^{d}	φ_{C2}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	100.16^{Sd} 101.26^{Td}
11.	**3**-H_2H_3:5.2		74.0	2.0728	-18.58^{Td}	102.87^T *101.41*^{d}	φ_{C3}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	100.38^{Sd} 101.41^{Td}
12.	**3**-H_3H_4: 0	89.96	69.3	1.9411	-88.99^S	106.37^T	φ_{C4}= $\cos^{-1}\sin\{-[60 - (\tan^{1}1/R_m)]/2\}$	106.37 109.66^d
13.	**4**-H_1H_2: 4.8	-2.159	68.4	1.9159	-2.923^{S2}	106.22^T	φ_{C1}=$\cos^{-1}\sin\{-[60 - (\tan^{-1}1/R_m)]/2\}$	106.219 109.18^{Td}
14.	**4**-H_2H_3:5.2	-18.16	72.5	2.2844	-18.65^S	101.82^T	φ_{C2}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	101.34^{Sd} 102.11^{Td}
15.	**4**-H_2H_3:5.2		72.7	2.0364	- 18.717^{Td}	103.07^T 101.28^d	φ_{C3}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	100.19^{Sd} 101.28^{Td}
16.	**4**-H_3H_4: 0	89.96	70.9	1.9859	89.766S	106.63^T	φ_{C4}=$\cos^{-1}\sin\{-[60 - (\tan^{-1}1/R_m)]/2\}$	106.63
17.	**5**-H_1H_2: 2.8	58.64	63.3	1.773	59.422^T	107.16^S	φ_{C1}=$\cos^{-1}\sin[-(\sin^{1}1/R_m)/2]$	107.16
18.	**5**-H_2H_3:3.6	38.16	72.1	2.0196	37.561^{Td}	103.82^T 101.21^d	φ_{C2}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	102.96
19.	**5**-H_2H_3:3.6		73.4	2.0560	37.291^{Td}	102.96^T 101.35^d	φ_{C3}= $\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	103.17
20.	**5**-H_3H_4: 8.8	167.44	63.9	1.7899	168.6^d 169.7^d	106.98^S 105.40^T	φ_{C4}=$\cos^{-1}\sin[-(\sin^{-1}1/R_m)/2]$ φ_{C4}=$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2]$	106.98^h

a. δ[ppm] ^{13}C-NMR, 75MHz, ^{1}H-NMR 400MHz: **1**, **3**, **4**-$CDCl_3$, **2**-D_2O, **5**-CD_3OD; b. *cis*, *trans-ee*: ϕ = $(^3J_{HH}x2)^2$, *trans-aa* ϕ = $(^3J_{HH})^2$, c. R_m[gauss] from δ_{Cn}[ppm]; d. eq. 6a,b, e. $\varphi_{C1} = \cos^{-1}\sin - \{[60 - (99.77 - 90)] / 1.5\} / 2$, f. $\varphi_{C2} = \cos^{-1}\sin - \{[60 - (115.31 - 90)] / 1.5\} / 2$, g. $\varphi_{C4} = \cos^{-1}\sin[(\theta^4 - 60)] / 2$, h. $\varphi_{C4} = \cos^{-1}\sin - (\phi - 60)$.

The Java Script program SetCnTETRAHEDRAL.html for calculation tetrahedral angles θ_{HnHn+1}[deg] from carbon chemical shift δ_{Cn}[deg] with eqs. 5a,b (Fig. 2) can be used with Notepad++. Relationship between dihedral θ_{HnHn+1}[deg] and tetrahedral angles φ_{Cn}[deg] on five sets angles: two possible tetrahedral angles and two units (C_n and T_n) with five sets angles results from the sin and tan trigonometric functions: $\theta^{C1Ni} = f(\sin^{-1}R_m)$, $\theta^{T1Ni} = f(\tan^{-1}R_m)$, both with $\theta^{U1N1} > 5$ deg, $\theta^{S1N1} < 5$ deg. In both units, the first and second angles of set A are equals with ϕ_2 of sets D and E. Dihedral angle almost equal with the calculated dihedral angle from vicinal coupling constant is choose from units C or unit T along its corresponding tetrahedral angle from unit T or C.

