Bull. Chem. Soc. Ethiop. **2011**, 25(3), 437-442.
Printed in Ethiopia
ISSN 1011-3924

EXPERIMENTAL AND THEORETICAL NMR STUDY OF 4-(1-PYRROLIDINYL)PIPERIDINE

Özgür Alver[1,2*], Cemal Parlak[3] and Metin Bilge[4]

[1] Plant, Drug and Scientific Research Centre, Anadolu University, Eskişehir, Turkey
[2] Department of Physics, Science Faculty, Anadolu University, Eskişehir, Turkey
[3] Department of Physics, Arts and Science Faculty, Dumlupınar University, Kütahya, Turkey
[4] Department of Physics, Science Faculty, Ege University, İzmir, Turkey

(Received April 1, 2010; revised December 8, 2010)

ABSTRACT. The possible stable forms and molecular structure of 4-(1-pyrrolidinyl)piperidine (4-pypp) have been studied experimentally and theoretically using nuclear magnetic resonance (NMR) spectroscopy. ^{1}H, ^{13}C, ^{15}N, DEPT, COSY and HETCOR NMR spectra of 4-pypp ($C_9H_{18}N_2$) have been reported. Solvent effects on nuclear magnetic shielding tensors have been investigated using chloroform-*d*, methanol-*d*, acetone-*d*, dimethylsulfoxide-*d* and water-*d*. The magnitude of $^{n}J(C,H)$ (n = 1, 2, 3) coupling constants of 4-pypp have been determined with selective ^{1}H decoupled ^{13}C NMR techniques. ^{1}H, ^{13}C, ^{15}N NMR chemical shifts and $^{1-3}J(C,H)$ coupling constants have also been calculated for the most stable two conformers, equatorial-equatorial (e-e) and axial-equatorial (a-e) forms of 4-pypp using DFT/6-311++G(d,p)//6-31G(d) level of theory. Results from experimental and theoretical data have showed that the molecular geometry and the mole fractions of stable conformers of 4-pypp are solvent dependent.

KEY WORDS: 4-(1-Pyrrolidinyl)piperidine, NMR, DFT, Axial, Equatorial

INTRODUCTION

The 4-(1-pyrrolidinyl)piperidine molecule consists of piperidine ($C_5H_{11}N$) and pyrrolidine (C_4H_9N). Piperidine has two distinguishable chair conformations; one with N–H bond in the axial position, and the other in the equatorial position. After much controversy during the 1950s–1970s, the equatorial conformation was found to be more stable by 0.72 kcal/mol in the gas phase [1]. Substituents on a piperidine ring have been found in the equatorial position [1, 2]. Pyrrolidine is expected the pure envelope conformation with apex at the N-atom and the pure twist conformation [3]. Many possible conformers could be proposed for 4-pypp, but here the discussion has confined for e-e, e-a, a-a and a-e conformers of 4-pypp (Figure 1). In these presentations, the former represents NH while the latter stands for pyrrolidine group. They are considered in axial and equatorial positions according to plane formed by C15, C18, C16 and C21 carbon atoms of 4-pypp.

This molecule has been identified as good inhibitor and used to synthesize some potent antagonists and substituted guanidines [4-6]. It has also been used in the study of carbon-14 labelling of 3-cyanoquinolines systems [7].

According to the literature, the experimental or theoretical NMR study of 4-pypp is not available. NMR spectroscopy has an enormous potential for investigating conformations and configurations in organic compounds [8]. After discovery of NMR, such potential rapidly increased to cover various kinds of compounds, including biological, inorganic and organometallic compounds [8]. 1D and 2D hetero- and homonuclear NMR methods enable to get full assignments and structural information of organic compounds [9-11].

For the theoretical NMR investigations, the gauge including atomic orbitals/density functional theory (GIAO/DFT) approach is widely used for various types of compounds [12-20]. DFT calculations are hardly expensive and provide accurate results for chemical shifts and coupling constant on systems such as large organic molecules [18].

