



TETRAHEDRAL ANGLES OF FIVE MEMBERED RING IMINOCYCLITOLS WITH RIBITOL STEREOCHEMISTRY BEYOND THE DIHEDRAL ANGLES

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Relationships between vicinal angles, angles result from vicinal coupling constant ${}^3J_{\text{HH}}[\text{Hz}]$, and tetrahedral angles of five membered ring iminocyclitols with ribitol stereochemistry are demonstrate with polyhedron and 3-sphere methods. Tetrahedral angles $\phi[\text{deg}]$ and internal angles $\gamma[\text{deg}]$ are calculated from ${}^{13}\text{C}$ -NMR, or ${}^1\text{H}$ -NMR chemical shift $\delta[\text{ppm}]$ in case of heteroatom, with energy-graph theory approach. The vicinal coupling constant can be calculated from one atom of carbon chemical shift $\delta_{\text{Cn}}[\text{ppm}]$, and also the corresponding dihedral angle under 3-sphere approach.

$$\begin{aligned}\tan(\phi/2) &= 1/E^n = 2\sin(\gamma/2) \\ \theta_{\text{HnHn+1}} &= \sin^{-1}\cos\phi \\ \phi &= f(\phi, \gamma) \\ {}^3J_{\text{HH}} &= (\phi)^{1/2}/n \\ n &= 1 \text{ trans-aa}, n = 2 \text{ cis, trans-ee}\end{aligned}$$

INTRODUCTION

The vicinal angle $\phi[\text{deg}]$ is in close relationship with the corresponding dihedral angle $\theta_{\text{HnHn+1}}[\text{deg}]$ under 3-sphere approach, and with tetrahedral angle $\phi[\text{deg}]$ under polyhedral approach.^{1,2} Dihedral angle and the vicinal angle under 3-sphere approach are angles at intersection of two intersecting discs (Fig. 1), the vicinal angle resulting from the vicinal constant coupling ${}^3J_{\text{HH}}[\text{Hz}]$. A method in three steps: 1. prediction of the dihedral angle only from vicinal coupling constant,³ 2. calculation of the angle of set A with manifold equation from the differences between

two atoms of carbon $\delta_{\text{Cn}}[\text{ppm}]$ and/or proton chemical shift $\delta_{\text{HnHn+1}}[\text{ppm}]$, 3. six dihedral angles with *cis*, *trans* stereochemistry under $\pm 60[\text{deg}]$ rule drowned on three concentric cons translated in 2D, gives set A. From set A are builds six sets angles on two units or seven sets angles on one unit. Hypersphere trigonometric equations giving the right sign and stereochemistry.^{4,5}

The 2D conic representation of 3-sphere approach with angle under $\pm 60[\text{deg}]$ rule, resulted from manifold equation [4,5] must contain the tetrahedral angle around the dihedral angle set on unit U or S.

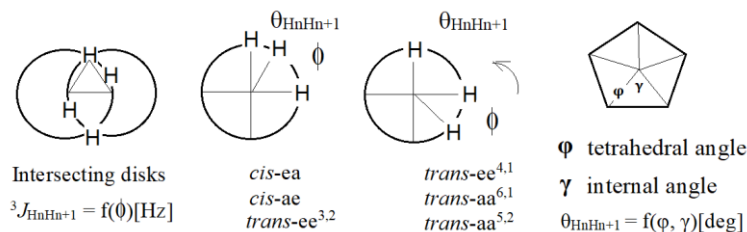


Fig. 1 – Relationships between dihedral angles $\theta_{\text{HH}}[\text{deg}]$ – vicinal angles $\phi[\text{deg}]$ and tetrahedral angles $\phi[\text{deg}]$ – internal angles $\gamma[\text{deg}]$ of five membered ring.

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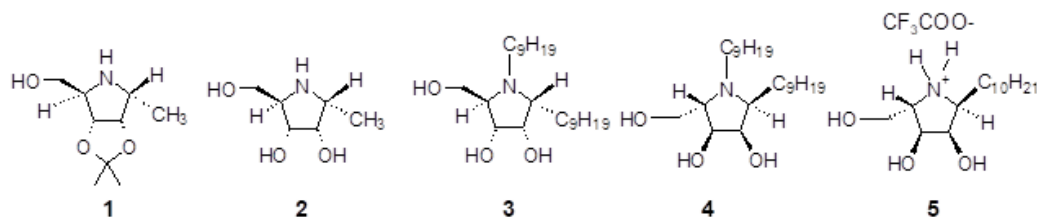


Fig. 2 – Five membered ring iminocyclitols with α -D-ribose (1-3) and β -L-ribose (4, 5) stereochemistry.

