

NMR SPECTROSCOPIC STUDY AND DFT CALCULATIONS OF VIBRATIONAL ANALYSES, GIAO NMR SHIELDINGS AND $^1J_{CH}$, $^1J_{CC}$ SPIN-SPIN COUPLING CONSTANTS OF 1,7-DIAMINOHEPTANE

Özgür Alver^{1,2*}, Cemal Parlak^{1,2} and Mustafa Şenyel¹

¹Department of Physics, Science Faculty, Anadolu University, 26470, Eskişehir, Turkey
²Plant, Drug and Scientific Research Centre, Anadolu University, 26470, Eskişehir, Turkey

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ABSTRACT. Vibrational frequencies and approximate mode descriptions of 1,7-diaminoheptane (dahp) have been determined via Becke-3-Lee-Yang-Parr (B3LYP) density functional method with 6-31G(d) basis set. 1H , proton coupled and uncoupled ^{13}C , ^{15}N , DEPT, COSY, HETCOR, INADEQUATE NMR spectra and the magnitude of one bond $^1J_{CH}$, $^1J_{CC}$ coupling constants of dahp ($C_7H_{18}N_2$) have been reported for the first time. 1H , ^{13}C , ^{15}N NMR chemical shifts and $^1J_{CH}$, $^1J_{CC}$ coupling constants of dahp have been calculated by means of B3LYP density functional method with 6-311++G(d,p) basis set. Comparison between the experimental and the theoretical results indicates that density functional B3LYP method is able to provide satisfactory results for predicting vibrational frequencies and NMR properties.

KEY WORDS: 1,7-Diaminoheptane, Vibrational assignments, NMR, GIAO, DFT

INTRODUCTION

1,7-Diaminoheptane has been extensively used in many different ways for scientific researches. For example, it has been used as a ligand in various complexes [1] and for the separation of low-molecular mass peptides by capillary electrophoresis [2]. This compound has also been used for synthesizing stable cationic monolayers under proper conditions [3] and as an internal standard for various types of studies [4-7].

Density functional theory (DFT) calculations provide excellent agreement with experimental vibrational frequencies of organic compounds, provided that the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, basis set deficiencies and anharmonicity [8-15]. Furthermore, GIAO/DFT (Gauge Including Atomic Orbitals/Density Functional Theory) approach is extensively used for the calculations of chemical shifts for various types of compounds [14-20]. 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 [19-23]. 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 [24, 25].

NMR is a sensitive and versatile probe of molecular-scale structure and dynamics in solids and liquids. It has been widely used in chemistry, materials and geochemistry [26, 27] and it enables to get faster and easier structural information. The standard 1D and 2D hetero and homonuclear NMR experiments are enough to afford complete assignment of organic compounds and effective to get molecular structure information [28, 29].

In this work, we have reported 1H , proton coupled and uncoupled ^{13}C , ^{15}N , DEPT, COSY, HETCOR, INADEQUATE NMR spectra and the magnitude of one bond $^1J_{CH}$, $^1J_{CC}$ coupling constants of 1,7-diaminoheptane (dahp) for the first time. We have also calculated the vibrational frequencies and 1H , ^{13}C , ^{15}N NMR chemical shifts, $^1J_{CH}$, $^1J_{CC}$ coupling constants of dahp by using B3LYP [30] method with 6-31G(d) and 6-311++G(d,p) basis sets, respectively.

*Corresponding author. E-mail: ozguralver@anadolu.edu.tr

Correlation values based on the least square method for the experimental and theoretical observations have also been determined.

EXPERIMENTAL

The pure dahp 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. The dahp was dissolved in MeOD. Chemical shifts were reported in ppm relative to TMS for ^1H and ^{13}C and relative to formamide for ^{15}N . ^1H , ^{13}C , ^{15}N NMR, DEPT, COSY, HETCOR and INADEQUATE NMR spectra were obtained at a base frequency of 125.76 MHz for ^{13}C and 500.13 MHz for ^1H and 50.66 MHz for ^{15}N nuclei. For proton coupled and uncoupled ^{13}C NMR spectroscopy, the pulse sequence used a delay (D1) and acquisition time (AQ) of 2.0 s and 5.62 s, respectively, a spectral width of 5822.98 Hz, 64 K data points, 90° pulse (8.30 μs) and 16 scans. DEPT spectra were obtained at $\theta_z = 45^\circ$ where CH, CH_2 and CH_3 appear in the positive phase and $\theta_z = 135^\circ$ where CH, CH_3 appear in the positive phase and CH_2 appears in the negative phase. For ^1H NMR experiment D1 = 1.0 s, AQ = 11.39 s, spectral width 2876.87 Hz, 64 K data points, 90° pulse (14.15 μs) and 8 scans were performed. For ^{15}N NMR experiment D1 = 10.0 s, AQ = 0.32 s, spectral width 51021.41 Hz, 32 K data points, 90° pulse (15.0 μs) and 128 scans were performed. Two-dimensional COSY, HETCOR and INADEQUATE techniques were measured using standard micro-programs provided by Bruker.

