

## Experimental and Theoretical $^{15}\text{N}$ NMR and $^1\text{J}_{\text{CH}}$ Spin-Spin Coupling Constants Investigation of 1-Phenylpiperazine

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Received: 11 December 2009, Accepted: 09 April 2010

**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 1-Phenylpiperazine (pp) have been reported for the first time.  $^{15}\text{N}$  NMR chemical shifts and  $^1\text{J}_{\text{CH}}$  coupling constants of pp ( $\text{C}_{10}\text{H}_{14}\text{N}_2$ ) have been calculated by means of the Becke-3-Lee-Yang-Parr (B3LYP) density functional method with the 6-311++G(d,p) basis set. Comparison between the experimental and theoretical results indicates that DFT/B3LYP method is in good agreement with the experimental data for predicting NMR properties.

**Key words:** 1-Phenylpiperazine, NMR, coupling constant, DFT, B3LYP.

## 1-Fenilpiperazinin $^{15}\text{N}$ NMR ve $^1\text{J}_{\text{CH}}$ Spin-Spin Çiftlenim Sabitlerinin Deneysel ve Kuramsal Olarak İncelenmesi

**Özet:** 1-Fenilpiperazin (pp) molekülünün proton çiftlenimli  $^{13}\text{C}$  ve  $^{15}\text{N}$  NMR spektrumları ilk kez elde edilmiştir. Fenilpiperin ( $\text{C}_{10}\text{H}_{14}\text{N}_2$ ) molekülünün  $^{15}\text{N}$  NMR kimyasal kayma değerleri 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 kuramsal sonuçlar arasındaki karşılaştırma tahmin edilen NMR özellikleri için DFT/B3LYP yönteminin deneysel veriler ile uyum içerisinde olduğunu göstermektedir.

**Anahtar kelimeler:** 1-Fenilpiperazin, NMR, çiftlenim sabiti, DFT, B3LYP.

### 1. Introduction

1-Phenylpiperazine consists of phenyl group attached to one of the nitrogens of piperazine an organic compound with a six-membered ring containing two opposing nitrogen atoms. Previously, we reported some experimental and theoretical infrared and NMR spectroscopic properties of pp [1]. We also prepared Hofmann-type complexes and clathrates by using this molecule as a ligand in our previous studies [2, 3]. The free pp exists in a chair conformation because of the steric crowding present in the boat form and prefers equatorial phenyl– axial NH chair form. However, this molecule can also coordinate in the boat form as a bidentate ligand, in the chair form as a bidentate ligand or as a unidentate ligand coordinating only through the NH nitrogen [1-3].

DFT methods with GIAO (Gauge Including Atomic Orbitals) approach are widely used for the calculations of chemical shifts for different types of compounds [1, 4-8]. During the last decade and important breakthrough in the calculation of NMR spin-spin coupling constants took place when the coupled-perturbed approach was implemented within the DFT framework [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 [9].

In this work, in order to get a deeper insight into the electronic structure of pp and to see the hybridization and type of the bond effects on  $^1J_{CH}$  coupling constants, we have decided to measure  $^1J_{CH}$  coupling constants. Henceforth, we have reported the magnitude of one bond  $^1J_{CH}$  coupling constants, proton coupled  $^{13}C$  NMR and  $^{15}N$  NMR spectra for the title molecule for the first time.  $^{15}N$  NMR chemical shifts and the magnitude of one bond  $^1J_{CH}$  coupling constants of pp have also been calculated at B3LYP level of theory using the 6-311++G(d,p) basis set.

## 2. Materials and Methods

The pure pp molecule in the liquid form was obtained from Aldrich Chemical Co. (% 99), USA and used without further purification. NMR experiments were performed in Bruker AVANCE 500 spectrometer using 5 mm BBO probe at 300 K. The pp was dissolved in MeOD deuterated solvent. Chemical shifts were reported in ppm relative to TMS and formamide for proton coupled  $^{13}C$  NMR and  $^{15}N$  NMR spectra, respectively. Proton coupled  $^{13}C$  NMR and  $^{15}N$  NMR spectra were obtained at a base frequency of 125.76 MHz for  $^{13}C$  and 50.66 MHz for  $^{15}N$  nuclei. For proton coupled  $^{13}C$  NMR spectroscopy, the pulse sequence used a delay (D1) and acquisition time (AQ) of 2.0 s and 5.19 s, respectively, a spectral width of 29761.904 Hz, 64K data points,  $90^0$  pulse (8.30  $\mu$ s) and 256 scans. For  $^{15}N$  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,  $90^0$  pulse (15.00  $\mu$ s) and 2000 scans. All spectra were recorded at room temperature.