In this paper our aim is to calculate the vicinal coupling constant ${}^3J_{\text{HH}}[\text{Hz}]$ of five membered ring (Fig. 1) only from one atom of carbon chemical shift $\delta_{\text{C}_n}[\text{ppm}]$, the vicinal angles ϕ [deg] with their corresponding dihedral angles $\theta_{\text{HH}}[\text{deg}]$ and tetrahedral angles φ [deg].

DISCUSSION

Euler character of the energy-graph theory ensures the calculation of the tetrahedral angles φ [deg] and internal angles γ [deg] of the five membered ring iminocyclitols (Fig. 2), with α -D-ribose (1-3) and β -L-ribose (4, 5) stereochemistry,⁶ from ${}^{13}\text{C}$ -NMR carbon chemical shift, or ${}^1\text{H}$ -NMR in case of heteroatom. Euler's polygon division applied on iminocyclitols 1-5 transforms the spherical coordinate on pentagonal surface, in fact polyhedral with Euclidean pentagons or triangles surfaces.⁷

The dihedral angle of polyhedral (dodecahedron eq. 1, icosahedron eq. 2)⁷ ensures a perfect conic distribution of the tetrahedral angle (φ) and internal angle (γ) of five membered ring under 180[deg] and tetrahedral rule, after replacing the golden ratio ($A = 1.618033952$) with inverse of energy [$\text{J/mol} \times 10^6$] [8] calculated from carbon chemical shift in polyhedral equations (eq. 3).^{1,2}

$$\text{Eq. 1: Dodecahedron: } \tan(D^D/2) = A = 2\sin(X/2),$$

$$\text{Eq. 2: Icosahedron: } \tan(D^I/2) = (A)^2 = 2\sin(X/2),$$

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

where: dihedral angle of polyhedral, dodecahedron D^D : 116.56506[deg], icosahedron D^I : 138.189685[deg], golden ratio $A = 1.618033952$, E^n – energy [$\text{J/mol} \times 10^6$], $n = 1, 2$, φ – tetrahedral angle [deg], γ – internal angle [deg].

In Table 1 are presented angles calculated from carbon chemical shift with polyhedron 1-3 and energy equations 4a-c for iminocyclitols 1-5.

$$\text{Eq. 4a-c: } \cos\theta^n/m = 1/E^n,$$

where: E^n – energy [$\text{J/mol} \times 10^6$], $n = 1, 1/2, 2$, $m = 1$ or 2, $\theta^n = \varphi$ or γ , φ – angle between two equivalent

orbitals – tetrahedral angle, [deg], γ – internal angle [deg], $180 - \gamma = \varphi$.

Three sets of six angles θ^n ($n = 1-6$) result from $1/E$, $1/E^{1/2}$, $1/E^2$ [8], with first three angles internal ($\gamma = \theta^{1-3} = 60 - 89$ [deg]) and last three angles tetrahedral ($\varphi = \theta^{4-6} = 119 - 90$ [deg]), giving information about the required tetrahedral (φ_{C_n} , $n = 1-5$), dihedral ($\theta_{\text{HnHn+1}}$), vicinal angles (ϕ), and no at list about the vicinal coupling constant ${}^3J_{\text{HnHn+1}}$.

The vicinal angle or the *cis*^{6,1} dihedral angle with positive sign (Tables 1, 2) result from set $1/E^2$ from the difference between θ^6 and 90[deg], multiplied by 1 (Table 1, entry 1: C_1 -1), 2 (entry 3: C_3 -1, entry 19: C_1 -5) or 4 (entry 20: C_2 -5), and in case of negative dihedral angle from angles θ^{4-6} of set $1/E^n$ having θ^6 dodecahedron, or transforming the angle θ^6 of set $1/E^n$ in dodecahedron angle (C_1 -4: 104.892– 115.526 – 118.823[deg], C_1 -3: 104.795 – 115.487 – 118.89[deg]). In case of *cis*^{5,2} dihedral angle with positive sign, the first angle of the set $1/E^n$ is equal with ϕ , if θ^6 is dodecahedron, or transformed into dodecahedron. The vicinal angle of the *trans-ee* stereochemistry results from $\phi/2$ of set C, set results under ± 60 [deg] rule from θ^6 of set $1/E^2$, and the vicinal angle of the *trans-aa*^{6,1} stereochemistry from the θ^{1-2} of set $1/E^2$, or or $\theta = 150 + (\theta^6 - 90)$.