Calculations

For the vibrational calculations, molecular structure of dahp was optimized by B3LYP with 6-31G(d) basis set. By using the same method and the basis set the vibrational frequencies of dahp were calculated, and then scaled by 0.9613 [14-15, 31-32]. In the calculations all frequencies were positive. Therefore, we were confident that a definite absolute minimum in the potential energy surface was found.

For the NMR calculations, molecular structure of dahp was first fully optimized at 6-31G(d) level in methanol ($\epsilon = 32.63$) by using the IEFPCM method [14-15, 33-34]. After optimization, ^1H , ^{13}C , ^{15}N NMR chemical shifts (δ_{H} , δ_{C} and δ_{N}) and $^1J_{\text{CH}}$, $^1J_{\text{CC}}$ coupling constants were calculated using the GIAO method [14-20] in methanol ($\epsilon = 32.63$) at the B3LYP/6-311++G(d,p)//6-31G(d) level under the keyword nmr = spinspin. Relative chemical shifts were then estimated by using the corresponding TMS and formamide shielding calculated in advance at the same theoretical level as the reference. All the calculations were performed by using GaussView molecular visualization program and Gaussian 03 program package on a personal computer [35, 36].

RESULTS AND DISCUSSION

Vibrational analysis of dahp

The experimental vibrational frequencies and assignments for the dahp molecule in the region of (4000-400) cm^{-1} have been reported by Kasap *et al.* [1]. We have calculated the theoretical vibrational frequencies of the title compound. Then, we have determined its approximate mode descriptions with the DFT calculations. For these calculations, the optimized molecular structure of dahp is shown in Figure 1. The theoretical vibrational frequencies and the assignments of dahp with the experimental data have been compared and the results are given in Table 1.

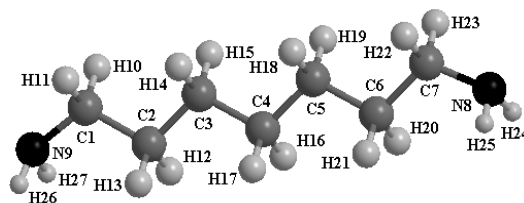


Figure 1. The optimized molecular structure of 1,7-diaminoheptane at used methods.

Table 1. Comparison of the experimental and calculated vibrational frequencies (cm^{-1}) of dahp.

