European Journal of Chemistry 5 (2) (2014) 343-350

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Ab initio calculations of ^{13}C NMR chemical shielding in some N_4O_2, N_4S_2 and N_6 Schiff base ligands containing piperazine moiety

Majid Rezaeivala [a,*] and Sam Daftari [b]

[a] *Department of Chemical Engineering, Hamedan University of Technology, Hamedan 65157, Iran*
[b] *Department of Environmental Sciences, University of Omran and Toseeh, Hamedan, 65157, Iran*

**Corresponding author at: Department of Chemical Engineering, Hamedan University of Technology, Hamedan 65155, Iran.*
Tel.: +98.811.8411501. Fax: +98.811.8411407. E-mail address: mrezaeivala@hut.ac.ir (M. Rezaeivala).

ARTICLE INFORMATION

DOI: 10.5155/eurjchem.5.2.343-350.959

Received: 27 October 2013
Received in revised form: 01 February 2014
Accepted: 04 February 2014
Online: 30 June 2014

KEYWORDS

DFT
GIAO
CSGT
Ab initio
Schiff base
Piperazine

ABSTRACT

The calculation of ^{13}C isotropic shielding constants by means of GIAO and CSGT methods of eight Schiff base ligands containing piperazine moiety at the Hartree-Fock and B3LYP levels of theory are presented. Good linear correlations between the calculated chemical shielding at gas-phase and experimental shift values in $CDCl_3$ solution were obtained. Density functional theory (DFT) calculations at the B3LYP/6-31G(2d,p) level of theory is used to optimize the geometry of ligands. Calculated nuclear magnetic resonance (NMR) chemical shifts ^{13}C are reported for the some N_4O_2, N_4S_2 and N_6 Schiff base ligands containing piperazine moiety. In order to establish a convenient and consistent protocol to be employed for confirming the experimental ^{13}C NMR spectra of Schiff base ligands, different combinations of models and basis sets were considered. The most reliable results were obtained at B3LYP/6-311G++ (d,p) level and CSGT method which can be used to predict ^{13}C NMR chemical shifts with a very high accuracy for latter compounds. These results show the agreement between theoretical and experimental ^{13}C NMR chemical shielding of mentioned ligands.

1. Introduction

Nuclear magnetic resonance spectroscopy is an important experimental tool to probe the local geometric and electronic structure of molecules. For quantum chemical calculations on large molecules, density functional theory has become a popular and powerful tool [1-5].

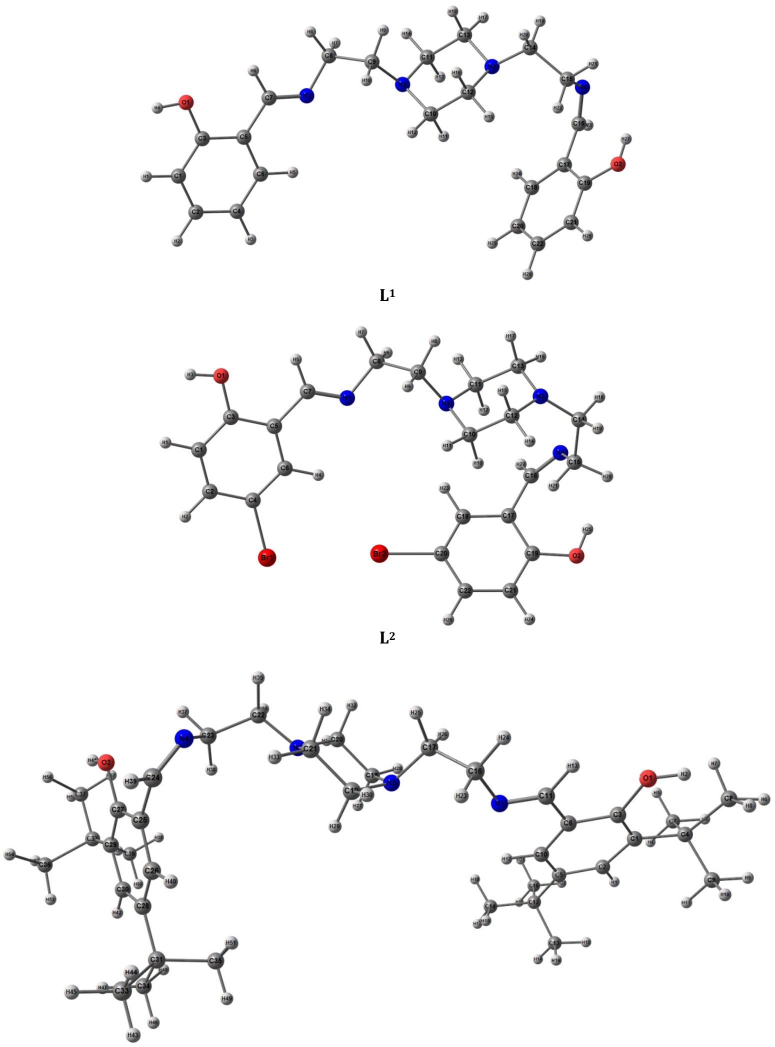
The chemical shift in nuclear magnetic resonance is closely linked to the environment of the nuclei. Thus, the measurement and theoretical calculation of the chemical shift tensors can provide useful information of the electronic structures of molecules [6,7]. In the next few years, it is likely that theoretical predictions of chemical shifts will become routinely used in the structural study of molecules. On the other hand, experimental improvements enable the determination of the principal values of ^{13}C chemical tensors in complex molecules to be made [8].

Even though we see a steady advancement in NMR techniques, this information may not lead to an unambiguous structure: among many possible causes there are difficulties in resolving crowded spectral regions, in determining small long-range couplings, or in assigning them. As a result, the confirmation of the proposed structure through X-ray analysis or total synthesis is required, but these avenues are not always available [9-11]. On the other hand, it is clear that the good correlation between the experimental and theoretical properties of the molecules will be achieved when the theoretically considered structure is the same or very close to the "actual" structure. In this work we have considered the latter structure for NMR study on upcoming ligands, and we were interested to know whether we can obtain a good correlation between the experimental and theoretical ^{13}C isotropic shielding constants.

