NMR SPECTROSCOPIC STUDY AND DFT CALCULATIONS OF GIAO NMR SHIELDINGS AND $^1J_{CH}$ SPIN-SPIN COUPLING CONSTANTS OF 1,9-DIAMINONONANE

Özgür Alver[1,2,*], Cemal Parlak[3] and Mustafa Şenyel[1]

[1]Department of Physics, Science Faculty, Anadolu University, 26470, Eskişehir, Turkey
[2]Plant, Drug and Scientific Research Centre, Anadolu University, 26470, Eskisehir, Turkey
[3]Department of Physics, Arts and Science Faculty, Dumlupinar University, Kütahya, Turkey

ABSTRACT. ^1H, proton coupled and decoupled ^{13}C, DEPT, HETCOR NMR spectra, the magnitude of one bond $^1J_{CH}$ coupling constants and ^{13}C NMR spin-lattice relaxation time (T_1) of 1,9-diaminononane (danon, $C_9H_{22}N_2$) have been reported for the first time. ^1H, ^{13}C NMR chemical shifts and $^1J_{CH}$ coupling constants of danon 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 NMR properties.

KEY WORDS: 1,9-Diaminononane, NMR, GIAO, DFT

INTRODUCTION

1,9-Diaminononane has been extensively subjected to many different types of scientific studies. For example, it has been used as a ligand in various complexes [1, 2] and has been used to synthesize various types of aliphatic-aromatic polyimides [3] which are very important for various fields of science and industry such as microelectronic and aerospace engineering [4-8]. This molecule has also been used for synthesizing liquid crystalline copolyimines and aliphatic polyurea films [9, 10].

GIAO/DFT (Gauge Including Atomic Orbitals/Density Functional Theory) approach is extensively used for the calculations of chemical shifts for various types of compounds [11-17]. 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 [16-18]. 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 [19, 20].

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 [21-23] and it enables one 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 [24-26].

The ^{13}C spin-lattice relaxation time is the important experimental quantity for examining the dynamical processes. The ^{13}C nucleus is of low natural abundance; therefore the relaxation is mainly governed by the dipolar interactions with the directly bonded hydrogen atoms. By analyzing the relaxation of the nuclei in different environments of the chain, it is possible to obtain a detailed picture of the motion occurring in different parts of the chain. The measured relaxation data can be used to obtain information about the dynamical processes occurring in various parts of the chain [27, 28].

_____

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

In this work, we have reported ^{1}H, proton coupled and decoupled ^{13}C, DEPT, HETCOR NMR spectra, the magnitude of one bond [1]J$_{CH}$ coupling constants and ^{13}C NMR spin-lattice relaxation time (T$_1$) of danon for the first time. We have also calculated ^{1}H, ^{13}C NMR chemical shifts, [1]J$_{CH}$ coupling constants of danon by using B3LYP [29] method with 6-31G(d) and 6-311++G(d,p) basis sets, respectively.

EXPERIMENTAL

The pure danon molecule 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 298 K. Danon was dissolved in MeOD deuterated solvent and chemical shifts were reported in ppm relative to TMS. ^{1}H, ^{13}C NMR, DEPT and HETCOR NMR spectra were obtained at a base frequency of 125.76 MHz for ^{13}C and 500.13 MHz for ^{1}H nuclei. For proton coupled and decoupled ^{13}C NMR spectroscopy, the pulse sequence used a delay (D1) and acquisition time (AQ) of 2.0 s and 7.63 s, respectively, a spectral width of 4290.61 Hz, 64000 data points, 90^0 pulse (8.30 µs) and 128 scans. DEPT spectra were obtained at $\theta_z = 45^0$ where CH, CH$_2$ and CH$_3$ appear in the positive phase and $\theta_z = 135^0$ where CH, CH$_3$ appear in the positive phase and CH$_2$ appears in the negative phase. For ^{1}H NMR experiment D1 = 1.0 s, AQ = 9.58 s, spectral width 3419.97 Hz, 64000 data points, 90^0 pulse (14.15 µs) and 32 scans were performed. Inversion recovery puls esequence (180°-τ-90°) was used to determine ^{13}C spin lattice relaxation time of the title molecule. The measurements were carried out using a range of τ varying from 0.25 s to 40 s divided into 9 numbers with 40 s of recycle delay.

