American Journal of Quantum Chemistry and Molecular Spectroscopy
2023; 7(1): 9-15
http://www.sciencepublishinggroup.com/j/ajqcms
doi: 10.11648/j.ajqcms.20230701.12

3-Sphere Torsional Angles and Six Membered Ring Conformation

Emerich Bartha, Carmen-Irena Mitan*, Petru Filip

Department of Chemistry, "C. D. Nenitescu" Institute of Organic and Supramolecular Chemistry, Bucharest, Romania

Email address:
cmitan@yahoo.com (Carmen-Irena Mitan)
*Corresponding author

To cite this article:
Emerich Bartha, Carmen-Irena Mitan, Petru Filip. 3-Sphere Torsional Angles and Six Membered Ring Conformation. *American Journal of Quantum Chemistry and Molecular Spectroscopy*. Vol. 7, No. 1, 2023, pp. 9-15. doi: 10.11648/j.ajqcms.20230701.12

Received: March 16, 2023; **Accepted**: April 4, 2023; **Published**: April 24, 2023

Abstract: The conformation of six membered ring, 1,3,4-tri-o-acetyl-2-azido-6-bromo-2,6-dideoxy-D-galactose α-1 and β-1, and 2,6-dideoxy-2,6-imino- D-talonic acid 2D and L-talonic acid 2L, is analyzed inscribing two five membered ring on six membered ring. Altona's five membered ring conformational parameters, phase angles of the pseudorotation P_1, P_2 [deg] and angle of deviation from planarity θ_m [deg] = f(P [deg]), are calculated with Java Script program using 3-Sphere torsional angles. The correlation between Altona map and six membered ring Stoddart's diagram conformations was confirmed with VISION molecular models. 3-Sphere torsional angles θ_{nn+1} [deg] for all *cis*, *trans*-ee, *-aa* stereochemistry are disclosed from trigonometric point of view, Hopf fibration confirmed by Lie algebra. The *cis*, *trans* stereochemistry on two units with six sets angles ensure relationships between dihedral θ_{HnHn+1} [deg]/vicinal angles ϕ [deg] ($\theta^{Bn} + A = \theta^{An}$, $\theta^{An} = \theta_{HnHn+1}$, $\theta^{Bn} = \phi$), and between dihedral θ_{HnHn+1} [deg]/torsional angles θ_{nn+1} [deg] ($\theta_{nn+1} = A +/- \theta_{HnHn+1}$); in first case A = 150 for *trans-aa*[6,1] and A = 90 for *trans-aa*[5,2] and *trans-ee* stereochemistry, in last case A = 180 [deg] for *cis* and *trans-aa* stereochemistry and A = 120 [deg] for *trans-ee* stereochemistry. The number of dihedral angles with positive and negative sign results from *3-sphere approach* for only one vicinal coupling constant $^3J_{HnHn+1}$ [Hz] are restricted by the VISION molecular models.

Keywords: 3-Sphere, Hopf Fibration, Lie Algebra, 6 Membered Ring Conformation, Altona Map, Stoddart's Diagrams, Carbasugar

1. Introduction

Conformational parameters of five membered ring, phase angle of the pseudorotation and angle of deviation from planarity (Figure 1), can be calculate with Altona model [1] from five torsional angles calculated with Karplus equations [2] or with 3-sphere approach [3-5]. Dihedral angles calculated with polynomial Karplus equations from vicinal coupling constant are in relationship of +/-120 [deg] for all *cis*, *trans* stereochemistry. PSEUDOROT program [6, 7] ensuring more exactly the relationship between endocyclic and exocyclic torsional angles: $\theta_{exo} = A\theta_{endo} + B$. Equations for calculation by hand are available in case of D-arabinose, D-lyxose, D-ribose and D-xylose endocyclic torsional angles [6].

Cano et all [8] reported a method for calculation conformational parameters of 6 membered ring [9] using two rectangles inscribed on six membered ring with the sign of the angles under Klyne and Prelog rule.

$$P = \tan^{-1}\frac{(\theta^2+\theta^4)-(\theta^1+\theta^3)}{2\theta^0(\sin 72+\sin 144)} \quad (1)$$

$$\theta_m = \frac{\theta^0}{\cos P} \quad (2)$$

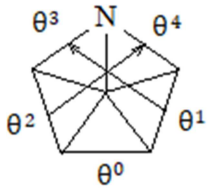

Figure 1. *Altona's conformational parameters: P phase angle of pseudorotation [deg], θ_m angle of deviation from planarity [deg], θ^n torsional angles [deg], with n = 0 - 4.*

In this paper we are presented a method for calculation conformational parameters of 6 membered ring using 3-Sphere-Altona model [10]. Torsional angles θ_{nn+1} [deg] with

right sign and stereochemistry, established with 3-Sphere approach based on Hopf fibration and Lie group theories, are used for analyzed the conformational parameters of six membered ring sugar.