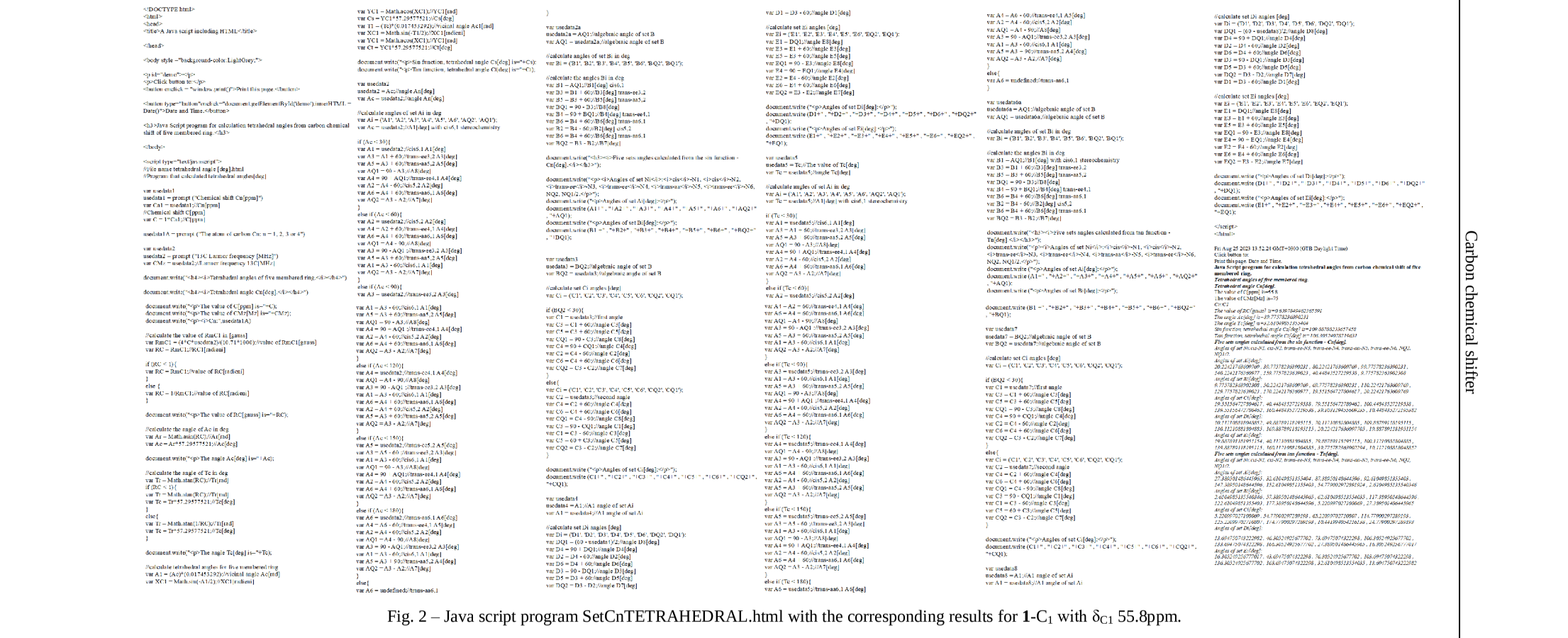


Fig. 2 – Java script program SetCnTETRAHEDRAL.html with the corresponding results for **1**-C_1 with δ_{C1} 55.8ppm.

