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

TETRAHEDRAL ANGLES OF SIX MEMBERED RING CALCULATED FROM NMR DATA WITH 3-SPHERE APPROACH

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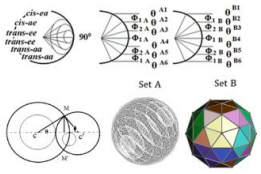
Hypersphere equations enable calculation tetrahedral angles φ_{Cn}[deg] of six membered ring from carbon chemical shift δ_{Cn}[deg]. The tetrahedral angles calculated directly from eqs. 2a, b are confirmed by the dihedral angles found in close relationship on the five sets unit (C_i and T_i, i = 1–5, C, T = U or S) having ϕ_{2X}, ϕ_{2Y} equal with θ^{Z1}, θ^{Z2} where Z is A or B and X, Y are D, E or F, G, angle of seven sets unit, or on two units with six sets. A method which is expected in case of six membered ring to ensure calculation of the tetrahedral angles for all conformations, *chair* – *boat* – *skew*.



Eq. 2a: **4D**: $\sin^{-1}\tan\{-\sin^{-1}[nx(1/R_m)]\} = -C$, **2c: 3D**: $\cos^{-1}\sin(-C/n) = \varphi_{Cn}^{sin}$

Eq. 2b: **4D**: $\tan^{-1}\sin\{-\tan^{-1}[nx(1/R_m)]\} = -D$, **2d**: **3D**: $\cos^{-1}\sin(-D/n) = \varphi_{Cn}^{tan}$

INTRODUCTION

Dihedral angles of five membered ring[1-3] are calculated to date from vicinal coupling constant[1,3] $^3J_{HH}$[Hz] with 3-sphere approach, relationships between dihedral θ_{HnHn+1}[deg] and vicinal angles ϕ[deg] ensuring the right sign, and proton or/and carbon chemical shift from manifold equations[2], conic section or Villarceau circles ensuring the right *cis*/*trans-ee*, *-aa* stereochemistry. The wave character of NMR data fitting well with the 3-sphere theory, Hopf fibration confirmed by Lie algebra. Hopf construction *versus* Riemannian symmetric space, octonionic Hopf fibration: $S^7 \rightarrow S^{15} \rightarrow S^8$ (R^{16} quaterionic multiplication) *versus* octonionic projective plane (dimension 16 = 2 × 8, F_4 symmetry, Cayley projective plane $P^2(O)$) for all *cis*/*trans* stereochemistry. A hypersphere with points in 4D and circle in S2,[4] with hypersphere – sphere – torus – circle available coordinates on seven sets units (C^{Ni} or T^{Ni}, N = A, B, C, D, E, F, G, i = 1–6) calculated from *sin* and *tan* function[2]. Seven sets angles with three pair of sets angles: A, B, C – D, E, A – F, G, B (Fig. 1). The transformation S to U giving angles almost equals with angles results from tan function, and U to S with angles results from sin function[2], resulting six sets on two units (U and S) under torus inversion to Dupin Cyclide or Dupin Cyclide inversion to torus circles, a tangential space ensuring the right *cis*/*trans-ee*, *-aa* stereochemistry, under 90[deg] rule for *trans-ee* stereochemistry and 180[deg] rule for *trans-aa* stereochemistry.[3]

Seven sets angles on two units: $C_n = U_n^{Ni}$, S_n^{Ni}, $T_n = U_n^{Ni}$, S_n^{Ni}.

θ^{CnNi} – unit calculated from *sin* function, θ^{TnNi} – unit calculated from *tan* function;

If $U_n^{N1} > 5$[deg]: $U_n = U_nA_i$, U_nB_i, U_nC_i, U_nD_i, U_nE_i, U_nF_i, U_nG_i, i = 1–6, n = 1–7.

If $Sn^{N1} < 5$[deg]: $S_n = S_nA_i$, S_nB_i, S_nC_i, S_nD_i, S_nE_i, S_nF_i, S_nG_i, i = 1–6, n = 1–7.

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Transformation from U to S and S to U:

$$\sin^{-1}\cos(\phi_{U1B}^{\text{trans-ee3,2}}) = \theta_{HnHn+1}^{S1A3} \quad (1a)$$

$$\phi_{1U1B} = (60 - \theta^{S1B1}) / 1.5, \quad \theta^{U1A1} = \phi_{1U1B}/2 \quad (1b)$$

The transformation from space-time to space, *i.e.* from Minkovski hyperbolic angle into Euclidean angle[5] was performed by transforming from Hz ($\delta_C \times \omega_L$[cycli/s]) in golden triangle – invers of dodecahedron under conic section, resulting one of the tesseract dimension.[2] Conic section a limit case of the cylindrical coordinates of torus, with helices as geodesics, a way to translate in two-dimension (geodesics on the unroll cone cut along meridian becomes straight lines in the plane). Villarceau circles result by cutting a torus oblique,[4] and polar curves at intersection of torus with a plane (Spiric section = Cassini oval, Lemniscate of Bernolli, hippopede),[4] the inverse of conic section (r = 1 + + e cos θ – limaçons of Pascal).[6]

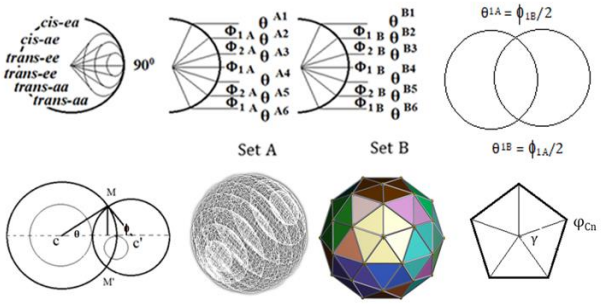


Fig. 1 – Dihedral angles θ_{HnHn+1}[deg] on set A and vicinal angles on set B with corresponding algebraic angles ϕ_2 and $\phi_1/2$ [deg] under 3-sphere theories with torus inversion to Dupin cyclide. Five and six membered rings inscribe on rhombic polyhedron geometries with corresponding tetrahedral φ_{Cn}[deg] and internal angles γ[deg].