2. Method

2.1. 3-Sphere-Altona Conformational Parameters

Conformational parameters of 6 membered ring are calculated using two five membered ring inscribed on six membered ring (Figure 2), and torsional angles with corresponding sign and stereochemistry under 3-sphere approach rule. [10] Altona's phase angle of the pseudorotation applied on six membered ring required six torsional angles (eq. 3), preferably four (eq. 4), since θ^1 and θ^6 are difficult to calculate in case of six membered ring bearing heteroatom X = 0, N. Two phase angles of the pseudorotation can be calculated from four torsional angles with eq. 6, 7 for two five membered ring inscribed on six membered ring, two conformations on Altona furanose map [1], one in left and on in right side, which fit well on Stoddart's circle [11] and spherical mapping of pyranose conformations [12, 13].

Schlafi Hess polygon [14]: icosahedron 120 cell{3,5,5/2} solid 60, 120, with internal angle 60 [deg] for 6 membered ring relative to 72 [deg] for 5 membered ring (Figure 2).

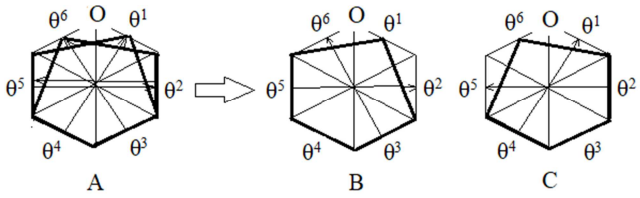

Figure 2. *Six membered ring with two five membered rings inscribed on six membered.*

$$P = \tan^{-1}\frac{1}{2(\sin 60+\sin 120)} \times \left[\frac{(\theta^4+\theta^1)-(\theta^2+\theta^5)}{\theta^3} + \frac{(\theta^3+\theta^6)-(\theta^5+\theta^2)}{\theta^4}\right] \quad (3)$$

$$P = \tan^{-1}\frac{1}{2(\sin 60+\sin 120)} \times \left[\frac{\theta^4-(\theta^2+\theta^5)}{\theta^3} + \frac{\theta^3-(\theta^5+\theta^2)}{\theta^4}\right] \quad (4)$$

Conformational parameters of six membered ring, P -phase angle of the pseudorotation [deg], θ_m – angle of deviation from planarity [deg], θ^n 3-sphere torsional angles [deg], with n = 1-6, are calculated with eq. 3, 4.

$$\theta_m = \frac{\theta^3+\theta^4}{2\cos P} \quad (5)$$

$$P_1 = \tan^{-1}\frac{\theta^4-(\theta^2+\theta^5)}{2\theta^3(\sin 60+\sin 120)} \quad (6)$$

$$P_2 = \tan^{-1}\frac{\theta^3-(\theta^5+\theta^2)}{2\theta^4(\sin 60+\sin 120)} \quad (7)$$

Six membered ring conformational parameters results from two five membered ring inscribed on six membered ring: P_1, P_2 – phase angles of pseudorotation of five membered ring on the left and right sides [deg] of six membered ring are calculated with eq. 6, 7.

The angle of deviation from planarity can be calculated with eq. 5 from eq. 3 or 4. The phase angle of the pseudorotation P_1 [deg] and P_2 [deg] fitting well on Altona map on Stoddart's diagram, two sequences on Altona map following the shape of one conformation on Stoddart's diagram (Table 1). The phase angle of the pseudorotation P [deg] gives information only about two atoms of carbon on Altona map, but is most helpfully for calculation the angle of deviation from planarity θ_m [deg]. The values of θ_{m2} [deg] calculated from P_2 [deg] is sometimes higher as 60 [deg] [10], probably also θ_{m1} [deg].

2.1.1. 3-Sphere Torsional Angles θ_{nn+1} [deg]

The calculation of the 3-sphere dihedral angles [3, 4] is to date well published. Root system in Euclidean space [14], Weyl group of A2 root system, fitting well with 60/120 rule of six angles θ^{nA} on set A (n = 1-6), angles from which result the algebraic angles ϕ [deg] (eq. 8, 9, 10, 11), namely also vicinal angles (Figures 3, 4).

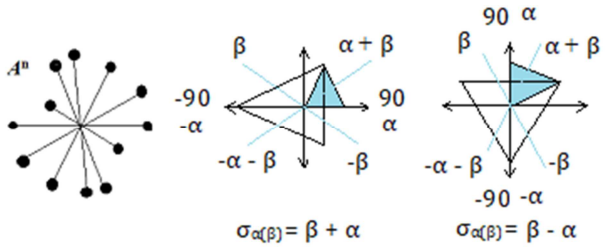

Figure 3. *Lie Algebra A^n. Weyl group of A2 root system on cis, trans-ee[3,2] (I) and trans-aa, trans-ee[4,1] stereochemistry (II): $\theta^{A1} +150 = \theta^{B6}$, $\theta^{A2} +90 = \theta^{B5}$, $\theta^{A3} +90 = \theta^{B6}$, $\theta^{A4} +90 = -\theta^{B1}$, $\theta^{A5} +90 = -\theta^{B2}$, $\theta^{A6} +90 = -\theta^{B3}$.*

