

Research Article

3-Angles Under 3-Sphere Approach for Conformational Analysis of 2,6-Dideoxy-2,6-Imino-D-Talonic Acid

Carmen-Irena Mitan^{*} , Emerich Bartha, Petru Filip

Department of Chemistry, Institute of Organic and Supramolecular Chemistry “Costin. D. Nenitescu”, Bucharest, Romania

Abstract

Relationships between vicinal ϕ - dihedral $\theta_{\text{HnHn}+1}$ - tetrahedral φ_{Cn} angles [deg] under Hopf fibration and Lie algebra theories enable conformational analysis with VISION molecular models on conformational routes that might be followed by six membered ring, *i.e.* ${}^4\text{C}_1$: ${}^0\text{H}_5$, ${}^0\text{H}_1$, ${}^2\text{H}_1$, ${}^2\text{H}_3$, ${}^4\text{H}_3$, ${}^4\text{H}_5$, ${}^0\text{S}_2$, ${}^3,0\text{B}$, ${}^3\text{S}_1$, $\text{B}^{1,4}$, ${}^5\text{S}_1$, ${}^{2,5}\text{B}$, ${}^2\text{S}_0$, $\text{B}_{3,0}$, ${}^1\text{S}_3$, ${}^{1,4}\text{B}$, ${}^1\text{S}_5$, $\text{B}_{2,5}$ of 2,6-dideoxy-2,6-imino-D-talonic acid 1D. Six dihedral angles with *cis*-, *trans-ee*, *trans-aa* stereochemistry calculated from only one vicinal coupling constant ${}^3J_{\text{HH}}[\text{Hz}]$ and *torus and invers of torus equations*, represented on 3-Sphere, a hypersphere in 4D, are restricted by the stereochemistry of sugar, by the combination of dihedral angles along its shape, tetrahedral angles and at list by the distorted boat B or skew S of relaxed ${}^4\text{C}_1$ or ${}^1\text{C}_4$ chair conformations. Dihedral angles at anomeric position calculated from vicinal coupling constant are compared with angles calculated from carbon chemical shift with Euler - Conic manifold. On VISION molecular models are simulated first two conformations $\text{B}_{0,3}$ and $\text{B}^{0,3}$ as etalon, followed by introduction the calculated exocyclic dihedral angles: 1. from dihedral angles calculated only from vicinal coupling constant ${}^3J_{\text{HH}}[\text{Hz}]$: S^1_3 ($\text{B}_{0,3}$), and $\text{B}^{0,3}$ (S^2_0), S^3_1 ; 2. or from carbon chemical shift $\delta[\text{ppm}]$ and vicinal coupling constant ${}^3J_{\text{HH}}[\text{Hz}]$: S^1_3 , $\text{B}_{0,3}$, S^2_0 and S^3_1 .

Keywords

3-Sphere, Hopf Fibration, Lie Algebra, Dihedral Angles, Tetrahedral Angles, Six Membered Ring, D-talonic Iminocyclitol

1. Introduction

Real Hopf fibration trigonometric equations for one vicinal coupling constant, or R^{32} octonionic Hopf fibration for all stereochemistry with positive and negative sign, in agreement with algebraic equations, in case of torus and other two equation results from invers of torus are applied on calculation dihedral angles in close relationships with tetrahedral angles from NMR data (vicinal coupling constant and / or carbon chemical shift) for conformational analysis. Six possible dihedral angles $\theta_{\text{HnHn}+1}[\text{deg}]$ results from vicinal angle $\phi[\text{deg}]$ calculated with characteristics equations (1, 2) for calculation dihedral angles

from vicinal coupling constant ${}^3J_{\text{HH}}[\text{Hz}]$. [1] Phase angle of the pseudorotation $\text{P}[\text{deg}]$ can be established with exocyclic 3-Sphere dihedral angles on VISION molecular models. Too higher number of dihedral angles are reduced by the relationship with the corresponding tetrahedral angle on seven set angles.

3-Sphere approach enable calculation dihedral angles from vicinal coupling constant ${}^3J_{\text{HH}}[\text{Hz}]$ and / or chemical shift $\delta[\text{ppm}]$. A hypersphere in 4D, where all *cis*, *trans-ee* and *trans-aa* stereochemistry can be drowned on three concentric

^{*}Correspondence: Carmen-Irena Mitan (cmitan@yahoo.com)

Received: 9 September 2026; Accepted: 27 September 2026; Published: 28 October 2026



Copyright: © The Author(s), 2026. Published by Science Publishing Group. This is an **Open Access** article, distributed under the terms of the Creative Commons Attribution 4.0 License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

cons, or on two sets angles with six angles on every set, having first angle of set A half of angle between angles 3 and 4 of set B. Hopf trigonometric equation ensuring relationships between dihedral angle $\theta_{HnHn+1}[\text{deg}]$ and vicinal angle $\phi[\text{deg}]$, angle result from vicinal coupling constant $^3J_{HH}[\text{Hz}]$. If dihedral angle $\theta_{HnHn+1}[\text{deg}]$ is the first angle of set A the vicinal angle is the third angle of set B resulting an angle with *cis*^{6,1} stereochemistry, if first angle of set A is a vicinal angle $\phi[\text{deg}]$ the dihedral angle can be the third or fourth angle of set B.

A method in 4 steps: 1. first are calculated the vicinal angles from vicinal coupling constant $^3J_{HH}[\text{Hz}]$, 2. with manifold equations will be calculated the first angle of unit, 3. Units with seven or six sets angles are builds, 4. Dihedral angles $\theta_{HnHn+1}[\text{deg}]$ are chosen in close relationships with tetrahedral angles $\varphi_{Cn}[\text{deg}]$. That must be mentioned in case of six membered ring tetrahedral angles $\varphi_{Cn}[\text{deg}]$ are in sets A or B and dihedral angles on sets D, E or F, G. In case of angles calculated only from vicinal coupling constant $^3J_{HH}[\text{Hz}]$ units are builds starting with dihedral angles $\theta_{HnHn+1}[\text{deg}]$. [2, 3].

2. Results

3-Sphere approach enable calculation dihedral $\theta_{HnHn+1}[\text{deg}]$ and tetrahedral $\varphi_{Cn}[\text{deg}]$ angles from vicinal angle $\phi^{\text{exp}}[\text{deg}]$, [1] angle calculated from vicinal coupling constant $^3J_{HH}^{\text{exp}}[\text{Hz}]$ or from carbon chemical shift $\delta_{Cn}[\text{deg}]$ with manifold [2, 3] equations. [4, 5] Six possible dihedral $\theta_{HnHn+1}[\text{Hz}]$ angles can be calculated from only one vicinal coupling constant $^3J_{HH}[\text{Hz}]$, angles in close relationship with tetrahedral $\varphi_{Cn}[\text{deg}]$ angles 1. on seven sets angles on one unit, having as keys angles θ^{A1} or $A2$ half of angles θ^{C1} or $C2$, ϕ_2 of sets D, E, and ϕ_2 of

sets F, G; 2. in six sets angles on two unit, based on transformation U to S and S to U. [2] The numbers of dihedral angles are reduced: I. by the stereochemistry of sugars, in this case negative sign of dihedral angle H_5H_4 restricted by D-talonic 1D stereochemistry [6], II. by relationship dihedral - tetrahedral with vicinal angle almost equal with recorded vicinal angle $\phi^{\text{exp}}[\text{deg}]$, III. conformational analysis. [7].

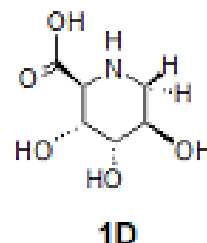


Figure 1. 2,6-Dideoxy-2,6-imino-D-talonic acid 1D.