The relationships between tetrahedral angle and dihedral angle (Fig. 1) are governed by the sphere or cyclide inversion, *sin versus trans* functions, and by rhombic polyhedron geometries[4] with both five and six membered ring inscribe on sphere.

As demonstrate recently, the shape of the five membered ring in function of the protective groups or alkyl chain varies between sinusoidal and tangential space from 2D to 4D with influence on biological activity.[7,8] The main advantage of the 3-sphere and Lie group theories is the huge number of trigonometric equations which fit well with the NMR data giving information about the physic constant of the molecules, *i.e.* tetrahedral – internal and dihedral – vicinal angles.

RESULTS

Hypersphere inversion[3] equations 2a, b enable calculation tetrahedral angles of six membered ring[9] from chemical shift δ_c[ppm], as demonstrated on α, β-1,3,4-tri-O-acetyl-2-azido-6-bromo-2,6-dideoxy-D-galactose **1a,b** and 2,6-dideoxy-2,6-imino D-talonic acid **2**[9] (Table 1, Fig. 2)

$$\textbf{4D}: \sin^{-1}\tan\{-\sin^{-1}[n\,(1/R_m)]\} = -C, \quad (2a)$$

$$\textbf{4D}: \tan^{-1}\sin\{-\tan^{-1}[n\,(1/R_m)]\} = -D, \quad (2b)$$

$$\textbf{3D}: \cos^{-1}\sin[-D/n] = \varphi_{Cn}^{\tan}, \quad (2c)$$

$$\textbf{3D}: \cos^{-1}\sin[-C/n] = \varphi_{Cn}^{\sin}, \quad (2d)$$

where: R_m chemical shift of C_n in gauss, n = ½, 1, 2, φ_{Cn} tetrahedral angle C_n in deg.

Dihedral angles (eqs. 3a–d) are angles[1] at intersection of two disks in close relationships with vicinal angles, angles result from vicinal coupling constant $^3J_{HH}$[Hz] under torus circle inversion to Dupin cyclide circle or *viceversa*. From both angles ϕ, θ_{HnHn+1}[deg] can be calculated $^3J_{HH}$[Hz] with eq. 4.

$$\sin^{-1}\cos\phi = \theta_{HnHn+1}, \quad (3a)$$

$$\cos^{-1}\sin(-\phi) = \theta_{HnHn+1}, \quad (3b)$$

$$\sin^{-1}\tan(-\phi) = \theta_{HnHn+1}, \quad (3c)$$

$$\sin^{-1}[1/\tan(-\phi)] = \theta_{HnHn+1}, \quad (3d)$$

$$\tan^{-1}\sin-\phi = \theta_{HnHn+1}, \quad (3e)$$

$$^3J_{HH} = (\phi + \cos^2\theta_{HnHn+1})^{1/2}/2, \quad (4)$$

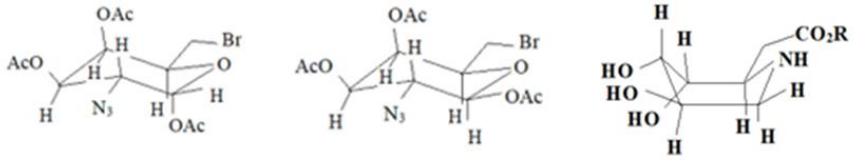
where ϕ – vicinal angle[deg], θ_{HnHn+1} – dihedral angle[deg], *cis*, *trans-ee*: $^3J_{HnHn+1} = (\phi)^{1/2}$, *trans-aa*: $^3J_{HnHn+1} = (\phi)^{1/2}/2$.

Table 1

Tetrahedral angles of α-**1a,** β-**1b, 2** calculated from δ_C[ppm] with 3-sphere approach eq. 2

