Dedicated to Dr. Maria. Zaharescu
on the occasion of her 85th anniversary

MANIFOLD INVERSION ON PREDICTION DIHEDRAL ANGLE FROM VICINAL COUPLING CONSTANT WITH 3-SPHERE APPROACH
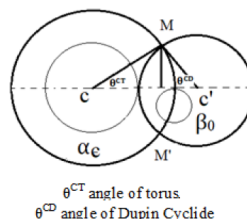
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Dihedral angles are predicted from vicinal coupling constants $^3J_{HH}$[Hz] with 3-sphere approach, sphere or torus trigonometric equations of circle 1, 2 and circle inversion 3–5 for all *cis-*, *trans-ee*, *trans-aa* stereochemistry. The existence of circle inversion was demonstrated with conformational analysis on five and six membered rings. The sign and the stereochemistry results from vicinal coupling constant under trigonometric equations confirmed by algebraic equations, Hopf and Lie algebra theory. 3-Sphere, a hypersphere in 4D enable for all stereochemistry calculation dihedral angles under magnetic wave (NMR data -$^3J_{HH}$[Hz]), and all isomers from only one vicinal coupling constant.

θ^{CT} angle of torus.
θ^{CD} angle of Dupin Cyclide

Eq. 3: **tan^{-1}sin(-ϕ) = θ$_{HnHn+1}$,**

Eq. 4: **sin^{-1}(cot(-ϕ)) = θ$_{HnHn+1}$,**

Eq. 5: **sin^{-1}(tan(-ϕ)) = θ$_{HnHn+1}$**

Where: ϕ – vicinal angle [deg], angle result from vicinal coupling constant $^3J_{HH}$[Hz], θ$_{HnHn+1}$[deg]

INTRODUCTION

The dihedral angle of the HCCH fragment with *cis*, *trans-ee* and *trans-aa* stereochemistry calculated from magnetic wave is an angle found at intersection of two congruent disks, centered on the perimeter of each other with equilateral triangles as vertices, six Hope fibration in terms of circles and ordinary sphere, nested tori of Vilarceau circles linking. The tandem vicinal ϕ deg (eq. 1) – dihedral angles θ$_{HnHn+1}$ deg (eq. 2) result from vicinal coupling constant $^3J_{HH}$[Hz] with Lie algebra – 3-sphere approach theory [1, 2].

Eq. 1: *cis, trans-ee*^{3,2}: $\sin^{-1}\cos\phi = \theta_{HnHn+1}$

Eq. 2: *trans-aa*$^{6,1 \text{ or } 5,2}$, *trans-ee*^{4,1}: $\cos^{-1}\sin(-\phi) = \theta_{HnHn+1}$

$$\varphi = (n \times {}^3J_{HnHn+1})^2$$

where: θ_{HH}[deg] – dihedral angle, φ[deg] – vicinal angle, $^3J_{HH}$[Hz] – vicinal coupling constant, with *cis, trans-ee*: $m = 2$, *trans-aa*: $m = 1$.

A torus is the stereogenic projection of the inverse image of a circle of 2-sphere latitude, having four characteristics circles: meridian, parallel and two Villarceau circles. Circles usefully for calculation angles from proton and carbon chemical shift or construction the six sets on two units [3].

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RESULT AND DISCUSSION

Two circles (α_0, β_0) intersecting each other on the point P$\epsilon\phi$ are transversal, and after moving the point P slightly along a geodesic in the normal direction to the circles can be drawn other two circles (α_ϵ, β_ϵ) through the resulting point P′ of ϕ. The pairs (α_ϵ, β_0), (α_0, β_ϵ) has 2 distinct intersecting points near P, points arbitrarily close to P with transversal circles through them as presented in Fig. 1 [4], two circles of torus and two circles of Dupin cyclide. Each point of the smooth closed surface homeomorhic to either a sphere or a torus ($\phi \in R^3$) able to build 4 distinct circles fully contained in the surface is a cyclide. Takeuchi claim that a surface with 7 circles through each point is a sphere [4].
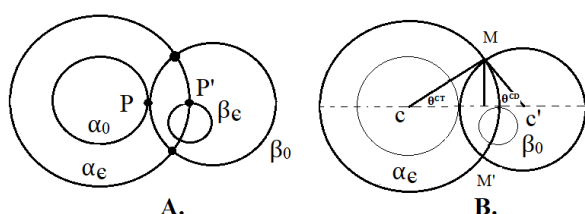

Fig. 1 – A) Torus circles intersecting Dumpin cyclide circles; B) Two angles of sets CT and CD.

The inversion of a ring torus is the image of ring Dupin cyclide, non-spherical algebraical surface of degree four[3].

The circles α_ϵ, β_0 reassemble the intersection of two right triangles inscribe on them, two half acute angle of rhombic dodecahedron which can be placed on two different sets under 3-sphere approach. The circle β_0 results from the tangent of circle α_ϵ, two intersecting circles on two points (M, M′) having four triangles between center (c, c′) of circles α_ϵ, β_0 and the points M, M′ (Fig. 1B). The circles α_0 and β_ϵ drawn concentric on the interior of circle α_ϵ and nonconcentric on the interior of circle β_0 reassembles the intersection of a torus with a Dupin cyclide (Fig. 1A). The angles θ^{CT} and θ^{CD} are equals with angles $C1\theta^{Ai}$ and $T1\theta^{Ai}$, angles of sets A resulting from *sin* function in the first case and *tan* function in the second case.
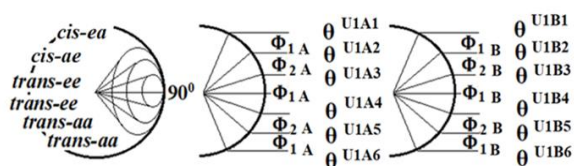

Fig. 2 – Six angles with *cis*, *trans* stereochemistry on two sets A, B.

