DFT Approach Chemical Shift Calculations to 13C for Bicyclical Epoxy-Himachlene Compound in the Presence of a Lewis Acid

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ABSTRACT

In the present study we were interested in determined tensioning of screen σ and the chemical shifts δ of carbon (^{13}C) relative to the epoxy-himachlene in the presence of a Lewis acid using GIAO (Gauge Independent Atomic Orbital), GTSB (Continuous Set of Gauge Transformations) and Individual Gauges for Atoms in Molecules IGAIM a slight variation on the GTSB method) methods. Theoretical calculations were performed using the method of the density functional theory DFT/B3LYP which is implanted in the program Gaussian 09 with a 6-31G (d,p) basis set.

Firstly, we obtained the following results for the reagent R1: [2α.3α-epoxy-cis- himachal-7.13-ene] showed that the GIAO method is the most reliable in the first place. Secondly, we calculated the chemical shifts of the reaction products: P_1[(1S.3R.7S)-(3.11.11)-trimethyltricyclo [5.4 (3.7)] dodecan-2-one] and compound: P_2[(1S.2S.3R.6R)-(3.10.10)-trimethyltricyclo [5.4.4] dodec-4-en-2-ol] formed from the epoxy-himachalene (R1) in the presence of the Lewis acid.

This theoretical study was also conducted using the method GIAO and different bases of atomic orbitals: 6-31G, 6-311G, 6-31G (d.p), 6-31G (2d.p), 6-31G(d), 6-311G(d.2p). The obtained theoretical calculations results show a perfect correlation between the experimental and theoretical results with the basis 6-31G (d.p).

Keywords: DFT, GIAO, CSGT, IGAIM calculation, NMR ^{13}C chemical shifts epoxy-himachalene

INTRODUCTION

Epoxy-himachaleneis is a sesquiterpenic bicyclical hydrocarbon product optically active; its epoxydation leads to pure oxygenated enantiomeric compounds. It has been used in many applications such as perfume industry, agrochemicals and pharmacology. Generally, himachalenes have been subjected to various modifications such ascyclopropanation [1-3], oxidation [4], hydroxylation [5] and epoxidation [6]. Epoxy-himachalene was synthesized from α-mixture β-γ-himachalene extract from the essential oil of Atlas cedar [7].

The conversion of epoxy-himachalene (R1) was studied in the presence of a catalytic amount of Lewis acid in dichloromethane. It leads predominantly to the formation of two tricyclic main products: [(1S.3R.7S)-(3.11.11)-trimethyltricyclo [5.4 (3.7)] dodecan-2-one] (P1) and [(1S.2S.3R.6R)-(3.10.10)-trimethyltricyclo [5.4.4] dodec-4-en-2-ol] (P2) according to the following equation in Figure 1.

The structures of [(1S,3R,7S)-(3,11,11)-trimethyltricyclo [5.4.(3,7)] (P1) and [(1S,2S,3R,6R)-(3,10,10)-trimethyltricyclo [5.4.4] dodec-4-én-2-ol] (P2) were determined by the spectral data ^{13}C and proton [1]H [8-11] by means of nuclear magnetic resonance NMR. This spectroscopic technique is based on the magnetic properties of certain atomic nuclide; it is one of the powerful methods for determining the structure of the molecular species.

The spectral parameters related to the compounds R1, P1 and P2 were investigated using the density functional theory (DFT) approach and the hybrid functional Becke, three-parameter, Lee-Yang-Parr (B3LYP).
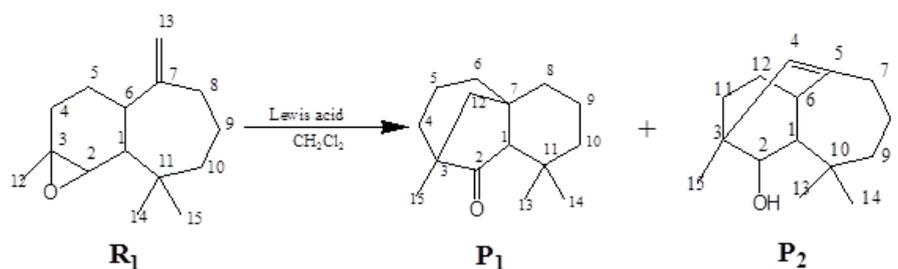
Figure 1: Reaction products of epoxy-himachalene conversion