Calculations

For the NMR calculations, molecular structure of danon was first fully optimized at B3LYP/6-31G(d) level in methanol (ε = 32.63) by using the IEFPCM method [30, 31]. By using the same method and the basis set, it was seen that all the vibrational frequencies of danon were positive. Hence, we were confident that a definite absolute minimum in the potential energy surface was found. After optimization, ^{1}H, ^{13}C NMR chemical shifts (δ_H and δ_C) and [1]J$_{CH}$ coupling constants of danon were calculated using the GIAO method [14-17, 30, 31] in methanol at the B3LYP/6-311++G(d,p)//6-31G(d) level under the keyword nmr=spinspin. Relative chemical shifts were then estimated using the corresponding TMS shieldings calculated in advance at the same theoretical level as the reference. Calculated ^{1}H and ^{13}C isotropic chemical shieldings for TMS in methanol at the same level of theory were 31.87 ppm and 183.97 ppm, respectively. The experimental values for ^{1}H and ^{13}C isotropic chemical shifts for TMS were 30.84 ppm and 188.1 ppm, respectively [32]. All the calculations were performed using Gaussian 03 program package on a personal computer [33].

RESULTS AND DISCUSSION

All the experimental results for ^{13}C, ^{1}H and [1]J(C, H) measurements of danon are given in Table 1. Danon molecule (Figure 1) shows five different carbon atoms, which is in agreement with the structure regarding the molecular symmetry. Due to that fact, in Figure 2, five carbon peaks are observed in ^{13}C NMR spectrum of danon. As it can be seen from DEPT 45 and DEPT 135 spectra (Figure 2), positive and negative phased peaks appear due to CH$_2$ groups.

Danon molecule is symmetric along the both sides of the C$_5$ atom. Therefore, only one side of danon has the complete NMR information. In other words, these nuclei are NMR equivalent.

The correlations between C_1-H_{12-13}, C_2-H_{14-15}, C_3-H_{16-17}, C_4-H_{18-19}, C_5-H_{20-21}, C_6-H_{22-23}, C_7-H_{24-25}, C_8-H_{26-27}, C_9-H_{28-29} are clearly observed in HETCOR spectrum (Figure 3).

Table 1. Experimental and calculated ^{13}C, ^{1}H NMR chemical shifts (ppm) and $^1J_{CH}$ NMR coupling constants (Hz) of danon.

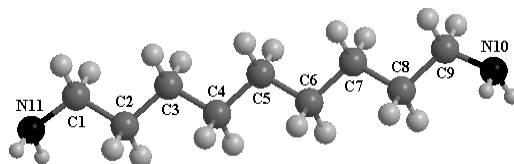| Nuclei	Experimental (ppm)	B3LYP (ppm)
C_3, C_7	28.2	31.1
C_4, C_6	30.5	34.6
C_5	30.6	34.9
C_2, C_8	33.2	37.9
C_1, C_9	42.4	48.9
$H_{16, 17}$, $H_{24, 25}$	1.3	1.2
$H_{18, 19}$, $H_{22, 23}$, $H_{20, 21}$	1.3	1.3
$H_{30, 31}$, $H_{32, 33}$	1.5	1.2
$H_{14, 15}$, $H_{26, 27}$	1.5	1.3
$H_{12, 13}$, $H_{28, 29}$	2.6	2.5
$^1J(C_nH_n)$	Experimental (Hz)	B3LYP (Hz)
$C_2H_{14}H_{15}$, $C_8H_{26}H_{27}$	122.4	118.2
$C_3H_{16}H_{17}$, $C_7H_{24}H_{25}$	122.9	119.1
$C_4H_{18}H_{19}$, $C_6H_{22}H_{23}$	123.8	119.7
$C_5H_{20}H_{21}$ $C_1H_{12}H_{13}$, $C_9H_{28}H_{29}$	135.2	132.1

Figure 1. The optimized molecular structure of danon at the used methods.