Schiff base compounds have attracted considerable attention due to their impressive and useful chemical and physical properties [12-15]. The instant and enduring popularity of Schiff base compounds undoubtedly stem from the ease with which they can be synthesized and their wide range complexing ability [16-19]. Besides, a wide variety of Schiff base ligands and their metal complexes have been extensively investigated because of their potential applicability as catalysts [20-23] and their magnetic properties [24].

On the other hand, the comparison between experimental and theoretical NMR data may be helpful in making correct assignments and understanding the relationship between chemical shielding and molecular structure. Therefore, nowadays the Gauge Independent Atomic Orbitals/Density Functional Theory (GIAO/DFT) [23,25] and Continuous Set of Gauge Transformations/Density Functional Theory (CSGT/DFT) [26,27] approaches are widely used to calculate chemical shifts for a variety of compounds [28-31].

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.5.2.343-350.959



L¹

L²

L³

Figure 1. B3LYP/6-31G(2d,p) geometry optimized structure of L¹, L² and L³.

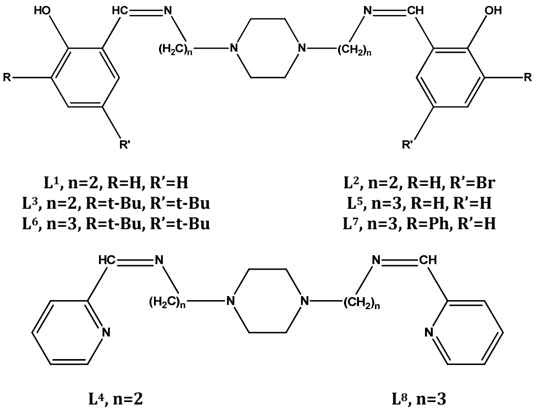
A comparison between the experimental and theoretical investigations on carbon-13 isotropic shielding constants of some tripodal tetraamine ligands has been reported [32].

The present work is focused on predicting NMR shielding tensors at the DFT/B3LYP level of theory with two different models: gauge-including atomic orbital (GIAO) and continuous sets of gauge transformations and two different basis sets, 6-31G (2d,p) and 6-311++G(d,p).

According to our knowledge, there are only few computational NMR studies on Schiff base compounds [33-35]. In this work, the ^{13}C NMR isotropic chemical shielding of eight Schiff base ligands in gas phase (Scheme 1) studied systematically by the GIAO [23,25] and CSGT [26,27] methods at the level of density functional theory (DFT) with two different basis sets, 6-31G(2d,p) and 6-311++G(d,p).

2. Experimental

The geometries of all Schiff base ligands investigated here, in gas-phase were fully optimized at the DFT (B3LYP) [36] level of theory using the Gaussian 03 package [37]. The standard 6-31G(2d,p) basis set was used for geometry optimization (Figure 1-3) and vibrational frequency analyses calculated at the same level of theory, indicate that optimized structures are at the stationary points corresponding to local minima without any imaginary frequencies. The NMR calculations were performed at the Hartree-Fock (HF) level of theory using the standard 6-31G(2d,p) and 6-311++G(d, p) basis sets.



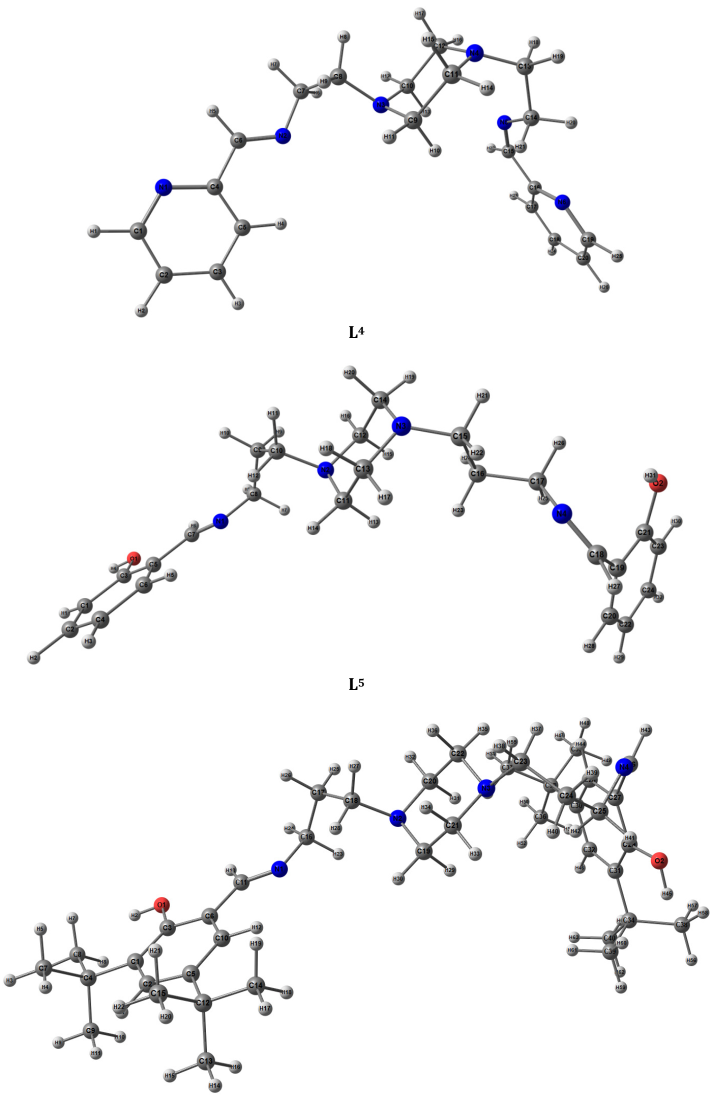
L¹, n=2, R=H, R'=H
L³, n=2, R=t-Bu, R'=t-Bu
L⁶, n=3, R=t-Bu, R'=t-Bu

L², n=2, R=H, R'=Br
L⁵, n=3, R=H, R'=H
L⁷, n=3, R=Ph, R'=H

L⁴, n=2

L⁸, n=3

Scheme 1



L^4

L^5

L^6

Figure 2. B3LYP/6-31G(2d,p) geometry optimized structure of L^4, L^5 and L^6.