RESULTS AND DISCUSSION

Molecular geometry optimization

Optimized geometries of studied molecules were carried out with the Gaussian 09 [12] and displayed in the program using its graphical interface Gauss View 03 [13].The minimum potential energy was calculated by the Berny algorithm using redundant internal coordinates [14]. The calculations were made using the DFT theory with B3LYP functional [15-17] and the orbital base 6-31G (d.p) [18-21].

Calculation of nuclear magnetic resonance parameters

Nuclear magnetic resonance (NMR) is a selective local probe. It can provide accurate information on nearby atomic environments. The most commonly studied nuclei are ^{1}H and ^{13}C NMR. The calculation of nuclear magnetic resonance parameters presents an important aspect in theoretical chemistry. For this is why, we used the DFT method combined with IGAIM methods [22], GIAO [23-27] and GTSB [26-28] which are restricted to finite and isolated systems (molecules or clusters). The σ tensor is a priori arbitrary but can be broken down into two parts: σ_s and σ_{as} according to the Eq. 1:

$$\sigma = \sigma_s + \sigma_{as} \tag{1}$$

where, σ_s and σ_{as} are the symmetric and anti-symmetric coefficient respectively. The anti-symmetric part has a small contribution in the NMR signals. The symmetric part can be diagonalized under its own axis system that can be written in the Cartesian coordinate system:

$$\begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

It is convenient to represent these three independent values of σ_{11}, σ_{22} and σ_{33} according to Haebrlen convention [28]. The isotropic screen constant is defined by the equation Eq. 2:

$$\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \tag{2}$$

where, σ11, σ22 and σ23 are the main normal constraints coefficients.

The isotropic chemical shifts were calculated following the formula Eq. 3:

$$\sigma_{iso} = \sigma_{iso}^{ref} + \sigma_{iso}^{molecule} \tag{3}$$

The inert compound tetramethylsilane abbreviated as TMS is taken as reference ($\sigma_{iso}^{ref} = 0$). The determination of the spectral parameters using the methods of theoretical chemistry and the comparison of results with their experimental counterparts allows us to easily identify the model that reflects the chemical shifts obtained.

Selection criteria of the calculation method

Displacements δ calculated with GIAO, CSGT and IGIAM methods and those obtained by the experience [29,30] are given in Table 1.

Table 1 shows that isotropic chemical shifts values obtained by the GIAO, GTSB and IGIM methods with the base 6-31G (d.p) and ^{13}C NMR for R1 compound are similar to their experimental homologue. The δ_{theo} obtained values for the carbon atoms in position 7 and 13 are normal because they are usually deshielded.

Table 1: Isotropic chemical shifts values (ppm) obtained by the GIAO, GTSB and IGIM methods with the base 6-31G (d.p) and ^{13}C NMR experimental for the reactant R1

C	δ_{exp}	δ_{GIAO}	δ_{CSGT}	δ_{IGIAM}
C_7	155.60	162.88	163.67	163.70
C_{13}	111.90	119.86	120.91	121.76
C_2	62.60	67.76	68.87	69.23
C_3	58.80	61.44	62.12	62.34
C_1	47.50	52.33	54.56	56.87
C_{10}	39.00	43.45	45.78	47.89
C_6	37.80	41.34	43.67	43.89
C_{11}	36.90	40.34	41.12	41.79
C_{14}	30.80	36.43	37.06	37.48
C_5	28.10	33.54	34.21	34.62
C_8	26.60	32.45	33.17	33.58
C_9	24.80	30.28	31.77	32.05
C_{15}	23.20	27.78	28.04	28.67
C_{12}	22.70	26.88	27.67	27.84