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

The essence of this study is briefly to report experimental and theoretical NMR features of 4-pypp and then to investigate solvent effects on NMR of 4-pypp using chloroform-*d*, methanol-*d*, acetone-*d*, dimethylsulfoxide-*d* and water-*d*. For these goals, we have reported ^{1}H, ^{13}C, ^{15}N, DEPT, COSY and HETCOR NMR spectra, ^{n}J(C,H) (n = 1-3) coupling constants of 4-pypp. Moreover, coupling constants and ^{1}H, ^{13}C and ^{15}N NMR chemical shifts of 4-pypp have been calculated for the most stable two conformers obtained form conformer search of 4-pypp using DFT with 6-311++G(d,p) basis set.

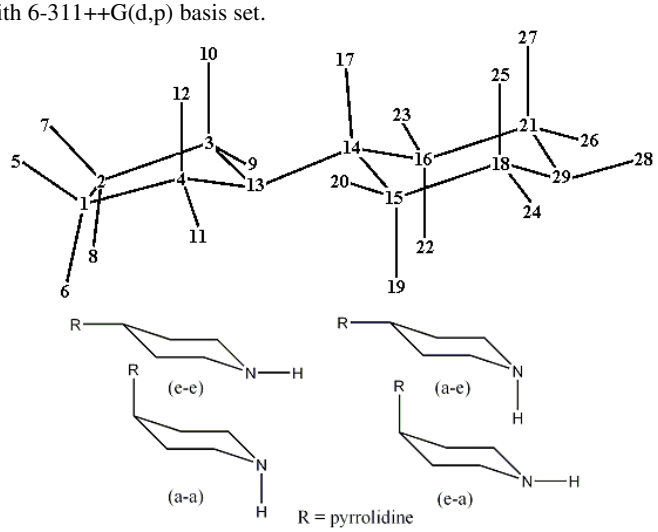

Figure 1. Conformations of 4-pypp showing atomic numbering.

EXPERIMENTAL

The pure 4-pypp was obtained as powder from Acros Organics (99%, Belgium) and used without further purification. All NMR spectra of 4-pypp were recorded on a Bruker AVANCE II 500 spectrometer using 5 mm BBO (broad band observe) probe [21, 22] at room temperature. The operating frequencies were 500.13 MHz, 125.76 MHz and 50.66 MHz for ^{1}H, ^{13}C and ^{15}N, respectively. All spectra were measured in 5 mm tubes containing $CDCl_3$, MeOD, DMSO-d_6, CD_3COCD_3 and D_2O with tetramethylsilane (TMS, 0.012 g/mL) and formamide (0.010 g/mL) as internal reference (TMS: ^{1}H, ^{13}C, 0 ppm and formamide: ^{15}N, 112 ppm [23]).

The pulse conditions used in the NMR experiments were as follows: ^{1}H: SF 500.13 MHz, SW 615.76 Hz, AQ 53.2 s, NS 32, PD 90^{o} (14.15 µs), ^{13}C: SF 125.76 MHz, SW 10593.2 Hz, AQ 3.1 s, NS 64, PD 90^{o} (8.3 µs), ^{15}N: SF 50.66 MHz, SW 30864.19 Hz, AQ 0.53 s, PD 90^{o} (15.0 µs). The abbreviations stand for: SF, spectrometer frequency; SW, spectral width; AQ, acquisition time; NS, number of scan; PD, pulse duration. DEPT spectra were obtained at θ_z = 135^{0} where CH, CH_3 appear in the positive phase and CH_2 appears in the negative phase. Two-dimensional COSY and HETCOR techniques were measured using standard micro-programs provided by Bruker [22, 24].

Calculations

All the calculations were performed with Gaussian 03 program package [25] on a personal computer, invoking gradient geometry optimization. All four forms of 4-pypp were first fully optimized at DFT/6-31G(d) level using the keyword volume in gas phase and five different

solvents with the IEFPCM method [26, 27]. The optimized geometric structures at minima on the potential energy surface were provided by solving self consistent field equation iteratively. After the optimizations, ^{1}H, ^{13}C and ^{15}N NMR chemical shifts (δ_H, δ_C and δ_N) and $^{1-3}J(C,H)$ coupling constants of the most stable two conformers of 4-pypp were calculated using the GIAO method [16-19] for related solvents at the DFT/6-311++G(d,p) level under the keyword nmr = spinspin. Relative chemical shifts were then estimated using the corresponding TMS and formamide shieldings computed at the same theoretical levels as the references.