The calculations of NMR shielding tensors were done using two common procedures, namely GIAO and CSGT. The obtained shielding tensors were referenced against tetramethylsilane (TMS) to yield relative chemical shifts {δ (cal) = δ (TMS, calc) - δ iso (calc)} [38]. Calculations were performed on a Pentium-PC computer with a 3200 MHz processor. A starting molecular-mechanics structure for the ab initio calculations was obtained using the HyperChem 5.02 program [39]. The experimental ^{13}C NMR data of Schiff base ligands derived from a previous paper [40].

3. Result and discussion

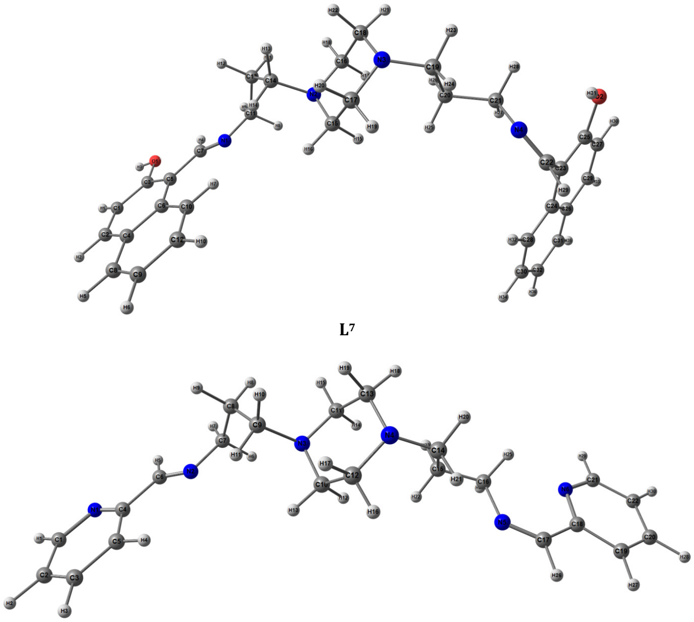
Piperazine is a water soluble cyclic diazine with rigid preorganized cyclohexane conformation [41]. As an amine, piperazine readily undergoes nucleophilic substitution reactions with proper halides. The so-called reinforced compounds have been introduced, namely, systems in which two amine groups are linked by a further aliphatic chain [42].

It has been experimentally/theoretically confirmed that the chair conformation is usually more stable than boat conformation for saturated six-membered rings [43]. In particular, when the ligand is complexed, the piperazine moiety should exist as a boat conformer, but when the ligand demetallates, the piperazine fragment assumes the thermodynamically more favorable chair conformation [44].

The standard 6-31G(2d,p) basis set was used for geometry optimization and vibrational frequency analyses, calculated at the same level of theory, indicate that optimized structures are at the stationary points corresponding to local minima without any imaginary frequencies (Figure 1-3).

The theoretical calculations of ^{13}C NMR chemical shifts for eight Schiff base ligands containing piperazine moiety were performed with GIAO and CSGT models, through HF and B3LYP level of theory applying two different basis sets.

The computed ^{13}C NMR chemical shifts at 6-31G(2d,p) and 6-311++G(d,p) levels of theory in comparison with experimental data for all Schiff base ligands are given in Tables 1-8. It is clear that the results of the B3LYP method are in a better agreement with experimental values in L^3, L^6 and L^8 and HF method have good agreement with experimental data in L^1, L^2 and L^5. In L^3 and L^8 with GIAO, B3LYP is better and with CSGT, HF is better.



L^7

L^8

Figure 3. B3LYP/6-31G(2d,p) geometry optimized structure of L^7 and L^8.

Table 1. Comparison between experimental and calculated chemical shifts (ppm) for L^1.

Atoms	GIAO		CSGT		Experimental
	HF	B3LYP	HF	B3LYP	
C1	111.0 [a]	110.6	113.4	110.7	117.0
	116.3 [b]	117.4	112.3	113.3	
C2	134.6	126.8	135.6	126.0	118.7
	142.2	136.7	138.9	133.6	
C3	154.7	151.5	158.6	153.6	161.1
	163.8	163.5	158.9	158.1	
C5	118.2	117.0	119.9	116.5	113.3
	124.7	125.6	122.0	122.8	
C6	120.3	120.0	122.6	120.4	118.6
	127.1	129.2	121.7	123.1	
C9	134.0	125.1	135.1	124.6	132.3
	141.7	134.9	136.5	130.2	
C10	156.1	150.0	158.6	151.1	165.8
	163.2	159.5	159.0	155.4	
C16	56.9	63.3	59.2	65.9	58.5
	59.8	68.3	57.6	66.2	
C17	50.4	55.4	52.2	57.7	56.8
	52.9	59.9	51.1	58.2	
C23	49.1	55.1	50.8	57.0	53.1
	51.7	59.7	50.4	58.4	
C24	43.6	48.8	45.5	50.9	53.1
	45.7	52.7	44.4	51.3	
C25	42.7	47.1	44.5	49.3	53.1
	44.5	50.3	43.5	49.5	
C26	44.2	48.0	46.0	50.1	53.1
	46.1	51.3	44.9	50.2	
C36	53.3	59.6	55.39	61.8	56.8
	55.5	63.8	53.48	61.8	
C37	47.0	51.9	55.4	54.7	58.5
	48. 8	55.5	47.0	53.5	
C43	159.4	155.6	162.8	157.9	165.8
	167.1	166.2	162.7	162.0	
C44	118.7	118.9	121.9	120.3	118.6
	125.6	127.8	120.3	121.7	
C46	131.9	124.9	133.2	124.5	132.3
	139.8	134.9	135.5	130.9	
C47	152.4	148.9	156.3	150.7	161.1
	160.9	160.3	156.2	154.8	
C48	118.4	116.0	120.2	116.1	131.3
	125.2	124.9	122.5	122.5	
C49	114.7	111.5	116.5	111.3	117.0
	121.8	120.4	117.4	116.0	
C52	133.7	126.4	134.6	125.6	118.7

[a] Computed data at 6-31G(2d,p) for all atoms.