	C_n	$^3J_{HnHn+1}{}^{pred}$ [Hz]	ϕ, θ_{HnHn+1} [deg]	δ_{Cn} [ppm]	$R_m{}^c$ [π]	φ [deg]	θ_{HnHn+1} [deg]	$^3J_{HnHn+1}{}^{calc}$ [Hz]
1.	**α-1**[a]							
2.	C_1	H_1H_2: 3.5	*49* 41	90.3	2.10784	I. 110.58 II. 113.2013	40.29 41.60	3.52 3.47
3.	C_2	H_2H_3: 11	*121* 149 –139.39[3f] 143.06[3d]	56.5	1.3188	I. 117.32[S] 110.44[StoU] II. 111.958 117.062[UtoS] III. 113.982	148.661 –139.107 –139.020 148.522 –138.008	11.015 10.95[h] 10.940 11.021 10.762
4.	C_3	H_3H_4: 3.0	*36* 54	67.1	1.5662	I. 111.147 113.117 II. 118.28 110.285StoU II. 111.106 III. 115.667 111.334	55.573 56.55 54.714 55.553 55.667	2.93 2.89 2.97 2.934 2.929
5.	C_4	H_4H_5: 1.0	*4* –4.0[eq.3d] –3.9[eq.3f]	68.0	1.5873	I. 117.108 II. 118.05 III. 115.787 111.579	– – – –4.21, 55.7	 1.02
6.	C_5			71.0	1.6573	I. 114.584 II. 117.82 115.643 III. 116.179	–5.41 –4.35 –3.82	 1.04 0.975
7.	**β-1**[a]							
8.	C_1	H_1H_2: 8.5	*72.2* 162.2	92.6	2.1615	I. 112.10 II. 114.82	161.05 162.41	8.42 8.50
9.	C_2	H_2H_3: 11	*121* 149 –139.39[3f] 143.06[3d]	59.3	1.3842	I. 115.28 110.56 II. 111.756 III. 114.75	 162.64 –137.3 160.89 –	 8.52 10.61 8.41 –
10.	C_3	H_3H_4: 3.0	*36* 54	66.5	1.5522	I. 111.409 III. 115.58 111.167	160.704 –139.29 55.70 160.58 –139.41 55.58	8.40 10.98 2.92 8.40 11.00 2.93
11.	C_4	H_4H_5: 1.0	*4* –4.0[eq.3d] –3.9[eq.3f]	71.2	1.6619	I. 114.43 II. 117.27	–2.78 57.21 –	0.83 2.86 –
12.	C_5			73.8	1.7226	I. 112.264 II. 116.658 113.316	–3.63 56.36 –3.34 56.65	0.95 2.9 –3.33 2.88
13.	**2**[b]							
14.	C_1	H_1H_2: 3.5 7.7	*49* –37.04[eq.3f] *59.29* –143.5[eq.3d]	44.8	1.2549	I. 114.65 II. 112.133 II. 115.98[g]	47.67[ϕ] 57.32[ϕ] 48.93[ϕ] 56.06[ϕ] 47.00[ϕ] 57.99[ϕ]	3.45 7.57 3.49 7.48 3.42 7.61
15.	C_2	H_2H_3: 7.3	*53.29* 143.29	60.3	1.6890	I. 113.637 116.818 II. 116.99	 143.63 143.99	 7.32 7.34
16.	C_3	H_3H_4: 2.6	*27.04* –24.44[eq.3] –30.69[eq.5]	65.7	1.8403	I. 110.16 119.495 III. 117.073	 29.49[ϕ] 27.07[ϕ]	 2.71 2.60
17.	C_4	H_4H_5: 6.4	*40.96* –146.75[eq.3]	68.2	1.9103	III. 117.37	27.37[ϕ] 58.68[ϕ] 46.31[ϕ] 40.87[ϕStoU]	2.61 7.66 3.40 6.39
18.	C_5			70.6	1.9775	III. 117.64	27.64[ϕ] 40.78[ϕStoU]	2.62 6.38

^{13}C NMR: a) ω_C = 62.5 MHz, b) ω_C = 75 MHz, c) $R_m = \Delta\delta_C \times \omega_L \times 4 \times 10^{-3}/\gamma$ [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]; R_m ~ 1.61803 dodecahedron, ~2.61803 icosahedron; d) unit build from calculated tetrahedral angle under five sets angles rule; e) transformation S to U; f) five membered ring with $\phi_2{}^D = \theta^{A1}$, $\phi_2{}^E = \theta^{B1}$; g) IIa. B/2 112.133, IIb. B/2 109.013, IIb. B 115.98; h) 180 – sin^{-1} tan – $\theta_{H2H3}{}^{cis} = \phi^{trans}$[deg], $^3J_{H2H3} = (\phi^{trans})^{1/2}$.



α-1 **β-1b** **2**

Fig. 2 – α, β-1,3,4-Tri-O-acetyl-2-azido-6-bromo-2,6-dideoxy-D-galactose **1a,b** and 2,6-dideoxy-2,6-imino D-talonic acid **2**[9].

Relationships between tetrahedral angle φ_{Cn}[deg] and dihedral angle θ_{HnHn+1}[deg] on five sets angles on one unit, or six sets angles on two units are demonstrated in Table 2, and established the trigonometric equation between two of them. From dihedral angle θ_{HnHn+1}[deg] or vicinal angle ϕ[deg] result the tetrahedral angle φ_{Cn}[deg] with eq. Ic, IIc, IIIc, or $\phi_2 = \theta^{N2}$ is subtracted from 60 deg (eq.7).

$$\cos^{-1}\sin(-\theta_{HnHn+1}/2) = \varphi_{Cn}, \quad (5)$$

$$\cos^{-1}\sin(-\phi_2/2) = \varphi_{Cn}, \quad (6)$$

$$60 - \phi_2 = \varphi_{Cn}, \quad (7)$$

where θ_{HnHn+1} – dihedral angle[deg], φ_{Cn} – tetrahedral angle[deg], ϕ_2 – algebraic angle, φ_{Cn} – tetrahedral angle[deg].