The vicinal angle $\phi = \theta^{Bn}$ is in close relationship with dihedral angle $\theta_{HnHn+1} = \theta^{An}$ on two intersecting torus circles [5] or torus - Dupin cyclide circles [15] for all *cis*, *trans* stereochemistry. Two chart and their transition map in differential topology: angle of set A multiply with invers of angle of set B and angle of set B multiply with inverse of angle of set A, ensuring the relationship between angles of set A and set B on trigonometric equations (eq. 12, 13) under Hopf fibration coordinates for all *cis*, *trans* stereochemistry (Figure 4). [5]

The equilateral triangles of angular velocity reveal the relationships between set A, set B and set C [5]. Six sets angles on two units (U and S) (Figure 4), totally seven set angles on unit U and seven on unit S covering all dihedral angles with *cis*, *trans* stereochemistry, three Ven diagrams: A - B - C, D - E - A, F - G - B. Analog to cube tesseract [14], the varies translation from 2D to 4D on Ven diagrams are quantified by the transformation from unit U1 to S1 and *viceversa* or from set A to set B or set C to set A of second

unit (U2 or S2). The tangential space of torus - Dupin cyclide [15] increasing the number of isomers for only one vicinal coupling constant $^3J_{HH}$ [Hz]. The transformation between U to S (eq. 15) and S to U (eq. 16) giving angles approximately equals with angles result from transformation torus – Dupin Cyclide (eq. 14). [4, 8]

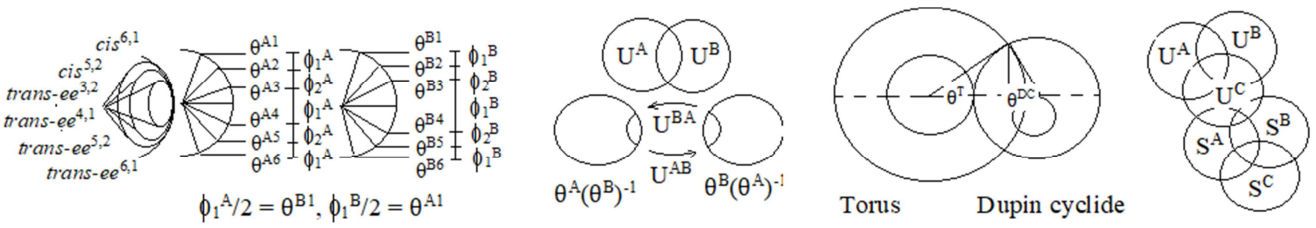

Figure 4. *Dihedral angles (θ^{A1} or θ^{B1} [deg]) and vicinal angles ($\phi = f(\phi_1, \phi_2)$ [deg]) under 3-sphere approach for all cis, trans stereochemistry.*

Dihedral angles can be calculated only from vicinal coupling constant [3, 4, 15] or from carbon or/and proton chemical shift [5] with 3-sphere approach. Relationships between dihedral θ_{HnHn+1} [deg]/vicinal angles ϕ [deg] ($\theta^{Bn} + A = \theta^{An}$, $\theta^{An} = \theta_{HnHn+1}$, $\theta^{Bn} = \phi$); with A = 150 for *trans-aa*^{6,1} and A = 90 for *trans-aa*^{5,2} and *trans-ee* stereochemistry (Figure 3), Vicinal angle ϕ [deg] result from vicinal coupling constant $^3J_{HnHn+1}$ [Hz].

Lie algebra - Algebraic equations (Figure 3):

$$\sigma_{\alpha(\beta)} = \beta - \alpha,\ \sigma_{\alpha(\beta)} = \beta + \alpha$$

$$cis,\ trans\text{-}ee^{3,2}\text{: } 90 - \theta^{A1\text{-}3} = \theta^{B1\text{-}3} \tag{8}$$

$$90 - \theta^{A4\text{-}6} = -\theta^{B1\text{-}3}$$

$$trans\text{-}aa,\ trans\text{-}ee^{4,1}\text{: } 90 + \theta^{A1\text{-}3} = \theta^{B4\text{-}6} \tag{9}$$

$$90 - \theta^{A4\text{-}6} = \theta^{B4\text{-}6} - 360.$$

Algebraic angle – vicinal angle ϕ [deg]:

$$cis^{6,1}\text{: } 60 + \phi_1{}^A/2,\ cis^{5,2}\text{: } \phi_2{}^A + \phi_1{}^A/2$$

$$trans\text{-}ee^{4,1}\text{: } \phi_1{}^A/2,\ trans\text{-}ee^{3,2}\text{: } \phi_2{}^A - \phi_1{}^A/2 \tag{10}$$

with *trans-ee*^{4,1} in unit U and *trans*-ee^{3,2} in unit S.