DISCUSSION

Golden ratio, the invers of Fibonacci number (0.6180339) is found in nature on polyhedron: dodecahedron – 1.61803, icosahedron – 2.61803. The five membered ring and six membered rings are inscribed on Rhombic polyhedron geometry eq. 1. Tetrahedral angles calculated from carbon chemical shift under electric (Table 2) and magnetic (Table 3) fields, with R_m around the polyhedron values, are in both cases with expected values for C_2 and C_3, but with planar (*i.e.* **1**) in Table 2 and nonplanar values in Table 3 for C_1 and C_4. Under the unit of 3-sphere rule the angles C_1 and C_4 of Table 2 can be found almost equals with angles calculated in Table 3. Planar angles are calculated with eq. 6 (6a: transformation S to U, 6b: U to S[1]) in case of **3**-H_3H_4, **3**-H_1H_2 (Table 3, entry 9, 12), but are angles from the pair C_n, C_{n+1}, with C_{n+1} ~ 100 deg. In case of isopropylidene protected iminocyclitol **1** (Table 3, Entry 1) from *sin* function result five sets angles with dihedral angle θ_{H1H2}^{CUA1} = 20.22 deg and two tetrahedral angles 109.88, 100.11[deg], and from tangent function five sets angles with dihedral angle θ_{H2H3}^{TSA1} = 27.38 deg and tetrahedral angles 106.305, 103.69 deg. Resulting that for a dihedral angle θ_{H1H2}^{CA1} the tetrahedral angle is $\varphi_{C1} = 106.305^{TD4}$ deg, and for a dihedral angle θ_{H2H3}^{TA1} the tetrahedral angle is $\varphi_{C2} = 100.11^{CE4}$ deg. The transformation TS1 to TU1 (Eq. 6a) [1] gives an angle of 21.74 deg on set C, having first and second angles of set C equals with ϕ_2 of sets A and B, and tetrahedral angles 109.12, 100.87. Remarkably, in this case unit has three sets angles. The transformation TS1 to TS2 having equal angles, but on five sets unit. The tetrahedral angle φ_{C2} calculated from δ_{C2}[ppm] is 101.57^{TUE4} deg with a dihedral angle $\theta_{H2H3} = -25.31^{CSA1}$ deg ($^3J_{H2H3}^{calc}$ = 5.36[Hz]), relative to θ_{H2H3} = –26.64 deg as calculated for $^3J_{H2H3}^{exp}$ = 5.4 Hz. The tetrahedral angle φ_{C3} = 101.476[deg] result from unit TUE4 in opposite with dihedral angle θ_{H2H3} -25.05^{CSA1} deg ($^3J_{H2H3}^{calc}$ = 5.36 Hz). As observation, the transformation S to U from unit CS1 result an angle of 101.648 deg. The dihedral angle θ_{H3H4} = 88.44 deg on unit TSA3 has a tetrahedral angle φ_{C4} = 106.40 deg on unit CSD4.

$$\text{S to U: } Z = [60 - (\theta^{S4} - 90)] / 1.5, \quad (6a)$$

if $\theta^{S4} < 100$ result φ_1 or φ_4; $\theta^{S4} > 100$ result φ_2 or φ_3, where: φ_n – tetrahedral angles [deg], n =1–4, θ^{S4} – the fourth angle[deg] of sets A or B in unit S.

$$\text{U to S: } Z = \phi_2^U - \phi_1^U / 2, \quad (6b)$$

where: $\phi_1^{UA} / 2 = \theta^{UB1}$ or $\phi_1^{UB} / 2 = \theta^{UA1}$, $\phi_2^{UA} = \theta^{UC1}$ or $\phi_2^{UB} = \theta^{UC2}$, the algebraic angles[deg]: $\phi_2^U = \theta^{U3} - \theta^{U2}$, $\phi_1^U / 2 = 90 - \theta^{U3}$, θ^{U3}, θ^{U2} – second and third angles[deg] of sets A or B in unit U.

In Table 2 close to polyhedron value are R_m of C_n (n = 1–4) relative to Table 3, but from eq. 5a,b results two possible tetrahedral angles, easy to choose between since only one is in opposite with the corresponding dihedral angle with values almost equals with the predicted one from the vicinal coupling constant[4]. The border line values of 1.9 indicate *trans* stereochemistry or *cis* with a dihedral angle equal with a *trans-ee* vicinal angle (ϕ). The sign of the dihedral angles results only from the eqs. I–IV for prediction dihedral angles; way prediction? Because the stereochemistry can be established only from manifold equations, conic section[1], Villarceau circles[1], rectangle[10], for building units from carbon or/and proton chemical shift. Between dihedral angles predicted and calculated differences are no more as 2 deg. The *trans-ee* stereochemistry in agreement with algebraic equations[1] has *trans-ee*^{4,1} in unit U (Eq. 7a) and *trans-ee*^{3,2} in unit S (eq. 7b). The vicinal coupling constant $^3J_{HnHn+1}$[deg] can be calculated from ϕ[deg] and θ_{HnHn+1}[deg] with eq. 8. If from vicinal coupling constant result an angle from unit S, the transformation S to U gives two units U. The wave character of NMR data fitting well on the 3-sphere unit approach, the dihedral angles can be calculated until the first unit has values almost equals with the last unit, resulting few dihedral angles[11] with values around the predicted dihedral angle

