

# $^{15}\text{N}$ NMR AND $^1\text{J}_{\text{CH}}$ SPIN-SPIN COUPLING CONSTANTS INVESTIGATIONS OF 2-(1-CYCLOHEXENYL)ETHYLAMINE AS EXPERIMENTAL AND THEORETICAL

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## ABSTRACT

The magnitude of one bond  $^1\text{J}_{\text{CH}}$  coupling constants, proton coupled  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR spectra for 2-(1-Cyclohexenyl)ethylamine (CyHEA) molecule have been reported for the first time.  $^{15}\text{N}$  NMR chemical shift and  $^1\text{J}_{\text{CH}}$  coupling constants of CyHEA ( $\text{C}_8\text{H}_{15}\text{N}$ ) have been calculated by means of the Becke-3-Lee-Yang-Parr (B3LYP) density functional method with 6-311++G(d,p) basis set. Comparison between experimental and theoretical results indicates that density functional B3LYP method is in good agreement with the experimental NMR data.

**Keywords:** 2-(1-Cyclohexenyl)ethylamine, coupling constant, NMR, DFT.

## 2-(1-SİKLOHEKZENİL)ETİLAMİNİN $^{15}\text{N}$ NMR VE $^1\text{J}_{\text{CH}}$ SPİN-SPİN ÇİFTLENİM SABİTLERİNİN İNCELENMESİ

### ÖZET

2-(1-Siklohekzenil)etilamin (CyHEA) molekülünün tek bağ  $^1\text{J}_{\text{CH}}$  çiftlenim sabitlerinin büyüklüğü ve proton çiftlenimli  $^{13}\text{C}$  ile  $^{15}\text{N}$  NMR spektrumları ilk kez elde edilmiştir. CyHEA ( $\text{C}_8\text{H}_{15}\text{N}$ ) molekülünün  $^{15}\text{N}$  NMR kimyasal kayma değeri ve  $^1\text{J}_{\text{CH}}$  çiftlenim sabitleri 6-311++G(d,p) baz seti ile Becke-3-Lee-Yang-Parr (B3LYP) yoğunluk fonksiyonel yöntemi kullanılarak hesaplanmıştır. Deneysel ve teorik sonuçlar arasındaki karşılaştırma B3LYP yoğunluk fonksiyonel metodunun deneysel NMR veriler ile uyum içerisinde olduğunu göstermektedir.

**Anahtar kelimeler:** 2-(1-Siklohekzenil)etilamin, çiftlenim sabiti, NMR, DFT.

### I. INTRODUCTION

GIAO/DFT (Gauge Including Atomic Orbitals/Density Functional Theory) approach is widely used for the calculations of chemical shifts for different types of compounds [1-4]. During the last decade an important breakthrough in the calculation of NMR spin-spin coupling constants took place when the coupled-perturbed approach

was implemented within the DFT framework [5-6]. At present with this methodology an interesting variety of spin-spin coupling constants can be calculated with good accuracy in polyatomic systems using reasonable computational resources [7].

Previously, we reported some experimental and theoretical infrared and NMR spectroscopic properties of CyHEA ( $\text{C}_8\text{H}_{15}\text{N}$ ) [4]. We also prepared Hofmann-type complexes by using this molecule as a ligand in our previous study [8]. In this work, we have decided to measure  $^1\text{J}_{\text{CH}}$  in order to get a deeper insight into the electronic structure of CyHEA and to see the hybridization and type of the bond effects on  $^1\text{J}_{\text{CH}}$  coupling constants. Hence, we have reported the magnitude of one bond  $^1\text{J}_{\text{CH}}$  coupling constants, proton coupled  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR spectra for the title molecule for the first time.  $^{15}\text{N}$  NMR chemical shift and the magnitude of one bond  $^1\text{J}_{\text{CH}}$  coupling constants of CyHEA have been calculated by using B3LYP method with 6-311++G(d,p) basis set.

## II. EXPERIMENTAL STUDY

The pure CyHEA in the liquid form was obtained from Aldrich Chemical Co., USA and used without further purification. NMR experiments were performed in Bruker AVANCE 500 spectrometer using 5 mm BBO probe at 300 K. In order to prevent the overlapping of the solvent and sample peaks, CyHEA was dissolved in  $\text{CDCl}_3$ . Chemical shifts were reported in ppm relative to TMS and formamide for proton coupled  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR spectra, respectively. Proton coupled  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR spectra were obtained at a base frequency of 125.76 MHz for  $^{13}\text{C}$  and 50.67 MHz for  $^{15}\text{N}$  nuclei. For proton coupled  $^{13}\text{C}$  NMR spectroscopy, the pulse sequence used a delay (D1) and acquisition time (AQ) of 2.0 s and 1.1 s, respectively, a spectral width of 29761.904 Hz, 64K data points,  $90^\circ$  pulse (8.30  $\mu\text{s}$ ) and 16 scans. For  $^{15}\text{N}$  NMR spectroscopy, the pulse sequence used a delay (D1) and acquisition time (AQ) of 5.0 s and 0.64 s, respectively, a spectral width of 25510.203 Hz, 32K data points,  $90^\circ$  pulse (15.00  $\mu\text{s}$ ) and 2000 scans. All NMR spectra were recorded using 5 mm sample tubes.