Six angles with *cis*, *trans-ee*, *trans-aa* stereochemistry can be drowned on three concentric cons, solid angle *versus* conic section; after decomposition in two circles, conic section reassembling the trigonometric eq. 2, the square of the solid angle is replaced by the sphere equation. Considering only the east side of the circles with positive angles, namely sets A, B, the trigonometric equations 2–5 [5, 6] have angles of set A equals with ϕ and angles of set B equals with θ_{HnHn+1} deg in combinations characteristics for all stereochemistry of the HCCH fragment. Sets A and B result from the sin and cos functions in case of torus circle and from the tan and inverse of tan function in case of the Dupin cyclide circle.

Eq. 3: $\tan^{-1}\sin(-\phi) = \theta_{HnHn+1}$

Eq. 4: $\sin^{-1}(\cot(-\phi)) = \theta_{HnHn+1}$

Eq. 5: $\sin^{-1}(\tan(-\phi)) = \theta_{HnHn+1}$

trans-aa[6,1 or 5,2]: $\theta_{HnHn+1}{}^{trans} = -180 - \theta_{HnHn+1}{}^{cis}$
trans-ee[4,1 or 3,2]: $\theta_{HnHn+1}{}^{trans} = -90 -/+ \theta_{HnHn+1}{}^{cis}$

All *cis*, *trans* stereochemistry results from the trigonometric equations 2–5 [5, 6] are found on six sets angles on two units U1 and S1 (sometimes on seven sets on one-unit U1 or S1). Seven sets unit contain three units of three sets angles: 1. A, B, C; 2. D, E, A; 3. F, G, B; U or S or combination of U or S. The number of units increasing until the calculated dihedral angles is almost equal with the predicted one. The unit C1 or T1 are equals with U1 or S1 if one of the first angle of seven sets angles are higher or smaller as 5 deg (Fig. 3). The Java Script program for transformation from unit U to unit S and unit S to unit U was published already [1].

$$\theta^{C1Ni} = f(sin^{-1}Rm), \quad \theta^{T1Ni} = f(tan^{-1}Rm)$$
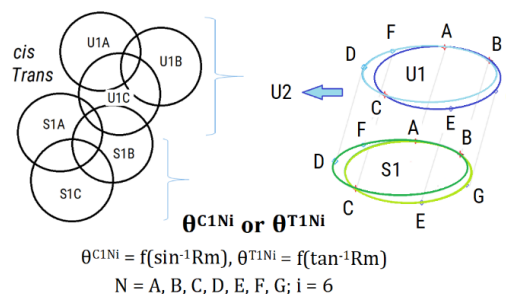$$N = A, B, C, D, E, F, G; i = 6$$

Fig. 3 – Six sets angles one two units, $C1\theta^{Ai}$ and $T1\theta^{Ai}$: unit C1 with one angle calculated from *sin* function, unit T1 with one angle calculated from *tan* function; C1 or T1 = U1 if one angle $\theta^{N1} > 1$ and C1 or T1 = S1 if one angle $\theta^{N1} < 1$.

The circle inversion eqs. 3–5 enable calculation for one vicinal coupling constant $^3J_{HH}$ Hz all the

isomers. Two torsional angles with *trans-aa*[6,1] stereochemistry between $^3J_{HH}$ of 6 – 6.3 and 7.1 – 7.9 Hz with negative sign [6] are prove for circle inversion, demonstrated with conformational analysis [6] on D-, L-talonic acid [7] or on D-, L-ribitol [8] series (Fig. 4), relative to one torsional angle with positive sign result from eq. 1, or alternatively directly the dihedral angle from eq. 2. For examples, for a vicinal coupling constant of 2.6 Hz from eq. 1 result a *gauche* angle of 62.96 deg with positive sign, instead of *cis* as recorded experimentally [7], negative *cis* angles resulting only from eq. 3 (–24.447 deg) and 5 (–30.69 deg). The conformation of 2,6-dideoxy-

2,6-imino-D and L-talonic acid **1D**, **1L** can't be established with molecular models using dihedral angles calculated with eq. 1, 2 from recorded *cis/trans* stereochemistry, introduction of the circles inversion eqs. 3–5 giving a good correlation between recorded vicinal coupling constant and the sign of the dihedral angles (Table 1). D-talonic acid **1D** has boat conformation $\mathbf{B^{0.3}}$ in case of *cis* recorded $^3J_{H3H4}$ = 2.6 [Hz] and skew $\mathbf{S^0_1}$ in case of *gauche* angle θ_{H3H4} = 62.96 [deg] result from eq. 1. L-talonic acid **1L** has skew $\mathbf{S^3_1}$ conformation on Stoddart's diagram [9]. The sign around the six membered ring reported in literature indicate skew conformation instead of $\mathbf{B^{0.3}}$ [10].