$$\textit{Trans-ee}^{4,1}\text{: } ^3J_{HnHn+1} \sim \cos^{-1}[(\sin\phi)]^{1/2} / 2, \quad \phi^{UA} = \phi_1^{UA}{}_{/2} = \theta^{UB1}, \quad (7a)$$

$$\textit{Trans-ee}^{3,2}\text{: } ^3J_{HnHn+1} \sim \text{tang}^{-1}[(\sin\phi)]^{1/2} / 2, \quad \phi^{UA} = \phi_2^{UA} - \phi_1^{UA}{}_{/2} = \theta^{SA1}, \quad (7b)$$

$$^3J_{HH} = (\phi + \cos^2\theta_{HnHn+1})^{1/2} / 2, \quad (8)$$

where: $^3J_{HnHn+1}$ – vicinal coupling constant [deg], ϕ – vicinal angle [deg], θ_{HnHn+1} – dihedral angle [deg].

The transformation U to S and S to U gives angles almost equals with the *tan* or sin functions (*i.e.* eq. 7b) [1], the opposite rule between dihedral and tetrahedral angles implied five + three sets angles, from two pair sets angles on unit U and two on S, angles results from 4D hypersphere equations (9a–c) and 3D sphere equations (I–IV), resulting

again the utility of calculation angles from both vicinal coupling constant $^3J_{HH}$[Hz] and chemical shift δ_{Cn}[ppm].

The transformation S to U increased the tetrahedral angle φ_{C1} from 105.939 deg to 107.311 deg, and decreased the tetrahedral angles φ_{C2}, φ_{C2} from 103.23, 103.309 deg to 101.17, 101.12 deg in case of deprotected iminocyclitol **2**.

The values calculated under magnetic field are at C_1 and C_4 with smaller differences; *i.e.* angles calculated with Hückel theory for conformational analysis of iminocyclitol **2**[12, 13]: a. cos / sin – Euler-Hückel I: 106.26, 102.63, 102.63, 106.25, 111.45 deg; b. Tan- Euler -Huckel 1 – dodecahedron: 102.68, 106.26, 106.25, 102.31, 112.29 deg.

$$\cos^{-1}\sin[-(\tan^{-1}1/R_m)/2] = \varphi_{C1} \quad (9a)$$

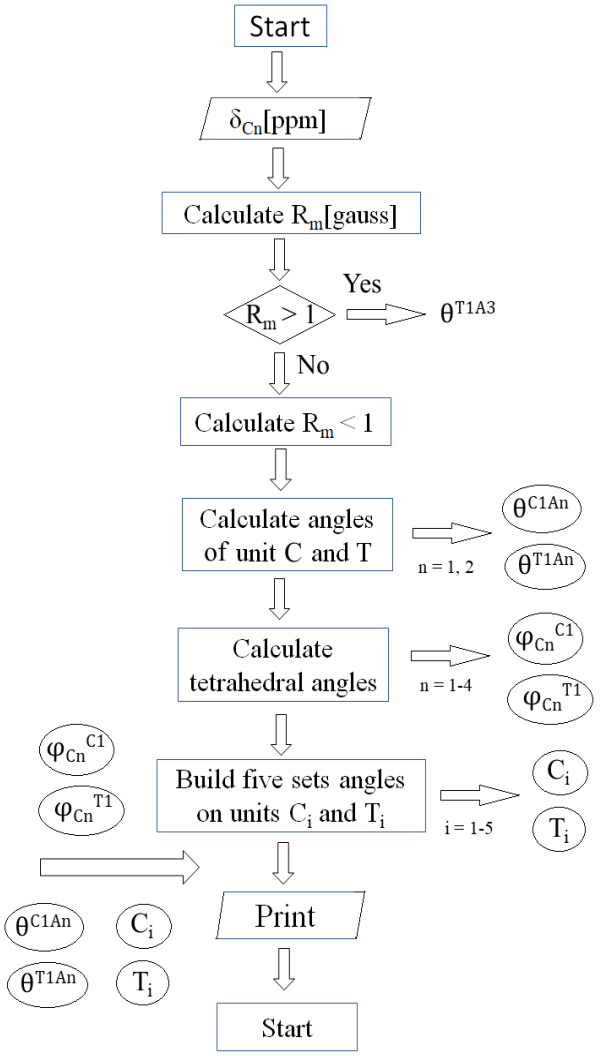
$$\cos^{-1}\sin\{-[60-(\tan^{-1}1/R_m)]/2\} = \varphi_{C2} \text{ or } \varphi_{C3} \quad (9b)$$