Mode	^a Approximate mode descriptions	^b Exp. ass.	^c dahp in CCl_4	^d B3LYP
ν_1	N(9)H ₂ asym. str.	$\nu_a(\text{NH}_2)$	3367 s	3385 (31.31)
ν_2	N(8)H ₂ asym. str.	-	-	3385 (0.52)
ν_3	NH ₂ sym. str.	$\nu_s(\text{NH}_2)$	3288 s	3304 (27.05)
ν_4	NH ₂ sym. str.	-	-	3304 (1.45)
ν_5	C(1;2;4;6;7)H ₂ asym. str.	-	-	2988 (3.77)
ν_6	C(1;3;4;5;7)H ₂ asym. str.	-	-	2985 (0.05)
ν_7	C(1;2;3;5;6;7)H ₂ asym. str.	-	-	2974 (4.15)
ν_8	C(1;2;3;5;6;7)H ₂ asym. str.	-	-	2958 (0.07)
ν_9	CH ₂ asym. str.	$\nu_a(\text{CH}_2)$	2927 vs	2936 (174.78)
ν_{10}	C(2;3;5;6)H ₂ asym. str.	-	-	2934 (0.11)
ν_{11}	CH ₂ sym. str.	-	-	2863 (1.19)
ν_{12}	C(1;2;6;7)H ₂ sym. str.	-	-	2851 (0.05)
ν_{13}	C(2;3;4;5;6)H ₂ sym. str.	-	-	2849 (2.61)
ν_{14}	CH ₂ sym. str.	$\nu_s(\text{CH}_2)$	2854 vs	2846 (69.08)
ν_{15}	C(1;2;3;5;6;7)H ₂ sym. str.	-	-	2832 (0.28)
ν_{16}	C(2;3;4;5;6)H ₂ sym. str.	-	-	2830 (0.61)
ν_{17}	C(2;4;6)H ₂ sym. str.	-	-	2823 (1.19)
ν_{18}	C(2;3;5;6)H ₂ sym. str.	-	-	2821 (1.93)
ν_{19}	NH ₂ sci.	$\delta(\text{NH}_2)$	1598 s	1606 (41.05)
ν_{20}	NH ₂ sci.	-	-	1606 (0.27)
ν_{21}	C(2;3;4;5;6)H ₂ sci.	-	-	1507 (0.85)
ν_{22}	C(1;2;3;5;6;7)H ₂ sci.	-	-	1499 (0.16)
ν_{23}	CH ₂ sci.	-	-	1489 (0.50)
ν_{24}	C(1;3;5;7)H ₂ sci.	-	-	1480 (0.28)
ν_{25}	CH ₂ sci.	-	-	1477 (0.09)
ν_{26}	C(1;2;3;5;6;7)H ₂ sci.	-	-	1473 (0.07)
ν_{27}	CH ₂ sci.	$\delta(\text{CH}_2)$	1464 s	1462 (5.61)
ν_{28}	C(1;3;4;5;7)H ₂ twi.	-	-	1442 (3.88)
ν_{29}	C(1;2;3;5;6;7)H ₂ twi.	$\delta(\text{CH}_2)$	1439 w	1436 (0.88)
ν_{30}	C(1;7)H ₂ wag.+NH ₂ wag.	$\rho_w(\text{CH}_2)$	1390 w	1391 (1.78)
ν_{31}	C(1;7)H ₂ wag.+NH ₂ wag.	-	-	1391 (0.05)
ν_{32}	CH ₂ wag.	$\rho_w(\text{CH}_2)$	1371 w	1370 (3.04)
ν_{33}	C(1;2;6;7)H ₂ twi.	-	-	1360 (1.66)
ν_{34}	C(1;3;5;7)H ₂ twi.	$\rho_t(\text{CH}_2)$	1356 vw	1358 (0.31)
ν_{35}	C(1;2;4;6;7)H ₂ twi.	-	-	1348 (0.72)
ν_{36}	C(2;3;4;5;6)H ₂ wag.	-	-	1317 (4.22)
ν_{37}	C(2;3;4;5;6)H ₂ wag.	-	-	1317 (0.36)

V ₃₈	CH ₂ wag.+NH ₂ wag.	$\rho_t(\text{NH}_2)$	1308 vw	1306 (0.55)
V ₃₉	C(2;3;5;6)H ₂ +NH ₂ wag.+ C(1;4;7)H ₂ twi.	-	-	1292 (0.12)
V ₄₀	C(4;5)H ₂ +NH ₂ wag.+ C(1;2;3;6;7)H ₂ twi.	-	-	1254 (0.43)
V ₄₁	C(2;3;4;5;6)H ₂ wag.	-	-	1218 (5.44)
V ₄₂	C(2;3;4;5;6)H ₂ +NH ₂ wag.+ C(1;7)H ₂ twi.	-	-	1208 (0.39)
V ₄₃	Skeletal str.	-	-	1105 (6.58)
V ₄₄	C-NH ₂ sym. str.	$\nu(\text{CN})$	1093 w	1090 (1.21)
V ₄₅	C-NH ₂ sym. str.	$\nu(\text{CN})$	1072 m	1072 (6.88)
V ₄₆	CH ₂ +NH ₂ wag.	-	-	1061 (0.56)
V ₄₇	C(1;2;5;6;7)H ₂ +NH ₂ wag.+ C(3;4)H ₂ twi.	$\rho_w(\text{NH}_2)$	1016 vw	1028 (1.65)
V ₄₈	C(4)-C(5) sym. str.	-	-	1021 (0.71)
V ₄₉	C(2)-C(3)+ C(5)-C(6) sym. str.	-	-	1013 (0.24)
V ₅₀	C(1;6)-C(2;7)-N(9;8) sym.; asym. str.	-	-	1003 (4.12)
V ₅₁	C-NH ₂ asym. str.+C(3)-C(4) sym. str.	-	-	968 (0.14)
V ₅₂	Skeletal str.	-	-	964 (0.11)
V ₅₃	C(3;4;5;6)H ₂ rock+NH ₂ wag.+ C(1;7)H ₂ twi.	$\rho_t(\text{CH}_2)$	954 s, sh	952 (8.94)
V ₅₄	C-NH ₂ sym. str.	-	-	879 (0.65)
V ₅₅	C-NH ₂ sym. str.	-	-	867 (2.82)
V ₅₆	C(2;3;4;5)H ₂ rock+NH ₂ wag.+ C(1;7)H ₂ twi.	$\rho_t(\text{CH}_2)$	840 m, br	842 (4.48)
V ₅₇	CH ₂ rock	-	-	798 (0.55)
V ₅₈	C(3)H ₂ wag.+ C(1;2;4;5;6;7)H ₂ twi.	-	-	749 (0.38)
V ₅₉	C(1;2;3;5;6;7)H ₂ twi.	-	-	731 (0.35)
V ₆₀	C(2;3;4;5)H ₂ rock.	$\rho_t(\text{CH}_2)$	725 w	725 (1.81)
V ₆₁	Skeletal bend	-	-	502 (1.37)
V ₆₂	Skeletal bend	-	-	435 (2.63)
V ₆₃	Skeletal bend	-	-	412 (4.17)