[b] Computed data at 6-311++G(d,p) for all atoms.

Table 2. Comparison between experimental and calculated chemical shifts (ppm) of L^2.

Atoms	GIAO		CSGT		Experimental
	HF	B3LYP	HF	B3LYP	
C1	112.1 [a]	111.5	114.6	112.1	109.9
	117.3 [b]	118.3	113.2		
C2	137.9	129.8	139.4	129.9	134.9
	145.7	139.7	140.4		
C3	154.4	150.7	158.6	153.2	160.4
	163.2	162.3	158.3		
C5	123.7	128.4	125.9	128.3	120.1
	130.4	137.6	129.2		
C6	121.8	121.7	124.3	122.4	119.9
	128.3	130.6	123.1		
C9	136.6	127.7	138.3	128.2	134.9
	144.3	137.3	137.1		
C10	155.3	149.6	157.8	150.6	164.4
	162.4	159.2	158.1		
C16	56.9	63.2	59.1	65.8	58.4
	59.7	68.1	57.3		
C17	50.4	55.3	52.3	57.9	56.8
	52.8	59.8	51.1		
C23	48.9	54.9	50.5	57.0	53.3
	51.3	59.6	49. 8		
C24	43.3	49.6	44.8	51.3	53.3
	45.1	53.2	43.6		
C25	40.8	45.2	42.9	47.4	53.3
	42.3	47.9	41.3		
C26	39.8	43. 9	41. 7	45.5	53.3
	41.0	46.0	40.1		
C36	53.6	60.0	55.7	62.4	56.8
	55.9	64.5	54.5		
C37	51.9	58.0	53.7	60.0	58.4
	54.0	61.9	51.9		
C43	160.1	155.6	163.3	157.9	164.4
	168.7	166.9	164.4		
C44	119.1	119.7	122.1	121.4	119.9
	125.7	128.2	120.1		
C46	135.3	128.1	136.9	128.4	134.9
	143.0	137.6	137.0		
C47	152. 8	148.4	156.9	150.7	160.4
	161.2	159.6	156.4		
C48	125.3	129.1	127.6	129.5	120.1
	132.4	138.8	130.2		
C49	115.5	112.6	117.4	112.7	109.9
	122.2	121.2	117.9		
C52	137. 9	130.3	139.1	130.2	134.9
	145.7	140.3	140.6		

[a] Computed data at 6-31G(2d,p) for all atoms.

[b] Computed data at 6-311++G(d,p) for all atoms.

Table 3. Comparison between experimental and calculated chemical shifts (ppm) of L3.

Atoms	GIAO		CSGT		Experimental
	HF	**B3LYP**	**HF**	**B3LYP**	
C1	125.2 [a]	125.0	128. 8	126.8	125.9
	132.8 [b]	134.6	128. 8	126.8	
C2	134. 7	126.8	137.7	128.9	127.0
	142.8	137. 7	137.7	128.9	
C3	151.4	149.2	157.2	153. 8	158.2
	159.4	160.2	157.2	153. 8	
C4	31.5	39.1	33.9	43.5	35.1
	33.6	43.0	33.9	43.5	
C5	136.0	135.0	138.2	135.7	140.1
	145.3	147.2	138.2	135.7	
C6	121.6	121.9	124.5	122.	118.0
	128.1	130.7	124.5	122.4	
C8	32.4	34.4	32.2	34.1	31.6
	34.1	36.4	32.2	34.1	
C9	27.7	29.2	28.4	29.6	31.6
	28.5	30.2	28.4	29.6	
C10	32.5	34.9	32.3	34.2	31.6
	34.2	37.0	32.3	34.2	
C12	128.5	120.4	131.3	122.2	125.9
	135.2	129.3	131.3	122.2	
C13	157. 7	151.6	160.1	152.4	166.8
	165.0	161.1	160.1	152.4	
C14	29.8	36.5	32.2	41.2	34.2
	31. 9	40.5	32.2	41.2	
C26	30.8	32.5	30.7	32.2	29.1
	32.4	34.4	30. 7	32.2	
C27	27.2	29.1	27.8	29.3	29.1
	28.4	30.3	27.8	29.3	
C28	30.9	32. 6	30.7	32.3	29.1
	32. 5	34.4	30.7	32.3	
C31	56.9	63.6	59.2	65.9	59.0
	59.8	68.4	59.2	65.9	
C41	50.5	55.6	52.3	57.8	57.1
	53.1	60.2	52.3	57.8	
C47	50.1	56.4	51.9	58.2	53.5
	53.1	61.4	51.9	58.2	
C48	43.2	48.2	45.0	50.3	53.5
	45.4	52.2	45.0	50.3	
C49	47.3	51. 8	49.2	54.1	53.5
	49.6	55.8	49.2	54.1	
C50	42.3	46.2	43.7	48.1	53.5
	44.4	49.8	43.7	48.1	
C60	53.4	59.3	55.3	61.6	57.1
	56.2	64.5	55.3	61.6	
C61	52.2	57.7	54.2	60.2	59.0
	55.0	62.4	54.2	60.2	
C67	157.3	154.0	160.6	156.0	166.8
	165.4	165.0	160.6	156.0	
C68	124. 6	123.1	127.5	124.0	118.0
	132.0	132.5	127.5	124.0	
C70	130.3	123.1	133.2	125.1	126.9
	137.5	132.7	133.2	125.1	
C71	148.6	146.1	154.4	150.0	158.2
	156.6	157.3	154.4	151.0	
C72	136.8	135.5	139.0	135.7	136.8
	146.4	148.3	139.0	135.7	
C73	125.6	124.4	128.7	126.3	125.9
	133.1	134.1	128.7	126.3	
C76	129.8	123.5	133.0	125.4	126.9
	137.0	133.1	133.0	125.4	
C77	29.9	37.7	32.3	41.3	34.2
	32.1	41.3	32.3	41.3	
C78	31.7	39.7	34.1	43.6	35.1
	33.8	43.4	34.1	43.6	
C80	31.7	32.6	30.2	31.9	29.1
	32.0	34.4	30.2	31.9	
C81	27.2	29.1	27.9	29.3	29.1
	28.3	30.4	27.9	29.3	
C82	31.0	32.7	30.8	32.6	29.1
	32.8	34.7	30.8	32.6	
C83	32.1	34.7	31.8	33.9	31.6
	33.9	36.5	31.8	33.9	
C84	27.7	29.4	28.4	29.6	31.6
	28.5	30.5	28.4	29.6	
C85	32.4	34.8	32.1	34.2	31.6
	34.1	36.6	32.1	34.2	

[a] Computed data at 6-31G(2d,p) for all atoms.
[b] Computed data at 6-311++G(d,p) for all atoms.