Table 2

Seven sets angles and relationships between tetrahedral angles and dihedral angles of **1a**

Entry	$^3J_{HnHn+1}$ [Hz]	θ^{Ni}	θ^{Ai}	θ^{Bi}	θ^{Ci}	θ^{Di}	θ^{Ei}	θ^{Fi}	θ^{Gi}
		θ^{N1}	9.4147	20.585	18.829	4.707	25.292	10.292	19.707
		$\theta^{N2\theta}$	50.585	39.414	41.705	55.292	34.707	49.707	40.292
		θ^{N3}	69.414	80.585	78.829	64.707	85.292	70.292	79.707
		θ^{N4}	110.58	99.414	101.17	115.292	94.707	109.70	100.29
1.	**1**-H_1H_2:3.5	θ^{N5}	129.41	140.58	138.82	124.707	145.292	130.292	139.70
		θ^{N6}	170.58	159.41	161.17	175.292	154.707	169.707	160.29
		ϕ_2	18.829	41.170	37.658	9.4147	50.585	20.585	39.414
		$\phi_1/2$	20.581	9.414	11.170	25.292	4.707	19.707	10.292
	Equations		$\cos^{-1}\sin\text{-}\theta_{H1H2}/2 = \varphi_{C1}$, where $\theta_{H1H2} = 40.292$, $\varphi_{C1} = 110.14$ deg $\cos^{-1}\sin\text{-}\phi_2/2 = \varphi_{C1}$, where $\phi_2 = 41.170$, $\varphi_{C1} = 110.58$ deg						
		θ^{N1}	2.678	27.321	5.357	1.339	28.660	13.660	16.339
		$\theta^{N2\theta}$	57.321	32.678	54.642	58.660	31.339	46.339	43.660
		θ^{N3}	62.678	87.321	65.357	61.339	88.660	73.660	76.339
		θ^{N4}	117.32	92.678	114.64	118.660	91.339	106.339	103.660
2.	**2**-H_2H_3:11	θ^{N5}	122.67	147.321	125.357	121.339	148.660	133.660	136.339
		θ^{N6}	177.32	152.678	174.642	178.660	151.339	166.339	163.66
		ϕ_2	5.357	54.642	10.714	2.677	57.321	27.321	32.678
		$\phi_1/2$	27.32	2.678	24.647	28.660	1.339	16.339	13.6606
		θ^{N1}	19.107	10.892	21.785	9.5535	20.446	5.446	24.553
		$\theta^{N2\theta}$	40.892	49.107	38.214	50.446	39.553	54.553	35.446
		θ^{N3}	79.107	70.892	81.785	69.553	80.446	65.446	84.553
		θ^{N4}	100.89	109.10	98.214	110.44	99.553	114.553	95.446
	S to U	θ^{N5}	139.10	130.89	141.785	129.553	140.44	125.446	144.55
3.		θ^{N6}	160.89	169.107	158.214	170.446	159.55	174.553	155.446
		ϕ_2	38.214	21.785	43.571	19.707	40.892	10.892	49.107
		$\phi_1/2$	10.892	19.107	8.214	20.446	9.553	24.553	5.446
	Equations		$\cos^{-1}\sin - \phi_2 = \varphi_{C2}$, where $\phi_2 = 27.321$, $\varphi_{C1} = 117.32$ deg, $\theta_{H2H3} = 43.66$ $\cos^{-1}\sin - \theta_{H2H3}/2 = \varphi_{C2}$, where $\theta_{H2H3} = 40.892$, $\varphi_{C2} = 110.44$ deg Eq.: 3b: $\theta = 31^{cis}$, 149^{trans}; 3d: 36.9^{cis}, 143.1^{trans}, 3e: -40.60^{cis}, -139.39^{trans}						

DISCUSSION

Relationship between tetrahedral angle and the dihedral angle of six membered ring, as demonstrated on Table 2 with eqs. 2a, b, can be established on five sets unit. Java script program used a system of equations Ia-c, IIa-c, IIIa-c result from *torus to invers of torus*, analog to cube tesseract from 4D to 2D – 3D. Five sets unit with trigonometric eqs. 2c, d between tetrahedral-dihedral or vicinal angles, relative to five membered iminocyclitols[3] where the relationship between the dihedral and the tetrahedral angle is established also trigonometric, but their position on two units is in opposite, one angle on unit results from sin function and one from tan function.

Building the unit (Table 1, entry 2, Table 2, entry 1) with tetrahedral angle φ_{C1} **I** 110.58 deg results from eq. 2a was observed that the dihedral angle $cis^{5,2} - \theta_{H1H2}{}^{UG2}$ 40.29 [deg] and the corresponding vicinal angle ϕ^{UF2} 49.70 [deg] are on two sets angles with ϕ_2 equals with first θ^{U1B1} deg and second θ^{U1B2}[deg] angles of set B. The tetrahedral angle $\varphi_{C1}{}^{UA4}$ deg results from angle θ^{U1B1} deg (eq. 3b with $\phi = \theta^{U1B1}$ or Ic), half of $cis^{5,2} - \theta_{H1H2}{}^{UG2}$. In this case between φ_{C1} **I** 110.58 deg and φ_{C1} **II** 113.20 deg are smaller differences, in last case $cis^{5,2} - \theta_{H1H2}{}^{UG2}$ 41.60 [deg].

The most suggestive example for building unit is that the tetrahedral angle φ_{C2} **I** 117.32 deg has a dihedral angle of 148.66 deg for a vicinal constant coupling $^3J_{H2H3}$ of 11[Hz] (Table 1, entry 3, Table 2 entry 2) with ϕ_2 of sets D, E equals with θ^{A1} and θ^{A2} of set A, since the dihedral angle θ_{H2H3} has negative sign as established with molecular model. Therefore, tetrahedral angle will be 110.44 [deg], angle result from transformation S to U in close relationship with dihedral angle $trans\text{-}aa^{5,2}$ θ_{H2H3} – 139.11 [deg], with value comparable with predicted dihedral angle θ_{H2H3} – 139.29 [deg] with eq. 3f. Tetrahedral angle on set D and dihedral angle on set A, with ϕ_2 of sets D and E equals with θ^{SA1} and θ^{SA2}, θ^{SA2} the corresponding torsional angle of the dihedral angle θ^{SA5}.