All the experimental $^1J_{CH}$ coupling constants were derived from proton coupled ^{13}C NMR spectrum. There is a simple correlation between $^1J_{CH}$ and the hybridization of the carbon atom involved; $^1J_{CH} = 500s$ (Hz) [34]. The quantity s can assume values which range from 0.25 to 0.5 as the hybridization changes from sp^3 to sp [34]. Calculated $^1J_{CH}$ coupling constants and experimentally obtained results for danon (Table 1) molecule are in good compliance. Moreover, substituents have considerable influence on C, H coupling constants [34]. It can be seen that electronegative amine groups lead to an increase in the $^1J_{CH}$ coupling constant values for danon molecule as expected.

Even in unsubstituted n-alkanes the CH$_2$ segments are found to have different T_1 values, as the mobility in the middle of the chain is less than near the ends [35]. ^{13}C spin-lattice relaxation curves of danon are given in Figure 4. When looking at the T_1 values it can be said that for C_3 and C_5 carbon atoms of danon molecule, molecular motions at the Larmor frequency have the largest number leading to shorter T_1 values. In a similar manner, the carbon atoms at the end of the danon chain with the longest T_1 are experiencing the least molecular motions at the Larmor frequency. In other words, flexibility of the danon molecule at near ends is larger than flexibility of its middle part.

We have calculated the theoretical ^{1}H, ^{13}C NMR chemical shifts and the magnitude of one bond $^1J_{CH}$ coupling constants of danon molecule. The shielding calculations were given the experimental shape but they were systematically a few ppm deviated because of the effects of

the finite basis used. 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 5. The correlation values for carbon chemical shifts and $^{1}J_{CH}$ coupling constants are found to be 0.99759 and 0.99931 for B3LYP with the 6-311++G(d,p) basis set, respectively. It can be seen that B3LYP findings are in good agreement with all the experimental results.
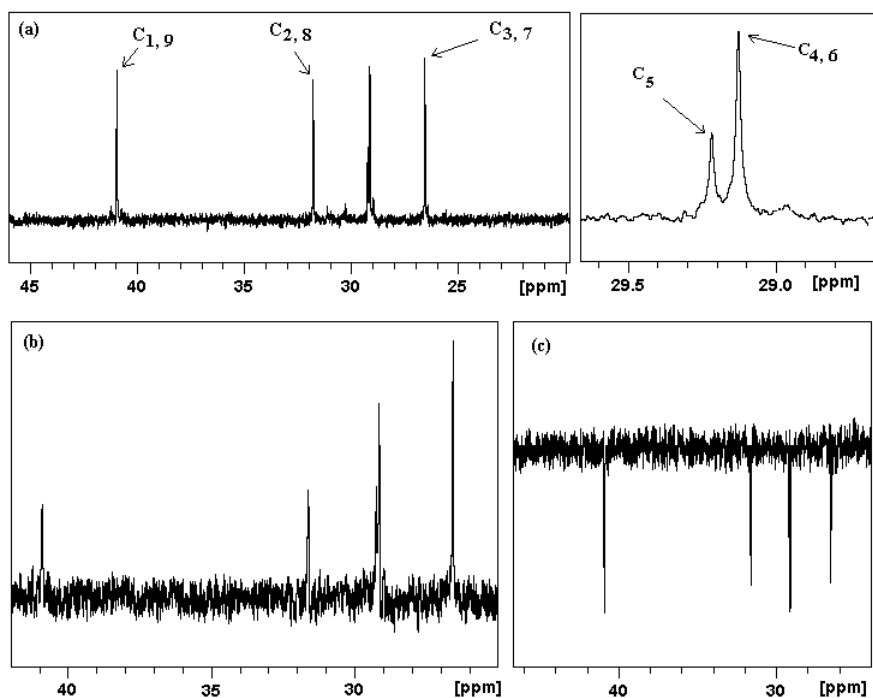