## 3. Calculations

For the NMR calculations, molecular structure of pp while phenyl group was in the equatorial position and NH group was in the axial position was first fully optimized at B3LYP/6-31G(d) level in methanol ( $\epsilon = 32.63$ ) by using the IEFPCM method [1, 4, 5]. After optimization,  $^{15}N$  NMR chemical shifts ( $\delta_N$ ) and coupling constants ( $^1J_{CH}$ ) were calculated using the GIAO [1, 4, 5] method in methanol at the B3LYP/6-311++G(d,p)//6-31G(d) levels under the keyword nmr = spinspin. Relative chemical shifts were then estimated by using the corresponding formamide shielding calculated in advance at the same theoretical level as the reference. All the calculations were performed by using Gaussian 03 program package on a personal computer [10].

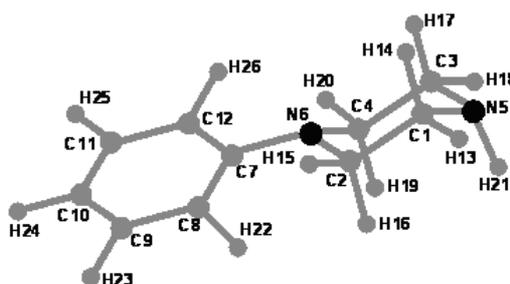


Figure 1. The optimized molecular structure of pp at used methods.

#### 4. Results and Discussion

The optimized molecular structure of pp is presented in Figure 1. All the experimental values for  $^1J_{CH}$  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.  $^1J_{CH}$  coupling constants of pp are derived from the proton coupled  $^{13}C$  NMR spectrum (Figure 2).  $C_8$ ,  $C_9$ ,  $C_{10}$ ,  $C_{11}$  and  $C_{12}$  carbon atoms on phenyl ring show  $sp^2$  hybridization so they have stronger C-H coupling constants than  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  carbon atoms possessing  $sp^3$  type hybridization on piperazine ring. In phenyl ring, owing to attached piperazine molecule, it was observed that the magnitude of  $^1J(C_{10}, H_{24})$  slightly bigger than  $^1J(C_{9,11}, H_{23,25})$  and  $^1J(C_{8,12}, H_{22,26})$ .

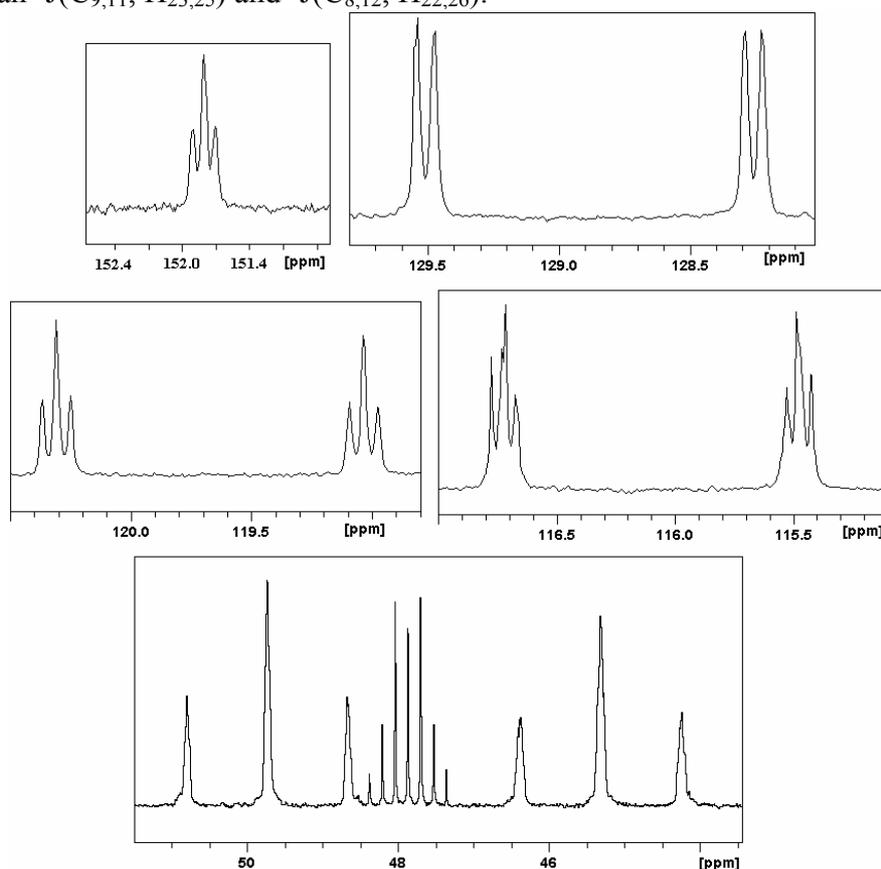


Figure 2. Proton coupled  $^{13}C$  NMR spectrum of pp.