Figure 2 shows the variation of experimental chemical shifts as a function of theoretical chemical shifts for GIAO, CSGT and IGIAM calculations.
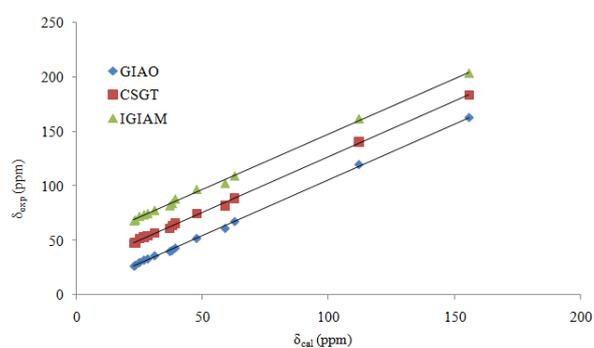
Figure 2: Variation curves of experimental chemical shifts as a function of theoretical chemical shifts for GIAO, CSGT and IGIAM calculations

The obtained curves are linear type Eq. 4:

$$\sigma_{exp} = a\delta_{calc} + b \tag{4}$$

where a and b are the slop and the intercept respectively.

Slop a, intercept b and determination coefficient r^2 of linear variation curves of δ_{theo} as a function of δ_{exp} are summarized in Table 2.

Table 2: Slope intercept and determination coefficient of linear variation curves of δ_{theo} as a function of δ_{exp}

Method	Basis	Slop, intercept and determination coefficient	GIAO	CSGT	IGIAM
DFT	6-31G (d.p)	a	1.0348	1.0471	1.0767
		b	6.0605	13.86	18.017
		r^2	0.9967	0.9893	0.9828

The obtained slop, intercept and the correlation coefficients, r^2, are given in Table 2. The table shows that the correlation coefficients for the GIAO are closer to one than that of the CSGT and IGIAM method. From these results it was concluded that the GIAO method describe better the NMR ^{13}C chemical shifts calculation for the compounds investigated in this work

CHOOSING THE GIAO METHOD AS BASIC CALCULATION

We applied the GIAO method to calculate the chemical shifts of carbon 13 for P1 and P2 products at different basis: 6-31G, 6-311G, 6-31G (d, p), 6-31G (2d,p), 6-31G (d), 6-311G (d,2p).

Chemical structure and isotropic chemical shift δ_{iso} calculation of the first product

The most stable conformer of the product P1 is shown in Figure 3. Its energy value was -435.0874 kcal/mol calculated by the DFT method and confirmed by AM1 method [31].
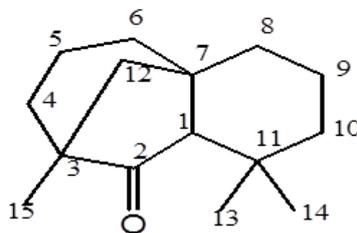
Figure 3: Chemical structure stable conformer of the product P1

Table 3 shows the isotropic chemical shift δ_{iso} (ppm) obtained by the DFT/GIAO method, at the bases 6-31G, 6-311G, 6-31G(d,p), 6-31G(2d,p), 6-31G (d), 6-311G (d,2p) and those obtained by NMR analysis of the first product.

Table 3: The isotropic chemical shift δ_{iso} (ppm) obtained by the DFT/GIAO method, at the bases 6-31G, 6-311G, 6-31G (d,p), 6-31G (2d,p), 6-31G (d), 6-311G (d,2p) and those obtained by NMR analysis of the first product