Once the vicinal angle ϕ , or the dihedral angle $\theta_{\text{HnHn+1}}$, is established with trigonometric equation will be calculated the corresponding dihedral angle or the vicinal angle. The vicinal coupling constant ${}^3J_{\text{HnHn+1}}[\text{Hz}]$ can be calculated from the vicinal angle (ϕ [deg] = θ^n) with eq. 5, and with trigonometric equation 6 the corresponding dihedral angle.³⁻⁵

$$\text{Eq. 5: } {}^3J_{\text{HH}} = (\theta^n)^{1/2}/n, \text{ with } \textit{cis}: n = 2, \textit{trans}: n = 1.$$

$$\text{Eq. 6: } \theta_{\text{HnHn+1}} = \sin^{-1}\cos(\phi), \text{ with } \phi = f(\theta^n), n = 1-6.$$

Dihedral angle $\theta_{\text{HnHn+1}}$ can be calculated from C_n or C_{n+1} , the representative value remains one with the calculated vicinal coupling constant almost equal with the recorded one.

Table 1

Tetrahedral angle φ [deg], vicinal angle Φ [deg], dihedral angle θ_{HH} [deg] and vicinal coupling constant ${}^3J_{HH}$ [Hz] calculated from carbon chemical shift with polyhedron equations 1-3