RESULTS AND DISCUSSION

Gibbs free energies, relative stabilities, equilibrium constants and mole fractions [28] of the optimized geometries in the five different solvent environments of four conformations of 4-pypp calculated with DFT/6-31G(d) are given in Table 1. Regarding the calculated free energies for gas phase, e-e form is more stable than a-e by 0.061 kcal/mol, e-a by 5.447 kcal/mol and a-a by 5.591 kcal/mol. The e-a and a-a forms could be neglected for calculation of equilibrium constant since their energy differences are larger than 2 kcal/mol. Consequently, 4-pypp in the gas phase prefers e-e and a-e forms with preference of 53% and 47%, respectively. Similarly, the calculated free energies in chloroform as a non-polar solvent show that e-e form is more stable than other forms and 4-pypp prefers e-e and a-e forms with preference of 57% and 43%, respectively. However, the calculated free energies in methanol, dimethylsulfoxide, acetone and deuteriumoxide as polar solvents show that the a-e form is more stable than the other forms and 4-pypp prefers a-e and e-e forms with approximate preference of 60% and 40%, respectively.

Table 1. Some characteristic features of optimized geometries in the various solvent environments of four different conformations of 4-pypp with B3LYP/6-31G(d).

Medium	Conformer			
Chloroform (ε = 4.9)	e-e	a-e	e-a	a-a
ΔG (Hartree)	-463.056122	-463.055851	-463.046901	-463.047017
Relative stability (δΔG; kcal/mol)	0.00	0.17	5.79	5.71
Equilibrium constant (K_c)	0.75		-	-
Mole fractions (%)	57	43	-	-
Methanol (ε = 32.63)				
ΔG (Hartree)	-463.058474	-463.058860	-463.049369	-463.049818
Relative stability (δΔG; kcal/mol)	0.24	0.00	5.96	5.67
Equilibrium constant (K_c)	0.66		-	-
Mole fractions (%)	40	60	-	-
Dimethylsulfoxide (ε = 46.7)				
ΔG (Hartree)	-463.058534	-463.058927	-463.049371	-463.049660
Relative stability (δΔG; kcal/mol)	0.25	0.00	6.00	5.82
Equilibrium constant (K_c)	0.66		-	-
Mole fractions (%)	40	60	-	-
Acetone (ε = 20.7)				
ΔG (Hartree)	-463.058065	-463.058484	-463.048968	-463.049153
Relative stability (δΔG; kcal/mol)	0.26	0.00	5.97	5.86
Equilibrium constant (K_c)	0.64		-	-
Mole fractions (%)	39	61	-	-
Deuteriumoxide (ε = 78.3)				
ΔG (Hartree)	-463.058869	-463.059307	-463.049937	-463.050138
Relative stability (δΔG; kcal/mol)	0.27	0.00	5.88	5.75
Equilibrium constant (K_c)	0.63		-	-
Mole fractions (%)	39	61	-	-

Calculated ^{1}H, ^{13}C and ^{15}N isotropic chemical shieldings for TMS and formamide as references are given in Table 2 together with their experimental values [29, 30]. It is seen that the theoretical ^{1}H chemical shifts in investigated solvents are similar and very close to experimental value. For ^{13}C and ^{15}N chemical shifts, the experimental data are in better agreement with computed values in deuteriumoxide and chloroform, respectively, than those of other solvents.

Table 2. Calculated and experimental isotropic shieldings (ppm) of references.

B3LYP / 6-311++G(d,p) // 6-31G(d)			
Medium	Nucleus / Reference		
	^{1}H / TMS	^{13}C / TMS	^{15}N / Formamide
Chloroform	31.87	183.76	135.06
Methanol	31.87	183.97	131.47
Dimethylsulfoxide	31.88	184.07	131.25
Acetone	31.88	184.05	131.89
Deuteriumoxide	31.88	184.10	131.03
Experimental	30.84 [a]	188.10 [a]	152.50 [b]

[a, b] Taken from Ref. [29] and [30], respectively.