## III. COMPUTATIONAL DETAILS

For the NMR calculations, molecular structure of CyHEA was first fully optimized at 6-31G(d) level in chloroform ( $\epsilon = 4.9$ ) by using the IEFPCM method [1-4]. After optimization,  $^{15}\text{N}$  NMR chemical shift ( $\delta_{\text{N}}$ ) and coupling constants ( $^1\text{J}_{\text{CH}}$ ) were calculated using the GIAO method [1-4] in chloroform at the B3LYP/6-311++G(d,p)//6-31G(d) level under the keyword nmr = spinspin. Relative chemical shift was then estimated by using the corresponding formamide shielding calculated in advance at the same theoretical level as the reference. Calculated  $^{15}\text{N}$  isotropic chemical shielding for formamide at the B3LYP/6-311++G(d,p)//6-31G(d) levels in chloroform by using the IEFPCM method was 135.06 ppm. All the calculations were performed by using Gaussian 03 program package on a personal computer [9].

## IV. RESULTS AND DISCUSSION

The optimized molecular structure of CyHEA is presented in Figure 1. All the experimental values for  $^1\text{J}_{\text{CH}}$  coupling constants of the title molecule are given in Table 1. Substituents and hybridization of the carbon atom have crucial effects on C-H coupling constants. CyHEA molecule is good example to see those effects.

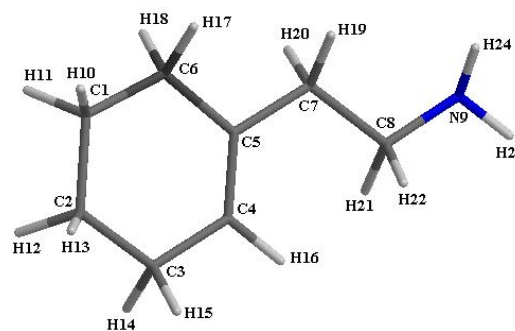


Figure 1. The optimized molecular structure of CyHEA at used method.

$^1\text{J}_{\text{CH}}$  coupling constants for the title molecule are derived from the proton coupled  $^{13}\text{C}$  NMR spectrum of this molecule (Figure 2). In the CyHEA molecule, owing to  $\text{sp}^2$  type hybridization of  $\text{C}_4$  carbon atom,  $\text{C}_4\text{-H}_{16}$  has the strongest coupling constant when compared the other C-H couplings in this molecule.  $\text{C}_7\text{-H}_{19, 20}$  has the second largest coupling constant value for CyHEA. Since in our previous study [4], we showed that  $\text{H}_{16}\text{-H}_{19, 20}$  and  $\text{H}_{19, 20}\text{-H}_{23, 24}$  have an interaction through space, this second largest value could be attributed to neighbouring  $\text{-C}_4=\text{C}_5\text{-}$  double bond and electronegative  $\text{N}_9$  atom.

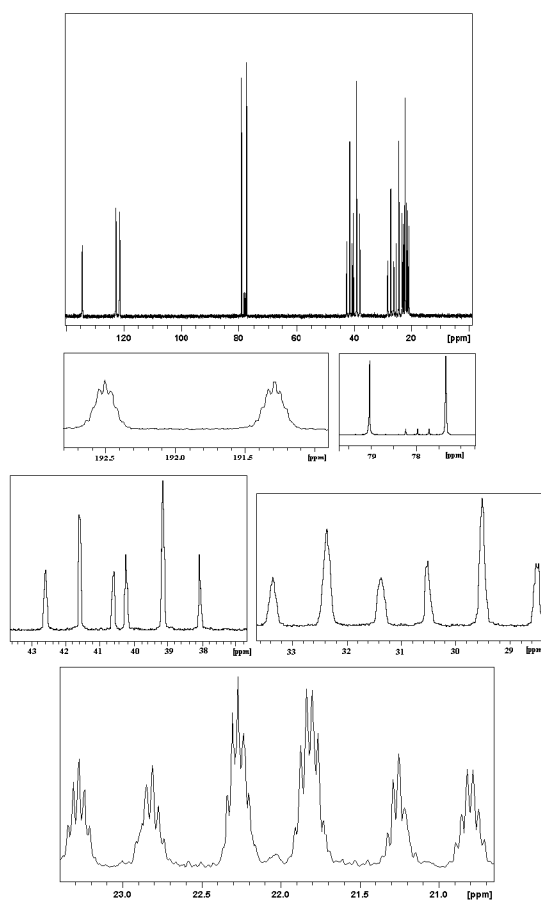


Figure 2. Proton coupled  $^{13}\text{C}$  NMR spectrum of CyHEA.