Based on recorded vicinal coupling constants $^3J_{HH}[\text{Hz}]$ reported in literature for 2,6-dideoxy-2,6-imino-talonic acid 1D, B^{0,3} conformation was established considering the following succession of dihedral angles (exocyclic angles): -39.10 *cis* / -139.78 *trans-aa*^{5,2}, +143.29 *trans-aa*^{5,2}, -30.69, *cis*, -146.76 *trans-aa*^{5,2} [8], considering the rule of vicinal angle: eq. (1) until now characteristics for *cis*, *trans-ee* for values smaller as 6[Hz] and eq. (2) for *trans-aa* stereochemistry with values higher as 6[Hz], now is applied without any restriction for *trans* stereochemistry (Eqs. (1 – 4)). Four possible cases are restricted at two combinations (a and b) of *trans-aa* and *trans-ee* with corresponding *cis* stereochemistry. [1].

Table 1. Tetrahedral angles $\varphi_{Cn}[\text{deg}]$ in close relationship with dihedral angles $\theta_{HnHn+1}[\text{deg}]$ calculated from vicinal angle $\phi[\text{deg}]$ for 2,6-dideoxy-2,6-imino-D-talonic acid 1D.

Entry	$^3J_{HH}[\text{Hz}]$	$(n \times ^3J_{HH})^2$	$\phi[\text{deg}]$	$\theta_{HnHn+1}[\text{deg}]$	$\varphi_{Cn}[\text{deg}]$ D, E	$\varphi_{Cn}[\text{deg}]$ F, G
1.	3.8	$(2 \times ^3J_{HH})^2$	57.76	32.24 (-32.24)	-	118.88
				-40.22	110.06	114.887
				-39.10	-	115.448
				75.56 (-75.56)	112.22	112.78
		$(^3J_{HH})^2$	14.44	-14.002	112.99	112.001
				-14.921	112.53	112.460
				30.71 (-30.71)	-	118.579
				-40.68	110.34	114.982
2.	7.7	$(2 \times ^3J_{HH})^2$	237.16	-36.44	-	114.900
				-32.84 (32.84)	-	119.645
				40.036	110.018	114.656
				-40.19	110.09	115.279

Entry	$^3J_{HH}[\text{Hz}]$	$(n \times ^3J_{HH})^2$	$\phi[\text{deg}]$	$\theta_{HnHn+1}[\text{deg}]$	$\varphi_{Cn}[\text{deg}]$ D, E	$\varphi_{Cn}[\text{deg}]$ F, G
3.	7.3	$(^3J_{HH})^2$	53.29	36.71 (-36.71)	-	116.645
				-38.71	-	115.640
				-48.21	114.10	110.893
		$(2 \times ^3J_{HH})^2$	213.16	-56.84 (56.84)	118.42	-
				28.67	-	119.338
				-40.797	110.398	114.601
4.	2.6	$(2 \times ^3J_{HH})^2$	27.04	62.96 (-62.96)	118.52	-
				-24.44	-	117.223
				-30.69	-	119.654
		$(^3J_{HH})^2$	6.76	83.24 (-83.24)	-	116.62
				-6.71	116.64	-
				-6.80	116.59	-
5.	6.4	$(^3J_{HH})^2$	40.96	49.04 (-49.04)	114.52	110.455
				-33.24	-	118.377
				-60.26	119.86	-
		$(2 \times ^3J_{HH})^2$	163.84	-73.84 (73.84)	113.08	111.92
				-15.55	112.22	112.776
				16.84	111.57	113.422

Vicinal angles $\phi[\text{deg}]$:

$$\theta_{HnHn+1} = \sin^{-1} \tan \phi \quad (7)$$

$$\text{trans-ee: } \phi = (2 \times ^3J_{HH})^2 \quad (1)$$

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

$$\text{trans-aa: } \phi = (2 \times ^3J_{HH})^2 \quad (3)$$

$$\text{trans-ee: } \phi = (^3J_{HH})^2 \quad (4)$$

Dihedral angles $\theta_{HnHn+1}[\text{deg}]$:

$$\theta_{HnHn+1} = \sin^{-1} \cos \phi \quad (5)$$

$$\theta_{HnHn+1} = \tan^{-1} \sin \phi \quad (6)$$

Dihedral [8] angles $\theta_{HnHn+1}[\text{deg}]$ with corresponding tetrahedral [4] angles $\varphi_{Cn}[\text{deg}]$ calculated from vicinal coupling constant $^3J_{HH}[\text{deg}]$ with eqs. (1 and 2) [1] are presented in Table 1. Thus, six dihedral angles $\theta_{HnHn+1}[\text{deg}]$ for only one vicinal coupling constant $^3J_{HH}[\text{deg}]$. Unit with seven sets angles are builds from the half calculated dihedral angle (angles of set A) with eq. (8 – 10), relationships between *cis*, *trans-ee* dihedral angles θ^{A1} , θ^{A2} , θ^{A3} and angle θ^{D4} equal with tetrahedral angle.

Relationships dihedral $\theta_{HnHn+1}[\text{deg}]$ angles and $\varphi_{Cn}[\text{deg}]$ tetrahedral angles:

$$\theta_{HnHn+1}^{A1} = f(^3J_{HH}): \varphi_{Cn} = 120 - (\theta_{HnHn+1}/2) \quad (8)$$

$$\theta_{HnHn+1}^{A2} = f(^3J_{HH}): \varphi_{Cn} = 120 - \cos^{-1} \sin [(-\theta_{HnHn+1})/2] \quad (9)$$

$$\theta_{HnHn+1}^{A3} = f(^3J_{HH}): \varphi_{Cn} = 120 - \cos^{-1} \sin \{-[60 - (\theta_{HnHn+1}/2)]\} \quad (10)$$

In light of new consideration [1], at anomeric position are distingue two cases: A. both *cis* and *trans* angles are negative,

B. *cis* positive and *trans* negative, with angles around 114 -

116[deg] under A, B and D, E sets rule or 110[deg] with relationships between dihedral and tetrahedral under A, B and F, G sets rule. Tetrahedral angles 110 and 113 - 115[deg] results from sets D and F for same values of dihedral angles

θ_{HnHn+1} [deg]. Between the two possible dihedral angles will be calculated the tetrahedral angle from set D conform with eq. (8 – 10).

Table 2. Tetrahedral angles φ_{Cn} [deg] in close relationship with dihedral angles θ_{HnHn+1} [deg] calculated from carbon chemical shift δ_{Cn} [ppm] of 1D from sets A, B and D, E.