^{1}H, ^{13}C and ^{15}N NMR data of 4-pypp are reported in Table 3. As in Figure 1, 4-pypp has nine carbon atoms but it shows five different carbon peaks in ^{13}C NMR spectrum, C1-2, C15-16, C18-21, C3-4, C14, as in agreement with the structure regarding molecular symmetry. In DEPT 135 spectrum, C14-H17 appears in the positive phase at 62.41 ppm. Regarding the ^{15}N NMR spectrum, two peaks are observed at 37.82 ppm and 66.49 ppm. According to the obtained ^{1}H NMR spectra of 4-pypp, proton of NH group can not be differentiated either axially or equatorially. This could be attributed to a fast conformational interconversion on the NMR time-scale. However, in piperidine ring, equatorially oriented protons (H24-26 and H20-23) appear at higher frequency field region compared to axially oriented protons (H25-27 and H19-22).

Table 3. Experimental and calculated ^{13}C, ^{1}H and ^{15}N NMR chemical shifts (ppm) of 4-pypp.

Nucleus	$CDCl_3$			MeOD			DMSO-d6			D_2O			CD_3COCD_3		
	Exp.	e-e	a-e	Exp.	e-e	a-e	Exp.	e-e	a-e	Exp.	e-e	a-e	Exp.	e-e	a-e
C-1, C-2	23.28	27.45	27.06	23.91	27.29	27.15	24.68	27.39	27.27	23.91	27.29	27.15	23.91	27.39	27.25
C-15, C-16	33.05	37.80	39.84	32.98	38.24	39.86	34.23	38.36	40.02	32.98	38.24	39.86	33.74	38.29	39.97
C-18, C-21	45.68	51.04	51.22	45.90	51.20	51.44	46.74	51.30	51.61	45.90	51.20	51.44	46.12	51.29	51.54
C-3, C-4	51.28	56.57	56.06	52.11	56.80	56.35	52.32	56.95	56.48	52.11	56.80	56.35	51.60	56.91	56.43
C-14	62.41	68.39	67.73	63.60	68.33	67.92	63.62	68.53	68.06	63.60	68.33	67.92	63.06	68.54	67.95
H19, H22	1.39	1.40	1.08	1.39	1.31	1.08	1.26	1.31	1.10	1.39	1.31	1.08	1.32	1.33	1.09
H5, H8	1.78	1.74	1.73	1.80	1.76	1.75	1.69	1.77	1.76	1.80	1.76	1.75	1.70	1.77	1.76
H20, H23	1.91	1.78	1.78	1.93	1.85	1.81	1.78	1.86	1.82	1.93	1.85	1.81	1.80	1.85	1.82
H17	2.08	1.82	1.96	2.16	1.92	2.04	2.00	1.93	2.06	2.16	1.92	2.04	2.02	1.91	2.04
H9-12	2.56	2.47	2.46	2.61	2.51	2.50	2.48	2.52	2.51	2.61	2.51	2.50	2.50	2.52	2.45
H25, H27	2.60	2.76	2.65	2.56	2.78	2.67	2.45	2.79	2.68	2.56	2.78	2.67	2.52	2.78	2.67
H28	2.30	1.63	1.00	-	2.05	1.39	2.56	2.07	1.41	-	2.05	1.39	2.59	2.00	1.32
H24,H26	3.10	3.01	3.03	3.04	3.02	3.04	2.94	3.03	3.05	3.04	3.02	3.04	2.99	3.03	3.05
N13	37.82	28.83	29.50	-	32.42	31.79	-	32.57	32.01	-	32.96	32.21	-	32.08	31.34
N29	66.49	65.54	61.95	-	66.27	70.20	-	66.53	70.22	-	65.21	70.73	-	65.76	69.54

As can be seen from Table 3, the noticeable chemical shifts have been observed in solvents of varying. It is easy to see these shifts when the results of $CDCl_3$ are compared to the values of DMSO-d_6, CD_3COCD_3 and D_2O solvents [31]. $CDCl_3$ as a non-polar solvent is poor in forming hydrogen bonds with electronegative atoms. CD_3COCD_3 and DMSO-d_6 have an interaction with

proton of NH due to strong hydrogen bonding. Henceforth, H28 appears at the most downfield frequency region in $CDCl_3$. When MeOD or D_2O have used as solvent, the peak coming from NH proton is vanished due to possible exchange between deuterium of MeOD or D_2O and proton of NH.