	R	C _n	$\delta_{C_n}^a$ [ppm]	E ^b [J/moli]	$\varphi^{1/E}$ [deg]	$\varphi^{1/E^{1/2}}$ [deg]	φ^{1/E^2} [deg]	Φ [deg]	${}^3J_{HH}$ [Hz]	θ_{HH} [deg]	${}^3J_{HH}^{exp}$ [Hz]
1.	1	C ₁	55.8	1.670	106.44	101.38	111.01 95.97	68.99 117.51 116.05	H ₁ H ₂ 4.15 H ₂ H ₃ 5.4 H ₂ H ₃ 5.38	21.00 -27.51 -26.05	H ₁ H ₂ 4.1
2.		C ₂	83.5	2.499	113.58	101.52	99.21 108.42	66.42 118.80	H ₁ H ₂ 4.07 H ₂ H ₃ 5.44	23.58 -28.80	H ₂ H ₃ 5.4
3.		C ₃	84.3	2.523	113.34	101.96	99.03 108.07	119.59 ^c 118.89 ^d	H ₂ H ₃ 5.46 H ₂ H ₃ 5.45	-29.59 -28.89	
4.		C ₄	65.9	1.972	119.07	90.78	104.89 119.78	119.07 116.45 ^d 0.23 0.798	H ₂ H ₃ 5.45 H ₂ H ₃ 5.39 H ₃ H ₄ 0.21 ^f H ₃ H ₄ 0.44	-29.07 -26.45 -89.78 -89.20	H ₃ H ₄ 0
5.		NH	2.64	0.421 2.372	114.93	99.04	100.23 110.46 114.93 ^e	-	-	-	-
6.	2	C ₁	57.4	1.718	108.81	99.44	109.80 100.79	39.60 63.17	H ₁ H ₂ 3.14 H ₂ H ₃ 3.97	50.39 ^c 26.82	H ₁ H ₂ 3.1
7.		C ₂	71.5	2.140	117.87 111.42	93.75	102.61 115.22	39.85 ^c 61.93	H ₁ H ₂ 3.15 H ₂ H ₃ 3.9	50.14 28.07	H ₂ H ₃ 3.9
8.		C ₃	71.7	2.146	117.77 111.07	93.90	102.53 115.07	61.62 ^g 77.46	H ₂ H ₃ 3.92 H ₃ H ₄ 8.80	28.36 -167.46 ^h	
9.		C ₄	66.8	1.999	119.98	90.01	104.48 115.88	60.01 78.46	H ₂ H ₃ 3.89 H ₃ H ₄ 8.85	29.98 -168.46 ^h	H ₃ H ₄ 8.8
10.		NH	3.33	0.531 1.881	115.77	93.622	106.41 116.04 ^d 114.34 115.77 ^e	-	-	-	-
11.	3	C ₁	63.7	1.906	116.73	92.80	105.96 116.13	92.73 107.90	H ₁ H ₂ 4.81 H ₂ H ₃ 5.19	-2.80 -17.90	H ₁ H ₂ 4.8
12.		C ₂	72.5	2.170	117.43 109.75	94.49	102.26 114.52	92.16 107.65	H ₁ H ₂ 4.86 H ₂ H ₃ 5.18	-2.16 -17.65	H ₂ H ₃ 5.2
13.		C ₃	74.0	2.214	116.83 107.35	95.56	101.76 113.52	108.18 3.58	H ₂ H ₃ 5.2 H ₃ H ₄ 0.95	-18.18 -86.41 ^f	
14.		C ₄	69.3	2.074	118.82 115.28	92.05	103.43 116.87	107.56 3.12	H ₂ H ₃ 5.18 H ₃ H ₄ 0.88	-17.56 -86.87 ^f	H ₃ H ₄ 0
15.	4	C ₁	68.4	2.047	119.23 116.95	91.32	103.80 117.60	92.02 108.49	H ₁ H ₂ 4.79 H ₂ H ₃ 5.20	-2.02 -18.49	H ₁ H ₂ 4.8
16.		C ₂	71.1	2.152	117.68 110.75	94.05	102.46 114.93	91.95 107.42	H ₁ H ₂ 4.79 H ₂ H ₃ 5.18	-1.956 -17.42	H ₂ H ₃ 5.2
17.		C ₃	72.7	2.176	117.36 109.43	94.64	102.19 114.38	108.39 4.10	H ₂ H ₃ 5.20 H ₃ H ₄ 1.01	-18.39 85.9 ^f	
18.		C ₄	70.9	2.122	118.11 112.45	93.30	102.82 115.65	108.70 4.34	H ₂ H ₃ 5.21 H ₃ H ₄ 1.04	-18.70 85.65 ^f	H ₃ H ₄ 0
19.	5	C ₁	63.3	1.894	116.28	93.185	106.17 115.302	32.34 ^c 52.57 ⁱ	H ₁ H ₂ 2.84 H ₂ H ₃ 3.62	57.65 37.42	H ₁ H ₂ 2.8
20.		C ₂	72.1	2.158	117.60 110.41	94.20	102.39 114.797	34.79 51.29 ^c	H ₁ H ₂ 2.94 H ₂ H ₃ 3.58	55.21 ⁱ 38.70	H ₂ H ₃ 3.6
21.		C ₃	73.4	2.929	109.95 100.17	108.50	96.689 103.379	50.09 76.09	H ₂ H ₃ 3.53 H ₃ H ₄ 8.72	39.91 ⁱ 166.09 ^h	
22.		C ₄	63.9	1.912	116.95	92.62	105.86 116.544	51.57 75.86 78.20	H ₂ H ₃ 3.59 H ₃ H ₄ 8.7 H ₃ H ₄ 8.8	38.43 ^j 165.86 ^h 168.20 ^h	H ₃ H ₄ 8.8 ^k

a. δ [ppm] ¹³C-NMR, 75MHz, ¹H-NMR 400MHz: **1, 3, 4**-CDCl₃, **2**-D₂O, **5**-CD₃OD; b. $E = \delta_{C_n} \omega_C x h x N_A [J/molix10^6]$, δ_{C_n} - carbon chemical shift[ppm], ω_C - Larmore frequency[MHz], $h = 6.626070080 \times 10^{-34} [Jxs]$, $N_A = 0.023 \times 10^{23} [moli^{-1}]$; c. θ or $\phi = nx(90 - \theta^6)$, $n = 2, 4$; d. eq.1 with $\theta^6 = \gamma$; e. $\varphi = f(1/E^3)$; f. $\phi_{1/2}$ of set C result from θ^6 [deg] under ± 60 [deg] rule; g. eq. c applied on set $1/E^{1/2}$; h. $trans-aa^{6,1}-\theta^{1-3} = \phi$ or $\theta = 150 + (\theta^6 - 90)$, i. eq. c applied on set $1/E$, j. $1/E: \theta^6$ under eq. 3 gives an angle of 109.21[deg], then is applied eq.c, k. in L-series $trans-H_3H_4$ has positive sign, relative to D-series with negative sign.