		δ_{cal}(DFT/GIAO)					
Position	δ_{exp}	**6-31G**	**6-311G**	**6-31G (d.p)**	**6-31G (2d.p)**	**6-31G (d)**	**6-311G (d.2p)**
C_2	220.7	233.54	238.33	225.14	228.78	243.81	241.53
C_1	66.6	77.43	74.88	71.34	75.33	83.8	85.03
C_{12}	53.3	78.86	69.24	65.12	79.17	76.12	80.89
C_3	48.3	63.78	6.82	55.34	59.88	65.56	67.67
C_{10}	43.5	59.67	62.31	54.37	64.67	60.48	62.66
C_7	40.3	58.58	60.38	51.23	55.54	57.98	61.49
C_8	39.6	53.77	55.67	49.33	56.87	60.23	58.22
C_4	38.9	48.34	51.35	45.12	49.45	50.66	51.67
C_{11}	33.3	51.55	50.54	46.66	49.02	54.66	50.12
C_6	32.7	54.34	52.32	47.55	53.02	58.56	56.97
C_{13}	31.9	48.45	47.12	43.50	50.23	53.22	50.55
C_{15}	21.6	38.23	37.34	36.81	39.33	41.19	39.53
C_{14}	20.7	39.31	37.39	31.78	38.43	42.11	45.66
C_5	20.5	37.12	38.08	36.33	38.34	41.05	42.58
C_9	19.4	39.54	34.28	36.24	33.23	37.02	39.23

We were able to mathematically determine the equation expressing the relationship between the theoretical values and the experimental values the isotropic chemical shift. This obtained values shows a small difference for linear regression r^2 at the bases 6-31G, 6-311G, 6-31G (d.p), 6-31G (2d.p), 6-31G (d) and 6-311G (d.2p).

A good similarity between the theoretical and experimental chemical shift was observed [28,29]. Furthermore these results show that the method GIAO at the base 6-31G (d, p) is the most reliable to calculate the chemical shifts of ^{13}C for the first product P1.

The variations of δ_{exp} as function of δ_{cal} at the bases 6-31G, 6-311G, 6-31G(d,p), 6-31G(2d,p), 6-31G (d) and 6-311G (d,2p) are shown in Figure 4. The figure indicates that all curves are linear. Their characteristics are summarized in Table 4.
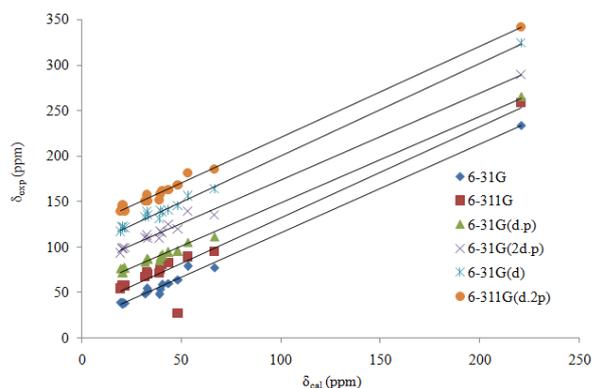
Figure 4: Variation curves of experimental chemical shifts as a function of theoretical chemical shifts at the bases 6-31G, 6-311G, 6-31G(d,p), 6-31G(2d,p), 6-31G(d) and 6-311G (d,2p) for the first product P1

Table 4: Slope, intercept and determination coefficient of linear variation curves of δ_{exp} as a function of δ_{cal}

Method	a, b and r^2	6-31G	6-311G	6-31G (d.p)	6-31G (2d.p)	6-31G (d)	6311G (d.2p)
	a	1.028	0.994	1.051	1.043	0.979	0.992
	b	-17.9	-16.48	-13.51	-19.074	-17.65	-19.65
DFT/GIAO	r^2	0.984	0.991	0.996	0.990	0.893	0.946

Chemical structure and isotropic chemical shift δiso calculation of the second product

The most stable conformer of the product P2 is shown in Figure 5. Its energy value was -387.1274 kcal/mol calculated by the DFT method.
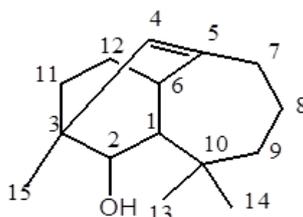
Figure 5: Chemical structure stable conformer of the product P2

The calculation we did for the P2 product are similar to those we have done for P1 product. The obtained results are summarized in the Tables 5 and 6.