IR intensities (km/mol) are in parenthesis. Exp., experimental; ass., assignments; ν , very; s, strong; m, medium; w, weak; sh, shoulder; br, broad; str., stretching; bend, bending; sci., scissoring; twi., twisting; wag., wagging; rock., rocking; sym., symmetric; asym., asymmetric; ^aOur vibrational frequency assignments on the basis of the DFT (B3LYP) calculations. ^{b,c} Taken from Ref. [1]. ^dScaling factor = 0.9613 for B3LYP [14-15, 31-32] with 6-31G(d) basis set.

The dahp molecule consists of 27 atoms, so it has 75 normal vibrational modes and it belongs to the point group C_1 with only identity (E) symmetry element or operation. It is difficult to determine the dahp molecule's experimental vibrational assignments due to its low symmetry (Table 1). According to the calculations the twelve normal vibrational modes of title molecule are below the 400 cm^{-1} . As it can be seen from Table 1, if the vibrational assignments are investigated one-by-one, the experimental assignments of the dahp are also consistent with that determined by DFT calculations, and there is a good agreement between the experimental and the theoretical vibrational frequencies in the region of (4000-400) cm^{-1} . The NH₂ asymmetric and symmetric stretching frequencies observed at 3367 cm^{-1} and 3288 cm^{-1} are theoretically predicted at 3385 cm^{-1} and 3304 cm^{-1} , respectively. Calculated ν_1 and ν_2 (or ν_3 and ν_4) vibrational modes have the same frequency values due to molecular symmetry of dahp molecule (Table 1). For CH₂ stretching bands between (3000-2800) cm^{-1} , the experimental findings are highly compatible with the theoretical predictions. The biggest difference between experimental and calculated frequencies is 18 cm^{-1} . In general, the calculated intensities are very high when compared to those in the higher frequency region. Among the calculated fundamentals, the best agreement between the experimental and the calculated intensities is in low frequency region. We have noted that the experimental results belong to liquid phase and theoretical calculations belong to gaseous phase.

In order to compare the experimental vibrational frequencies, the correlation graphic based on the calculations has been presented in Figure 2. The correlation value is found to be 0.99995 for B3LYP with 6-31G(d) basis set. It can be seen that the results of B3LYP calculations are in compliance with experimental findings.

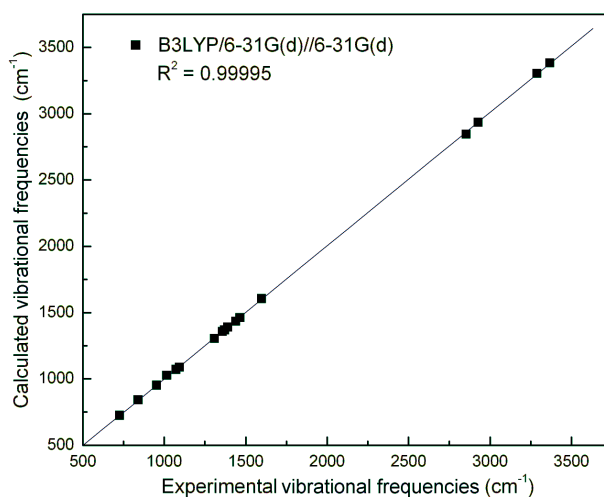


Figure 2. Plot of the calculated vs. the experimental vibrational frequencies of dahp molecule.