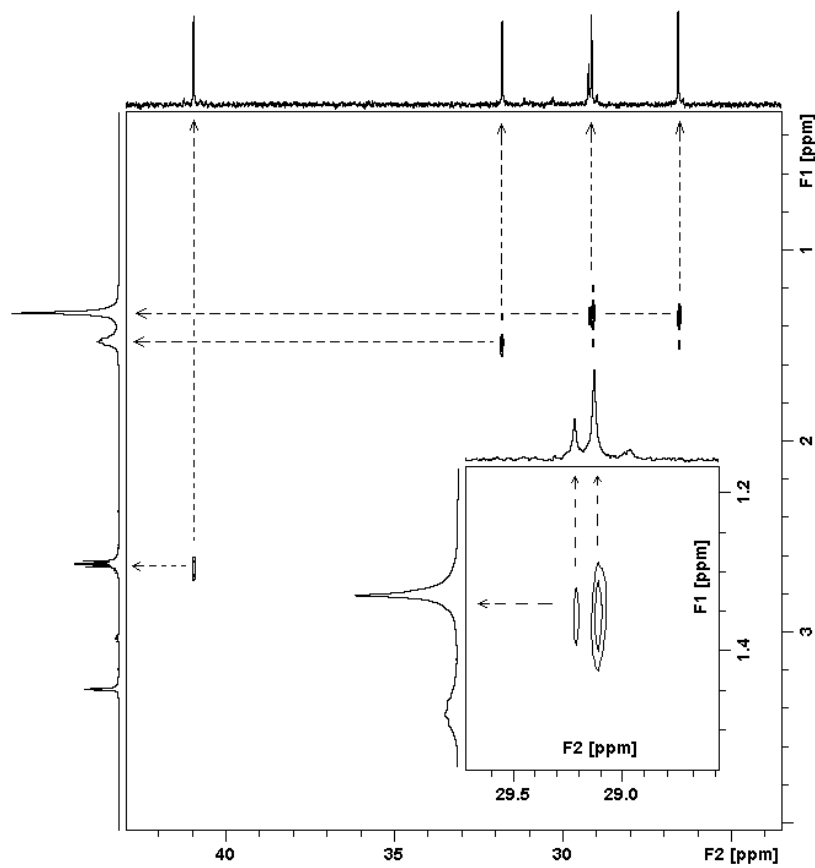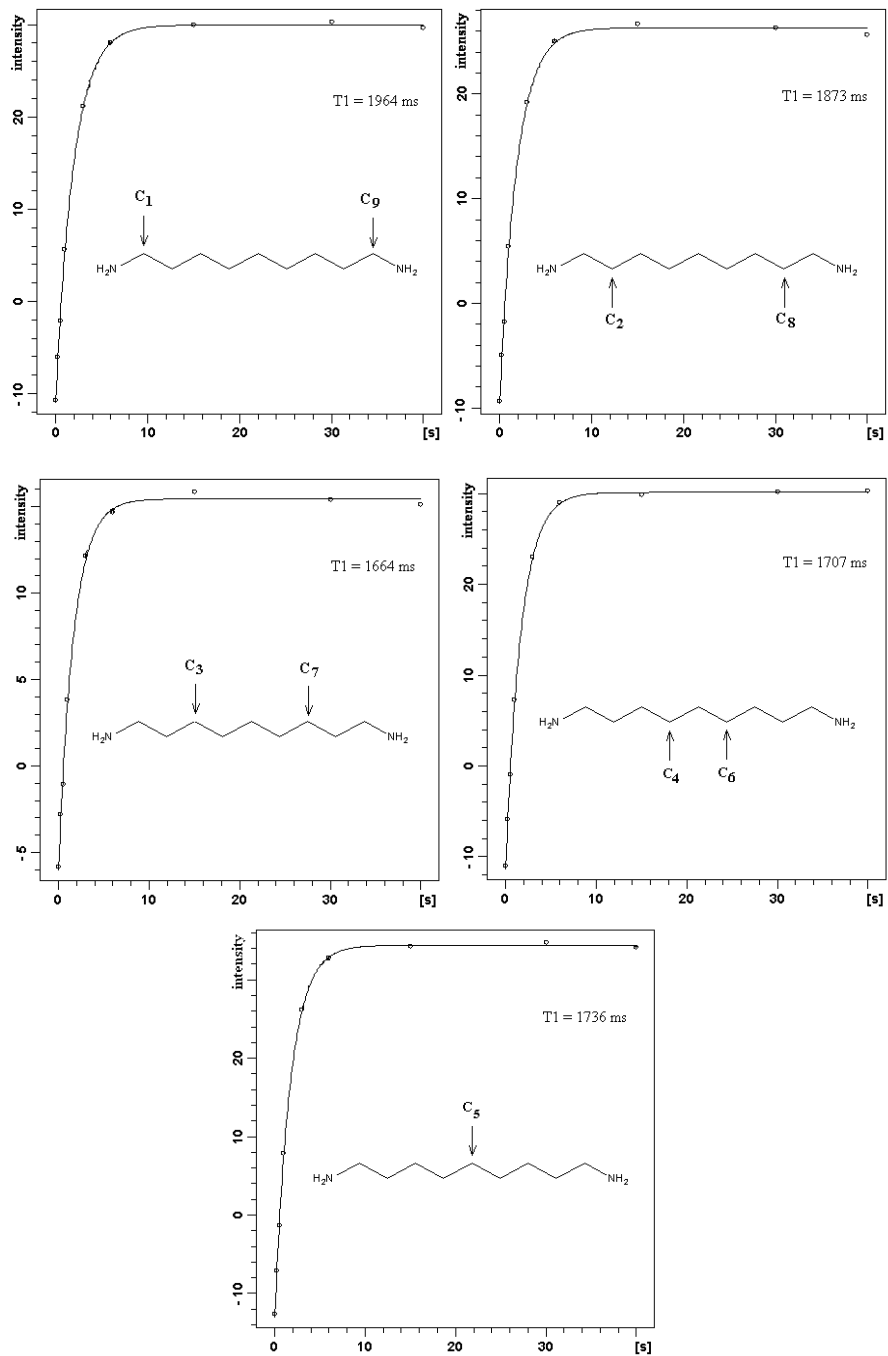Figure 2. ^{13}C NMR (a), DEPT 45 (b) and DEPT 135 (c) NMR spectra of danon.