$$trans\text{-}aa^{6,1}\text{: } 120 - \phi_1{}^A/2,\ trans\text{-}aa^{5,1}\text{: } 120 + \phi_1{}^A/2$$

$$trans\text{-}ee^{4,1}\text{: } 120 + \phi_2{}^A + \phi_1{}^A/2 \tag{11}$$

Hopf fibration – trigonometric equations:

$$cis\text{: } \sin^{-1}\cos\phi = \theta_{HnHn+1}{}^{cis}$$

$$trans\text{: } 180 - \theta_{HnHn+1}{}^{cis} = \theta_{HnHn+1}{}^{trans}$$

$$\sim \cos^{-1}\sin{-\phi} = \theta_{HnHn+1}{}^{trans} \tag{12}$$

$$cis\text{: } \sin^{-1}\cos\phi = -\theta_{HnHn+1}{}^{cis}$$

$$trans\text{: } \theta_{HnHn+1}{}^{cis} - 180 = -\theta_{HnHn+1}{}^{trans} \tag{13}$$

Tangential space – Torus to Dupin cyclide or viceversa:

$$\theta_{HnHn+1} = \sin^{-1}(\tan\phi);\ \theta_{HnHn+1} = \tan^{-1}(\sin\phi) \tag{14}$$

Transformation U to S:

$$\phi^{S1A1} = \phi_2{}^{U1A} - \phi_1{}^{U1A}/2 \tag{15}$$

Transformation S to U:

$$\phi^{U1A1} = [(60 - \phi_1{}^{S1A1})/1.5]/2 \tag{16}$$

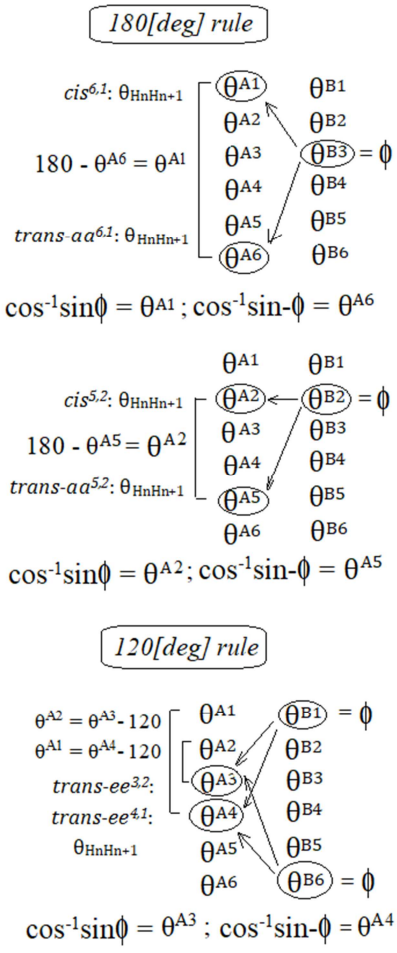

Figure 5. *3-Sphere torsional angles calculated from 3-sphere dihedral angles with cis/trans stereochemistry.*

A method in three steps based on Hopf fibration and Lie group theories: 1. Prediction of the dihedral angles only from vicinal coupling constant with torus [3] and torus inversion [4, 15] trigonometric equations. 2. Calculation one angle of the first set with manifold conic section [5], Vilarceau circles [5] and rectangles [16]. 3. Building units and choose the dihedral angle with values almost equal with the calculated one, since only from this step can be established the