NMR study of dahp

All the experimental chemical shift values for ^{13}C and ^1H measurements of dahp are given in Table 2-3. As shown in Figure 1, dahp molecule shows four different carbon atoms, which is in agreement with the structure regarding the molecular symmetry. Due to that fact, in Figure 3, four carbon peaks are observed in ^{13}C NMR spectrum of dahp. In DEPT 45 and DEPT 135 spectra (Figure 4), all the peaks are upward and downward, respectively, because of CH_2 groups. As can be seen from Figure 3 and Figure 5, $\text{C}_{1,7}$ and $\text{H}_{10,11}$, $\text{H}_{22,23}$ are observed at the most upfield magnetic region.

Table 2. Experimental and calculated ^{13}C and ^1H NMR chemical shifts (ppm) of dahp.

Carbon	Experimental (ppm)	B3LYP (ppm)
C_1, C_7	43.11	50.86
C_2, C_6	34.35	41.51
C_4	30.81	37.58
C_3, C_5	28.38	34.13
Proton	Experimental (ppm)	B3LYP (ppm)
$\text{H}_{10,11}, \text{H}_{22,23}$	2.65	2.52
$\text{H}_{12,13}, \text{H}_{20,21}, \text{H}_{24,25}, \text{H}_{26,27}$	1.50	1.27
$\text{H}_{14,15}, \text{H}_{16,17}, \text{H}_{18,19}$	1.38	1.20

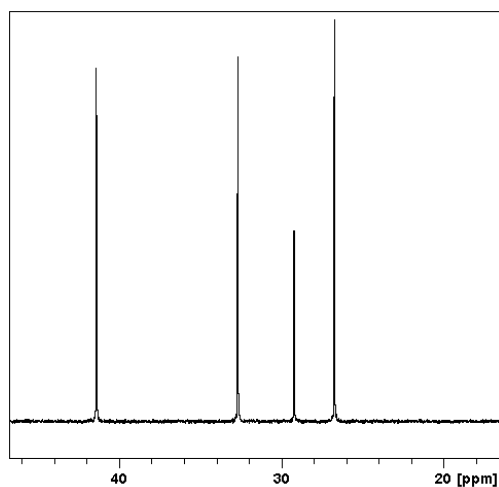


Figure 3. ^{13}C NMR spectrum of dahp (δ , ppm).

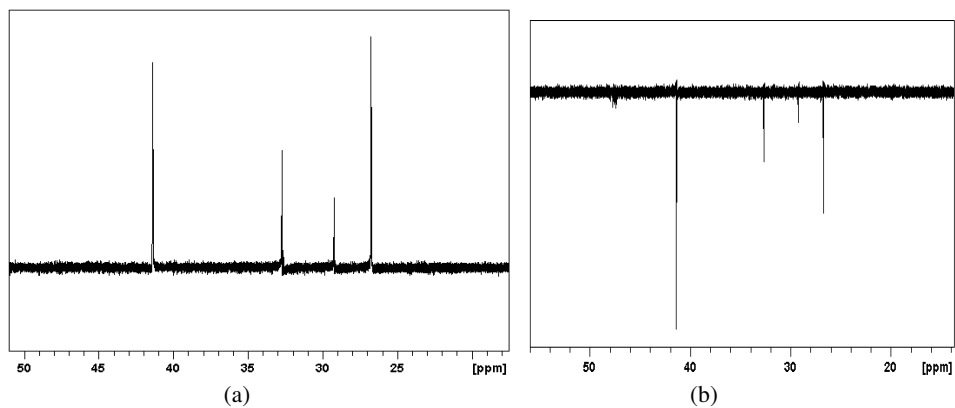


Figure 4. DEPT 45 (a) and DEPT 135 (b) NMR spectra of dahp (δ , ppm).

Formamide (^{15}N) has a chemical shift $\delta = 112$ ppm (downfield of liquid ammonia) [37]. The experimental ^{15}N chemical shift appears at 21.24 ppm (Figure 6). The theoretically calculated ^{15}N chemical shift is 86.74 ppm. The theoretical calculation of ^{15}N nucleus was performed relative to formamide. Henceforth, the experimental ^{15}N value of the title molecule was rescaled relative to formamide. Therefore, it can be said that experimental ^{15}N peak of the dahp is 90.76 ppm upfield of formamide ^{15}N peak.