Figure 3. 2D HETCOR NMR spectrum of danon.

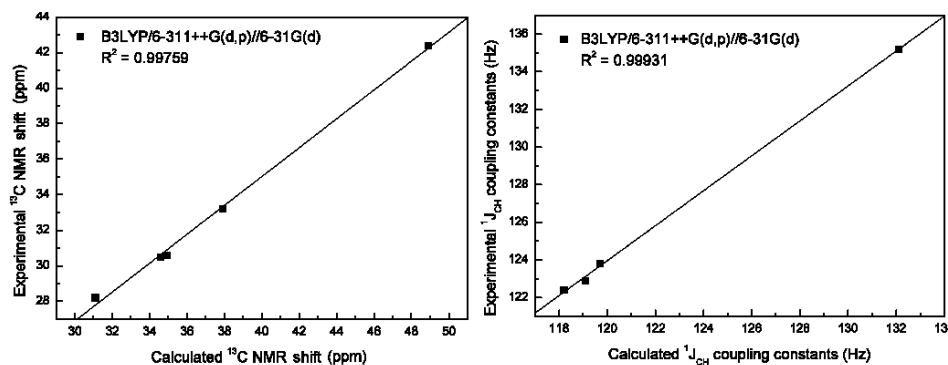Figure 4. ^{13}C spin-lattice relaxation (T_1) curves of danon.

Figure 5. Plot of the calculated vs. the experimental ^{13}C NMR chemical shifts (ppm) and $^1J_{CH}$ coupling constants (Hz) of danon

CONCLUSIONS

The experimental and the theoretical investigation of danon molecule have been performed successfully by using NMR and quantum chemical calculations. Both experimental and theoretical calculations suggest that the danon has a very symmetrical alignment as expected. Regarding the calculations, it is shown that the results of DFT (B3LYP) method are in good agreement with all the experimental findings.