Entry	δ_{Cn}^a [ppm] [gauss]	$^3J_{HH}^a$ [Hz]	$(n \times ^3J_{HH})^2$	ϕ [deg] <i>recorded</i>	θ_{HnHn+1} [deg] <
-------	-------------------------------------	----------------------	-------------------------	--	---

Entry	δ_{Cn}^a [ppm] [gauss]	$^3J_{HH}^a$ [Hz]	$(n \times ^3J_{HH})^2$	ϕ [deg] <i>recorded</i>	θ_{HnHn+1} [deg]	ϕ [deg]	$^3J_{HH}$ [Hz]	θ_{HnHn+1} [deg] <i>calculated</i>	ϕ_{Cn} [deg]
4.	C ₄ 68.2 1.9103	2.6	$(n \times ^3J_{HH})^2$	27.04	62.96 -24.44 -30.69	212.94	7.29	62.499	(58.518)
						28.536	2.67	H ₃ H ₄ : -	110.228
						28.536	2.67	32.499	(58.51)
						27.349 ^b	2.61	H ₂ H ₃ : -	114.771
						212.157	7.28	55.001	
						28.0238	2.64	H ₃ H ₄ : -	
						27.904 ^b	2.64	25.0009	
						214.886	7.32	H ₂ H ₃ :	
						27.951 ^b	2.64	28.536	
						211.200	7.26	H ₃ H ₄ :	
						27.385	2.61	61.462	
						28.323 ^b	2.66	H ₃ H ₄ : -	
								32.940	
								H ₃ H ₄ : -	
								31.463	
								H ₂ H ₃ :	
								28.023	
								H ₃ H ₄ :	
								61.976	
								H ₃ H ₄ : -	
								31.976	
								H ₂ H ₃ : -	
								55.114	
								H ₃ H ₄ : -	
								25.113	
								H ₂ H ₃ :	
								27.385	
								H ₃ H ₄ :	
								62.614	
								H ₃ H ₄ : -	
								32.614	
			$(^3J_{HH})^2$	6.76	83.24 -6.71 -6.80			H ₃ H ₄ :	
								61.976	
								H ₃ H ₄ : -	
								31.976	
						28.024	2.646	H ₄ H ₅ : -	
						27.904 ^b	2.64	63.952	I. 108.95:
						41.689	6.45	H ₃ H ₄ :	116.0475
						26.047	2.55	63.952	112.094
						41.089	6.41	H ₄ H ₅ : -	105.22:
						40.924	6.39	60.696	118.607
						40.956	6.39	H ₄ H ₅ : -	119.778
						41.280	6.42	60.116	119.557
						28.608	2.67	H ₄ H ₅ : -	117.216
						41.535	6.44	60.221	II. 109.705:
						41.258	6.42	H ₄ H ₅ : -	115.294
						28.688	2.67	61.392	117.375
						-	-	H ₃ H ₄ :	III. 110.0924
						41.477	6.44	61.392	115.7334
						27.866	2.639	H ₄ H ₅ : -	
								62.353	
								H ₄ H ₅ : -	
								61.312	
								H ₃ H ₄ :	
								61.312	

Entry	δ_{Cn}^a [ppm] [gauss]	$^3J_{HH}^a$ [Hz]	$(n \times ^3J_{HH})^2$	ϕ [deg] <i>recorded</i>	θ_{HnHn+1} [deg]	ϕ [deg]	$^3J_{HH}$ [Hz]	θ_{HnHn+1} [deg] <i>calculated</i>	ϕ_{Cn} [deg]
5.	C ₅ 70.6 0.50566	6.4	$(2 \times ^3J_{HH})^2$	163.84	-73.84 -15.55 16.84	41.301 28.529 27.567 ^b 41.177 28.986 41.343 28.372 41.218 28.837 41.498 27.788 40.229 41.664 27.142 ^b 40.377 41.685 27.063 39.540 ^b 41.568 27.517	6.426 2.67 2.625 6.41 2.69 6.429 2.66 6.42 2.685 6.44 2.63 6.342 6.454 2.60 6.354 6.456 2.601 6.288 6.44 2.517	- H ₄ H ₅ : - 62.133 H ₃ H ₄ : 62.133 - H ₄ H ₅ : - 61.470 H ₃ H ₄ : 61.470 H ₃ H ₄ : - 31.470 H ₄ H ₅ : - 61.013 H ₃ H ₄ : 61.013 H ₄ H ₅ : - 61.627 H ₃ H ₄ : 61.627 H ₄ H ₅ : - 61.162 H ₃ H ₄ : 61.162 H ₄ H ₅ : - 62.2119 H ₃ H ₄ : 62.211 H ₄ H ₅ : - 32.856 H ₄ H ₅ : - 62.856 H ₃ H ₄ : 62.856 H ₄ H ₅ : - 32.936 H ₄ H ₅ : - 62.936 H ₃ H ₄ : 62.936 H ₄ H ₅ : - 32.482 H ₄ H ₅ : - 62.482 H ₃ H ₄ : 62.482	I. 107.94 117.0588 107.0279 117.972 108.255 116.745 117.675 II. 109.413 115.576 114.287 III. 114.1275 115.0355

a. ^{13}C -RMN 75[MHz], D₂O [6]: Euler conic $R_m = \delta_{Cn} \times 75 \times 4 \times 10^{-3} / 10.71 [\pi]$ [3]; b. $\tan^{-1} \sin(-A/n) = -B$, $\cos^{-1} \sin(-B/m) = C$, $n, m = 1, 2$; b. ϕ calculated from dihedral angle, angle of set E: $\tan^{-1} \sin(-x) = -\theta^E$.

Table 3. Tetrahedral angles φ_{Cn} [deg] in close relationship with dihedral angles θ_{HnHn+1} [deg] calculated from carbon chemical shift δ_{Cn} [ppm] for 2,6-dideoxy-2,6-imino-D-talonic acid 1D from sets A, B and F, G.

Entry	δ_{Cn} [ppm] [gauss]	$^3J_{HH}$ [Hz]	$(n \times ^3J_{HH})^2$	ϕ [deg] <i>recorded</i>	θ_{HnHn+1} [deg]	ϕ [deg]	$^3J_{HH}$ [Hz]	θ_{HnHn+1} [deg] <i>calculated</i>	φ_{Cn} [deg]
1.	C ₁ 44.8 1.2549	3.8	$(2 \times ^3J_{HH})^2$	57.76	32.24				
					-40.22				
					-39.10				
			$(^3J_{HH})^2$	14.44	75.56				
					-14.002				
					-14.921	57.894	3.80	H ₁ H ₂ : -40.267	
			$(^3J_{HH})^2$	59.29	30.71	237.896	7.71	H ₁ H ₂ : 40.267	II.
					-40.68	237.123	7.69	H ₁ H ₂ : -40.267	110.535
					-36.44	57.458	3.79	H ₁ H ₂ : -40.131	(61.25)
						237.45	7.7	H ₁ H ₂ : 40.131	110.262
2.	C ₂ 60.3 1.6890	7.7	$(2 \times ^3J_{HH})^2$	237.16	-32.84	237.196	7.7	H ₁ H ₂ : -40.131	(58.740)
					40.02				
					-40.19				
			$(2 \times ^3J_{HH})^2$	213.16	-56.84				
					28.67				
					61.32				
			$(2 \times ^3J_{HH})^2$	27.04	62.96	163.083	6.38	H ₄ H ₅ : -73.023	
					-24.44	163.723	6.39	H ₄ H ₅ : -16.976	
					-30.69	162.225	6.36	H ₄ H ₅ : 16.976	
						41.047	6.4	H ₄ H ₅ : 48.953	I. 116.0475
						162.007	6.36	H ₄ H ₅ : 18.952	112.094
						40.184	6.33	H ₄ H ₅ : 49.815	105.22:
						164.303	6.4	H ₄ H ₅ : -74.303	110.369
						163.679	6.39	H ₄ H ₅ : 15.6963	118.607
						164.889	6.42	H ₄ H ₅ : -74.889	119.778
						164.334	6.4	H ₄ H ₅ : 15.1108	119.557
3.	C ₄ 68.2 1.9103	2.6	$(^3J_{HH})^2$	6.76	83.24	164.778	6.41	H ₄ H ₅ : -74.778	117.216
					-6.71	164.210	6.407	H ₄ H ₅ : 15.221	II. 109.705:
					-6.80	163.608	6.39	H ₄ H ₅ : -73.608	115.294
			$(^3J_{HH})^2$	40.96		164.240	6.40	H ₄ H ₅ : 16.392	110.588
						162.646	6.37	H ₄ H ₅ : -72.646	III. 117.375
						40.294	6.34	H ₄ H ₅ : 49.706	110.098
						164.311	6.409	H ₄ H ₅ : 16.312	115.733
						40.046	6.328	H ₄ H ₅ : 49.953	
						163.585	6.39	H ₄ H ₅ : 17.133	
					49.04	164.170	6.406	H ₄ H ₅ : 16.470	
					-33.24	164.170	6.406	H ₄ H ₅ : -16.470	
					-60.26	163.529	6.39	H ₄ H ₅ : -73.529	
						164.577	6.414	H ₄ H ₅ : 16.013	I. 117.0588
4.	C ₅ 70.6 0.50566	6.4	$(^3J_{HH})^2$	163.84		164.577	6.414	H ₄ H ₅ : -16.013	117.972
						163.986	6.4	H ₄ H ₅ : -73.986	116.745
						164.031	6.403	H ₄ H ₅ : 16.627	117.675
			$(2 \times ^3J_{HH})^2$	163.84	-73.84	164.031	6.403	H ₄ H ₅ : -16.627	115.576
					-15.55	163.372	6.390	H ₄ H ₅ : -73.372	II. 114.287
					16.84	164.444	6.41	H ₄ H ₅ : 16.162	114.127
						164.444	6.41	H ₄ H ₅ : -16.162	III. 110.872
						162.143	6.36	H ₄ H ₅ : -72.143	115.0355
						163.516	6.39	H ₄ H ₅ : 17.211	
						161.954	6.36	H ₄ H ₅ : -17.211	
						162.788	6.37	H ₄ H ₅ : -72.788	
						40.437	6.359	H ₄ H ₅ : 49.563	