Table 1. The experimental and calculated  $^1J_{CH}$  NMR coupling constants (Hz) and chemical shifts (ppm) of pp.

$^1J(C_nH_n)$	Exp.	B3LYP	Nucleus	Exp.*	B3LYP*
$C_2H_{15}H_{16}$ , $C_4H_{19}H_{20}$	133.26	130.33	$C_1, C_3$	45.31	46.10
$C_1H_{13}H_{14}$ , $C_3H_{17}H_{18}$	135.13	131.48	$C_2, C_4$	49.72	51.05
$C_8H_{22}$ , $C_{12}H_{26}$	155.54	151.76	$C_8, C_{12}$	116.11	112.85
$C_9H_{23}$ , $C_{11}H_{25}$	157.32	153.44	$C_{10}$	119.68	114.53
$C_{10}H_{24}$	160.11	157.48	$C_9, C_{11}$	128.88	123.88
			$C_7$	151.87	147.80

\* Reported by ALVER et al. [1], Exp.: Experimental.

All the experimental and theoretical investigations for nitrogen atom were performed relative to formamide ( $\delta = 112$  ppm, downfield of liquid ammonia) [11]. The calculated  $^{15}\text{N}$  chemical shift values of pp are 69.03 ( $\text{N}_5$ ) ppm and 32.19 ( $\text{N}_6$ ) ppm while the experimental values are 65.20 ppm and 31.70 ppm, respectively. The  $^{15}\text{N}$  chemical shift values of pp are absolute  $^{15}\text{N}$  values rescaled relative to formamide. Therefore, it can be said that  $^{15}\text{N}$  peaks of pp are about 65 ppm and 32 ppm upfield of formamide in the magnetic field region.  $^{15}\text{N}$  NMR spectrum of the title molecule is given in Figure 3. The basic relaxation mechanism is due to dipole dipole interactions. Henceforth, for a given relaxation delay,  $\text{N}_6$  nucleus can easily be observed in  $^{15}\text{N}$  NMR spectrum as in the case of pp molecule. As for  $\text{N}_5$ , larger relaxation values are required.

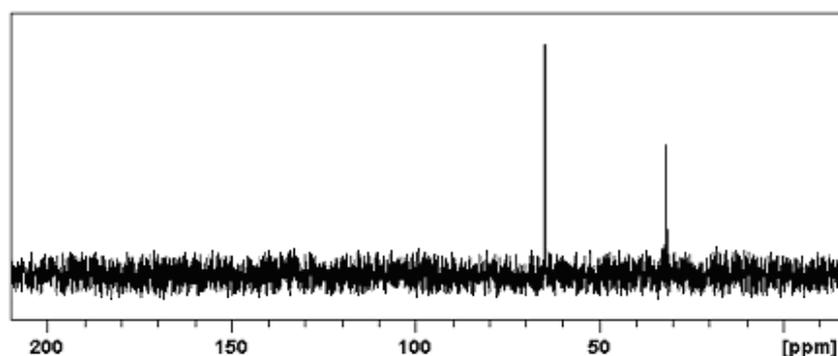


Figure 3.  $^{15}\text{N}$  NMR spectra of pp.

We have also computed the magnitude of one bond  $^1\text{J}_{\text{CH}}$  coupling constants of pp (Table 1). The biggest difference between the experimental and calculated  $^1\text{J}_{\text{CH}}$  coupling constants is 3.88 Hz. In order to compare the experimental and calculated  $^1\text{J}_{\text{CH}}$  coupling constants, the correlation graphics are presented in Figure 4. The correlation value is found to be 0.99907. Regarding the results, it can be seen that B3LYP calculations are in good agreement with all the experimental findings.