Table 5: The isotropic chemical shift δ_{iso} (ppm) obtained by the DFT/GIAM method, at the bases 6-31G, 6-311G, 6-31G (d,p), 6-31G (2d,p), 6-31G (d) , 6-311G (d,2p) and those obtained by NMR analysis of the second product

	δ_{cal}(DFT/GIAO)						
Position	δ_{exp}	6-31G	6-311G	6-31G(d.p)	6-31G(2d.p)	6-31G(d)	6-311G(d.2p)
C_5	146.0	157.11	159.35	154.23	163.23	168.08	173.88
C_4	130.3	147.34	156.99	139.88	149.35	166.22	163.22
C_2	78.0	89.22	94.54	84.67	90.34	98.98	93.08
C_1	57.1	68.02	72.77	63.56	75.11	81.02	79.65
C_3	39.8	49.78	46.34	44.43	55.67	61.09	63.12
C_{10}	36.10	52.65	49.87	43.05	58.98	60.11	62.87
C_9	35.4	51.54	55.81	45.67	61.32	59.09	63.11
C_6	34.6	40.43	41.02	38.76	40.24	41.38	42.57
C_7	32.5	48.33	54.04	47.09	58.77	63.02	68.11
C_{14}	28.6	44.46	49.67	40.99	54.32	51.89	59.71
C_{13}	27.4	43.41	44.52	33.87	39.29	48.77	51.54
C_{12}	26.1	42.33	38.42	38.18	46.87	50.67	51.45
C_{11}	24.7	39.17	42.38	33.87	40.75	51.65	49.98
C_{15}	21.8	37.44	35.21	29.97	40.76	42.44	48.89
C_8	19.0	29.33	32.19	27.78	35.97	40.09	46.77

Table 6: Slope, intercept and determination coefficient of linear variation curves of δ_{exp} as a function of δ_{cal} by the DFT/GIAM method, at the bases 6-31G, 6-311G, 6-31G (d,p), 6-31G (2d,p), 6-31G (d), 6-311G (d,2p) and those obtained by NMR analysis of the second product

Method	a, b and r^2	6-31G	6-311G	6-31G (d.p)	6-31G(2d.p)	6-31G(d)	6311G(d.2p)
	a	1.028	0.994	1.051	1.043	0.979	0.992
DFT/GIAO	b	-17.9	-16.48	-13.51	-19.074	-17.65	-19.65
	r^2	0.984	0.991	0.996	0.990	0.893	0.946

The comparison of theoretical and experimental results show a perfect match between calculated isotropic chemical shift δ_{iso} obtained by the DFT/GIAM method, at the bases 6-31G, 6-311G, 6-31G(d,p), 6-31G(2d,p), 6-31G (d) , 6-311G (d,2p) and experimental chemical shift δ_{exp}.

ERROR ESTIMATION OF ISOTROPIC CHEMICAL SHIFTS OF TWO PRODUCTS P1 AND P2

The error estimate of the isotropic chemical shift is given by the equation Eq. 5:

$$\text{Error(\%)} = \frac{\delta_{cal} - \delta_{exp}}{\delta_{cal}} \times 100 \tag{5}$$

The obtained result chemical shift percentage error estimation of δ_{cal} by the DFT/GIAO method of the product P1 and P2, are given respectively in Tables 7 and 8. From these results we conclude that the basis 6-31G (d,p) has a lower estimate error, which confirms the compatibility of the theoretical and experimental values of chemical shift the epoxy-himachalene conversion products (Figure 6).

Table 7: Chemical shift percentage error estimation of δ_{cal} by the DFT/GIAO method of the P1 product

Position	6-31G	6-311G	6-31G (d.p)	6-31G (2d.p)	6-31G (d)	6-311G (d.2p)
C_2	5.49	7.39	1.97	3.25	9.47	8.62
C_1	13.98	11.05	6.64	11.58	20.55	21.67
C_{12}	32.41	23.02	18.15	32.67	24.31	34.10
C_3	24.27	30.06	12.72	19.33	26.32	28.62
C_{10}	27.09	30.18	19.99	32.73	28.07	30.57
C_7	31.20	33.25	21.33	27.43	30.49	50.41
C_8	26.35	28.86	19.32	30.36	24.25	31.98
C_4	19.52	24.24	13.78	21.33	23.21	24.71
C_{11}	35.40	34.11	28.63	32.06	39.07	33.55
C_6	39.82	37.50	31.24	38.32	44.15	42.60
C_{13}	34.15	32.30	26.66	36.49	40.06	36.89
C_{15}	43.49	42.15	41.32	45.08	47.56	45.10
C_{14}	47.34	44.63	32.23	46.13	50.84	54.66
C_5	44.77	47.34	43.57	46.53	50.06	51.86
C_9	50.93	43.58	46.46	41.61	43.40	50.93