Entry	δ_{Cn} [ppm] [gauss]	$^3J_{HH}$ [Hz]	$(n \times ^3J_{HH})^2$	ϕ [deg] <i>recorded</i>	θ_{HnHn+1} [deg]	ϕ [deg]	$^3J_{HH}$ [Hz]	θ_{HnHn+1} [deg] <i>calculated</i>	φ_{Cn} [deg]
						163.279	6.38	H4H5: 17.482	
						163.279	6.38	H4H5: -17.482	
						162.5177	6.374	H4H5: -72.517	
						162.883	6.38	H4H5: 17.936	
						161.114	6.34	H4H5: -17.936	
						162.067	6.36	H4H5: -72.063	
						40.437	6.35	H4H5: 49.563	
						163.279	6.38	H4H5: 17.482	
						161.641	6.35	H4H5: -17.482	
						162.517	6.37	H4H5: -72.517	

Dihedral angles θ_{HnHn+1} [deg] with corresponding tetrahedral angles φ_{Cn} [deg] calculated from carbon chemical shift δ_{Cn} [deg] and vicinal angles ϕ [deg] with eqs. (1 – 4) are presented in Tables 2, 3. All dihedral and tetrahedral angles are calculated from direct relationship between five sets angles, from strict trigonometric point of view from sets A, B and D, E (Table 2) or A, B and F, G (Table 3). In set A is placed the tetrahedral angle calculated from *sin*, *tan* and *cot* functions with eqs. (11, 12) in 4D and eq. (13) in 3D, with first and second angles of set A as ϕ_2 in sets D, E and or with first and second angles of set B as ϕ_2 in sets F, G.

Dihedral angles are calculated from sets D, E or F, G using three characteristics equations for every vicinal angle ϕ [deg] (eqs. (5 – 7)) calculated from vicinal coupling constant $^3J_{HH}$ [Hz] (eqs. (1 – 4)), totally six angles, having in mind that the calculated dihedral angle must have almost equal value as dihedral angles results only from vicinal coupling constant $^3J_{HH}$ [Hz].

Tetrahedral angles φ_{Cn} [deg]:

$$4D: \sin^{-1}\tan\{-\sin^{-1}[nx(1/R_m)]\} = -\phi_2^{FS} \quad (11)$$

$$4D: \tan^{-1}\sin\{-\tan^{-1}[nx(1/R_m)]\} = -\phi_2^{FT \text{ or } FIT} \quad (12)$$

$$3D: \cos^{-1}\sin[-n_b \times \phi_2^F] = \varphi_{Cn} \quad (13)$$

where: φ_{Cn} [deg] - tetrahedral angle of C_n , $n = 1 - 5$, $R_m - [\pi]$ - values calculated from chemical shift δ [ppm] with manifold equation.

Relationship between dihedral angles and tetrahedral angles on seven sets angles ensured by eqs. (14 – 16).

$$\theta^{A1} = \phi_2^D = 2x(120 - \varphi_{Cn}); \theta^{B1} = \phi_2^F = 2x(120 - \varphi_{Cn}) \quad (14)$$

Equation (5) on Hopf fibration:

$$R^4: X_0 = \cos\phi\sin\theta, X_1 = \sin\phi\sin\theta,$$

$$X_2 = \cos\theta\sin\phi, X_3 = \sin\theta\sin\phi,$$

$$\theta^{A2} = \phi_2^E = 60 - \theta^{A1}; \theta^{B2} = \phi_2^G = 60 - \theta^{B1} \quad (15)$$

$$2x\cos^{-1}\sin\phi_{Cn}^{D \text{ or } F} = \theta^{N2} \quad (16)$$

where: tetrahedral angle φ_{Cn} [deg] = θ^{A4}

$\phi_2^D, \phi_2^E, \phi_2^F, \phi_2^G$ - algebraic angles of sets D, E, F and G, $N = A, B$.

3. Discussion

Phase angle of pseudorotation P [deg] can be established on VISION molecular models using exocyclic 3-Sphere dihedral angles in close relationship with corresponding tetrahedral angles φ_{Cn} [deg]. Dihedral and tetrahedral angles φ_{Cn} [deg] calculated only from vicinal coupling constant $^3J_{H2H3}$ [Hz] or carbon chemical shift results in both pairs of angles D, E and F, G. In first case, seven sets angles are builds from calculated dihedral angles with eqs. (5 – 7), in second case with calculated tetrahedral angles φ_{Cn} [deg] from carbon chemical shift δ_{Cn} [ppm] with Euler-conic [2, 3] and characteristics equations for calculation tetrahedral [4, 5] angles φ_{Cn} [deg] in opposite with dihedral angles *sin versus tan* function on 4D equations (eq. (11, 12)).

Six possible dihedral angles can be calculated from vicinal angles ϕ [deg] with torus and invers of torus equations (5 – 7), real Hopf fibration [2, 9, 10] for only one vicinal coupling constant or R^4 complex Hopf fibration for two possible vicinal coupling constants $^3J_{HH}$ [Hz], in close relationships between set A and B. In case of invers of torus equations (8, 9) the unit is build starting with calculated dihedral angle following the rule of unit C (U or S), angles are not all under *sin* and *tan* functions on sets A and B.