Table 4. Comparison between experimental and calculated chemical shifts (ppm) of L4.

Atoms	GIAO		CSGT		Experimental
	HF	**B3LYP**	**HF**	**B3LYP**	
C1	150.5 [a]	145.0	152.9	145.6	149.3
	158.2 [b]	155.1	152.5	149.6	
C2	121.2	120.0	122.4	118.8	120.7
	127.6	128.5	124.6	125.5	
C5	138.5	130.3	140.0	130.2	136.9
	146.1	140.3	142.0	136.6	
C6	157.8	151. 7	159.7	152.1	162.4
	165.8	162.4	159.3	155.9	
C8	120.0	118.2	121.7	117.9	125.1
	126.4	126.5	121.3	121.7	
C9	161.2	157.5	164.0	159.0	153.9
	169.1	168.6	164.6	164.1	
C14	57.0	63.4	59.3	66.0	57.7
	59.9	68.2	57.6	66.1	
C15	49.9	55.1	51.8	57.4	57.7
	52.5	59.4	50.7	57.8	
C21	50.5	57.1	52.3	59.0	52.8
	53.3	61.8	51.7	60.5	
C22	43.2	48.5	44.9	50.5	52.8
	45.2	52.1	43.6	50. 8	
C23	41.5	45.6	43.7	48.4	52.8
	43.2	49.0	42.2	48.2	
C24	40.2	44.1	42.2	46.3	52.8
	41.5	46.8	40.6	45.9	
C34	54.1	59.5	56.4	62.4	57.7
	56.9	64.8	55.4	63.2	
C35	52.7	59.7	54.9	62.3	58.0
	55.2	64.4	52.9	62.0	
C41	153.6	151.5	156.9	153.8	153.9
	160.8	162.2	157.2	158.7	
C42	155.1	148.3	157.0	148.2	162.4
	163.0	158.6	156.3	151.2	
C44	125.1	124.7	126.6	124.2	125.1
	131.3	133.0	127.4	129.2	
C46	139.6	131.7	140.8	131.3	136.9
	147.4	142.0	143.0	137.9	
C47	151.4	145.3	153.7	145.8	149.3
	158.9	155.1	153.0	149.6	
C49	120.8	118.7	121.9	117.5	120.7
	127.2	127.3	123.8	123.9	

[a] Computed data at 6-31G(2d,p) for all atoms.
[b] Computed data at 6-311++G(d,p) for all atoms.

Table 5. Comparison between experimental and calculated chemical shifts (ppm) of L5.

Atoms	GIAO		CSGT		Experimental
	HF	**B3LYP**	**HF**	**B3LYP**	
C1	111.2 [a]	110.8	113.6	110.8	116.9
	142.1 [b]	142.1	138.8	133.6	
C2	134.6	127.1	135.5	126.0	131.0
	131.0	142.1	142.1	138.8	
C3	154.8	151.6	158.7	153. 7	161.3
	163.9	163.9	159.0	158.1	
C5	118.2	116.7	119.9	116.4	118.3
	124.7	124.7	122.0	122.7	
C6	120.3	119.6	122.7	120.3	118.8
	127.2	127.2	121.8	123.0	
C9	133.5	124.4	134.5	124.2	132.0
	141.1	141.1	135.9	129.6	
C10	155.5	149.3	158.0	150.3	164.9
	162.6	162.6	158.4	154.6	
C16	52.6	59.5	54.7	61.8	57.3
	55.3	55.3	53.6	62.4	
C17	30.0	32.8	29.7	33.1	27.8
	31.9	31.9	31.0	35.6	
C20	42.7	47.2	44.8	49.9	55.7
	44.0	44.0	43.0	49.3	
C26	50.1	56.8	51.8	58.5	53.1
	52.6	52.6	51.1	59.8	
C27	42.9	48.4	44.7	50.5	53.1
	44.8	44.8	43.6	51.1	
C28	42.4	47.1	44.4	49.4	53.1
	44.3	44.3	43.2	49.5	
C29	39.4	43.3	41.3	45.5	53.1
	40.9	40.9	39. 9	45.2	
C39	51.0	57.2	53.1	59.9	55.7
	53.6	53.6	52.7	61.2	

[a] Computed data at 6-31G(2d,p) for all atoms.
[b] Computed data at 6-311++G(d,p) for all atoms.

Table 5. Continued.

Atoms	GIAO		CSGT		Experimental
	HF	B3LYP	HF	B3LYP	
C40	31.9	36.6	31.4	37.1	27.8
	33.9	40.2	33.1	40.2	
C43	47.7	53.4	50.0	56.3	57.3
	49.7	49.7	48.0	55.3	
C49	158.8	154.7	161.9	156.8	164.9
	166.5	166.5	161.9	161.1	
C50	117.6	117.6	120.8	119.3	118.8
	124.3	124.3	118.9	120.4	
C52	131.7	124.8	133.0	124.5	132.0
	138.8	138.8	134.89	130.4	
C53	153.7	149. 9	157.5	151.8	161.3
	162.3	162.3	157.4	155.9	
C54	118.1	116.0	119.8	115.7	118.3
	124.8	124.8	122.0	122.2	
C55	114.9	112.0	116.7	111.6	116.9
	122.1	117.6	116.4	122.1	
C58	134.6	127.3	135.4	126.2	131.0
	142.2	138. 7	133.9	142.2	

[a] Computed data at 6-31G(2d,p) for all atoms.