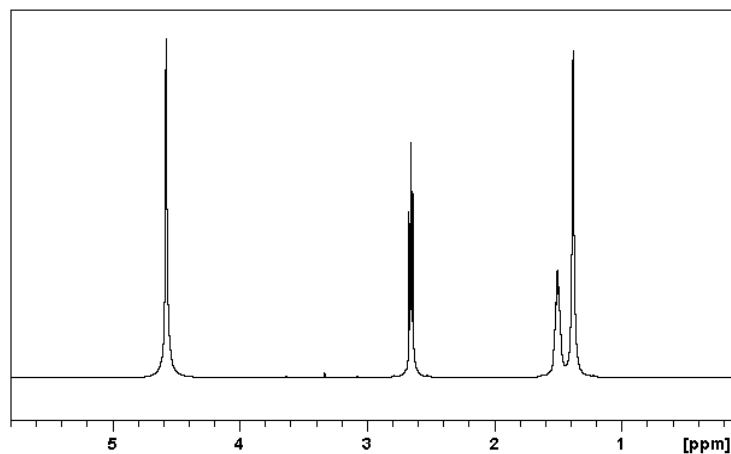


Figure 5. ^1H NMR spectrum of dahp (δ , ppm).

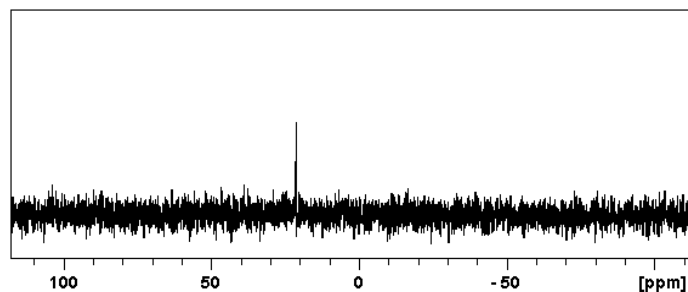


Figure 6. ^{15}N NMR spectrum of dahp (δ , ppm).

The title molecule is symmetric along the both sides of C_4 atom. Therefore, only one side of dahp has the complete NMR information. From 2D COSY NMR spectrum (Figure 7), all the connections between the hydrogen atoms are clearly observed. The correlations between $\text{C}_1\text{-H}_{10-11}$, $\text{C}_2\text{-H}_{12-13}$, $\text{C}_3\text{-H}_{14-15}$, $\text{C}_4\text{-H}_{16-17}$, $\text{C}_5\text{-H}_{18-19}$, $\text{C}_6\text{-H}_{20-21}$, $\text{C}_7\text{-H}_{22-23}$ are clearly observed in HETCOR spectrum (Figure 7). If 2D INADEQUATE spectrum (Figure 7) is investigated, the carbon skeletal structure of the title molecule and carbon-carbon couplings can be clearly identified.

In order to determine $^1J_{\text{CC}}$ and $^1J_{\text{CH}}$ coupling constant values (Table 3), proton coupled ^{13}C NMR and 2D INADEQUATE NMR spectra (Figure 7) were used, respectively. There is a simple correlation between $^1J_{\text{CH}}$ and the hybridization of the carbon atom involved; $^1J_{\text{CH}} = 500s$ [38]. The quantity s can assume values which range from 0.25 to 0.5 as the hybridization changes from sp^3 to sp . If we take into account the mentioned relation for $^1J_{\text{CH}}$ coupling constants, the experimentally obtained results for dahp (Table 3) seem reasonable. Moreover substituents have considerable influence on C, H coupling constants [38]. It can be seen that electronegative amine groups lead to an increase in the $^1J_{\text{CH}}$ coupling constant values for dahp molecule (Table 3) as expected. It is possible to see the same effect for $^1J_{\text{CC}}$ coupling constants as well (Table 3).