All the $^{1-3}J(C,H)$ coupling constants derived from proton coupled ^{13}C NMR spectrum of 4-pypp are given in Table 4. As can be seen from Table 4, due to electronegative N29 atom, ^1J(C18-H24,25) and ^1J(C21-H26,27) are larger than ^1J(C15-H19,20) and ^1J(C16-H22,23). The magnitude of $^3J(C,H)$ is bigger than $^2J(C,H)$ for benzene and its derivatives [32]. It is also seen from Table 4 that $^3J(C,H)$ is bigger than $^2J(C,H)$ for piperidine ring of 4-pypp.

Table 4. Some experimental and calculated $^{1-3}J(C, H)$ coupling constants (Hz) of 4-pypp.

$^nJ(C, H)$	$CDCl_3$		
	Exp.	e-e	a-e
^1J(C1-H5,6), ^1J(C2-H7,8)	132.0	125.0	125.0
^1J(C3-H9,10), ^1J(C4-H11,12)	137.0	129.0	128.0
^1J(C14-H17)	128.0	121.0	122.0
^1J(C15-H19,20), ^1J(C16-H22,23)	125.0	124.0	121.0
^1J(C18-H24,25), ^1J(C21-H26,27)	133.0	126.0	128.0
^2J(C1-H7,8), ^2J(C2-H5,6)	3.1	2.5	2.5
^2J(C16-H26)	*	3.1	0.9
^2J(C16-H27)	*	1.5	1.2
^3J(C15-H22), ^3J(C16-H19)	*	2.0	2.0
^3J(C15-H23), ^3J(C16-H20)	*	0.6	5.4
^3J(C3-H11,12), ^3J(C4-H9,10)	4.3	5.6	5.8
^3J(C18-H26), ^3J(C21-H24)	9.1	9.4	9.1
^3J(C18-H27), ^3J(C21-H25)	*	3.4	1.5

* Mark indicates the peaks which can not be resolved experimentally.

From COSY NMR spectrum, all the bonds between the hydrogen atoms on pyrrolidine and piperidine ring are clearly observed. In HETCOR spectrum, two marks are seen for both C18-21 and C15-16 which indicates that related protons have different chemical environment or different orientations. However, proton couples on pyrrolidine ring show similar behaviours. Henceforth, at room temperature, there is no preferred axial or equatorial orientation or conformational interconversion is fast on the NMR time-scale for protons on pyrrolidine ring of 4-pypp. The experimental and theoretical NMR investigations of 4-pypp have been performed by using NMR and quantum chemical calculations. In order to compare the experimental and theoretical results, the correlation graphics have been investigated. For e-e conformer, the best correlation values obtained for proton and carbon chemical shifts are 0.97035 (CD_3COCD_3) and 0.99994 ($CDCl_3$). For a-e conformer, on the other hand, the best correlation values for proton and carbon chemical shifts are found to be 0.98419 ($CDCl_3$) and 0.99578 (CD_3COCD_3).

CONCLUSIONS

Applications of DFT calculation method yield ^1H, ^{13}C, ^{15}N NMR chemical shifts and $^{1-3}J(C,H)$ coupling constants that are in reasonable agreement with the experimental results. Thus, the DFT/6-311++G(d,p)//6-31G(d) level of theory makes it easier to understand NMR spectra of 4-pypp. Comparison between the experimental and calculated results indicates that, with less polar solvent such as $CDCl_3$, 4-pypp adopts mainly the e-e conformer. However, with increasing solvent polarity, the a-e conformer becomes more dominant. The conformational exchange is more apparent with polar solvents which suggest that conformational energy barrier is solvent dependent. It is also possible to see axially and equatorially oriented protons in piperidine ring of 4-pypp; equatorial proton signals appear at higher frequencies when compared to those of the axial ones.