stereochemistry, the sign of the calculated dihedral angle resulting only from first step.

```
<!DOCTYPE html>
<html>
<head>
<title1>A Java script including HTML</title1>

</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 of the six membered ring conformation.</h3>

</body>

<script type="text/javascript">
//File name Conformation.html
//Program that calculate the conformation of six membered ring

var usedata1
usedata1 = prompt ("The value of torsional angle H1H2")
var H1H2 = usedata1;//angle H1H2[deg]
//calculate angle H2[deg]
var H2 = 1*(H1H2);//angle H1[deg]

document.write("<h4>Torsional angles.</h4>")
document.write("<p> H2[deg]="+H2);

var usedata2
usedata2 = prompt ("The value of torsional angle H2H3")
var H2H3 = usedata2;//angle H2H3[deg]
//calculate angle H3[deg]
var H3 = 1*(H2H3);//angle H3[deg]

document.write("<p>H3[deg]="+H3);

var usedata3
usedata3 = prompt ("The value of torsional angle H3H4[deg]")
var H3H4 = usedata3;//angle H3H4[deg]
 //calculate angle H4[deg]
 var H4 = 1*(H3H4);//angle H4[deg]

 document.write("<p> H4[deg]="+H4);

 var usedata4
 usedata4 = prompt ("The value of torsional angle H4H5[deg]")
 var H4H5 = usedata4;//angle H4H5[deg]
 //calculate angle H5[deg]
 var H5 = 1*(H4H5);//angle H5[deg]

 document.write("<p> H5[deg]="+H5);

 //calculate the angle of deviation from planarity M[deg]
 var a = (H4 - H2 - H5)/H3;//value of a
 var b = (H3 - H5 - H2)/H4;//value of b
 var A = (a + b)/3.464101617;//value of A
 var Pr = Math.atan(A);//value of Pr[rad]
 var Pd = (Pr)*(57.29577521);//value of Pd[deg]
 var P = Pd;//value of P[deg]

 if (H3 > 0){
 var P = Pd;//value of P[deg]
 }
 else{
 var P = 180 - Pd;//value of P[deg]
 }

 var constrad = 0.017453292;//constant rad
 var Mm = (P)*(constrad);//value of Mm [rad]
 var Mr = Math.cos(Mm);//value Mr[radians]
 var H = (H3 + H4);//angle of deviation from planarity
 var M = H/(2*Mr);//angle of deviation from planarity

 document.write("<p>The angle of deviation from planarity, the angle M[deg]:"+M);

 //calculate the value of P1
 var A1 = [(H4 - H2 - H5)/(3.464101617*H3)];//value of A1
 var P1r = Math.atan(A1);//value of P1r[rad]
 var P1d = (P1r)*(57.29577521);//value of P1d[deg]
 var P1 = P1d;//value of P[deg]

 if (H3 > 0){
 var P1 = P1d;//value of P1[deg]

     else{
     var P1 = 180 + P1d;//value of P1[deg]
     }
 }

 document.write("<p>The phase angle of the pseudorotation, the angle P1[deg]:"+P1);

 //calculate the value of P2
 var A2 = [(H3 - H5 - H2)/(3.464101617*H4)];//value of A2
 var P2r = Math.atan(A2);//value of P2r[rad]
 var P2d = (P2r)*(57.29577521);//value of P2d[deg]
 var P2 = P2d;//value of P2[deg]

 if (H4 > 0){
 var P2 = P2d;//value of phase angle of the pseudorotation[deg]
     if (P2 < 180){
     var P2 = 180 - P2d;//value of P2[deg]
     }

     else{
     var P2 = 180 + P2d;//value of P2[deg]
     }
 }
 else{
 var P2 = 180 - P2d;//value of P2[deg]
     if (P2 < 180){
     var P2 = 180 - P2d;//value of P2[deg]
     }

     else{
     var P2 = 180 + P2d;//value of P2[deg]
     }
 }

 document.write("<p>The phase angle of the pseudorotation, the angle P2[deg]:"+P2);

 alert("Hello World!");

 </script>
 </html>
```

Figure 6. *Java script program for calculation the conformational parameters.*

A long presentation for demonstrating apparently the strange rule of 3-Sphere torsional angles relative to polynomial torsional angle, respectively under 120 [deg] rule for trans-ee stereochemistry and 180 [deg] rule for trans-aa stereochemistry (Figure 5). 3D-Trigonometric equations for trans-aa stereochemistry, relationship between angle θ^{A1} or θ^{A6} of set A and angle $\theta^{B3} = \phi$ of set B for cis, trans-aa^{6,1} stereochemistry or angle $\theta^{A2} = \phi$ and θ^{B2} or θ^{B5} for cis, trans-aa^{5,2} stereochemistry are under 180 [deg] rule. The trans-ee stereochemistry from the trigonometric point of view shown relationship between angles of set B, $\phi = \theta^{B1}$ or θ^{B6} and angles of set A, $\theta_{HnHn+1} = \theta^{A3}$ or θ^{A4} for trans-ee^{3,2} and trans-ee^{4,1} stereochemistry both under 120 [deg] rule relative to torsional angle θ^{A1} and θ^{A2}. Thus, dihedral angles with trans-ee stereochemistry result from θ^1 and not from θ^2, since an angle θ^2 able to fit into a vicinal coupling constant with values between 0 – 2.7 [Hz] can't be found on torus equations [3]. The highest θ^1 angle of 29.16 [deg] giving a gauche dihedral angle (trans-ee^{3,2}) of 60.84 [deg] for a vicinal coupling constant of 2.7 [Hz]. The torsional angle θ^2 result

only from invers of torus [4] for vicinal coupling constant of 2.6 and 2.7 [Hz], respectively -30.69 and -33.91 [deg] (2D, 2L: Table 1, entry 12 and 17).

2.1.2. Java Script Program for Calculation of the Conformational Parameters

Java script program (Figure 6) for calculation the conformational parameters [4]: the phase angle of the pseudorotation from four torsional angles with eq. 6, 7, and angle of deviation from planarity with eq. 5 can be used on Notepad+ or Java Script Editor. Four torsional angles with corresponding sign are introduced on program and value of phase angle of the pseudoroatation P_1, P_2 [deg] and angle of deviation from planarity M [deg] are display.

2.2. 3-Sphere Dihedral Angles on VISION Molecular Models

The conformation of six membered ring sugar can be established placing the 3-Sphere dihedral angles θ_{HnHN+1} [deg] around the VISION molecular model, then placed on Stoddart's diagram.

3. Results

The Altona conformational parameters, phase angle of the pseudorotation P [deg] and the angle of the deviation from planarity θ_m [deg], characteristics for five membered ring are calculated with 3-Sphere torsional angles in case of 1,3,4-tri-o-acetyl-2-azido-6-bromo-2,6-dideoxy-D-galactose α-1 and β-1, and 2,6-dideoxy-2,6-imino- D-talonic acid 2D and L-talonic acid 2L. [17] As shown in Table 1, 3-Sphere dihedral angles are calculated only from vicinal coupling constant [3, 4, 15], from carbon or proton chemical shift δ_X [ppm] (X = ^{13}C, ^{1}H) with conic section and from ratio proton and carbon chemical shift with Villarceau circles [5].