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

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

Equation (6) on Hopf fibration:

$$\begin{aligned} R^4: X_0 &= \tan\phi \sin\theta^T, X_1 = \sin\phi \sin\phi, \\ X_2 &= \tan\theta^T \sin\phi, X_3 = \sin\theta^T \sin\theta^T, \end{aligned}$$

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

$$\begin{aligned} R^{16}: \text{octonionic Hopf fibration } S^3 \rightarrow S^7 \rightarrow S^4 \\ trans-aa^{6,1}: X_0 &= \tan\theta^{U1A6} \sin\phi, X_1 = \sin\theta^{U1A6} \sin\theta^{U1A6}, \\ trans-aa^{5,2}: X_2 &= \tan\theta^{U1A5} \sin\phi, X_3 = \sin\theta^{U1A5} \sin\theta^{U1A5}, \\ trans-ee^{4,1}: X_4 &= \tan\theta^{U1A5} \sin\phi, X_5 = \sin\theta^{U1A5} \sin\theta^{U1A5}, \\ trans-ee^{3,2}: X_6 &= \tan\theta^{U1A3} \sin\phi, X_7 = \sin\theta^{U1A3} \sin\theta^{U1A3}, \\ trans-ee^{3,2}: \phi_{ee3,2}^{U1B} &= \theta^{S1B1}, X_8 = \tan\theta^{S1A3} \sin\phi, X_9 = \sin\theta^{S1A3} \sin\theta^{S1A3}, \\ trans-ee^{4,1}: \phi_{ee4,1}^{U1B} &= \theta^{S1B1}, X_{10} = \tan\theta^{S1A4} \sin\phi, X_{11} = \sin\theta^{S1A4} \sin\theta^{S1A4}, \\ cis-ae/ea^{1,6}: X_{12} &= \tan\theta^{U1A1} \sin\phi, X_{13} = \sin\theta^{U1A1} \sin\theta^{U1A1}, \\ cis-ae/ea^{2,5}: X_{14} &= \tan\theta^{U1A2} \sin\phi, X_{15} = \sin\theta^{U1A2} \sin\theta^{U1A2}. \end{aligned}$$

Equation (7) on Hopf fibration:

$$\begin{aligned} R^4: X_0 &= \sin\phi \tan\theta^{ST}, X_1 = \tan\phi \tan\phi, \\ X_2 &= \sin\theta^{ST} \tan\phi, X_3 = \tan\theta^{ST} \tan\theta^{ST}, \end{aligned}$$

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

$$\begin{aligned} R^{16}: \text{octonionic Hopf fibration } S^3 \rightarrow S^7 \rightarrow S^4 \\ trans-aa^{6,1}: X_0 &= \sin\theta^{U1A6} \tan\phi, X_1 = \tan\theta^{U1A6} \tan\theta^{U1A6}, \\ trans-aa^{5,2}: X_2 &= \sin\theta^{U1A5} \tan\phi, X_3 = \tan\theta^{U1A5} \tan\theta^{U1A5}, \end{aligned}$$

$$trans-ee^{4,1}: X_4 = \sin\theta^{U1A5}\tan\phi, X_5 = \tan\theta^{U1A5}\tan\theta^{U1A5},$$

$$trans-ee^{3,2}: X_6 = \sin\theta^{U1A3}\tan\phi, X_7 = \tan\theta^{U1A3}\tan\theta^{U1A3},$$

$$trans-ee^{3,2}: \phi_{ee3,2}^{U1B} = \theta^{S1B1}, X_8 = \sin\theta^{S1A3}\tan\phi, X_9 = \tan\theta^{S1A3}\tan\theta^{S1A3},$$

$$trans-ee^{4,1}: \phi_{ee4,1}^{U1B} = \theta^{S1B1}, X_{10} = \sin\theta^{S1A4}\tan\phi, X_{11} = \tan\theta^{S1A4}\tan\theta^{S1A4},$$

$$cis-ae/ea^{1,6}: X_{12} = \sin\theta^{U1A1}\tan\phi, X_{13} = \tan\theta^{U1A1}\tan\theta^{U1A1},$$

$$cis-ae/ea^{2,5}: X_{14} = \sin\theta^{U1A2}\tan\phi, X_{15} = \tan\theta^{U1A2}\tan\theta^{U1A2}.$$

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

$$\phi = \sin^{-1}\sin\phi \quad (18)$$

$$\theta_{HnHn+1} = \tan^{-1}(1/\sin\phi) \quad (19)$$

Hopf fibration ensures trigonometric equations between dihedral angles θ_{HnHn+1} [deg] and vicinal ϕ [deg] angles, for example the already published equations (5, 6, 7), [9] and the equations (17) [11] and (19) in tangential space. Relationships between dihedral and vicinal angles results from eqs. (17, 19), relative to eq. (18). Dihedral angles calculated from vicinal angles with eq. (5) have sign in opposite with dihedral angles calculated with eq. (17). Relationships between dihedral / vicinal angle are established with eq. (17), since with eq. (18) result only the angle analyzed.

Negative sign for vicinal angle don't gives the *trans-ee*^{4,1} stereochemistry and only a negative dihedral angle with *trans-ee*^{3,5} stereochemistry. Homotopic behavior of Hopf fibration trigonometric equations giving from the invers of vicinal angle under *tan* function the dihedral angle under the *cot* function. As shown in Table 2, between vicinal coupling constants 3.8 and 7.7[Hz] the vicinal angles 57.76 and 237.16[deg] gives two angles almost equals: +/-32.24 and +/-32.84[deg], with vicinal coupling constants 3.78, 7.7[Hz] and 3.76, 7.69[Hz].

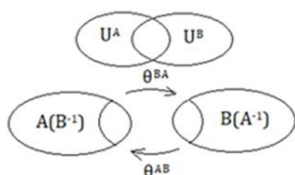


Figure 2. Differential topology, relationship between angles of set A and B: i. *e*³J_{HH} 3.8[Hz], ϕ 57.76[deg], θ_{HnHn+1} +/-32.24[deg] (positive eq. (3), negative eq. (17)), +/- 89.75 = $\tan^{-1}(1/\sin \pm 0.25)$ (eq. (19)).

The anomeric position on molecular models shown two combinations of angles (Table 4): S₁³ *cis*- θ_{H1H2} -40.22 [deg] for 3.8[Hz], *trans-aa* θ_{H1H2} -139.32 [deg] for 7.7[Hz] (entry 1), S₂⁰ or S₃¹ *trans-ee* θ_{H1H2} -79.78 [deg] for 3.8[Hz] and *cis*- θ_{H1H2} -40.03[deg] for 7.7[Hz] (entry 2 and 5), or S₂⁰ (entry 3) S₃¹ for

cis- θ_{H1H2} 32.24[deg] for 3.8[Hz] and *trans-ee* θ_{H1H2} -87.15 [deg] for 7.7[Hz] (entry 6) with higher value of the vicinal coupling constant for *trans-ee* stereochemistry. The most preferred conformations are S₁³ (entry 1) and S₃¹ (entry 6) as demonstrated with VISION molecular models, also the conformation B_{0,3}(S₂⁰) *cis*- θ_{H1H2} -14.002 [deg] for 3.8[Hz], *trans-aa* θ_{H1H2} -139.31 [deg] for 7.7[Hz] (entry 4).

Tetrahedral angles at anomeric position calculated from vicinal coupling constant (Table 1) are 118.88 and 119.64[deg] with *cis* 32.24[deg] for a vicinal coupling constant 3.7[Hz] and *trans-ee*^{3,2} -87.159[deg] for a vicinal coupling constant 7.7[Hz] or other pair of angles 110.06 and 110.01[deg] with *trans-ee*^{3,2} -79.78[deg] for a vicinal coupling constant of 3.7[Hz] and *cis* 40.02[deg] for a vicinal coupling constant of 7.7[Hz]. Tetrahedral angles ϕ_{C1} [deg] calculated at anomeric position from carbon chemical shift have calculated vicinal coupling constants almost equal with recorded vicinal coupling constant for angles 113.63, 114.65, 115.98 and 116.347[deg] (Tables 2 and 5), in all cases with *cis* positive and *trans-ee*^{3,2} negative calculated from eq. (1).

Conformation S₁³ with negative *cis* -40.22[deg] / *trans-aa*^{5,2} -138.32[deg] stereochemistry at anomeric position and dihedral angles H₂H₃ 91.323[deg], 83.29[deg], H₃H₄ 57.039[deg], H₄H₅ -146.75[deg] for all stereochemistry (Table 4, entry 1), relative to S₂⁰ with *trans-ee* -79.78[deg] and *cis* 40.02[deg] at anomeric position, and as possible dihedral angles H₂H₃ 63.16[deg], H₃H₄ 57.04 (36.76)[deg], H₄H₅ -73.84 (-60.26)[deg] (Table 4, entry 2) difficult to simulate on VISION molecular models.