REFERENCES

1. Carballeira, L.; Perez-Juste, I. *J. Comput. Chem.* **1998**, 19, 961.
2. Komasa, A.; Katrusiak, A.; Szafran, M.; Barczynski, P.; Szafran, Z.D. *J. Mol. Struct.* **2008**, 889, 112.
3. El-Gogary, T.M.; Soliman, M.S. *Spectrochim. Acta A* **2001**, 57, 2647.
4. Waelchli, R.; Bollbuck, B.; Bruns, C.; Buhl, T.; Eder, J.; Feifel, R.; Hersperger, R.; Janser, P.; Revesz, L.; Zerwes, H.G.; Schlapbach, A. *Bioorg. Med. Chem. Lett.* **2006**, 16, 108.
5. Yokoyama, K.; Ishikawa, N.; Igarashi, S.; Kawano, N.; Masuda, N.; Hamaguchi, W.; Yamasaki, S.; Koganemaru, Y.; Hattori, K.; Miyazaki, T.; Ogino, S.; Matsumoto, Y.; Takeuchi, M.; Ohta, M. *Bioorg. Med. Chem.* **2009**, 17, 64.
6. Zhang, W.X.; Nishiura, M.; Hou, Z. *Chem. Eur. J.* **2007**, 13, 4037.
7. Olszewski, J.D.; Berger, D.M.; May, M.K.; Label, J. *Compd. Radiopharm.* **2007**, 50, 578.
8. Contreras, R.H.; Peralta, J.E. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000,** 37, 321.
9. Dodziuk, H.; Demchuk, O.M.; Schilf, W.; Dolgonos, G. *J. Mol. Struct.* **2004,** 693, 145.
10. Beraldo, H.; Nacif, W.F.; West, D.X. *Spectrochim. Acta A* **2001**, 57, 1847.
11. Abdel-Shafi, A.A. *Spectrochim. Acta A* **2001**, 57, 1819.
12. Alver, Ö.; Parlak, C.; Şenyel, M. *Bull. Chem. Soc. Ethiop.* **2009**, 23, 437.
13. Alver, Ö.; Parlak, C.; Şenyel, M. *Phys. Lett. A* **2007**, 371, 300.
14. Parlak, C.; Alver, Ö.; Şenyel, M. *Bull. Chem. Soc. Ethiop.* **2009**, 23, 85.
15. Şenyel, M.; Alver, Ö.; Parlak, C. *Spectrochim. Acta A* **2008**, 71, 830.
16. Barone, G.; Paloma, L.G.; Duca, D.; Silvestri, A.; Riccio, R.; Bifulco, G. *Chem. Eur. J.* **2002**, 8, 3233.
17. Bagno, A.; Rastrelli, F.; Saielli, G. *Chem. Eur. J.* **2006**, 12, 5514.
18. Helgaker, T.; Jaszunski, M.; Ruud, K. *Chem. Rev.* **1999**, 99, 293.
19. Bagno, A.; Rastrelli, F.; Saielli, G. *J. Phys. Chem. A* **2003**, 107, 9964.
20. Bifulco, G.; Bassarello, C.; Riccio, R.; Paloma, L.G. *Org. Lett.* **2004**, 6, 1025.
21. Hoffman, R.E. *J. Magn. Reson.* **2003,** 163, 325.
22. Lycka, A.; Holecek, J. *Dyes and Pigments* **2003,** 57, 115.
23. Martin, G.E.; Hadden, C.E. *J. Am. Chem. Soc.* **2000**, 63, 543.
24. XWINNMR Version 3.0. Bruker; **2001**.
25. 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**.
26. Cancès, M.T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, 107, 3032.
27. Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, 286, 253.
28. Hür, D.; Güven, A. *J. Mol. Struct. (Theochem)* **2002**, 583, 1.
29. Cheeseman, J.R.; Trucks, G.W.; Keith, T.A.; Frisch, M.J. *J. Chem. Phys.* **1996**, 104, 5497.
30. Vaara, J.; Kaski, J.J.; Jokisaari, J.; Diehl, P. *J. Phys. Chem. A* **1998**, 101, 5069.
31. De Morais, L.P.F.; Hallwass, F.; Malvestiti, I.; Srivastava, R.M. *J. Mol. Struct.* **2006**, 782, 200.
32. Friebolin, H; *Basic One and Two Dimensional NMR Spectroscopy*, VCH Publishers: Weinheim; **1991**.