Angle calculated with eq. **III** 115.789 [deg] is under three sets rule (Table 1, entry 5) with tetrahedral angle φ_{C4} 111.579 [deg], since θ^{C1} and θ^{C2} are equals with ϕ_2 of sets A and B, three sets rule because two sets of second unit are omitted. Seven sets angles (Table 1, entry 10) ensuring relationships between φ_{C3} 110.409[deg] and the tandem dihedral/vicinal angles: θ_{H3H4} 55.70, ϕ 34.29 [deg] in sets D and E, θ_{H1H2} 160.70, ϕ 70.70, [deg], θ_{H2H3} – 139.29, ϕ 120.56 [deg] in sets F, G. Thus, two pair of five set angles A-D-E and A(B)-F-G, the last one with two dihedral angles. If half of the dihedral angle or vicinal angle is on set B and tetrahedral angle on set A is applied eq. 3b, alternatively $\phi_2 = \theta^{N2}$ is subtracted from 60 [deg] (eq. 7). D-talonic acid with *cis*/*trans*-θ_{H1H2} stereochemistry is also under seven sets rule (Table 1, entry 14) in close relationship with ϕ^{cis} 47.67 deg and ϕ^{trans} 57.32 [deg].

2D: $\sin^{-1}[n\times(1/R_m)] = A,$ (Ia)

3D: $\sin{-1}\tan(-n\times A) = -C,$ (Ib)

3D: $\cos^{-1}\sin(-C/n) = \varphi_{Cn}{}^{sin}$[deg], (Ic)

2D: $\tan^{-1}[n\times(1/R_m)] = B,$ (IIa)

3D: $\tan^{-1}\sin(-n\times B) = -D,$ (IIb)

3D: $\cos^{-1}\sin(-D/n) = \varphi_{Cn}{}^{tan}$[deg], (IIc)

2D: $\tan^{-1}[n\times(R_m)] = B,$ (IIIa)

3D: $\tan^{-1}\sin(-n\times B) = -D,$ (IIIb)

3D: $\cos^{-1}\sin(-D/n) = \varphi_{Cn}{}^{tan}$[deg], (IIIc)

where: n = ½, 1, 2; A, B, C < or > 40[deg], R_m chemical shift of C_n in gauss, φ_{Cn} tetrahedral angle C_n in deg, C, D = f(θ_{HH}, ϕ): $\cos^{-1}\sin[-(\phi \text{ or } \theta_{HH})/n] = \varphi$, n = 1, 2.

Tetrahedral angles φ_{Cn}[deg] of six membered ring can be calculated from carbon chemical shift δ_{Cn}[ppm] with equations Ia-c, IIa-c, IIIa-c, angles results from hypersphere equations 2a, b, analog to cube tesseract from 4D to 2D (Fig. 2). With the calculated tetrahedral angle is build only one unit with seven sets angles and analyzed its relationship with the corresponding dihedral angle, angle with values almost equals with angle predicted from vicinal coupling constant[3] and confirmed with molecular models, since from only one vicinal coupling constant

with known stereochemistry result three possible angles with positive or negative sign. The values of the choose dihedral angle can be confirmed by the eq. 5–7. The transformation from unit U to S or S to U (eqs. 1a,b) can be made with programs already published in literature[2], also the prediction of the dihedral angles only from vicinal coupling constant.[1,3] Alternatively, can be predicted dihedral angles with eqs. 3a–f only from vicinal coupling constant $^3J_{HH}$[Hz] by hand.

EXPERIMENTAL

Tetrahedral angles of six membered ring can be calculated by hand using the equations Ia-c, IIa-c, IIIa-c. The angles result from eq. IIIa-c can be analyzed building seven sets unit or six sets units, and found the best relationship tetrahedral – dihedral or vicinal angle on five sets angles, as well as the sign and the stereochemistry of the dihedral angle calculated from carbon chemical shift δ_{Cn}[ppm] in relationship with tetrahedral angle φ_{Cn}[deg] to be almost equal with dihedral angle result only from vicinal coupling constant $^3J_{HnHn+1}$[Hz]. An example for calculation of the tetrahedral angle φ_{C1}[deg] of **α-1** for a vicinal coupling constant $^3J_{H1H2}$ = 3.5 Hz, chemical shift δ_{C1} 90.3 ppm and ω_C = 62.5 [MHz] with Java Script program (under work at this moment) is presented in Fig. 3. Three possible tetrahedral angles result from eq. I, II, III: T1 110.585 deg. T2 113.201[deg] and T3 118.124 deg. Building unit with seven set angle (Table 2, entry 1) on set U1G is found the dihedral angle θ_{H1H2} 40.292 [deg] with its corresponding vicinal angle ϕ 49.707 deg in set U1F. The angle ϕ_2 of set U1F is the angle θ^{U1B1} of set B in close relationship with tetrahedral angle T1 = θ^{U1A4} = 110.585 [deg] of set A

$$\cos^{-1} \sin\theta_{HnHn+1} = \phi \text{ [deg]}, \quad (8)$$

$$^3J_{H1H2} = (\phi)^{1/2} / 2 \text{ Hz}, \quad (9)$$

where dihedral angle – θ_{HnHn+1}[deg], vicinal angle – ϕ, vicinal coupling constant – $^3J_{H1H2}$[Hz].