The conformation B_{0,3} can be simulated probably with calculated angle of -104.46[deg], since on VISION molecular models can be observed an angle smaller to 120[deg], but difficult to simulate 57.03[deg] θ_{H3H4} relative to combination 57.03 / -146.75 [deg] θ_{H3H4} / θ_{H4H5} for S₁³ configuration. Negative angle (-83.29[deg]) calculated for a vicinal coupling constant of 7.3[Hz] with eq. (5) cannot be simulated (Table 4, entry 1). The most important observation, the tetrahedral angle at C₁ is not compatible with combination *cis* angle of -

32.24[deg] and *trans-aa* angle -139.32[deg] with vicinal coupling constant of 3.8: 7.7[Hz] (entry 1), between two possible dihedral angles only one is compatible, -40.22[deg]. In case of conformation S^2_0 with *cis* 32.24[deg] and *trans-ee* -87.15[deg] at anomeric position, between dihedral angles H_2H_3 63.16[deg], H_3H_4 36.76[deg], H_4H_5 -73.84[deg] only the dihedral angle H_4H_5 look higher on molecular models. The *Gauche* angle of 63.16[deg] with positive sign results from eq. (17). The conformation S^3_1 with *cis* 32.24[deg] and *trans-ee* -87.15[deg] at anomeric position (entry 6), and the following dihedral angles H_2H_3 151.32[deg], H_3H_4 -62.96[deg], H_4H_5 -104.44[deg] is preferred relative to conformation with H_4H_5 -73.84[deg] (entry 5). Angles higher as 90[deg] are preferred for *trans-ee* stereochemistry (entry 5, 6). As demonstrated recently, the relationship between *cis*, *trans-aa* in agreement with Hopf trigonometric equation is under 180[deg] and between *cis*, *trans-ee* under 120[deg], but once calculated the *cis* angle corresponding to *trans-aa* stereochemistry the rule of 120[deg] must be applied as demonstrated with VISION molecular models.[11] Excepting *cis* -14.002[deg] at anomeric

position (entry 4), all the *cis*, *trans* values are in close relationship exocyclic-torsional/dihedral, i. e. -40.22/-139.32 (-40.68) [Hz].

The conformation $B^{0,3}$ simulated in Table 4, entry 4, required as shown VISION molecular models an angle $\theta_{H_2H_3}$ close to 180[deg] or higher as 180[deg]. The combination *cis* / *trans-ee*^{4,1} at anomeric position decreasing the dihedral angle $\theta_{H_2H_3}$ from 180[deg], but only two calculated positive dihedral angles are possible 151.33, 143.29[deg].

Angle calculated from vicinal coupling constant versus angle calculated from carbon chemical shift, conformations simulated with *gauche* / *cis*, instead of *trans-ee* / *cis* (Tables 4, 5), angles calculated only from vicinal coupling constant 7.3[Hz] $\theta_{H_2H_3}$ 63.16[deg], 2.6[Hz] $\theta_{H_3H_4}$ 36.76[deg] (Table 4, entry 3), relative to angles $\theta_{H_2H_3}$ 91.32[deg] and $\theta_{H_3H_4}$ 57.03[deg] (Table 4, entry 1) and angles $\theta_{H_2H_3}$ 91.50[deg] and $\theta_{H_3H_4}$ 57.38[deg] (Table 5, entry 1), in last case all attempt to find dihedral angle with calculated values almost equal with recorded $\theta_{H_3H_4}$ 36.76[deg] failed.

Table 4. Conformation, phase angle of pseudorotation P [deg] established with tetrahedral φ_{Cn} [deg] and dihedral θ_{HnHn+1} [deg] angles calculated from vicinal coupling constant $^3J_{HH}$ [Hz] of 1D.

Entry	Conformation $B_{0,3}$	$^3J_{HH}$ [Hz]	3.8	7.7	7.3	2.6	6.4
1.	S^1_3 ($B_{0,3}^*$)	ϕ [deg]	57.76	59.29	213.16 53.29	27.04	40.96
		θ_{HnHn+1} [deg]	-40.22 (-32.24) ^{eq.17,*}	-139.32 -139.81	91.323 +/-83.29	57.039 (62.96)	-146.75 -104.44*
		φ_{Cn} [deg]	110.112 (118.88)	110.34 110.09	119.338 116.645	118.52	118.377 112.22
		ϕ [deg]	57.76	237.16	213.16	27.04	163.84 40.96
2.	S^2_0	θ_{HnHn+1} [deg]	-79.78	40.036	63.16 ^{eq. 17}	57.04	-73.84 -60.26
		φ_{Cn} [deg]	110.06	110.01	118.42	118.52	113.08 119.86
		ϕ [deg]	57.76	237.16	213.16	6.76	163.84 40.96
3.	S^2_0 $B_{0,3}$	θ_{HnHn+1} [deg]	32.24	-87.159	63.16 ^{eq. 17}	36.76	-73.84 ^{eq.1} -60.26 ^{eq.2}
		φ_{Cn} [deg]	118.88	119.645	118.42	116.62	113.08 119.86
		ϕ [deg]	14.44	237.16	213.16 53.29	27.04	163.84
		θ_{HnHn+1} [deg]	-14.002	-139.31	< or = 180 151.323 220.797*	-24.44 -30.69	-130.91
4.	$B^{0,3}$ ($S^0_{2^*}$)	φ_{Cn} [deg]	112.999	110.018 or 114.982	119.338 110.398*	117.223 119.654	114.545

Entry	Conformation $B_{0,3}$	$^3J_{HH}[\text{Hz}]$	3.8	7.7	7.3	2.6	6.4
5.	S^3_1	$\phi[\text{deg}]$	57.76	237.16	213.16 53.29	27.04	163.84 40.96
		$\theta_{HnHn+1}[\text{deg}]$	-79.78	40.02	151.33 143.29	-24.44 -30.69	-73.84 -60.26
		$\varphi_{Cn}[\text{deg}]$	110.06	110.01	119.338 116.645	117.223 119.654	113.08 119.86
		$\phi[\text{deg}]$	57.76	237.16	213.16 53.29	27.04	163.84
6.	S^3_1	$\theta_{HnHn+1}[\text{deg}]$	32.24	-87.159 -92.84	151.323 ^{eq.1} 143.29 ^{eq.2}	-62.96 ^{eq.17} -57.039 ^{eq.17}	-104.448
		$\varphi_{Cn}[\text{deg}]$	118.88	118.579	119.338 116.645	118.52	112.776

The conformations simulated from dihedral angles calculated from carbon chemical shift $\delta[\text{ppm}]$ and vicinal coupling constant $^3J_{HH}[\text{Hz}]$: S^1_3 , $B_{0,3}$, S^2_0 and S^3_1 are presented in Table 5. Conformations S^1_3 , $B_{0,3}$ (entry 1) with different dihedral angles θ_{H4H5} , -133.023 versus -104.303 [deg] fit well on molecular models. The dihedral angles θ_{H3H4} and θ_{H4H5} on conformation S^2_0 ensures the better simulation, i. e. 57.39 and -

102.26 (entry 2) or 57.39 and -87.06 (entry 4) relative to 57.39 and -102.86 (entry 3). The conformation S^3_1 (Table 5, entry 5, 6, 7) result from the calculated angles without any uncertainty, probably only in case of entry 7 required an angle smaller as θ_{H2H3} 151.5[deg].