Table 1

Predicted dihedral angles θ_{nn+1} deg of D-talonic acid **1D** and L-talonic acid **1L**

|	H_nH_{n+1}	$^3J_{HH}$ [Hz] **1D**	θ_{HnHn+1} [deg]	$^3J_{HH}$ [Hz] **1L**	θ_{HnHN+1} [deg]
1.	*cis*-H_1H_2	3.8	–39.10[eq.4]	3.8	32.23[eq.1]
2.	*trans*-H_1H_2	7.7	–143.56[eq.4]	7.7	149.29[eq.2]
3.	*trans*-H_2H_3	7.3	143.29[eq.2]	7.3	–141.28[eq.3] –131.786[eq.4]
4.	*cis*-H_3H_4	2.6	–24.44[eq.3] –30.69[eq.5]	2.4	–21.37[eq.3] –25.169[eq.5]
5.	*trans*-H_3H_4	2.6	62.96[eq.1]	2.4	66.96[eq.1]
6.	*trans*-H_4H_5	6.4	–146.75[eq.3]	6.0	126[eq.2]
7.	**1D**: $\mathbf{B^{0.3}}$ *cis/trans* H_1H_2 – *trans* H_2H_3 – *cis* H_3H_4 – *trans* H_4H_5 –39/–143.56, 143.29, –30.69, –146.75				
8.	**1L**: $\mathbf{S^3_1}$ *cis/trans* H_1H_2 – *trans* H_2H_3 – *cis* H_3H_4 – *trans* H_4H_5 34.24/149.29, –141.28, –21.37, 126				
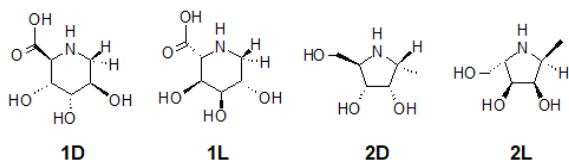
Fig. 4 – Six **1** (D, L talonic acid) and five membered ring iminocyclitols **2** (α-D, β-L ribitol).

For vicinal coupling constant of 8.8 Hz the dihedral angles θ_{H3H4} calculated with Karplus equations [9] are *trans-aa*[5,2] and *trans aa*[6,1] with positive sign, and from 3-sphere equations *trans-aa*[6,1] with positive and negative sign in agreement with θ_{H3H4} of D, L ribitol stereochemistry [8] and *trans-aa*[5,2] with positive sign.

Karplus equations [11]: $^3J_{HH}$ = 8.8 Hz

Eq. 6[12] $^3J_{HH} = 9.5\cos^2\theta – 0.28$: 132.13 deg

Eq. 7[13] $^3J_{HH} = 1.1 + 17\cos^2\theta$: 167.70 deg

Eq. 8[14] $^3J_{HH} = 7.76\cos^2\theta – 1.1\cos + 1.4$: 137.7 deg

3-Sphere equations [5]: $\phi = (8.8)^2 = 77.44$ deg

Eq. 1: $\sin^{-1}\cos\phi = 167.44$ deg,   *β L-ribitol*

Eq. 4: $\sin^{-1}(\cot-\phi) = –167.12$ deg,   α *D-ribitol*

Eq. 3: $\tan^{-1}(\sin-\phi) = 135.69$ deg

The 3-sphere dihedral angles with *trans-aa* and *trans-ee* stereochemistry results from "torsional angles", the corresponding *cis* angles +/–180 deg (eq. 2U) for *trans-aa* or +/–120 deg for *trans-ee*, relationships between dihedral angle on set A and vicinal angle on set B and *viceversa*. 3-Sphere *trans-ee* dihedral angles results from trigonometric equations are *ee*[3,1] and *ee*[4,1] relative to *convention rule ee*[3,2] and *ee*[4,1]. Way the *tans-aa* angles are not under +/–120 deg? Certainly, on conformational analysis with molecular models are used dihedral angles and not torsional angles as on Altona model [15]; eq. 1 giving the corresponding *cis* angle which must be subtracted from 180 deg and the eq. 2 the *trans-aa* dihedral angle. The 3-sphere dihedral angles are *cis* torsional angles used recently on conformational analysis [16].

In Table 2 are presented angles of six sets on two units C1Ni, with units S1 and U1

calculated for a vicinal coupling constant of 0.1 Hz. The Hopf coordinates (I) applied on *cis/trans-aa*[6,1] stereochemistry reveals the relationship between *cis/trans*[6,1] and *cis/trans*[5,2] of 180 deg. R^4 complex Hopf fibration for *cis/trans-aa*[6,1] stereochemistry, analog to *cis/trans-aa*[5,2], quaternionic multiplication $S^3 \rightarrow S^7 \rightarrow S^4$ for both, totally R^{16} octonionic Hopf fibration $S^7 \rightarrow S^{15} \rightarrow S^8$ with $\theta^{U1A6} = \phi$ and $\theta^{U1B3} = \theta_{HnHn+1}$.

Table 2

Six sets angles C1Ni on two units S1Ni and U1Ni calculated for a vicinal coupling constant of 0.1 Hz

Entry	θ^{S1Ni}	θ^{S1Ai}	θ^{S1Bi}	θ^{S1Ci}	Entry	θ^{U1Ni}	θ^{U1Ai}	θ^{U1Bi}	θ^{U1Ci}
1.	$\theta^{S1}\theta^{N1}$	29.95	0.04	0.08	9.	θ^{U1N1}	10.01	19.98	20.02
2.	θ^{S1N2}	30.04	59.95	59.91	10.	θ^{U1N2}	49.98	40.013	39.97
3.	θ^{S1N3}	89.96	60.04	60.08	11.	θ^{U1N3}	70.01	79.98	80.02
4.	θ^{S1N4}	90.04	119.96	119.91	12.	θ^{U1N4}	109.98	100.01	99.97
5.	θ^{S1N5}	149.95	120.04	120.91	13.	θ^{U1N5}	130.01	139.98	140.02
6.	θ^{S1N6}	150.04	179.95	179.92	14.	θ^{U1N6}	169.98	160.01	159.97
7.	ϕ_2	59.91	0.08	0.16	15.	ϕ_2	20.02	39.97	40.01
8.	$\phi_1/2$	0.04	29.95	29.91	16.	$\phi_1/2$	19.98	10.01	9.97