[b] Computed data at 6-311++G(d,p) for all atoms.

Table 6. Comparison between experimental and calculated chemical shifts (ppm) of L^6.

Atoms	GIAO		CSGT		Experimental
	HF	B3LYP	HF	B3LYP	
C1	125.6 [a]	124.5	129.1	127.1	126.8
	144.0 [b]	134.1	129.0	130.5	
C2	134.8	126.5	129.1	129.1	136.7
	147.9	137.5	139.3	134.4	
C3	151.5	149.6	157.3	153.9	158.2
	169.7	160.5	155.5	156.2	
C4	31.5	39.9	33.9	43.5	35.0
	59.2	43.4	34.9	45.7	
C5	135.9	135.3	138.1	135.6	136.7
	156.5	147.5	141.4	143.0	
C6	121.4	121.7	124.3	122.2	117.8
	139.4	130.6	124.2	125.9	
C8	32.6	35.0	32.3	34.2	31.5
	49.2	36.9	32.5	35.7	
C9	27.7	29.2	28.3	29.6	31.5
	41.8	30.0	26.0	28.3	
C10	32.4	34.8	32.1	34.0	31.5
	49.0	36.7	32.3	35.5	
C12	127.9	120.4	130.7	121.7	126.8
	137.7	129.0	129.5	124.2	
C13	157.3	151.2	159.8	151.8	166.0
	169.9	160.6	160.5	156.4	
C14	29.8	37.1	32.2	41.2	34.1
	56.8	40.9	33.2	43.3	
C26	30.8	32.8	30.7	32.3	29.4
	47.1	34.6	30.8	33.5	
C27	27.2	28.4	27.8	29.2	29.4
	42.4	29.9	26.3	28.9	
C28	30.8	32.7	30.6	32.2	29.4
	47.0	34.4	30.8	33.5	
C31	52.4	59.2	54.6	61.6	57.6
	75.8	63.7	53.5	62.2	
C41	30.0	32.7	29.7	33.2	28.1
	49.2	35.6	31.0	35.7	
C44	42.9	47.8	44.9	50.3	56.1
	63.3	50.8	43.2	49.8	
C50	49.5	55.6	51.3	57.5	53.3
	72.3	60.0	50.8	58.8	
C51	42.7	48.0	44.5	50.1	53.3
	64.2	51.9	43.6	50.7	
C52	42.5	46.9	44.4	49.2	53.3
	63.0	50.2	43.4	49.5	
C53	44.4	48.7	46.2	50.6	53.3
	64.2	51.8	45.1	50.7	
C63	48.7	55.3	50.7	57.3	56.1
	71.3	58.8	49.3	57.8	
C64	26.8	29.3	27.1	30.3	28.1
	45.4	31.9	27.4	32.0	
C67	45.5	51.6	47.8	53.9	57.6
	66.7	54.8	45.9	53.2	
C73	157.2	154.3	160.6	156.4	166.0
	174.4	165.0	160.7	160.9	
C74	123.6	121.8	127.1	123.3	117.8
	140.1	131.7	127.1	126.6	
C76	130.7	124.2	133.4	125.4	117.8
	143.6	133.9	134.3	130.0	
C77	150.2	147.1	155.4	151.6	139.8
	168.5	158.1	154.8	154.9	
C78	137.0	135.6	138.9	135.8	158.2
	157.2	148.1	142.6	143.6	
C79	126.9	125.4	129.9	127.5	136.7
	144.8	135.7	130.0	131.25	
C82	126.6	120.7	129.9	122.7	126.8
	138.6	129.2	128.5	125.1	
C83	30.0	36.5	32.4	41.4	126.8
	57.0	40.5	33.4	43.5	
C84	29.6	37.5	31.5	40.9	34.1
	56.7	41.1	32.6	43.1	
C86	31.0	32.9	30.8	32.5	35.0
	47.5	35.2	31.0	34.0	
C87	27.2	28.9	27.8	29.3	29.4
	42.3	30.3	26.2	28.8	
C88	31.2	33.2	30.8	32.5	29.4
	47.6	35.2	31.1	34.1	
C89	27.3	29.1	27.2	28.8	29.4
	43.0	30.4	26.8	29.5	
C90	27.1	29.2	27.0	28.5	31.5
	42.5	30.3	26.5	29.0	
C91	30.1	32.6	30.6	32.3	31.5
	45.6	33.9	29.0	32.1	

[a] Computed data at 6-31G(2d,p) for all atoms.

[b] Computed data at 6-311++G(d,p) for all atoms.

Table 7. Comparison between experimental and calculated chemical shifts (ppm) of L^7.

Atoms	GIAO		CSGT		Experimental
	HF	B3LYP	HF	B3LYP	
C1	112.9 [a]	111.9	116.1	113.3	117.7
	118.1 [b]	119.0	115.0	115.8	
C2	137.1	129.3	138.8	129.2	137.3
	144.3	138.7	140.9	135.5	
C3	156.0	152.2	160.1	155.1	137.3
	164.0	163.7	159.7	159.0	
C5	126.4	124.6	128.8	125.1	126.2
	134.4	134.9	129.3	129.6	
C6	111.3	111.8	115.2	113.8	106.5
	117.3	119.9	112.6	114.3	
C9	136.7	130.0	139.2	131.1	134.0
	144.2	139.6	138.6	134.3	
C10	159.5	153.3	161.9	153.7	158.2
	166.6	162.8	162.4	158.3	
C11	128.4	124.0	130.6	124.5	127.9
	135.3	133.2	132.2	130.3	
C14	123.1	120.1	124.9	120.0	125.2
	129.7	129.1	127.0	126.2	
C15	128.0	125.2	129.8	125.4	122.6
	135.1	134.42	130.8	130.4	
C18	54.0	61.3	56.2	63.5	54.8
	56.8	65.6	55.1	64.1	
C19	129.87	124.9	131.3	124.6	129.3
	136.7	134.2	133.4	131.0	
C22	30.2	32.8	29.8	33.2	27.4
	32.0	35.6	31.1	35.6	
C26	43.2	47.7	45.2	50.4	50.7
	44.5	50.6	43.5	49.8	
C32	50.3	57.2	52.1	58.9	53.0
	52.9	61.7	51.4	60.2	
C33	42.9	48.5	44.7	50.6	53.0
	44.8	52.2	43.6	51.1	
C34	42.4	47.2	44.4	49.4	53.0
	44.2	50.5	43.1	49.4	
C35	39.7	43.6	41.6	45.8	53.0
	41.3	46.6	40.2	45.5	
C45	51.2	57.3	53.3	60.0	50.7
	53.8	62.1	52.8	61.3	
C46	32.0	36.4	31.5	37.21	27.4
	34.0	40.3	33.3	40.5	
C49	48.1	53.9	50.3	56.8	54.8
	50.1	57.6	48.6	56.1	
C55	159.3	154.4	162.6	157.1	158.2
	167.3	165.6	162.5	161.0	
C56	108.4	110.4	113.0	114.0	106.5
	114.4	118.2	109.3	113.0	