Table 2

Tetrahedral approach: 2D-Conic representation of the internal angles θ^{1-3} and tetrahedral angles θ^{4-6} , in close relationship with vicinal ϕ and dihedral angles θ_{HH} [deg]. 3-Sphere approach: sets A, B, C and relationships between ϕ and θ_{HH} [deg]

Entry	$1/E^n$	1/E	$1/E^{1/2}$	$1/E^2$	1/E	$1/E^{1/2}$	$1/E^2$
1.	θ^n [deg]	C ₁ -1			C ₁ -2		
2.	θ^{180-D}						61.20
	$\theta^{180-D'}$	63.95		62.488	61.72		64.55
	θ^1	73.557	78.611	68.992	66.415	78.475	75.304
	θ^2	75.911	77.808	74.141	73.12	77.75	78.601
	θ^3	79.730	76.569	82.878	84.789	76.650	80.788
	θ^4	100.269	101.388	97.121	95.210	101.524	99.211
	θ^5	104.088	102.191	105.859	106.210	102.242	101.398
	θ^6	106.442	103.430	111.007	113.879	103.349	104.695
	$\theta^{D'}$	116.05 ^a		117.511 ^a	118.275 ^a		115.453 ^a
	$\theta^{D''}$						118.803 ^a
3.	$H_n H_{n+1}$ ${}^3J_{HH}$ [Hz] ϕ [deg] θ_{HH} [deg]	$H_1 H_2$ 4.15, 68.99, 21.006 $cis^{6,1}-\theta_{HH} = 111.007 - 90 = 21.007$ $H_2 H_3$ 5.4, 117.51, -27.51			$H_1 H_2$ 4.07, 66.42, 23.58 $\phi = 113.879 - 90 = 66.42 = \theta^1$ $H_2 H_3$ 5.44, 118.80, -28.80		
4.	θ^{nN}	Set A	Set B	Set C	Set A	Set B	Set C
5.	θ^{1N}	8.993	21.0064	17.987	20.788	9.211	18.423
	θ^{2N}	51.006	38.9935	42.012	39.211	50.788	41.576
	θ^{3N}	68.993	81.0064	77.987	80.788	69.211	78.423
	θ^{4N}	111.006	98.9935	102.012	99.211	110.788	101.576
	θ^{5N}	128.993	141.006	137.987	140.788	129.211	138.423
	θ^{6N}	171.006	158.993	162.012	159.211	170.788	161.576
	ϕ_2	17.987	42.012	35.975	41.576	18.423	36.847
	$\phi_{1/2}$	21.006	8.993	12.012	9.211	20.788	11.576
6.	$\phi = f(\theta, \phi)$ $\theta = f(\phi)$	$\cos^{-1} \sin 111.006 = 21.0064$ $\sin^{-1} \cos 21.0064 = 68.993, 4.15$ [Hz]			$\cos^{-1} \sin 99.2118 = 9.2118^b$ $\sin^{-1} \cos 99.2118 = 20.788, 4.15$ [Hz]		
7.	θ^n [deg]	C ₂ -2			C ₄ -4		
8.	$\theta^{180-D''}$						
	$\theta^{180-D'}$	62.36			70.78		
	θ^1	68.574	64.537	64.778	63.044	71.80	74.136
	θ^2	73.976	72.368	72.464	71.766	80.91	76.132
	θ^3	83.182	86.245	86.055	87.442	87.382	79.352
	θ^4	96.817	93.754	93.944	92.557	92.618	100.647
	θ^5	106.023	107.631	107.535	108.233	99.09	103.867
	θ^6	111.425	115.462	115.221	116.955	108.20	105.863
	$\theta^{D'}$	117.856 ^a			109.22		
	$\theta^{D''}$						
	θ^4		101.380	101.814			
	θ^5		103.435	103.176			
	θ^6		104.724	104.036			
9.	$H_n H_{n+1}$ ${}^3J_{HH}$ [Hz] ϕ [deg] θ_{HH} [deg]	$H_1 H_2$ 3.12, 39.07, 50.925 $cis^{5,2}-\theta_{HH} = 2x(115.46 - 90) = 50.9$ $H_2 H_3$ 3.89, 60.55, 29.44 $cis^{6,1}-\theta_{HH} = 2x(104.72 - 90) = 29.44$			$H_2 H_3$ 5.4, 117.51, -27.51 $cis^{5,2}-\theta_{HH} = 2x(109.22 - 90) = 38.43$ $H_3 H_4$ 8.8, 77.44, 12.56, 167.44 $trans^{6,1}-\theta_{HH} = 108.2 - 90 = 18.20, 168.2$		