$$\cos^{-1} \sin 40.2926 = 49.707 \text{ [deg]}, \quad (8)$$

$$^3J_{H1H2} = (49.707)^{1/2} / 2 = 3.52 \text{ [Hz]}, \quad (9)$$

$$\cos^{-1} \sin - 40.292 / 2 = 110.525 \text{ [deg]}. \quad (5)$$

Second angle calculated T2 of 113.201 deg has θ^{U1B1} = = ϕ_2^F = 23.20 deg and a dihedral angle of $\theta_{H1H2} = \theta^{U1G2}$ 41.60 deg.

$$\cos^{-1} \sin 41.6006 = 48.399 \text{ [deg]}, \quad (8)$$

$$^3J_{H1H2} = (48.399)^{1/2} / 2 = 3.47 \text{ [Hz]}, \quad (9)$$

$$\cos^{-1}\sin - 23.201 = 113.201 \text{ [deg]}. \quad (6)$$

Third angle T3 118.124[deg] result in unit S with a higher difference between the calculated dihedral angle from vicinal coupling constant and dihedral angles result from set G (44.062 deg). The transformation S to U gives a dihedral angle of 40.625 deg in set A and a tetrahedral angle of 110.312[deg] in set D.

$$\cos^{-1} \sin 44.062 = 45.937 \text{ deg}, \quad (8)$$

$$^3J_{H1H2} = (45.937)^{1/2} / 2 = 3.38 \text{ Hz}, \quad (9)$$

$$\cos^{-1}\sin - 28.124 = 118.124 \text{ deg}. \quad (6)$$

CONCLUSION

Three tetrahedral angles are calculated with equations Ia-c, IIa-c, IIIa-c (2D, 3D, 3D), equations result from hypersphere equations 2 (4D + 3D), ensuring the relations between sinusoidal in opposite with tangential space of tetrahedral and dihedral angles on only one unit. Five sets angles result from seven sets angles on one unit, or from six sets angles on two units in relationship sin/tan, or from three sets angles on unit 1 and three on unit 2. The hypersphere equations proposed for calculation of the tetrahedral angles of six membered ring from chemical shift probably can be used for all conformations, *chair – boat – skew*, to date was demonstrated only for chair (α-**1a,** β-**1b**) and boat (**2**) conformation. A method easy to used for calculation of the tetrahedral angles in close relationships with dihedral angles of six membered ring with Java Script. Recently was reported the conformational analysis[10] of six membered ring based on 3-sphere dihedral angles, and the differences between the 3-sphere torsional angles and polynomial torsional angles. 3-Sphere tetrahedral angles can be other parameters[11] used in future on conformational analysis. To date 3-sphere approach has been applied on calculation of the dihedral angles[1–3, 12], tetrahedral angles of five membered ring[13], conformational analysis of five[14] and six[10] membered rings, configurational/ conformational analysis at anomeric position[15], and analysis of antiviral activity of three alkyl chain imnocyclitols with D and L ribitol stereochemistry with hypersphere equations.[16]

```
<!DOCTYPE html>
<html>
<head>
<title>A Java script including HTML</title>

</head>

<body style ="background-color:LightGrey;">

<p id="demo"></p>
<p>Click button to:</p>
<button onclick = "window.print()">Print this page.</button>

<button type="button"onclick="document.getElementById('demo').innerHTML =
Date()">Date and Time.</button>

<h3>Java Script program for calculation tetrahedral angles from carbon chemical
shift of pyranose.</h3>

</body>

<script type="text/javascript">
//File name tetrahedral angle [deg].html
//Program that calculated tetrahedral angles[deg]

var usedata1
usedata1 = prompt ("Chemical shift Cn[ppm]")
var Ca1 = usedata1;//Ca1[ppm]
//Chemical shift CP[ppm]
var CP = 1*Ca1;//CP[ppm]

usedata1A = prompt ("The atom of carbon Cn: n = 1, 2, 3, 4 or 5")

var usedata2
usedata2 = prompt ("13C Larmor frequency [MHz]")
var C13 = usedata2;//Larmor frequency 13C[MHz]

document.write("<h4><i>Tetrahedral angle Cn of six membered ring.</i></h4>")

document.write("<p>The value of CP[ppm] is="+CP);

document.write("<p>The value of C13[MHz] is="+C13);
document.write("<p><i>Cn:",usedata1A)

//calculate the value of RmC in [gauss]
var RC = (4*CP*usedata2)/(10.71*1000);//value of RC[gauss]
var RmC = RC;//RmC[radieni]

if (RmC < 1){
var RmC = RC;//value of RmC[radieni]
}
else {
var RmC = 1/RC;//value of RmC[radieni]
}

document.write("<p>The value of RmC[radieni] is="+RmC);

//calculate the angle A in deg
var Ar1 = Math.asin(RmC);//Ar1[rad]
var A1 = Ar1*57.29577521;//A1[deg]

document.write("<p>The angle Ar1[rad] is="+Ar1);
document.write("<p><i>I.</i>The angle A1[deg] is="+A1);

//calculate the angle B in deg
var Br1 = Math.atan(RmC);//Br1[rad]
var B1 = Br1*57.29577521;//B1[deg]

document.write("<p>The angle Br1[rad] is="+Br1);
document.write("<p><i>II.</i>The angle B1[deg] is="+B1);

//calculate the angle C in deg
var Cr1 = Math.atan(1/RmC);//Cr1[rad]
var C1 = Cr1*57.29577521;//C1[deg]

document.write("<p>The angle Cr1[rad] is="+Cr1);
document.write("<p><i>III.</i>The angle C1[deg] is="+C1);

var usedata3
usedata3 = Ar1;//angle Ar1[rad]
var Ar1 = usedata3;//angle Ar1[radI

//calculate the angle A in deg
var Ar = Math.tan(-2*usedata3);//Ar[radieni]
if (usedata3 < 0.52){
var Ar = Math.tan(-2*usedata3);//Ar[radieni]
   var Arr = Ar;//Arr[radieni]
       if (Ar > -1){
       var Arr = Ar;//Arr[radieni]
   var Aa = Math.asin(Arr);//Aa[rad]
   var A = Aa*57.29577521;//A[deg]
       }
       else{
   var Arr = 1/Ar;//Arr[radieni]
   var Aa = Math.asin(Arr);//Aa[rad]
   var A = Aa*57.29577521;//A[deg]
       }
}
else{
var Ar = Math.tan(-usedata3/2);//Ar[radieni]
   var Arr = Ar;//Arr[radieni]
       if (Ar > -1){
       var Arr = Ar;//Arr[radieni]
   var Aa = Math.asin(Arr);//Aa[rad]
   var A = Aa*57.29577521;//A[deg]
       }
       else {