REFERENCES

1. Kartal, Z.; Parlak, C.; Şentürk, Ş.; Aytekin, M.T.; Şenyel, M. *Croat. Chem. Acta* **2007**, 80, 9.
2. Hashimoto, M.; Kitazava, T.; Hasegawa, T.; Iwamoto T. *J. Incl. Phenom. Macro.* **1991**, 11, 153.
3. Balcerzak, E.S.; Sęk, D.; Volozhin, A.; Chamenko, T.; Jarząbek, B. *Eur. Polym. J.* **2002**, 38, 423.
4. İde, S.; Topaçlı, A. *J. Mol. Struct.* **2000**, 526, 201.
5. Hougham, G.; Tesoro, G.; Viehbeck, A. *Macromolecules* **1996**, 29, 3453.
6. Hougham, G.; Tesoro J.G.; Shawt, J. *Macromolecules* **1994**, 27, 3642.
7. Zhao, X.; Li, Y.F.; Zhang, S.J.; Shao, Y.; Wang, X.L. *Polymer* **2007**, 48, 5241.
8. Jang, W.; Lee, H.S.; Lee, S.; Choi, S.; Shin, D.; Han, H. *Mater. Chem. Phys.* **2007**, 104, 342.
9. Yang, H.X.; Natansohn, A. *Polym. Bull.* **1992**, 29, 159.
10. Hattori, T.; Iijima, M.; Takahashi, Y.; Fukada, E.; Suziki, Y.; Kakimoto, M.; Imai Y. *Jpn. J. Appl. Phys.* **1994**, 33, 4647.
11. Şenyel, M.; Alver, Ö.; Parlak, C. *Spectrochim. Acta A* **2008**, 71, 830.
12. Parlak, C.; Alver, Ö.; Şenyel, M.; *Spectrochim. Acta A* **2008**, 69, 1252.
13. Zhang Y.; Li, T.; Teng, Q. *Bull. Chem. Soc. Ethiop.* **2009**, 23, 77.
14. Barone, G.; Paloma, L.G.; Duca, D.; Silvestri, A.; Riccio, R.; Bifulco, G. *Chem. Eur. J.* **2002**, 8, 3233.
15. Bagno, A.; Rastrelli, F.; Saielli, G. *Chem. Eur. J.* **2006**, 12, 5514.
16. Helgaker, T.; Jaszunski, M.; Ruud, K. *Chem. Rev.* **1999**, 99, 293.
17. Bagno, A.; Rastrelli, F.; Saielli, G. *J. Phys. Chem. A* **2003**, 107, 9964.
18. Pratum, T.K. *J. Magn. Reson. A* **1995**, 117, 132.

19. Bifulco, G.; Bassarello, C.; Riccio, R.; Paloma, L.G. *Org. Lett.* **2004**, 6, 1025.
20. Williamson, R.T.; Marquez, B.L.; Gerwick, W.H.; Koehn, F.E. *Magn. Reson. Chem.* **2001**, 39, 544.
21. Jordan, E.; Koller, H. *Stud. Surf. Sci. Catal.* **2004**, 154, 1555.
22. Krushelnitsky, A.; Reichert, D. *Biopolymers* **2005**, 78, 129.
23. Krushelnitsky, A.; Reichert, D. *Prog. NMR Spectrosc*. **2005**, 47, 1.
24. Dodziuk, H.; Demchuk, O.M.; Schilf, W.; Dolgonos, G. *J. Mol. Struct.* **2004**, 693, 145.
25. Beraldo, H.; Nacif, W.F.; West, D.X. *Spectrochim. Acta A* **2001**, 57, 1847.
26. Abdel-Shafi, A.A. *Spectrochim. Acta A* **2001**, 57, 1819.
27. Gisser, D.J.; Glowinkowski, S.; Ediger, M.D. *Macromolecules* **1997**, 30, 3159.
28. Ravindranathan, S.; Sathyanarayana, D.N. *Macromolecules* **1995**, 28, 2396.
29. Becke, A.D. *J. Chem. Phys.* **1993**, 98, 5648.
30. Alver, Ö.; Parlak, C.; Şenyel, M. *Spectrochim. Acta A* **2007**, 67, 793.
31. Alver, Ö.; Parlak, C.; Şenyel, M. *Bull. Chem. Soc. Ethiop.* **2009**, 23, 85.
32. Cheeseman, J.R.; Trucks, G.W.; Keith T.A.; Frisch, M.J. *J. Chem. Phys.* **1996**, 104, 5497.
33. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A.; Vreven, 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.; Bakken, V.; 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.; Gonzalez, C.; Pople, J.A., *Gaussian 03*, Revision C.02, Gaussian, Inc., Wallingford CT, **2004**.
34. Friebolin, H.; *Basic One and Two Dimensional NMR Spectroscopy*, VCH Publishers: Weinheim, **1991**.
35. Abraham R.J.; Loftuus, P. *Proton and Carbon-13 NMR Spectroscopy*, Heyden Publishers: London, **1978**.