a. eq.1 with $\theta^6 = \gamma$, b. $\phi = 60 - \phi_{1/2}$.

Tetrahedral angles of β -D-ribofuranoside have been determined with X-ray and neutron diffraction crystal structure in comparison with B3LYP,⁹ resulting comparative values with the tetrahedral angles at C₁, C₂, C₃, C₄, but no at list comparative value with the total sum of the five tetrahedral angles lower as 540[deg], explained as defect⁷ on polyhedral surface. The angles of the crystal natural pyrite are 106.6, 102.6, 102.6,

106.6, 121.6[deg], totally 540[deg].⁷ The conformation of the iminocyclitols **1 - 5** change the values of the tetrahedral angles relative to regular pentagon. The differences between the angles calculated at C₁ - C₄ highlighted major change, the values of energy in J/molix10⁶ varies between the 1.6-2.5, from dodecahedron (eq. 1) to icosahedron (eq. 2). For example: 1.6 corresponding to tetrahedral angles of 111.01[deg], 1.97 to

104.8[deg] and 2.14 – 2.5 to 102.6 - 99.03[deg] (Table 1).

In Table 2 are presented few representative examples for the calculation of the vicinal coupling constant ${}^3J_{\text{HnHn+1}}$ [Hz] from sets $1/E$, $1/E^{1/2}$, $1/E^2$. The values of the vicinal coupling constant calculated for an angle $C_1\text{-1}$ of 106.44[deg] (set $1/E$) or 111.006[deg] (set $1/E^2$) and 106.478[deg] (result from 95.971[deg]) apparently are not significant, 4.28[Hz] relative to 4.15[Hz], but in case of 111.006[deg] the calculated dihedral angle (eq. 7, 8) has value near to predicted one.

The dihedral angles ($\theta_{\text{HH}} = 2x(\theta^6-90)$) result from set $1/E^{1/2}$ of C_1 , C_2 , $C_3\text{-1}$ are almost equals with the predicted dihedral angles in case of tetrahedral angles 101.38, 101.524, 101.968[deg]. The main question, are tetrahedral angles at C_2 and $C_3\text{-1}$ 99.21 and 99.03[deg] or 101.52 and 101.96[deg]. For a vicinal coupling constant of 4.1[Hz] the calculated tetrahedral angles are 111.0[Hz] at C_1 and 99.2[Hz] and C_2 (Table 2, entry 6).

$$\text{Eq. 7: } \cos^{-1}\sin\phi = \theta_{\text{HnHn+1}}, \text{ Eq. 8: } \sin^{-1}\cos \theta_{\text{HnHn+1}} = \phi.$$

The dihedral angle θ_{H1H2} calculated from tetrahedral angle $C_2\text{-1}$ of 99.211[deg] is smaller with 0.22[deg], and in eq. 7 instead of $\theta_{\text{HnHn+1}}$ result $\phi/2$ of set A. The algebraic angle ϕ for an angle with $\text{cis}^{6,1}$ stereochemistry is equal with $60 + \phi/2$ (Eq. 9, 10).

$$\text{Eq. 9: } \cos^{-1}\sin\phi = \phi/2,$$

$$\text{Eq. 10: } \sin^{-1}\cos \phi = \theta_{\text{HnHn+1}}, \phi = 60 + \phi/2.$$

For an angle of 111.006[deg] $C_1\text{-1}$ the internal angle γ is equal with θ^3 of set A, the vicinal angle ϕ for $\text{cis}^{6,1}$ stereochemistry, relative to an angle of 99.211[deg] $C_1\text{-2}$ with the vicinal angle on set B (Table 2, entry 6).