[a] Computed data at 6-31G(2d,p) for all atoms.

[b] Computed data at 6-311++G(d,p) for all atoms.

Table 7. Continued.

Atoms	GIAO		CSGT		Experimental
	HF	B3LYP	HF	B3LYP	
C58	134.2	128.6	136.7	129.7	134.0
	141.8	138.4	136.2	132.9	
C59	152.4	148.2	156.9	151.1	137.3
	160.3	159.0	156.2	154.5	
C60	125.9	123.8	128.4	124.5	126.2
	133.9	134.3	128.7	128.7	
C61	116.1	113.5	118.8	114.1	117.7
	122.7	122.2	119.3	118.5	
C63	121.8	119.3	123.9	119.7	122.6
	128.3	127.9	125.0	124.6	
C64	135.1	128.7	137.0	128.7	137.3
	142.3	138.1	139.2	135.0	
C65	129.5	123.4	130.8	123.0	129.3
	136.7	132.9	133.3	129.8	
C66	130.1	125.4	132.1	125.3	127.9
	137.2	134.5	133.7	131.0	
C70	122.5	119.9	124.3	119.6	125.2
	129.2	128.9	124.3	119.6	

[a] Computed data at 6-31G(2d,p) for all atoms.
[b] Computed data at 6-311++G(d,p) for all atoms.

Table 8. Comparison between experimental and calculated chemical shifts (ppm) of L^8.

Atoms	GIAO		CSGT		Experimental
	HF	B3LYP	HF	B3LYP	
C1	150.8 [a]	145.3	153.1	145.7	148.4
	158.5 [b]	155.4	152.7	149.8	
C2	121.4	120.0	122.5	119.0	123.7
	127.7	128.7	124.7	125.7	
C5	138.7	130.3\	140.0	130.2	135.5
	146.2	140.4	142.1	136.6	
C6	157.6	151.5	159.5	151.9	153.7
	165.6	162.2	159.0	155.6	
C8	119.6	117.9	121.4	117.6	120.2
	125.9	126.1	120.9	121.3	
C9	160.9	156.9	163.6	158.4	161.1
	168.7	167.8	164.2	163.4	
C14	52.3	58.8	54.4	61.5	58.4
	54.9	63.3	53.2	62.0	
C15	29.4	32.2	29.1	32.6	27.0
	31.3	35.0	30.3	35.0	
C18	42.8	47.2	44.8	50.0	55.2
	44.1	50.1	43.0	49.3	
C24	50.2	56.8	51.9	58.6	52.3
	52.8	61.3	51.3	59.9	
C25	42.7	48.0	44.5	50.2	52.3
	44.6	51.7	43.3	50.7	
C26	42.2	46.9	44.2	49.2	52.3
	44.0	50.2	42.9	49.2	
C27	39.6	43.6	41.6	45.8	52.3
	41.3	46.6	40.2	45.5	
C37	51.1	57.6	53.3	60.3	55.2
	53.7	62.3	53.0	61.6	
C38	32.3	36.5	32.1	37.6	27.0
	34.2	40.4	33.3	40.3	
C41	48.5	54.9	50.9	57.8	58.4
	50.9	59.2	48.9	57.1	
C47	152.9	150.6	156.2	152.7	161.1
	160.2	161.3	156.4	157.6	
C48	155.2	148.3	157.0	148.2	153.7
	163.1	158.6	156.3	151.2	
C50	124.8	124.5	126.4	124.0	120.2
	131.0	132.9	127.2	129.1	
C52	139.5	131.6	140.7	131.2	135.5
	147.3	141.9	142.9	137.8	
C53	151.4	145.4	153.6	145.7	148.4
	158.9	155.2	153.0	149.5	
C55	120.6	118.3	121.7	117.3	123.7
	127.1	127.0	123.6	123.5	

[a] Computed data at 6-31G(2d,p) for all atoms.
[b] Computed data at 6-311++G(d,p) for all atoms.

The results show that when the molecular weight of ligands is higher, B3LYP is more appropriate than HF as it is obvious in comparison of L^3 and L^6, L^4 and L^8.

B3LYP/6-311G(2d, p) is the recommended method by Cheeseman *et al.* for calculating isotropic NMR chemical shifts [40]. The best basis set for ^{13}C NMR chemical shifts calculation of these ligands is B3LYP/6-311G++(d,p) because all of my ligands are neutral.

To clarify the relation between theoretical and experimental values of NMR shielding tensors, the experimental data are plotted versus computed values. The r^2 values as shown in Table 9. There are good linear relationships between experimental and theoretical chemical shifts. Differences between the calculated and measured values may be a result of solvent interactions.