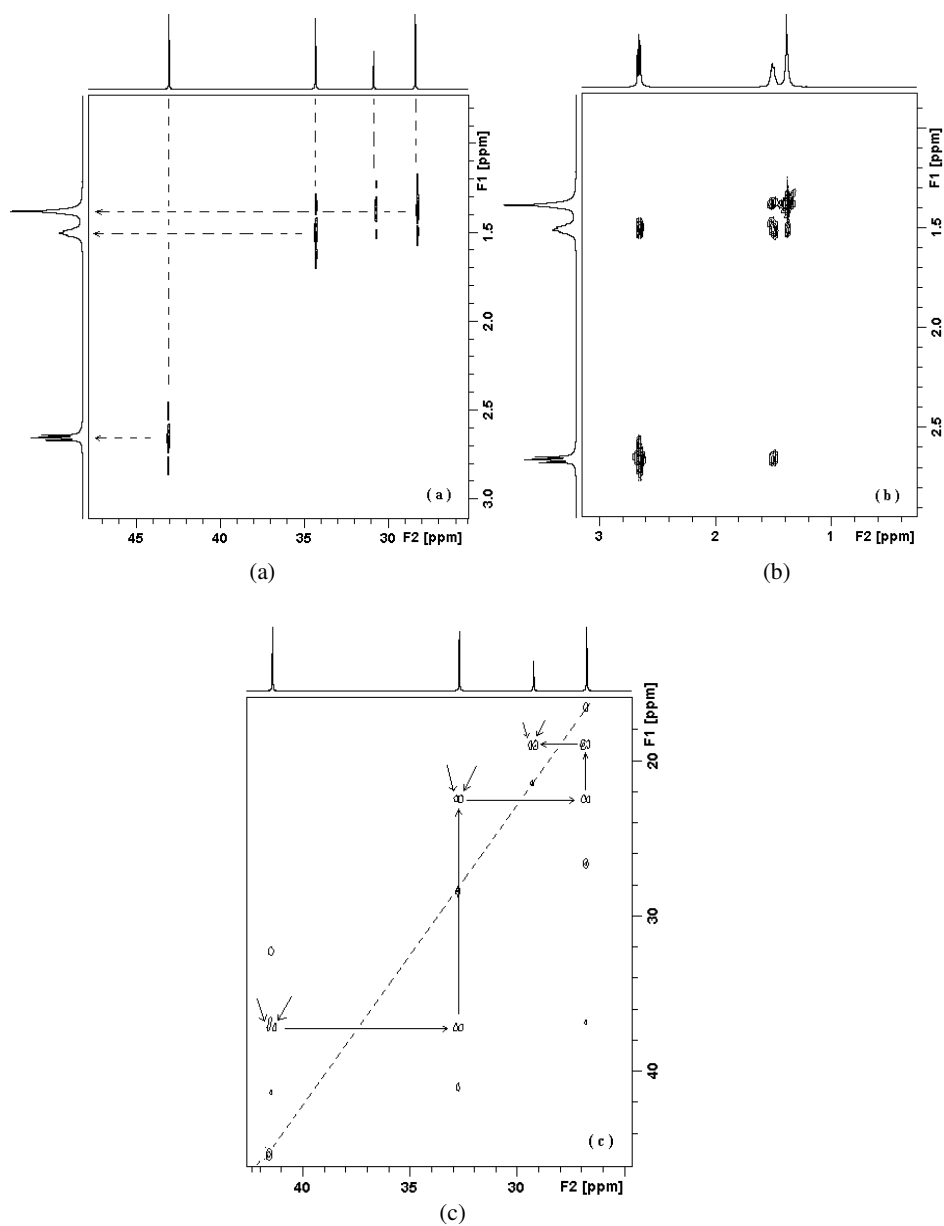
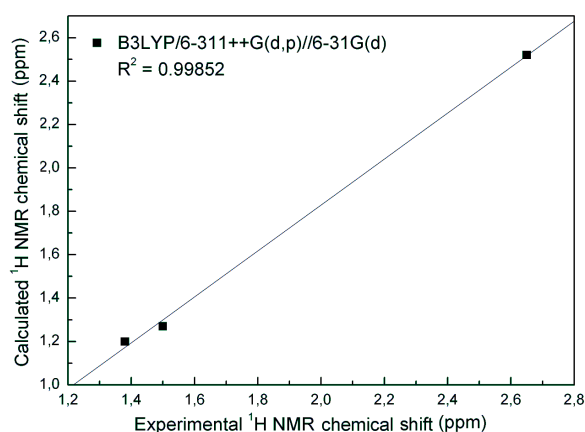


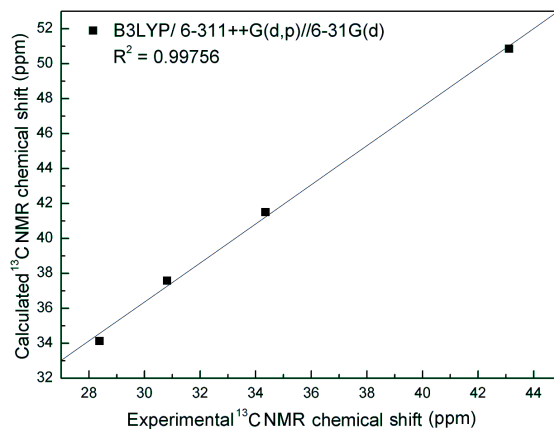
Figure 7. HETCOR (a), COSY (b) and inadequate (c) NMR spectra of dahp (δ , ppm).

Table 3. Experimental and calculated $^1J_{CC}$ and $^1J_{CH}$ NMR coupling constants (Hz) of dahp.