Angles of 102.61 and 115.22[deg] of $1/E^2 - C_2\text{-2}$ gives two six set angles with ${}^3J_{\text{H2H3}}$ 4.01[Hz] and 4.02[Hz]. The third six set angles resulting from 115.22[deg] with eq. 3 has ${}^3J_{\text{HH}}$ of 3.9[Hz], with dihedral angle of θ_{H2H3} 28.07[deg], almost equal with the recorded, as well as ${}^3J_{\text{H1H2}}$ 3.14[Hz], with θ_{H1H2} 50.44[deg], result from second set.

The angles $1/E^2 - C_4\text{-2}$, 118.97, 104.485 or 115.883, results by multiplied the manifold value with 1, 2, or 4, containing in their six set angles information about the tetrahedral angle $C_4\text{-2}$. The transformation from 104.485 to corresponding set angles with θ^6 115.598, leading to an angle of 107.59[deg], relative to 107.801[deg] result from

115.883[deg], or 109.051[deg] from 118.97[deg]. Successive transformation from 118.97[deg] with eq. 3 giving an angle of 106.469[deg].

The tetrahedral angles C_4 of all iminocyclitols **1-5** are much smaller as C_1 in accord with the values of E 1.9 -2.1 KJ/molix 10^6 , or must be extracted from sets $1/E^2$ resulting: 107.65 (**1**), 107.59 (**2**), 108.20 (**3**), 107.71 (**4**), 108.54 (**5**). As an observation, in case of iminocyclitols **3** and **4** the vicinal angles of ${}^3J_{\text{HH}}$ 5.2[Hz] are 107.56 and 108.70[deg] (Table 1, entry 14, and 18).

As an observation, in case of 3-sphere approach[4, 5], with manifold angle calculated from the differences between two atoms of carbon chemical shift, the tetrahedral angle 107.02[deg] of $C_1\text{-2}$ was found on set C with calculated dihedral angle of 53.26[deg] and vicinal coupling constant of 3.03[Hz]. Increasing the number of sets under seven sets unit or six sets units result the following angles: 51.73 U2F2 , 3.09[Hz] or 50.209 US1B2 , 3.15[Hz]. Tetrahedral approach (Table 2, $C_1\text{-1}$) giving an angle of 109.80[deg] in third set ($1/E^2$), with a vicinal angle of 39.60[deg] ($\phi = 2x(109.801 - 90)$) and a dihedral angle of 50.40[deg]. The tetrahedral angle 109.80[deg] under the +/-60[deg] rule has the corresponding vicinal angle on set C of first unit and the dihedral angle on set B of second unit. Thus, for $\text{cis}^{5,2}$ stereochemistry the half of θ^{U1B3} is equal with vicinal angle and half of θ^{U1B4} with dihedral angle.

CONCLUSIONS

Tetrahedral angles ϕ [deg] are calculated under polyhedral approach from carbon chemical shift δ_{cn} [ppm], demonstrating their relationship with vicinal angles ϕ [deg] and corresponding dihedral angles $\theta_{\text{HnHn+1}}$ [deg]. The value of E [J/molix 10^6] gives information about the tetrahedral angle, and no at list about the differences between the protected **1** and deprotected **2-5**, or *N*-alkylated and/or C-alkylated **3-5** iminocyclitols free based **1-4** or salt **5**, enabling the calculation of the vicinal coupling constant ${}^3J_{\text{HH}}$ [Hz]. The dihedral angle with positive or negative sign is in close relationship with the corresponding vicinal angle,¹⁰ the internal or the tetrahedral angle at one of the atoms of carbon implicate on vicinal coupling.

The tetrahedral angles can be predicted from $1/E^2$ or $1/E^{1/2}$ in function of the values of polyhedron using the set of six angles under the polyhedron rule as presented in Table 3.

Table 3

Tetrahedral angles φ [deg] predicted under polyhedron rule

Entry	φ_{C1} [deg]	φ_{C2} [deg]	φ_{C3} [deg]	φ_{C4} [deg]	φ_{NH} [deg]
1.	108.45 106.47	101.39	101.33	107.65	110.46
2.	108.116	102.61	102.53	107.79	106.41
3.	107.902	102.26	101.76	108.702	-
4.	108.49	102.46	102.19	108.23	-
5.	106.17	102.39	103.37	108.06	-

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