Table 1. *Calculated dihedral angles θ_{HnHn+1} [deg] of 1,3,4-tri-o-acetyl-2-azido-6-bromo-2,6-dideoxy-D-galactose α-1 and β-1, and 2,6-dideoxy-2,6-imino- D-talonic acid 2D and L-talonic acid 2L [17].*

Entry	H_nH_{n+1}	δ_{Cn} [ppm]	Δ_{Hn} [ppm]	$^3J_{HH}$ [Hz]	$\theta_{HnHn+1}{}^{J}$ [deg]	$\theta_{HnHn+1}{}^{c}$ [deg]	$\theta_{HnHn+1}{}^{d}$ [deg]	$\theta_{HnHn+1}{}^{e}$ [deg]	Conformation	
				α-1					Altona[13C]	Stoddart[13C]
1.[a]	*cis*-H_1H_2	C_1: 90.3	H_1: 6.30	3.5	40.99	41.04	41.77	42.77		
2.[a]	*trans*-H_2H_3	C_2: 56.5	H_2: 3.91	11	-148.99 -139.39	-148.68 -139.67	-146.174 -140.28	-146.769 -140.08	P_1 171.25: $^2T_1$ - ^2E - $^2T_3$ P_2 200.68: $_3E$ – $^4T_3$	$C_1{}^4$
3.[a]	*cis*-H_3H_4	C_3: 67.1	H_3: 5.33	3.0	53.99	54.85	54.85	54.95		
4.[a]	*cis*-H_4H_5	C_4: 68.8 C_5: 71.0	H_4: 5.66 H_5: 4.23	1.0	-3.99	-2.939	-3.843	-3.257	θ_m -6.628	
				β-1					Altona[13C]	Stoddart[13C]
5.[a]	*cis*-H_1H_2	C_1: 92.6	H_1: 5.55	8.5	162.24	160.507	162.668	162.279		
6.[a]	*trans*-H_2H_3	C_2: 59.3	H_2: 3.82	11.0	-148.99 -139.39	-145.83 -140.393	-147.037 -140.00	-147.451 -139.871	P_1 162.59: $^2T_1$ - ^2E - $^2T_3$ P_2 195.26: $_3E$ – $^4T_3$	$C_1{}^4$
7.[a]	*cis*-H_3H_4	C_3: 66.5	H_3: 4.92	3.0	53.99	53.70	54.70	55.33		
8.[a]	*cis*-H_4H_5	C_4: 71.2 C_5: 73.8	H_4: 5.57 H_5: 3.98	1.0	-3.99	-2.939	-2.848	-3.257	θ_m -5.651	
				2D					Altona[13C]	Stoddart[13C]
9.[b]	*cis*-H_1H_2	C_1: 44.8	H_1: 3.16	3.8	-39.10	-38.912	-38.4023	-41.920 -39.7434		
10.[b]	*trans*-H_1H_2	C_2: 60.3	H_2: 4.05	7.7	-139.31 -143.56	-139.74 -141.088	-139.83 -140.61	-140.25 -138.08	P_1 18.67: $^3T_4$ P_2 136.19: $_1E$ θ_m 0.659	$B^{0,3}$
11.[b]	*trans*-H_2H_3	C_3: 65.7	H_3: 3.71	7.3	143.29	145.650	144.847	144.818		
12.[b]	*cis*-H_3H_4	C_4: 68.2	H_4: 4.34	2.6	-24.44 -30.69	-32.108	-32.583	-30.246		
13.[b]	*trans*-H_4H_5	C_5: 70.6	H_5: 3.89	6.4	-146.75	-146.583	-147.049	-146.436		
				2L						
14.[b]	*cis*-H_1H_2	C_1: 44.6	H_1: 3.21	3.8	32.23	32.916	32.396	32.985		
15.[b]	*trans*-H_1H_2	C_2: 65.5	H_2: 4.10	7.7	149.29	147.083	148.801	148.507		
16.[b]	*trans*-H_2H_3	C_3: 68.0	H_3: 3.76	7.3	-141.28 -131.786	-128.54 -141.177	-140.73	-135.45 -140.69	P_1 141.41: $^2T_1$ P_2 120.16 $_4E$ θ_m 40.521	$S_1{}^3$
17.[b]	*cis*-H_3H_4	C_4: 70.4	H_4: 4.39	2.4	-21.37 -25.169	-20.99 -24.55	-22.69 -27.40	-19.13 -21.71		
18.[b]	*trans*-H_4H_5	C_5: 60.1	H_5: 3.94	6.0	126	126.61	125.201	126.533		

δ [ppm], $^3J_{HH}$ [Hz]: [a] $CDCl_3$, ^{13}C-NMR 62.5 [MHz], ^1H-NMR 500 [Mz], [b] D_2O, ^{13}C-NMR 75 [MHz], ^1H-NMR 500 [Mz] [17], [c] conic section $\Delta\delta_{CnCn+1}$ [ppm] [5], [d] conic section $\Delta\delta_{HnHn+1}$ [ppm] [5], [e] Villarceau [5].