*180 – 90.04 = 89.96 deg; 90 + 0.04 = 90.04 deg, 90 – 0.04 = 89.96 deg

Cis/Trans-aa[6,1] – Hopf coordinates I (eq. 2U):
$X_0 = \cos\theta^{U1A6}\sin-\theta^{U1B3}$, $X_1 = \sin\theta^{U1A6}\sin\theta^{U1A6}$
i.e.: $\cos^{-1}\sin-79.986 = 169.986$ deg
$\sin^{-1}\sin169.986 = 10.013$ deg

$180 - \theta^{U1A1} = \theta^{U1A6}$; *i.e.*: $180 - 10.013 = 169.986$ deg
$X_2 = \cos\theta^{U1A1}\sin\theta^{U1B3}$, $X_3 = \sin\theta^{U1A1}\sin\theta^{U1A1}$
i.e.: $\cos^{-1}\sin79.986 = 10.013$.

Between 1.2 – 2.5 Hz dihedral angles are on unit U with *trans-ee*[4,1] stereochemistry, the Hopf coordinates I (eq. 2aU) ensuring the calculation of the dihedral angles *trans-ee*[4,1] from θ^{U1A1} and θ^{U1B1} in agreement with the algebraic equations 11c [1], $\theta^{U1A1} = \phi_{1B}/2$ and $\theta^{U1B1} = \phi_{1A}/2$. Hopf coordinates I (eq. 2bU) gives the dihedral angles with *trans-ee*[3,2] stereochemistry but totally in disagreement with algebraic equation 11d.

Cis/Trans-ee[4,1] – Hopf coordinates I (eq. 2aU):

$X_0 = \cos\theta^{U1B4}\sin-(\theta^{U1A1})$, $X_1 = \sin\theta^{U1B4}\sin\theta^{U1B4}$ (2aU)

with θ^{U1A1} positive in sign

$X_2 = \cos\theta^{U1A4}\sin-(\theta^{U1B1})$, $X_3 = \sin\theta^{U1A4}\sin\theta^{U1A4}$ (2aU)

with θ^{U1B1} positive in sign;

Cis/Trans-ee[3,2] – Hopf coordinates I (eq. 2bU):

$X_0 = \cos\theta^{U1B3}\sin\theta^{U1A1}$, $X_1 = \sin\theta^{U1B3}\sin\theta^{U1B3}$ (2bU)

$X_2 = \cos\theta^{U1A3}\sin\theta^{U1B1}$, $X_3 = \sin\theta^{U1A3}\sin\theta^{U1A3}$.   (2bU)

The transformation unit U1 to unit S1 gives angles with *trans-ee*[3,2] stereochemistry since $\phi^{U1} = \phi_2^{U1} - \phi_1^{U1}/2 < 5$ deg. Hopf coordinates I (2bS) indicate *trans-ee*[3,2] in unit S if ϕ has positive sign and *trans-ee*[4,1] if ϕ has negative sign, in comparation with Hopf coordinates I (eq. 2aS) and II (eq. 1S) where both negative or positive ϕ^{U1} are under *trans-ee*[3,2] stereochemistry. Between 0 – 1.1 Hz and 2.6 – 2.7 Hz dihedral angles *trans-ee*[3,2]

are on unit S1. Unit S1 is builds for $\phi^{U1} = \theta^{S1N1} < 5$ deg, *gauche* angles resulting between 0 – 0.8 Hz (60.04 – 63.24 deg) and 2.6 – 2.7 Hz (62.96, 60.84 deg).

Trans-ee[4,1], *-ee*[3,2] – Hopf coordinates I (eq. 2S):

Trans-ee[3,2]: $X_0 = \cos\theta^{S1A3}\sin(-\theta^{S1B1})$,
$X^1 = \sin\theta^{S1A3}\sin\theta^{S1A3}$ (2aS)

i.e.: $\cos^{-1}\sin-(-0.040) = 89.96$ deg

Trans-ee[3,2]: $X_0 = \cos\theta^{S1A3}\sin+\theta^{S1B1}$,
$X_1 = \sin\theta^{S1A3}\sin\theta^{S1A3}$ (2bS)

i.e.: $\cos^{-1}\sin+0.040 = 89.96$ deg

Trans-ee[4,1]: $X_0 = \cos\theta^{S1A4}\sin(-\theta^{S1B1})$,
$X_1 = \sin\theta^{S1A4}\sin\theta^{S1A4}$ (2bS)

i.e.: $\cos^{-1}\sin-0.040 = 90.04$ deg
Equation 2aS is equivalent with $\theta^{S1A4} = 180 - \theta^{S1A3}$. Negative algebraic angle giving also *trans-ee*[3,2] stereochemistry.

Trans-ee[3,2] – Hopf coordinates II (eq. 1S):

1S: Trans-ee[3,2]: $X_0 = \sin\theta^{S1A3}\cos+\theta^{S1B1}$, $X_1 = \sin\theta^{S1A3}\sin\theta^{S1A3}$

i.e.: $\sin^{-1}\cos+0.040 = 89.96$ deg

1S: Trans-ee[3,2]: $X_0 = \sin\theta^{S1A4}\cos(-\theta^{S1B1})$, $X_1 = \sin\theta^{S1A4}\sin\theta^{S1A4}$

i.e.: $\sin^{-1}\cos-0.040 = 89.96$ deg

with θ^{S1A1} and θ^{S1B1} negative in sign for *trans-ee*[4,1] stereochemistry if $\phi_2 < \phi_1/2$ (eq. 2bS) and the *gauche* angle positive.