Table 8: Chemical shift percentage error estimation of δ_{cal} by the DFT/GIAO method of the P2 product

Position	6-31G	6-31G	6-31G(d.p)	6-31G(2d.p)	6-31G(d)	6-311G(d.2p)
C_5	7.07	8.37	5.33	10.55	13.13	16.03
C_4	29.89	17.00	6.84	12.75	21.60	20.16
C_2	36.00	17.49	7.87	13.69	21.19	16.20
C_1	16.05	21.53	10.16	23.97	29.64	38.31
C_3	20.04	14.11	10.42	25.50	34.85	36.94
C_{10}	31.43	27.61	16.14	38.79	39.94	42.57
C_9	31.31	36.57	22.48	42.27	40.09	43.90
C_6	14.41	15.65	10.73	12.01	16.38	18.72
C_7	32.75	39.85	30.98	14.01	48.44	52.28
C_{14}	35.67	42.41	30.22	44.69	48.42	52.10
C_{13}	36.38	38.45	15.78	47.34	47.19	46.83
C_{12}	38.34	32.06	31.63	44.31	45.92	46.74
C_{11}	36.94	41.71	27.07	39.38	52.17	50.58
C_{15}	41.77	38.08	27.26	46.51	48.63	55.41
C_8	35.21	40.97	31.60	47.17	45.60	59.37
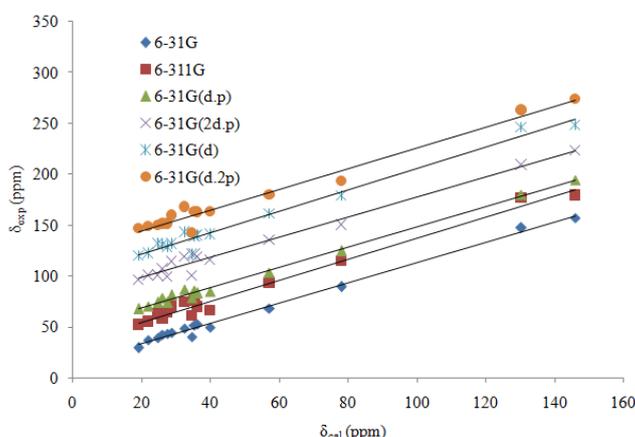
Figure 6: Variation curves of experimental chemical shifts as a function of theoretical chemical shifts at the bases 6-31G, 6-311G, 6-31G(d,p), 6-31G(2d,p), 6-31G(d) and 6-311G (d,2p) for the second product P2

We can see that the relative difference between the calculated values and the experience becomes increasingly systematically lower when the chemical shift believes. Indeed, this error does not exceed the threshold of 20 % for chemical shifts of less than 50 ppm in the most reliable basis 6-31G (d,p).

CONCLUSION

In this study, we used the quantum *ab initio* DFT method to reproduce nuclear magnetic properties of the carbon 13 of the epoxy-himachalene conversion in the presence of a catalytic amount of dichloromethane Lewis acid. The obtained results show that:

- The theoretical calculation of chemical shifts of the reactive R1 shows that the theoretical values calculated by the GIAO method are similar to the experimental results.

- The calculations of the chemical shifts of carbon 13 of the products P1 and P2, have been made by quantum *ab initio* DFT method using the B3LYP functional, at the basies 6-31G, 6-311G, 6-31G (d,p), 6-31G (2d,p), 6-31G (d) and 6-311G (d,2p). This study shows that the theoretical values obtained by the basis 6-31G (d,p) are in good agreement with the experimental values of the P1 and P2 products.

Finally, the density functional theory can be used as an effective approach chemical shift calculations to ^{13}C.

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