       var Arr = 1/Ar;//Arr[radieni]
   var Aa = Math.asin(Crr);//Aa[rad]
   var A = Ca*57.29577521;//A[deg]
       }
}

document.write("<h4><i>Tetrahedral angles I.</i></h4>")
document.write("<p>The angle Ar[radieni] is="+Ar);
document.write("<p>The angle Aa[rad] is="+Aa);
document.write("<p>The angle A[deg] is="+A);

var usedata4
usedata4 = Aa;//angle Aa[rad]
var Aa = usedata4;//angle Aa[rad]

//calculate the angle T1 in deg
var T1r = Math.sin(usedata4/2);//T1r[radieni]
if (usedata4 < -0.68){
var T1r = Math.sin(usedata4/2);//T1r[radieni]
   var T1rr = T1r;//T1rr[radieni]
       if (T1r > -1){
       var T1rr = T1r;//T1rr[radieni]
   var T1a = Math.acos(T1rr);//T1a[rad]
   var T1 = T1a*57.29577521;//T1[deg]
       }
       else{
   var T1rr = 1/T1r;//T1rr[radieni]
   var T1a = Math.acos(T1rr);//T1a[rad]
   var T1 = T1a*57.29577521;//T1[deg]
       }
}
else{
var T1r = Math.sin(-usedata4);//T1r[radieni]
   var T1rr = T1r;//T1rr[radieni]
       if (T1r > -1){
       var T1rr = T1r;//T1rr[radieni]
   var T1a = Math.acos(T1rr);//T1a[rad]
   var T1 = T1a*57.29577521;//T1[deg]
       }
       else {
       var T1rr = 1/T1r;//T1rr[radieni]
   var T1a = Math.acos(T1rr);//T1a[rad]
   var T1 = T1a*57.29577521;//T1[deg]
       }
}


document.write("<p>The angle T1[deg] is="+T1);

var usedata5
usedata5 = Br1;//angle Br1[rad]
var Br1 = usedata5;//angle Br1[rad]

//calculate the angle B in deg
var Br = Math.sin(-usedata5);//Br[radieni]
if (usedata5 < 0.5233){
var Br = Math.sin(-usedata5);//Br[radieni]
   var Brr = Br;//Brr[radieni]
       if (Br > -1){
       var Brr = Br;//Brr[radieni]
   var Ba = Math.atan(Brr);//Ba[rad]
   var B = Ba*57.29577521;//B[deg]
       }
       else{
   var Brr = 1/Br;//Brr[radieni]
   var Ba = Math.atan(Brr);//Ba[rad]
   var B = Ba*57.29577521;//B[deg]
       }
}
else{
var Br = Math.sin(-2*usedata5);//Br[radieni]
   var Brr = Br;//Brr[radieni]
       if (Br > -1){
       var Brr = Br;//Brr[radieni]
   var Ba = Math.atan(Brr);//Ba[rad]
   var B = Ba*57.29577521;//B[deg]
       }
       else {
       var Brr = 1/Br;//Brr[radieni]
   var Ba = Math.atan(Brr);//Ba[rad]
   var B = Ba*57.29577521;//B[deg]
       }
}

document.write("<h4><i>Tetrahedral angles II.</i></h4>")

document.write("<p>The angle Br[radieni] is="+Br);
document.write("<p>The angle Ba[rad] is="+Ba);
document.write("<p>The angle B[deg] is="+B);

var usedata6
usedata6 = Ba;//angle Ba[rad]
var Ba = usedata6;//angle Ba[rad]

//calculate the angle T2 in deg
var T2r = Math.sin(usedata6);//T2r[radieni]
if (usedata6 > -0.5233){
var T2r = Math.sin(usedata6);//T2r[radieni]
   var T2rr = T2r;//T2rr[radieni]
       if (T2r > -1){
       var T2rr = T2r;//T2rr[radieni]
   var T2a = Math.acos(T2rr);//T2a[rad]
   var T2 = T2a*57.29577521;//T2[deg]
       }
       else{
   var T2rr = 1/T2r;//T2rr[radieni]
   var T2a = Math.acos(T2rr);//T2a[rad]
   var T2 = T2a*57.29577521;//T2[deg]
       }
}
else{
var T2r = Math.sin(-usedata6/2);//T2r[radieni]
   var T2rr = TTr;//TTrr[radieni]
       if (T2r > -1){
       var T2rr = T2r;//T2rr[radieni]
   var T2a = Math.acos(T2rr);//T2a[rad]
   var T2 = T2a*57.29577521;//T2[deg]
       }
       else {
       var T2rr = 1/T2r;//T2rr[radieni]
   var T2a = Math.acos(T2rr);//T2a[rad]
   var T2 = T2a*57.29577521;//T2[deg]
       }
}

document.write("<p>The angle T2[deg] is="+T2);

var usedata7
usedata7 = Cr1;//angle Cr1[rad]
var Cr1 = usedata7;//angle Cr1[rad]

//calculate the angle C in deg
var Cr = Math.sin(-usedata7);//Cr[radieni]
if (usedata7 < 0.5233){
var Cr = Math.sin(-usedata7);//Cr[radieni]
   var Crr = Cr;//Crr[radieni]
       if (Cr > -1){
       var Crr = Cr;//Crr[radieni]
   var Ca = Math.atan(Crr);//Ca[rad]
   var C = Ca*57.29577521;//C[deg]
       }
       else{
   var Crr = 1/Cr;//Crr[radieni]
   var Ca = Math.atan(Crr);//Ca[rad]
   var C = Ca*57.29577521;//C[deg]
       }
}
else{
var Cr = Math.sin(-usedata7/2);//Cr[radieni]
   var Crr = Cr;//Crr[radieni]
       if (Cr > -1){
       var Crr = Cr;//Crr[radieni]
   var Ca = Math.atan(Crr);//Ca[rad]
   var C = Ca*57.29577521;//C[deg]
       }
       else {
       var Crr = 1/Cr;//Crr[radieni]
   var Ca = Math.atan(Crr);//Ca[rad]
   var C = Ca*57.29577521;//C[deg]
       }
}

document.write("<h4><i>Tetrahedral angles III.</i></h4>'

document.write("<p>The angle Cr[radieni] is="+Cr);
document.write("<p>The angle Ca[rad] is="+Ca);
document.write("<p>The angle C[deg] is="+C);

var usedata8
usedata8 = Ca;//angle Ca[rad]
var Ca = usedata8;//angle Ca[rad]

//calculate the angle T3 in deg
var T3r = Math.sin(usedata8);//T3r[radieni]

 if (usedata8 > -0.5233){
 var T3r = Math.sin(usedata8);//T3r[radieni]
    var T3rr = T3r;//T3rr[radieni]
        if (T3r > -1){
        var T3rr = T3r;//T3rr[radieni]
    var T3a = Math.acos(T3rr);//T3a[rad]
    var T3 = T3a*57.29577521;//T3[deg]
        }
        else{
    var T3rr = 1/T3r;//T3rr[radieni]
    var T3a = Math.acos(T3rr);//T3a[rad]
    var T3 = T3a*57.29577521;//T3[deg]
        }
 }
 else{
 var T3r = Math.sin(-usedata8/2);//T3r[radieni]
    var T3rr = T3r;//T3rr[radieni]
        if (T3r > -1){
        var T3rr = T3r;//T3rr[radieni]
    var T3a = Math.acos(T3rr);//T3a[rad]
    var T3 = T3a*57.29577521;//T3[deg]
        }
        else {
        var T3rr = 1/T3r;//T3rr[radieni]
    var T3a = Math.acos(T3rr);//T3a[rad]
    var T3 = T3a*57.29577521;//T3[deg]
        }
 }


document.write("<p>The angle T3[deg] is="+T3);

</script>
</html>
```