Excepting the rule of ϕ, positive angle result from eqs. 1, 2 and negative angles from eqs. 3–5. From unit S calculated only from vicinal coupling constant, the transformation S to U don't give information about the sign of ϕ^{U1}. In case of eqs. 3–5 the tan function is compatible with transformation S to U or on seven sets angles sequence U-S-U.
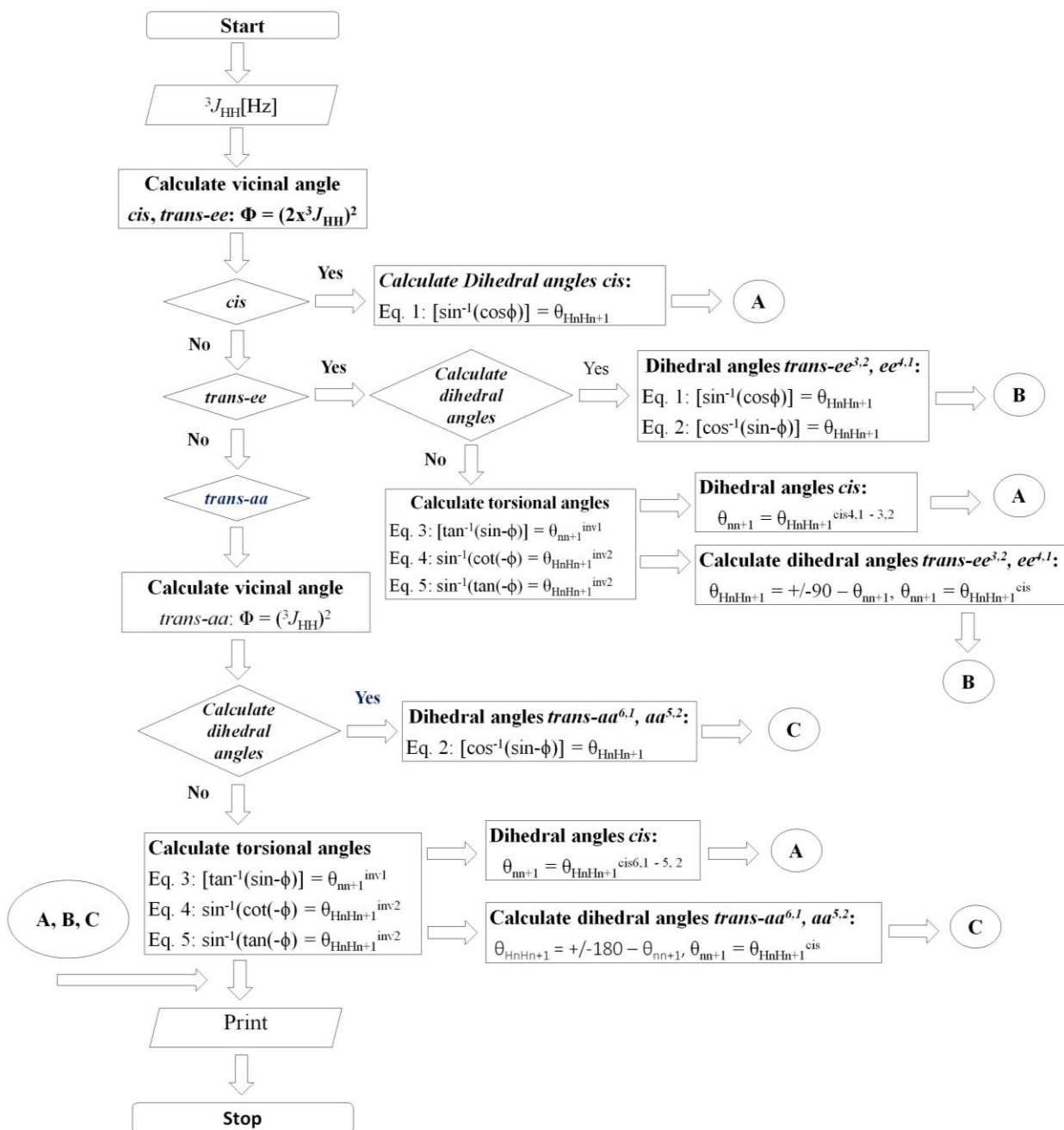
Scheme 1 – Flow-chart for prediction dihedral angles with 3-sphere approach and Java Script.

The differences between 3-sphere trigonometric equations under 180 deg for *trans-aa* stereochemistry and 90 deg for *trans-ee* stereochemistry and Karplus angles under 120 deg (eqs. 6–8), in contradiction to IUPAC rule: *trans-ee^{4,1}* and *-ee^{3,2}* stereochemistry, was overcome considering *trans-aa* stereochemistry under 180 deg and *trans-ee* stereochemistry under 120 deg (eqs. 9, 10) [5]. The presented trigonometric equations are in agreement with algebraic equations 11 [1].

$$\theta^{trans\text{-}ee3,2} = 120 - \theta_{HnHN+1}{}^{trans\text{-}ee3,2} \qquad (9)$$

$$\theta^{cis\text{-}aa6,1} = 120 - \theta_{HnHN+1}{}^{trans\text{-}ee4,1} \qquad (10)$$

Algebraic equations 11a–c for dihedral angles with *cis*-, *trans*-stereochemistry on unit U and S:

$$cis/trans\text{-}aa^{6,1}: \phi_{aa6,1} = 60 + (\phi_1{}^A/2) \qquad (11a)$$

$$cis/trans\text{-}aa^{5,2}: \phi_{aa5,2} = \phi_{2A} + (\phi^{1A}/2) \qquad (11b)$$

$$cis/trans\text{-}ee^{4,1}: \phi_{ee4,1} = \phi_{1A}/2 = \theta^{B1} \qquad (11c)$$

$$cis/trans\text{-}ee^{3,2}: \phi_{ee3,2} = \phi_2{}^{1A} - (\phi_1{}^{1A}/2) \qquad (11d)$$