Torsional angles θ_{nn+1} [deg] (θ_{nn+1} = A +/- θ_{HnHn+1}) calculated with 3-sphere approach are under 120 [deg] for *trans-ee* and 180 [deg] for *trans-aa* stereochemistry [4]. The vicinal angle ϕ [deg], calculate from vicinal coupling constant $^3J_{HnHn+1}$ [Hz] with algebraic equations under Lie group theory for *cis*, *trans-ee*, *trans-aa* stereochemistry, is in close relationship with corresponding dihedral angle $\theta_{HnHn+}1$ [deg] under Hopf fibration coordinates. [5] The Altona's phase angles of the pseudorotation P_1, P_2 [deg] are placed on Stoddart's diagram [11] (Table 1).

4. Discussions

The conformation of five membered ring with D and L-ribitol stereochemistry was analyzed recently with Java Script program [18]. Attempt to inscribed two five membered ring on six membered ring work properly as demonstrated with VISION molecular. Theoretical, pyranose ring sugars have two distinct chair ($^4C_1$ and $^1C_4$) conformation with intermediate conformers corresponding to boat (B) and skew (S) conformations. [19, 20]

The Altona's phase angles of the pseudorotation P_1 and P_2 giving on Stoddart's diagram C_1^4 conformation for 1,3,4-tri-o-acetyl-2-azido-6-bromo-2,6-dideoxy-D-galactose α-1 and β-1, $B^{0,3}$ for 2,6-dideoxy-2,6-imino- D-talonic acid 2D, and S_1^3 for L-talonic acid 2L (Table 1). As an observation, for chair conformation the sign of torsional angles alternates between positive and negative, and for boat and skew as two consecutive torsional angles with same sign. The phase angles of pseudorotation calculate from two five membered ring inscribed on six membered ring, therefore two five membered conformations on Altona map, are corelated with one conformation on Stoddart's diagram [11] following the succession of carbon atoms down or up of plane: *i.e.* envelop C_1^4 = Twist-Twist: $^4T_3 - {}_3E - {}^2T_3 - {}^2E - {}^2T_1$ (α-1 and β-1, Table 1). The sign of the 3-Sphere dihedral angle restricting the possible conformation for only on vicinal coupling constant $^3J_{HH}$ [Hz] on VISION molecular models. With Java Script program presented in scheme 8 are calculated the phase angles of the pseudorotation P_1 and P_2 (eq. 6, 7) from 3-Sphere torsional angles and the angle of deviation from planarity θ_m [deg] from P [deg] (eq. 4).

5. Conclusions

The conformation of six membered ring can be analyzed very easy using the phase angles of the pseudorotation P_1, P_2 [deg] of two five membered rings inscribed in six membered ring, calculated from 3-Sphere torsional angles θ_{nn+1} [deg] with Java Script program (Figure 6). Two Altona conformations are placed on Stoddart's diagram resulting: chair C_1^4 conformation for 1,3,4-tri-o-acetyl-2-azido-6-bromo-2,6-dideoxy-D-galactose α-1 and β-1, and boat $B^{0,3}$ for 2,6-dideoxy-2,6-imino- D-talonic acid 2D, and skew S_1^3 for L-talonic acid 2L. Conformations confirmed with 3-Sphere dihedral angles with right sign and stereochemistry around the VISION molecular model of six membered ring.

The wave character of NMR data fit well with 3-Sphere approach, a hypersphere in 4D. The Hopf fibration and Lie algebra theories, through the unit system ensuring the calculation of the 3-Sphere dihedral angles and the corresponding 3-Sphere torsional angles with right sign and stereochemistry, angles usefully for calculation of the conformational parameter. The six sets angles on two units U and S or seven sets angles U or S at first pair of sets followed by other two pair of sets angles with U or S character having the finger print of all manifolds (*i.e.* torus, Dupin cyclide) inscribed on hypersphere.

References

[1] C. Altona, M. Sundaralingam, Conformational analysis of the sugar ring in nucleosides and nucleotides. A new description using the concept of pseudorotation, *J. Am. Chem. Soc.* 1972, 94, 8205; doi.org/10.1021/ja00778a043.

[2] A. Navarro-Vazquez, J. C. Cobas, F. J. Sardina, A graphical tool for the prediction of vicinal proton-proton $^3J_{HH}$ coupling constants, *J. Chem. Inf. Comput. Sci.* 2004, *44*, 1690; doi.10.1021/ci049913f.

[3] E. Bartha, C.-I. Mitan, C. Draghici, M. T. Caproiu, P. Filip, R. Moriarty, Program for prediction dihedral angle from vicinal coupling constant with 3-sphere approach, *Rev. Roum. Chim.* 2021, 66, 178-183; DOI: 10.33224/rrch.2021.66.2.08 (Eng).