$$\cos^{-1}\sin[-(\sin^{-1}1/R_m)/2] = \varphi_{C4} \quad (9c)$$

$$\theta_{H3H4} = 2\times\tan^{-1}\cos[-(\sin^{-1}1/R_m)/2]^{[13, 14]} \quad (9d)$$

$$\theta_{H3H4} = 2\times\tan^{-1}\cos[-(\tan^{-1}1/R_m)/2] \quad (9e)$$

Tetrahedral angles φ_{Cn}[deg] can be calculated from carbon chemical shift building five sets angles from sin and tan functions with eq. 5, or using the generalized 4D hypersphere equations (9a–c) as presented in Table 2: Dupin cyclide inversion to torus, and torus inversion to Dupin cyclide resulting from eqs. 5a,b. Equation 9c enable calculation tetrahedral angle φ_{C4} (Table 3, entry 8, 12, 13, 16) from θ^2. Torus inversion to Dupin cyclide, analog to sphere inversion, under tangential space between the intersection of circles and middle of circles results a rhombic/kite geometry. Rhombic polyhedron geometry is specific for five and six membered rings, half of the kite is a triangle with three consecutive atoms of carbon $C_nC_{n+1}C_{n+2}$. Tetrahedral angles are calculated with hypersphere eq. 9c in case of *trans-ee*^{3,2}, *cis/ trans-aa*^{6,1} stereochemistry (Table 3, entry 4, 8, 9, 17) [13, 14]. Dihedral angles θ_{H3H4} are calculated from hypersphere eqs. 9d, e (torus inversion to Dupin cyclide and *viceversa*) and the corresponding tetrahedral angles from 9c; in case of **3**-H_3H_4 result a dihedral angle of 88.36 deg from 9e almost equals with angle result from *sin* function (88.99 deg) for a tetrahedral angle of 106.37 deg. Equation 9c explain better the differences between R_m of carbon atoms C_1 (1.5–1.6 gauss) and C_4 (1.8 – 1.9 gauss) with almost same values of tetrahedral angles (Table 3).



Scheme 1 – Flow-chart for calculation tetrahedral angles with 3-sphere approach and Java Script.

The Java Script program (Fig. 2, Scheme 1) for calculation of the tetrahedral angles φ_{Cn}[deg] of five membered ring (Table 2) from carbon chemical shift δ_{Cn} ppm under magnetic field (eqs. 5a, b): a. calculated two angles (θ^{C1An}, θ^{T1An}, n = 1, 2) from *sin* and *tan* functions, b. calculate two tetrahedral angles (φ_{Cn}^{C1}, φ_{Cn}^{T1}, n = 1–4), c. builds five sets units (C_i or T_i, i = 1–5) from angles θ^{C1An}, θ^{T1An}, d. display results. Java Script programs for transformation S to U and U to S are available in literature [1]. Between calculated tetrahedral angles is choose one in opposite with the calculated dihedral angles, angles with values almost equals with the predicted dihedral angles [4] only from vicinal coupling constant $^3J_{HH}$[Hz]. The units for calculation of the tetrahedral angles are builds starting with angles $\theta^{C1An} = f(\sin^{-1}R_m)$, $\theta^{T1An} = f(\tan^{-1}R_m)$, five sets angles (A, B, C, D, E or F, G relative to seven sets unit [1]) from *sin* function and five sets angles

from *tan* function. The angles θ^{A1}, θ^{A2} of set A are equals with ϕ_2 of sets D, E or F, G.

CONCLUSION

3-Sphere approach for calculation of the dihedral (I–IV) and tetrahedral angles (5a–f) from chemical shift and/or vicinal coupling constant used Lie algebra and Hopf fibration theories. Hypersphere equations 5a,b, equations of circles and circles inversion, ensure the *sin-trans* relationships between the tetrahedral angles and dihedral angles of sugars, angles calculated with Java Script program SetCnTETRAHEDRAL.html (Fig. 1). Dihedral angles are calculated with 3D-sphere equations I–IV [1] and tetrahedral angles with 4D-hypersphere equations **5**, generalized **9**. On the twenty sets angles (*sin* and *tan*: five sets angles U and S) are found circles of hypersphere – sphere – torus/Dupin cyclide – circles.

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