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

</head>

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

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

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

<h3>Java Script program for calculation dihedral angle from NMR data with 3-
sphere approach and skew circles.</h3>

<h4>Step 1:<i>Program for prediction dihedral angle from vicinal coupling
constant.</i></h4>

</body>

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

var usedata1A

usedata1A = prompt ("The value of cis vicinal coupling constant[Hz]")
usedataA = prompt ("The number of protons HnHn+1")

//calculate the value of X
var X = usedata1A*usedata1A;//value of X
if ( X < 100){
var X = usedata1A*usedata1A;//value of X
var BCd = 4*X;//angle of set B in deg
var BCr = (BCd)*(0.017453292);//vicinal angle BCr[rad]
var Rmc = Math.cos(BCr);//value Rmc in radians
var ACr = Math.asin(Rmc);//dihedral angle ACr[rad] with cis stereochemistry
var ACd = (ACr)*(57.29577521);//dihedral angle ACd[deg] with cis
stereochemistry

document.write("<h4><i>Dihedral angle cis[deg].</i></h4>")
document.write("<p><b>The <i>cis</i> vicinal coupling constant
<sup>3</sup><i>J</i><sub>HH</sub>[Hz]</b>=",usedata1A)
document.write("<p><i>cis</i>-HnHn+1:",usedataA)
document.write("<p>The angle of set B, the vicinal angle BCd[deg]:"+BCd);
document.write("<p>The angle of set A, the dihedral angle <i>cis</i>
ACd[deg]:"+ACd);

}
else{
var X = undefined;//value of X
}

//calculate the inversion I
var BC1 = [4*(usedata1A*usedata1A)];//angle of set B in deg
var BCn = (BC1)*(0.017453292);//vicinal angle BCn[rad]
var Rm1c = Math.sin(-BCn);//value Rm1c in radians
var Ac = Math.atan(Rm1c);//dihedral angle Ac[rad] with cis stereochemistry
var AC1 = (Ac)*(57.29577521);//angle of set A, the dihedral angle AC[deg]

document.write("<h4><i>The inversion I, cis[deg].</i></h4>")
document.write("<p>The angle of set B, the vicinal angle BC1[deg]:"+BC1);
document.write("<p>The angle of set A, the <i>cis</i> angle AC1[deg]:"+AC1);

//calculate the inverseion II
var BC2 = [4*(usedata1A*usedata1A)];//angle of set B in deg
var BC = (BC2)*(0.017453292);//vicinal angle BC[rad]
var Rm2c = Math.tan(-BC);//value Rm2a in radians

var Rm2 = Rm2c;//value Rm2 in radians
if (Rm2c < 0){
var Rm2 = Rm2c;//value Rm2 in radians
  if (Rm2c < -1.0){
      var Rm2 = 1/Rm2c;//value Rm2 in radians
      }
      else{
      var Rm2 = Rm2c;//value Rm2 in radians
      }
}
else{
var Rm2 = 1/Rm2c;//value Rm2 in radians
}

var AnC = Math.asin (Rm2);//dihedral angle AnC[rad] with cis stereochemistry
var AC2 = (AnC)*(57.29577521);//angle of set A, the dihedral angle AC2[deg]
if ( AC2 < 60){
var AC2 = (AnC)*(57.29577521);//angle of set A, dihedral angle cis AC2[deg]
}
else{
var AC2 = trans-ee;//angle of set A, trans-ee
}

document.write("<h4><i>The inversion II, cis[deg].</i></h4>")
document.write("<p>The angle of set B, the vicinal angle BC2[deg]:"+BC2);
document.write("<p>The angle of set A, the angle <i>cis</i> AC2[deg]:"+AC2);

var usedata2B

usedata2B = prompt ("The value of trans-ee vicinal constant coupling[Hz]")
usedataB = prompt ("The number of protons HnHn+1")

//calculate the value of X
```

```
var Y = usedata2B*usedata2B;//value of Y

if (Y < 100){
var Y = usedata2B*usedata2B;//value of Y
var BTed = 4*Y;//vicinal angle BTed[deg]
var BTer = (BTed)*(0.017453292);//vicinal angle BTer[rad]
var RmTe = Math.cos(BTer);//value RmTe in radians
var ATer = Math.asin(RmTe);//dihedral angle ATer[rad] with trans-ee
stereochemistry
var ATed = (ATer)*(57.29577521);//dihedral angle ATed[deg] with trans-ee3,2
stereochemistry
var ATeed = 180 - ATed;//dihedral angle ATeed[deg] with trans-ee4,1
stereochemistry

document.write("<h4><i>Dihedral angle trans-ee[deg].</i></h4>")
document.write("<p><b>The <i>trans-ee</i> vicinal coupling constant
<sup>3</sup><i>J</i><sub>HH</sub>[Hz]</b>=",usedata2B)
document.write("<p><i>Trans-ee</i>-HnHn+1:",usedataB)
document.write("<p>The angle of set B, the vicinal angle BTed[deg]:"+BTed)
document.write("<p>The angle of set A, the dihedral angle <i>trans-
ee</i><sup>3,2</sup> ATed[deg]:"+ATed);
document.write("<p>The angle of set A, the dihedral angle <i>trans-
ee</i><sup>4,1</sup> ATeed[deg]:"+ATeed);