[4] C.-I. Mitan, E. Bartha, P. Filip, C. Draghici, M. T. Caproiu, R. M. Moriarty, Two isomers with *trans-aa*^{5,2} stereochemistry are calculated with 3-sphere trigonometric equations approach at circle inversion motion from NMR data. ACS National Meeting in Chicago, IL, August 21- 25, 2022, CARB 3717658, 22 august 2022; doi.org/10.1021/scimeetings.2c00523.

[5] C.-I. Mitan, E. Bartha, C. Draghici, M. T. Caproiu, P. Filip, R. M. Moriarty, Hopf fibration on relationship between dihedral angle θ_{HnHn+1} [deg] and vicinal angle ϕ [deg], angles calculated from NMR data with 3-sphere approach and Java Script, Science Journal of Chemistry, *SciencePG* 2022, 10, 21; DOI: 10.11648/j.sjc.20221001.13 (Eng).

[6] J. B. Houseknecht, C. Altona, C. M. Hadad, T. L. Lowary, Conformational Analysis of Furanose Rings with PSEUROT: Parametrization for Rings Possessing the Arabino, Lyxo, Ribo, and Xylo Stereochemistry and Application to Arabinofuranosides, *J. Org. Chem.* 2002, *67*, 4647; doi.org/10.1021/jo025635q.

[7] P. MS Hendrickx, J. C. Martins, A new friendly Matlab program and GUI for the pseudorotation analysis of saturated five membered ring system based on scalar coupling constants, *Chemistry Central Journal* 2008, 2, 20; doi: 10.1186/1752-153X-2-4.

[8] F. H. Cano, C. Forces-Forces, S. Garcia-Blanco, A model for describing the conformation of flexible 6-membered rings. I. *Tetrahedron* 1977, *33*, 797; doi.org/10.1016/0040-4020(77)80195-6.

[9] J. C. A. Boeyens, The conformation of six membered rings, *J. Cryst. Molec. Struct.*, 1978, 8 (6), 317; doi 10.1007/BF01200485.

[10] 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, 22 august 2022; doi.org/10.1021/scimeetings.2c00876.

[11] X. Biarnés, A. Ardeval, A. Planas, C. Rovira, A. Laio, M. Parrinello, The conformational free energy landscape of β-glucopyranose. Implications for substrate preactivation in β-glucoside hydrolases, *J. Am. Chem. Soc.* 2007, *129*, 10686; Doi: 10.1021/ja068411a.

[12] A. R. Ionescu, A. Bérces, M. Z. Zgierski, D. M. Whitfield, T. Nukada, Conformational pathways of saturated six-membered rings. A static and dynamical density functional study, *J. Phys. Chem. A* 2005, *109*, 8096; doi.10.1021/jp052197t.

[13] E. Lescrinier, M. Froeyen, P. Herdewijn, Difference in conformational diversity between nucleic acids with a six-membered "sugar" unit and natural "furanose" nucleic acids, *Nucleic Acids Research* 2003, 31 (12), 2975; Doi: 10.1093/nor/gkg407.

[14] Wikipedia: Root system, cube tesseract, Schlafi Hess polygon.

[15] C.-I. Mitan, E. Bartha, P. Filip, 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, in press.

[16] E. Bartha, C.-I. Mitan, C. Draghici, M. T. Caproiu, P. Filip, R. Moriarty, Rectangle as manifold on relationships between vicinal constant couplings $^{3}J_{HH}$, ^{1}H and ^{13}C-chemical shifts and dihedral angles, *Rev. Roum. Chim.,* 2022, *67* (3), 167 – 172; DOI: 10.33224/rrch.2022.67.3.05 (Eng).

[17] B. M. Malle, I. Lundt, T. M. Wrodnigg, Regioselective intramolecular ring closure of 2-amino-6-bromo-2,6-dideoxyhexano-1,4-lactones to 5- or 6-membered iminuroic acid analogues: synthesis of 1-deoxymannojirimycin and 2.5-dideoxy-2,5-imino-D-glucitol, *Organic&Biomolecular Chemistry*, 2008, 6, 1779; doi.org/10.1039/B719631H.

[18] C.-I. Mitan, E. Bartha, P. Filip, C. Draghici, M. T. Caproiu, R. M. Moriarty, Dihedral angles calculated with 3-sphere approach as integer in conformational analysis on D-, L-ribitol series, *Rev. Roum. Chim.* 2022, *66* (21), 941, DOI: 10.33224/rrch.2021.66.12.07 (Eng).

[19] J. Iglesias-Fernández, L. Raich, A. Ardèval, C. Rovira, The complete conformational free energy landscape of β-xylose reveals a two fold catalytic itinerary for β-xylanases, *Chemical Science*, 2015, *6*, 1167; DOI: 10.1039/c4sc02240h.

[20] P. E. Marszalek, Y-P. Pang, H. Li, J. El Yazal, A. F. Oberhauser, J. M. Fernandez, Atomic levers control pyranose ring conformations, *Proc. Natl. Acad. Sci. USA*, 1999, 96, 7894; doi.org/10.1073/pnas96.14.7894.