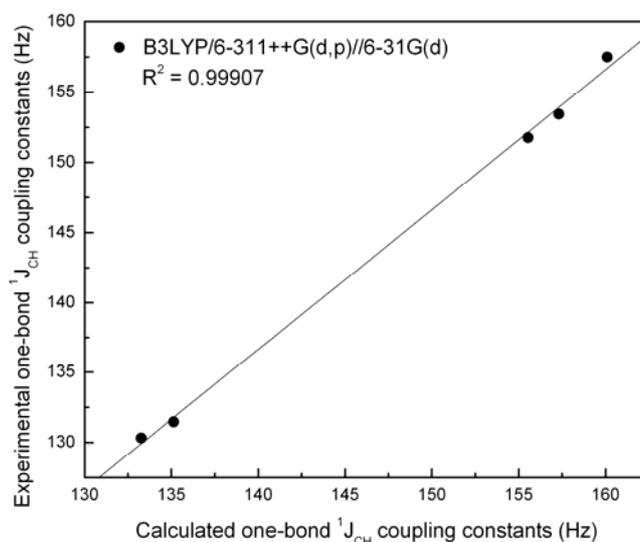


Figure 4. Plot of the calculated and experimental  $^1\text{J}_{\text{CH}}$  coupling constants (Hz) of pp.

## 5. Conclusion

The experimental and theoretical investigations of pp have been performed successfully by using NMR and quantum chemical calculations. Moreover, hybridization and type of the bond effects on  $^1J_{CH}$  coupling constants for title molecule have been clearly observed in present study. Any differences observed between the experimental and the calculated coupling constants and chemical shifts could be due to the fact that the calculations have been performed for a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. For all calculations, it is shown that the results of B3LYP method are excellent agreement with all the experimental findings.

## References

- [1] Alver Ö., Parlak C., Şenyel M., 2007. FT-IR and NMR investigation of 1-Phenylpiperazine: A combined experimental and theoretical study, *Spectrochimica Acta A*, 67: 793–801.
- [2] Şenyel M., Parlak C., Alver Ö., 2008. FT-IR spectroscopic investigation of some Hofmann type complexes:  $M(1\text{-Phenylpiperazine})_2Ni(CN)_4$  ( $M = Ni, Co, Cd, Pd$  or  $Mn$ ), *Spectrochimica Acta A*, 70: 367–375.
- [3] Parlak C., Alver Ö., Şenyel M., 2009. Vibrational spectroscopic study on some Hofmann type clathrates:  $M(1\text{-Phenylpiperazine})_2Ni(CN)_4 \cdot 2G$  ( $M = Ni, Co$  and  $Cd$ ;  $G = Aniline$ ), *Journal of Molecular Structure*, 919: 41–46.
- [4] Alver Ö., Parlak C., Şenyel M., 2007.  $^1H$ ,  $^{13}C$  NMR and  $^nJ_{CH}$  coupling constants investigation of 4-Phenylpyridine: A combined experimental and theoretical study, *Physics Letters A*, 371: 300–306.
- [5] Parlak C., Alver Ö., Şenyel M., 2008. Experimental and theoretical NMR study of 4-(3-Cyclohexen-1-yl)pyridine. *Spectrochimica Acta A*, 69: 1252–1256.
- [6] Helgaker T., Jaszunski M., Ruud K., 1999. Ab-initio methods for the calculations of NMR shielding and indirect spin-spin coupling constants, *Chemical Reviews*, 99: 293-352.
- [7] Barone G., Paloma L.G., Duca D., Silvestri A., Riccio R., Bifulco G., 2002. Structure Validation of Natural Products by Quantum-Mechanical GIAO Calculations of  $^{13}C$  NMR Chemical Shifts. *Chemistry A European Journal*, 8 (14): 3233-3239.
- [8] Atalay Y., Avcı D., 2008. GIAO Calculations of Chemical Shifts in Ethene-1,1,2, 2-tetrahydropyridine tetrathiocyanate, *Spectroscopy Letters*, 41: 116–121.
- [9] Bifulco G., Bassarello C., Riccio R., Paloma L.G., 2004. Quantum mechanical calculations of NMR J coupling values in the determination of relative configuration in organic compounds, *Organic Letters*, 6: 1025-1028.
- [10] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A., Vreven J.R.T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzales C., Pople J.A., 2003. Gaussian 03 Revision C.02, Gaussian Inc., Pittsburgh.
- [11] Martin G.E., Hadden C.E., 2000. Long-range  $^1H$ - $^{15}N$  heteronuclear shift correlation at natural abundance. *Journal of Natural Products*, 63 (4): 543–585.

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