}
else{
var Y = undefined;//value of Y
}

//calculate the inversion I
var BE1 = [4*(usedata2B*usedata2B)];//angle of set B in deg
var BEn = (BE1)*(0.017453292);//vicinal angle BEn[rad]
var Rme1 = Math.sin(-BEn);//value Rme1 in radians
var AEn = Math.atan(Rme1);//dihedral angle ATn[rad] with trans-ee
stereochemistry
var AE1 = (AEn)*(57.29577521);//angle of set A, the dihedral angle AE1[deg]

var A1E = -90 - AE1;//dihedral angle A1E[deg] with trans-ee stereochemistry
if (AE1 < 0){
var A1E = -90 - AE1;//dihedral angle A1E[deg] with trans-ee stereochemistry
}
else{
var A1E = 90 - AE1;//dihedral angle A1E[deg] with trans-ee stereochemistry
}

var A1EE = -(180 + A1E);//dihedral angle A1EE[deg] with trans-ee4,1
stereochemistry

document.write("<h4><i>The inversion I, dihedral angle trans-ee[deg].</i></h4>")

document.write("<p>The angle of set B, the vicinal angle BE1[deg]:"+BE1);
document.write("<p>The torsional angle of set A, the torsional angle
AE1[deg]:"+AE1);
document.write("<p>The angle of set A, the dihedral angle <i>trans-
ee</i><sup>3,2</sup> A1E[deg]:"+A1E);
document.write("<p>The angle of set A, the dihedral angle <i>trans-
ee</i><sup>4,1</sup> A1EE[deg]:"+A1EE);

//calculate the inversion II
var BE2 = [4*(usedata2B*usedata2B)];//angle of set B in deg
var BE = (BE2)*(0.017453292);//vicinal angle BE[rad]
var Rm3e = Math.tan(-BE);//value Rm3e in radians
var Rm3 = 1/Rm3e;//value Rm3 in radians

if (Rm3 > 1){
var Rm3 = 1/Rm3e;//value Rm3 in radians
}
else{
var Rm3 = Rm3e;//value Rm3 in radians
}

var AnE = Math.asin(Rm3);//dihedral angle AnE[rad] with trans-ee
stereochemistry
var AE2 = (AnE)*(57.29577521);//angle of set A, the dihedral angle AE2[deg]

var A2E = -90 - AE2;//dihedral angle A2E[deg] with trans-ee stereochemistry
if (AE2 < 0){
var A2E = -90 - AE2;//dihedral angle A2E[deg] with trans-ee stereochemistry
}
else{
var A2E = 90 - AE2;//dihedral angle A2E[deg] with trans-ee stereochemistry
}

var A2EE = -(180 + A2E);//dihedral angle A2EE[deg] with trans-ee4,1
stereochemistry

document.write("<h4><i>The inversion II, dihedral angle trans-
ee[deg].</i></h4>")
document.write("<p>The angle of set B, the vicinal angle BE2[deg]:"+BE2);
document.write("<p>The torsional angle of set A, the torsional angle
AE2[deg]:"+AE2);
document.write("<p>The angle of set A, the dihedral angle <i>trans-
ee</i><sup>3,2</sup> A2E[deg]:"+A2E);
document.write("<p>The angle of set A, the dihedral angle <i>trans-
ee</i><sup>4,1</sup> A2EE[deg]:"+A2EE);

var usedata3C
usedata3C = prompt ("The value of trans-aa vicinal constant coupling[Hz]")
usedataC = prompt ("The number of protons HnHn+1")

//calculate the vicinal angle BTd[deg]
var BTd = usedata3C*usedata3C;//angle of set B in deg

if (BTd < 150){
```

```
var BTd = usedata3C*usedata3C;//angle of set B in deg
var BTr = (BTd)*(0.017453292);//vicinal angle BTr[rad]
var Rmta = Math.sin(-BTr);//value Rmta in radians
var ATr = Math.acos(Rmta);//dihedral angle ATr[rad] with trans-aa
stereochemistry
var ATad = (ATr)*(57.29577521);//angle of set A, the dihedral angle ATad[deg]
var ATd = ATad;//the dihedral angle ATd[deg] with trans-aa stereochemistry
if (BTd < 81){
//calculate the angle of set A, the dihedral angle ATd[deg]
var ATd = ATad;//dihedral angle ATd[deg]
}
else{
//calculate the angle of set A, the dihedral angle ATd[deg]
var ATd = -ATad;//dihedral angle ATd[deg]
}

document.write("<h4><i>Dihedral angle trans-aa[deg].</i></h4>")
document.write("<p><b>The <i>trans-aa</i> vicinal coupling constant
<sup>3</sup><i>J</i><sub>HH</sub>[Hz]</b>=",usedata3C)
document.write("<p><i>Trans-aa</i> HnHn+1:",usedataC)
document.write("<p>The angle of set B, the vicinal angle BTd[deg]:"+BTd);
document.write("<p>The angle of set A, the dihedral angle <i>trans-aa</i>
ATd[deg]:"+ATd);