Table 5. Conformation, phase angle of pseudorotation $P[\text{deg}]$ established with tetrahedral $\varphi_{Cn}[\text{deg}]$ and dihedral $\theta_{HnHn+1}[\text{deg}]$ angles calculated from carbon chemical shift $\delta_{Cn}[\text{ppm}]$ for 2,6-dideoxy-2,6-imino-D-talonic acid 1D.

Entry/Confor- mation $B_{0,3}$	$^3J_{HH}[\text{Hz}]$	3.8	7.7	7.3	2.6	6.4	6.4
1. S^1_3 $B_{0,3}^*$	$\phi[\text{deg}]$	56.697	237.16	212.94	27.385	163.023	163.837
	$^3J_{HH}[\text{Hz}]$	3.76	7.7	7.29	2.61	6.38	6.39
	$\theta_{HnHn+1}[\text{deg}]$	-41.066	-138.933	91.501	57.385	-133.023 -104.303*	-133.867 -103.98*
	$\varphi_{Cn}[\text{deg}]$	C1: 112.133	C1: 112.133	C2: 116.996	C3: 114.771	C4: 116.046 118.607	C5: 117.675 117.972
2. S^2_0	$\phi[\text{deg}]$	57.32	237.33	212.94	27.385	41.477	41.177
	$^3J_{HH}[\text{Hz}]$	3.78	7.7	7.29	2.61	6.44	6.41
	$\theta_{HnHn+1}[\text{deg}]$	32.67	-87.33	91.501	57.385	-62.133	-61.013
	$\varphi_{Cn}[\text{deg}]$	C1: 114.65	C1: 114.64	C2: 116.996	C3: 114.771	C4: 115.733	C5: 117.972
3. S^2_0	$\phi[\text{deg}]$	57.32	237.33	212.94	27.385	163.58	164.577
	$^3J_{HH}[\text{Hz}]$	3.78	7.7	7.29	2.61	6.39	6.41
	$\theta_{HnHn+1}[\text{deg}]$	32.67	-87.33	91.501	57.396	-102.86	-103.98
	$\varphi_{Cn}[\text{deg}]$	C1: 114.65	C1:	C2:	C3:	C4:	C5:

Entry/Conformation B _{0,3}	³ J _{HH} [Hz]	3.8	7.7	7.3	2.6	6.4	6.4
4. S ₀ ² B ^{0,3}			114.64	116.996	114.771	115.733	117.972
	φ[deg]	57.32	237.33	212.94	27.385	41.477	40.377
	³ J _{HH} [Hz]	3.78	7.7	7.29	2.61	6.44	6.35
	θ _{HnHn+1} [deg]	32.67	-87.33	91.501	57.396	-62.133	-87.064
	φ _{Cn} [deg]	C ₁ : 114.65	C ₁ : 114.64	C ₂ : 116.996	C ₃ : 114.771	C ₄ : 115.733	C ₅ : 114.127
5. S ₁ ³	φ[deg]	58.173	238.174	212.88	27.349	41.477	41.177
	³ J _{HH} [Hz]	3.81	7.71	7.29	2.61	6.44	6.41
	θ _{HnHn+1} [deg]	31.826	-88.174	-116.84 ^{eq,17}	-31.463 ^b -32.941 ^c	-62.133	-61.013
	φ _{Cn} [deg]	C ₁ : 116.347	C ₁ : 116.347	C ₂ : 118.42	C ₃ : 117.073 ^a	C ₄ : 115.733	C ₅ : 117.972
	φ[deg]	58.173	238.174	212.88	27.349	163.58	164.577
6. S ₁ ³	³ J _{HH} [Hz]	3.81	7.71	7.29	2.61	6.39	6.41
	θ _{HnHn+1} [deg]	31.826	-88.174	151.501	-31.463 ^b -32.941 ^c	-102.86	-103.98
	φ _{Cn} [deg]	C ₁ : 116.347	C ₁ : 116.347	C ₂ : 116.996	C ₃ : 117.073 ^a	C ₄ : 115.733	C ₅ : 117.972
	φ[deg]	58.173	238.174	212.88	27.349	41.477	40.377
	³ J _{HH} [Hz]	3.81	7.71	7.29	2.61	6.44	6.35
7. S ₁ ³	θ _{HnHn+1} [deg]	31.826	-88.174	151.501	-31.463 ^b -32.941 ^c	-62.133	-87.064
	φ _{Cn} [deg]	C ₁ : 116.347	C ₁ : 116.347	C ₂ : 116.996	C ₃ : 117.073 ^a	C ₄ : 115.733	C ₅ : 114.127

a. ³J_{H3H4} 2.63[Hz], φ 27.796[deg], θ_{H3H4} -25.046[deg], φ_{C3} 110.092[deg], b. dihedral angle calculated from unit, c. dihedral angle with vicinal angle calculated from unit, d. dihedral angle calculated from sets D, E.

Relationship between tetrahedral angle φ_{Cn}[deg] and vicinal angle φ[deg], [9] between sets A, B and F, G and A. B and D, E presented in Table 6, are totally in agreement with dihedral angles results from eq. (5 – 7).

Table 6. Relationship between tetrahedral angle φ_{Cn}[deg] and vicinal angle φ[deg].

Entry	φ _{Cn} [deg]	φ	³ J _{HH} [Hz]	θ _{H1H2} [deg]	Equations
1.	C ₁ : 116.347	58.173 238.173	3.8 7.7	31.826 -31.826	φ: sin ⁻¹ cos[60 - (θ ^{A2} /2)] φ: sin ⁻¹ cos{[60 - [(60 - θ ^{A1})/2]]} φ: 180 + φ
2.	C ₂ : 116.996	31.5047 211.504	7.27	151.409	φ: sin ⁻¹ cos{60 - [(60 - θ ^{A2})/2]} φ: sin ⁻¹ cos[60 - (θ ^{A1} /2)]
3.	C ₃ : 117.073	31.463 211.463	7.27	152.437	φ: sin ⁻¹ cos[60 - (60 - θ ^{A2} /2)] φ: sin ⁻¹ cos[60 - (θ ^{A1} /2)]
4.	C ₃ : 117.073	28.536	2.67	61.46 (58.536)	φ: sin ⁻¹ cos[60 + (θ ^{A1} /2)]

Entry	$\varphi_{\text{Cn}}[\text{deg}]$	ϕ	$^3J_{\text{HH}}[\text{Hz}]$	$\theta_{\text{H1H2}}[\text{deg}]$	Equations
				-25.534 -35.941	
5.	C4: 115.733	162.866	6.38	-103.585	$\phi: 180 - \sin^{-1}\cos[60 + (\theta^{\text{B1}}/2)]$
6.	C5: 117.972	163.986	6.40	-104.576	$\phi: 180 - \sin^{-1}\cos[60 + (\theta^{\text{B1}}/2)]$
7.	C5: 114.127	162.063	6.36	-102.063	$\phi: 180 - \sin^{-1}\cos[60 + (\theta^{\text{B1}}/2)]$

4. Conclusions

Two main conformations are simulated $\text{B}_{0,3}$ and $\text{B}^{0,3}$ on VISION molecular models resulting the following conformations: 1. from dihedral angles calculated only from vicinal coupling constant $^3J_{\text{HH}}[\text{Hz}]$ (Table 4): S^1_3 ($\text{B}_{0,3}$), and $\text{B}^{0,3}$ (S^2_0 , S^3_1 ; 2. or from carbon chemical shift $\delta[\text{ppm}]$ and vicinal coupling constant $^3J_{\text{HH}}[\text{Hz}]$ (Table 5): S^1_3 , $\text{B}_{0,3}$, S^2_0 and S^3_1 .