Fri Aug 25 2023 12:40:16 GMT+0300 (GTB Daylight Time)

Click button to:

Print this page. Date and Time.

Java Script program for calculation tetrahedral angles from carbon chemical shift of pyranose.

Tetrahedral angle Cn of six membered ring.

The value of CP[ppm] is=90.2

The value of C13[MHz] is=62.5

Cn:C1

The value of RmC[radieni] is=0.47494456762749443

The angle Ar1[rad] is=0.4949010404385589

I.The angle A1[deg] is=28.355738764162794

The angle Br1[rad] is=0.44340310760720625

II.The angle B1[deg] is=25.405124780887793

The angle Cr1[rad] is=1.1273932191876903

III.The angle C1[deg] is=64.59486845985616

Tetrahedral angles I.

The angle Ar[radieni] is=-1.5230195328602338

The angle Aa[rad] is=-0.7162892787276961

The angle A[deg] is=-41.04034949931511

The angle T1[deg] is=110.52016799039165

Tetrahedral angles II.

The angle Br[radieni] is=-0.4290159599605437 6

The angle Ba[rad] is=-0.40526727821208386

The angle B[deg] is=-23.220102872408088

The angle T2[deg] is=113.22009611314219

Tetrahedral angles III.

The angle Cr[radieni] is=-0.5343145328546923

The angle Ca[rad] is=-0.49072092466310374

The angle C[deg] is=-28.11623579034054

The angle T3[deg] is=118.11622903107464

Fig. 3 – Java Script program for calculation tetrahedral angle φ_{C1} of **α-1** with $^3J_{H1H2}$ = 3.5[Hz] and the corresponding results.

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