Formamide has a chemical shift  $\delta = 112$  ppm [10], and the theoretical calculation we conducted for nitrogen nucleus was performed relative to formamide.  $^{15}\text{N}$  NMR spectrum of

the title molecule is given in Figure 3. As seen in Figure 3,  $^{15}\text{N}$  peak of CyHEA is 91.31 ppm (Table 1).

Table 1.  $^{15}\text{N}$  NMR chemical shifts (ppm) and  $^1\text{J}_{\text{CH}}$  coupling constants (Hz) of CyHEA.

$^1\text{J}(\text{C}_n\text{H}_n)$	Experimental	B3LYP
$\text{C}_4\text{H}_{16}$	152.72	148.25
$\text{C}_7\text{H}_{19}\text{H}_{20}$	135.66	133.39
$\text{C}_1\text{H}_{10}\text{H}_{11}$	127.13	126.61
$\text{C}_2\text{H}_{12}\text{H}_{13}$	126.22	125.09
$\text{C}_3\text{H}_{14}\text{H}_{15}$	125.54	124.22
$\text{C}_6\text{H}_{17}\text{H}_{18}$	124.36	122.87
$\text{C}_8\text{H}_{21}\text{H}_{22}$	123.47	121.73
$^{15}\text{N}$ NMR	Experimental	B3LYP
$\text{N}_9$	91.31	99.13

We have calculated the theoretical and experimental magnitude of one bond  $^1\text{J}_{\text{CH}}$  coupling constants, proton coupled  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR spectra for the title compound. Then, we have compared the theoretical and experimental  $^{15}\text{N}$  chemical shifts and  $^1\text{J}_{\text{CH}}$  coupling constants of CyHEA. The results are shown in Table 1. According to these results, the calculated chemical shift and coupling constants are in compliance with the experimental data. The  $^1\text{J}_{\text{CH}}$  correlation graphic is also presented in Figure 4 based on the calculation. The correlation value for  $^1\text{J}_{\text{CH}}$  coupling constants of CyHEA is found to be 0.99701 for B3LYP with the 6-311++G(d,p) basis set. It can be seen that B3LYP calculations are in good agreement with all the experimental findings.

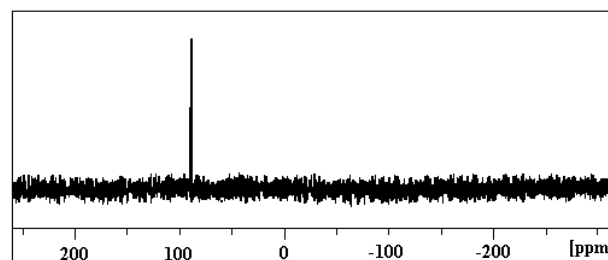


Figure 3.  $^{15}\text{N}$  NMR spectrum of CyHEA.

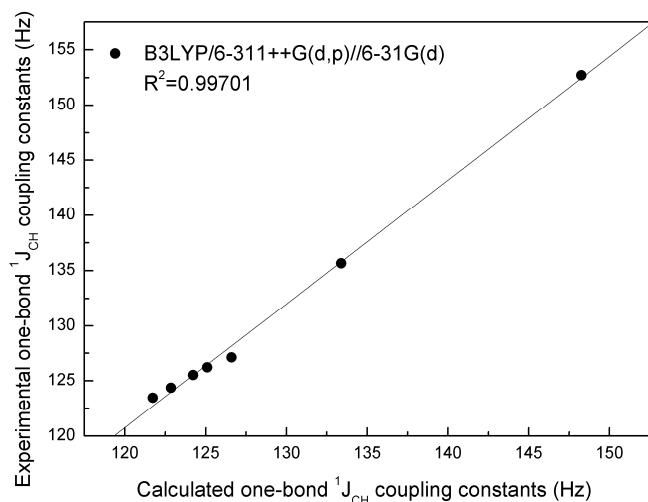


Figure 4. Plot of the calculated vs. the experimental  $^1\text{J}_{\text{CH}}$  coupling constants (Hz) of CyHEA.

## V. CONCLUSIONS

The experimental and theoretical investigations of CyHEA molecule have been performed successfully by using NMR and quantum chemical calculations. Moreover, hybridization and type of the bond effects on  $^1\text{J}_{\text{CH}}$  coupling constants for title molecule have been clearly observed in present study. For all calculations, it is shown that the results of B3LYP method are excellent agreement with all the experimental findings.

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