From vicinal coupling constant $^3J_{\text{HH}}[\text{Hz}]$ are calculated six dihedral angles in close relationship with θ^{D4} and θ^{F4} on seven sets angles. From carbon chemical shift are calculated first tetrahedral angles $\varphi_{\text{Cn}} = \theta^{\text{A4}}[\text{deg}]$ then the dihedral angles on pairs D, E and F, G on seven sets angles. Direct relationships between dihedral and tetrahedral angles on seven sets angles are established in Table 6.

The relationships between dihedral / tetrahedral angles in tangential space was analyzed, also on five and six membered ring using polyhedron equations [12], and five membered ring with Euler conic [13] and Conic projection [14] approach.

The distorted (boat or skew) conformations are simulated with VISION molecular models, boat – first and forth toms of carbon up or down and remaining atoms of carbon down or up; skew – three atoms of carbon in increased or decreased line. Stoddart's diagram in 2D named also itinerary map with six boat type conformers and six skew type conformers. The conformation of six membered ring is defined by three coordinates: a radius Q and two phase angles ϕ , θ . The Q coordinates is the sum of the perpendicular distance of each ring atom to the ring average plane. Cremer and Pople sphere for the north side is case of $^4\text{C}_1$ chair conformation corresponding to the Stoddart's pseudorotation itinerary. Characteristic for $^4\text{C}_1$ or $^1\text{C}_4$ conformations at anomeric position equatorial or axial position. [15-18].

Abbreviations

RMN Nuclear Magnetic Resonance

Author Contributions

Carmen-Irena Mitán: Conceptualization, Methodology, Resources

Emerich Bartha: Conceptualization, Methodology, Resources

Petru Filip: Methodology, Resources

Conflicts of Interest

The authors declare no conflicts of interest.

References

- [1] C.-I. Mitán, E. Bartha, P. Filip, C. Draghici, M.-T. Caproiu, R. M. Moriarty, 3-Sphere dihedral angles under wave character of the NMR data with applications on conformational analysis, ACS Spring, San Diego march 23 - 27, CARB 623, ID 4175487; <https://doi.org/10.1021/scimeetings.5c11051>
- [2] C.-I. Mitán, E. Bartha, C. Draghici, M. T. Caproiu, P. Filip, R. M. Moriarty, Hopf fibration on relationship between dihedral angle $\theta_{\text{HnHn+1}}[\text{deg}]$ and vicinal angle $\phi[\text{deg}]$, angles calculated from NMR data with 3-sphere approach and Java Script, *Science Journal of Chemistry* 2022, 10, 21. <https://doi.org/10.11648/j.sjc.20221001.13>
- [3] C.-I. Mitán, E. Bartha, P. Filip, C. Draghici, M.-T. Caproiu, R. M. Moriarty, Java Script programs for calculation of dihedral angles with manifold equations, *Science Journal of Chemistry* 2024, 12(3), 42; <https://doi.org/10.11648/j.sjc.20141203.11>
- [4] C.-I. Mitán, E. Bartha, P. Filip, Tetrahedral angles of six membered ring calculated from NMR data with 3-sphere approach, *Rev. Roum. Chim.* 2023, 68(5-6), 269; <https://doi.org/10.33224/rch.2023.68.5-6.10>
- [5] R. M. Moriarty, C.-I. Mitán, E. Bartha, P. Filip, R. Naithani, T. Block, *American Journal of Quantum Chemistry and Molecular Spectroscopy* 2024, 8(1), 1; *SciencePG*: <https://doi.org/10.11648/ajqcms.20240801.11>
- [6] B. M. Malle, I. Lundt, T. M. Wrodnigg, *Org. Biomol. Chem.* 2008, 6, 1779; doi.org/10.1039/B719631H.
- [7] E. Bartha, C.-I. Mitán, P. Filip, 3-Sphere torsional angles and six Membered ring conformation, *American Journal of Quantum Chemistry and Molecular Spectroscopy* 2023, 7(1), 9; <https://doi.org/10.11648/j.ajqcms.20230701.12>

- [8] C.-I. Mitan, E. Bartha, F. Petru, C. Draghici, M.-T. Caproiu, R. M. Moriarty, Manifold inversion on prediction dihedral angle from vicinal coupling constant with 3-sphere approach, *Rev. Roum. Chim.* 2023, 68(3-4), 185; <https://doi.org/10.33224/rch.2023.68.3-4.08>
- [9] C. I. Mitan, E. Bartha, P. Filip, R. Moriarty, Nuclear Magnetic Resonance Spectroscopy - Recent Research and Applications, chapter book: Dihedral and tetrahedral angles of five and six membered ring calculated from NMR data with 3-Sphere approach, IntachOpen 2025 ISBN 978-1-83635-220-4; <https://dx.doi.org/10.5772/intechopen.1009208>
- [10] C.-I. Mitan, P. Filip, E. Bartha, C. Draghici, M.-T. Caproiu, R. M. Moriarty, Stereochemistry of *cis* - *trans* vicinal coupling constant $^3J_{HH}$ [Hz] on 3-Sphere approach with application in conformational analysis, ACS Spring, San Diego march 23 - 27, Sci-Mix CARB - ANYL 632, ID 4175485; <https://doi.org/10.1021/scimeetings.5c11052>
- [11] C.-I. Mitan, E. Bartha, Stereochemistry of D, L-ribitol Iminocyclitols Between 4 and 2 Dimensions, *Science Journal of Chemistry* 2026, <https://doi.org/10.11648/j.sjc.20261405.11>
- [12] C.-I. Mitan, E. Bartha, P. Filip, C. Draghici, M. T. Caproiu, R. M. Moriarty NMR data on conformational analysis of five and six membered ring under 3-sphere approach. Vicinal constant coupling $^3J_{HH}$ on relationships between dihedral angles and tetrahedral angles. Sustainability in a changing world” ACS National Meeting in Chicago, IL, August 21- 25, 2022, CARB 3717557, 23 august 2022, 37 pag. Publisher: American Chemical Society, Washington, D. C.; <https://doi.org/10.1021/scimeetings.2c00876>
- [13] C.-I. Mitan, E. Bartha, P. Filip, V. dragutan, I. dragutan, C. Deleanu, C. Draghici, M.-T. Caproiu, R. M. Moriarty, 3-Spherical conformation insights into iminocyclitols with 1- α -D-ribose and 1- β -L-ribose stereochemistry under homotopic behavior of nuclear magnetic resonance data, *Science Journal of Chemistry* 2026, 14(1), 1; <https://doi.org/10.11648/j.sjc.20261401.11>
- [14] C.-I. Mitan, E. Bartha, P. Filip, M.-T. Caproiu, C. Draghici, C. Deleanu, V. Dragutan, E. M. Moriarty, Conic projection as manifold and 3-sphere dihedral angles θ_{HnHn+1} [deg] under homotopy, *Science Journal of Chemistry* 2026, 14(1), 12; <https://doi.org/10.11648/j.sjc.20261401.12>
- [15] X. Biarnes, A. Ardeval, A. Planas, C. Rovira, A. Laio, M. Parrinello, *J. Am. Chem. Soc.* 2007, 129, 10686; <https://doi.org/10.1021/ja0684110>
- [16] K. Fukaya, T. Sato, N. Chida, D. Urabe, *J. Org. Chem.* 2023, 88, 13655; <https://doi.org/10.1021/acs.joc.3c0134>
- [17] B. M. Sattelle, S. U. Hansen, J. Gardiner, A. Alnond, *J. Am. Chem. Soc.* 2010, 132, 13132; <https://doi.org/10.1021/ja1054143>
- [18] K. Omoto, K. Marusaki, H. Hirao, M. Imade, H. Fujimoto, *J. Phys. Chem. A*. 2000, 104, 6499; <https://doi.org/10.1021/jp994165>