}
else{
var BTd = undefined;//value of BTd
}

//calculate the inversion I, vicinal angle BT1[deg]
var BT1 = {usedata3C*usedata3C};//angle of set B in deg
var BTn = (BT1)*(0.017453292);//the vicinal angle BTn[rad]
var Rm1a = Math.sin(-BTn);//value Rm1 in radians
var ATn = Math.atan (Rm1a);//dihedral angle AT1[rad] with trans-aa
stereochemistry
var AT1 = (ATn)*(57.29577521);//angle of set A, the dihedral angle AT1[deg]

var A1T = -180 - AT1;//dihedral angle A1T[deg] with trans-aa stereochemistry
if (AT1 < 0){
var A1T = -180 - AT1;//dihedral angle A1T[deg] with trans-aa stereochemistry
}
else{
var A1T = 180 - AT1;//dihedral angle A1T[deg] with trans-aa stereochemistry
}

document.write("<h4><i>The inversion I, dihedral angle trans-aa[deg].</i></h4>")

document.write("<p>The angle of set B, the vicinal angle BT1[deg]:"+BT1);
document.write("<p>The torsional angle of set A, the torsional angle
AT1[deg]:"+AT1);
document.write("<p>The angle of set A, the dihedral angle <i>trans-aa</i>
A1T[deg]:"+A1T);

//calculate the inversion II, vicinal angle BT2[deg]
var BT2 = {usedata3C*usedata3C};//angle of set B in deg
var BT = (BT2)*(0.017453292);//the vicinal angle BT[rad]
var Rm4a = Math.tan(-BT);//value Rm4a in radians
var Rm4 = Rm4a;//value Rm2 in radians

if (Rm4 < 0){
var Rm4 = Rm4a;//value Rm2 in radians
  if (Rm4a < -1.0){
      var Rm4 = 1/Rm4a;//value Rm2 in radians
      }
      else{
      var Rm4 = Rm4a;//value Rm2 in radians
      }
  }
else{
var Rm4 = 1/Rm4a;//value Rm2 in radians
}

var AnT = Math.asin(Rm4);//the dihedral angle AnT[rad] with trans-aa
stereochemistry
var AT2 = (AnT)*(57.29577521);//the angle of set A, the dihedral angle AT2[deg]

var A2T = -180 - AT2;//dihedral angle A2T[deg] with trans-aa stereochemistry
if (AT2 < 0){
var A2T = -180 - AT2;//dihedral angle A2T[deg] with trans-aa stereochemistry
}
else{
var A2T = 180 - AT2;//dihedral angle A2T[deg] with trans-aa stereochemistry
}

document.write("<h4><i>The inversion II, dihedral angle trans-
aa[deg].</i></h4>")
document.write("<p>The angle of set B, the vicinal angle BT2[deg]:"+BT2);
document.write("<p>The torsional angle of set A, the torsional angle
AT2[deg]:"+AT2);
document.write("<p>The angle of set A, the dihedral angle <i>trans-aa</i>
A2T[deg]:"+A2T);

alert("Hello World!");
</script>
</html>
```

Fig. 5 – Java script program PREDICTIEACS2022.txt for prediction dihedral angles from vicinal coupling constant $^3J_{HH}$ Hz.

The flow-chart for prediction dihedral angles with 3-sphere approach (Scheme 1) starts with calculations of the vicinal angle for *cis* and *trans-ee* stereochemistry from vicinal coupling constant $^3J_{HH}$Hz. In case of *cis*, *trans-ee* stereochemistry the 3-sphere angles are calculated with eq. 1 and in case of *trans-ee* stereochemistry with eqs. 1–2.

From eqs. 3–5 results *cis* angles or *trans-ee* after multiplied or subtracted ϕ from +/–90 deg. The vicinal angle calculated for *trans-aa* stereochemistry from $^3J_{HH}$ Hz gives with eq. 2 dihedral angles with *trans-aa* stereochemistry and with eqs. 3–5 the corresponding *cis* angles transformed in *trans-aa* under 180 deg rule.

Results are display for all stereochemistry; R^{32} Hopf coordinates covered by five trigonometric equations for all isomers results from only one vicinal coupling constant.

The Java Script program for prediction dihedral angles from vicinal coupling constants $^3J_{HH}$[Hz] is presented in Fig. 5. Dihedral angles are calculated for all *cis*, *trans* stereochemistry, and torsional angles transformed in dihedral angles conformed with Scheme 1. Java Script code and Notepad++ are used for realization of the program.

CONCLUSION

Dihedral angles with corresponding stereochemistry and sign can be predicted only from vicinal coupling constant $^3J_{HnHn+1}$[Hz], introduction the chemical shift [1] in step 2 giving differences no more than 2 deg, a decisive step in analysis all aspects of stereochemistry under 3-sphere theories on next steps. In step two with conic section, Vilarceau circles [1] or rectangle equations [17] can be calculate from carbon and/or proton chemical shift the first angle of unit U or S. In step three are builds units U and S until the calculate angle is almost equal with the predicted one. Step 4 is just a verification step for calculation of the vicinal coupling constant from calculated dihedral angle. The positive (eqs. 1, 2) or negative (eq. 3–5) sign in case of five and six membered ring can be established with molecular models. From Java script program for prediction dihedral angle from vicinal coupling constant (vicinal angle) results six angles for only one vicinal coupling constant. Póncare conjunction – Lie algebra fitting well into the wave character of the NMR data, characteristics are torsional angles under 180 deg for *cis/trans-aa* or 120 deg for *cis/trans-ee* stereochemistry on two sets angles, particularly two intersecting circles. That be mentioned the Java Script programs with its trigonometric and algebraic equations work properly for vicinal coupling constants $^3J_{HH}$ between 0 – 6.1 Hz for *cis* and *trans-ee* stereochemistry and between 5.5 – 13.4 Hz for *trans-aa* stereochemistry. Higher $^3J_{HH}$ = 7.5 Hz for *cis* stereochemistry or smaller $^3J_{HH}$ = 4.5 Hz for *trans* stereochemistry are recorded to date, the algebraic and trigonometric equation for *cis* $^3J_{HH}$

between 2.8 – 6.1 Hz considered in this paper becomes compatible for *trans* stereochemistry, and *viceversa*.

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