$^1J(C, C)$	Experimental (Hz)	B3LYP (Hz)
C ₁ C ₂ , C ₆ C ₇	34.07	35.21
C ₂ C ₃ , C ₅ C ₆	30.55	33.96
C ₃ C ₄ , C ₄ C ₅	27.85	33.08
$^1J(C, H)$	Experimental (Hz)	B3LYP (Hz)
C ₁ H ₁₀ H ₁₁ , C ₇ H ₂₂ H ₂₃	133.27	126.67
C ₂ H ₁₂ H ₁₃ , C ₆ H ₂₀ H ₂₁	125.28	120.05
C ₄ H ₁₆ H ₁₇	124.95	119.71
C ₃ H ₁₄ H ₁₅ , C ₅ H ₁₈ H ₁₉	122.76	118.17

Figure 8. Plot of the calculated vs. the experimental 1H NMR chemical shift of dahp.

In order to compare the experimental and theoretical chemical shifts and coupling constants, the correlation graphics based on the calculations have been presented in Figure 8-11. The correlation values for proton-carbon chemical shifts and $^1J_{CH}$ - $^1J_{CC}$ coupling constants are found to be 0.99852, 0.99756 and 0.99917, 0.99942 for B3LYP with the 6-311++G(d,p) basis set, respectively.

Figure 9. Plot of the calculated vs. the experimental ^{13}C NMR chemical shift of dahp.

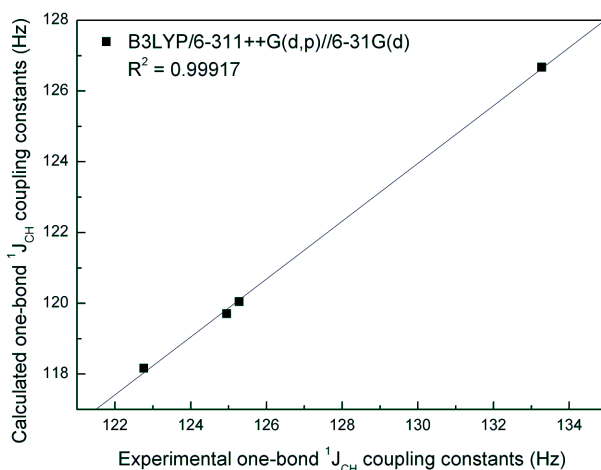


Figure 10. Plot of the calculated vs. the experimental $^1J_{CH}$ coupling constants (Hz) of dahp.

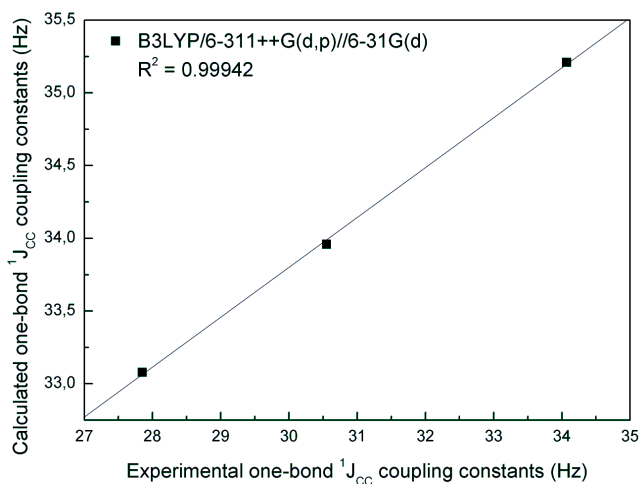


Figure 11. Plot of the calculated vs. the experimental $^1J_{CC}$ coupling constants (Hz) of dahp.

CONCLUSIONS

We have calculated both theoretical and experimental 1H , ^{13}C , ^{15}N NMR chemical shifts. The magnitude of one bond $^1J_{CH}$, $^1J_{CC}$ coupling constants and theoretical vibrational frequencies of 1,7-diaminoheptane. The theoretical ^{13}C , 1H NMR chemical shifts, the magnitude of one bond $^1J_{CC}$, $^1J_{CH}$ coupling constants and vibrational frequencies of dahp have been compared with the experimental data. According to these results, the calculated chemical shifts, coupling constants and vibrational frequencies are in good agreement with the experimental findings. Both experimental and theoretical calculations suggest that the dahp has a very symmetrical alignment towards both sides of C_4 atom as expected. Regarding the calculations, it is shown that the results of DFT (B3LYP) method are in good agreement with all the experimental findings.

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