The convergence of GIAO and CSGT methods with respect to the basis set is demonstrated in Tables 2-9 for absolute shielding and refers to TMS calculated at the Hartree-Fock and DFT levels of theory. The shielding constants are found to converge to the same value as the basis set used here. The overall quality of linear correlation between the experimental carbon shift and calculated shielding is very good. Regarding the method for achievement of ^{13}C chemical shifts, for the present case at the B3LYP level, the CSGT algorithm is slightly superior to GIAO. One of the most valuable properties of the chemical shielding is their sensitivity to the molecular geometry and environment. The experiments provided only the values of chemical shifts, which were later assigned into the molecular framework by comparison with the calculated values. The high accuracy achievable by modern chemical shielding calculations allows its use in revising questionable assignments.

An important finding is that the deviations from experimental data appear to be related to the atomic weight of the ligands, the higher the atomic weight the larger deviation.

Table 9. Correlation between theoretical (ppm, refer to TMS) and experimental chemical shifts (ppm) for ligands.

Methods	L^1	L^2	L^3	L^4	L^5	L^6	L^7	L^8
GIAO HF	0.989 [a]	0.985	0.991	0.992	0.992	0.989	0.982	0.991
	0.988 [b]	0.984	0.990	0.992	0.985	0.988	0.982	0.989
GIAO B3LYP	0.975	0.977	0.993	0.987	0.987	0.991	0.977	0.991
	0.973	0.976	0.991	0.987	0.987	0.990	0.976	0.990
CSGT HF	0.992	0.987	0.992	0.992	0.990	0.991	0.981	0.992
	0.988	0.984	0.991	0.990	0.985	0.988	0.982	0.991
CSGT B3LYP	0.991	0.979	0.992	0.986	0.984	0.992	0.972	0.991
	-	0.979	0.990	0.984	0.987	0.989	0.976	0.989

[a] 6-31G(2d,p).
[b] 6-311G++(d,p).

4. Conclusion

In order to suggest a convenient and consistent protocol to be employed to confirm the experimental ^{13}C spectra of Schiff base ligands, different combinations of models and basis sets were considered. The most reliable results were obtained at B3LYP/6-311++G(d,p) level and CSGT model and can be used to calculate ^{13}C NMR chemical shifts with high accuracy for latter ligands. These results show that the agreement between theoretical and experimental ^{13}C NMR chemical shielding of Schiff base ligands containing piperazine moiety could be used to evaluate the intrinsic relationship between structure and exclusive properties.

References

[1]. Gauss, J.; Bunsen-Ges, B. *Phys. Chem.* **1995**, *99*, 1001-1008.
[2]. Ziegler, T. *Chem. Rev.* **1991**, 91, 651-667.
[3]. Hohenberg, P.; Kohn, W. *Phys. Rev. B.* **1964**, *136*, 864-871.
[4]. Vignale, G.; Rasolt, M.; Geldard, D. J. W. *Adv. Quant. Chem.* **1990**, *21*, 235-253.
[5]. Lee, A. M.; Handy, N. C.; Colwell, S. M. *J. Chem. Phys.* **1995**, *103*, 10095-10109.
[6]. Ando, I.; Webb, G. A. Theory of NMR Parameters, Academic Press, London, 1983.
[7]. Facelli, J. C.; Hu, J. Z.; Orendt, A. M.; Arif, A. M.; Pugmire, R. J.; Grant, D. M. *J. Phys. Chem.* **1994**, *98*, 12186-12190.
[8]. Zheng, G.; Hu, J.; Zhang, X.; Shen, L.; Yea, C.; Webb, G. A. *J. Mol. Struct. (Theochem)* **1998**, *428*, 283-286.
[9]. Bagno, A.; Rastrelli, F.; Saielli, G. *Chem. Eur. J.* **2006**, *12*, 5514-5525.
[10]. Price, W. S.; Hwamg, J. L. P. *J. Chin. Chem. Soc.* **1992**, *39*, 497-507.

[11]. Jiang, B. C.; Miao, X. J.; Hwang, L. P.; Ye, C. H. *J. Chin. Chem. Soc.* **1995**, *42*, 887-892.
[12]. Borisova, N. E.; Reshetova, M. D.; Ustynyuk, Y. A. *Chem. Rev.* **2007**, *107*, 46-79.
[13]. Vigato, P. A.; Tamburini, S.; Bertolo, L. *Coord. Chem. Rev.* **2007**, *251*, 1311-1620.
[14]. Beckmann, U.; Brooker, S. *Coord. Chem. Rev.* **2003**, *245*, 17-29.
[15]. Radecka-Paryzek, W.; Patroniak, V.; Lisowski, J. *Coord. Chem. Rev.* **2005**, *249*, 2156-2175.
[16]. Bouwman, E.; Reedijk, J. *Coord. Chem. Rev.* **2005**, *249*, 1555-1581.
[17]. Vigato, P. A.; Tamburini, S. *Coord. Chem. Rev.* **2008**, *252*, 1871-2154.
[18]. Okawa, H.; Furutachi, H.; Fenton, D. E. *Coord. Chem. Rev.* **1998**, *174*, 51-75.
[19]. Cozzi, P. G. *Chem. Soc. Rev.* **2004**, *33*, 410-421.
[20]. Grigoropoulou, G.; Clark, J. H.; Elings, J. A. *Green Chem.* **2003**, *5*, 1-7.
[21]. Sheldon, R. A.; Kochi, J. K. In Metal-catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.
[22]. Hudlicky, M. In Oxidation in Organic Chemistry, ACS Monographs 186. Washington, DC, 1990.
[23]. Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789-807.
[24]. Keith, T.; Bader, R. *Chem. Phys. Lett.* **1993**, *179*, 479-482.
[25]. Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260.
[26]. Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *194*, 1-8.
[27]. Keith, T. A, Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223-231.
[28]. Prakash, R. V.; Rasul, G.; Surya, P. G. K.; Olah, G. A. *J. Org. Chem.* **2003**, *68*, 3507-3510.
[29]. Katritzky, A. R.; Akhmedov, N. G.; Güven, A.; Doskocz, J.; Akhmedova, R. G.; Majumder, S.; Dennis Hall, C. *J. Mol. Struct.* **2006**, *787*, 131-147.
[30]. Meng, Z.; Carper, W. R. *J. Mol. Struct. (Theochem.)* **2002**, *588*, 45-53.
[31]. Gallant, A. J.; Hui, J. K. H.; Zahariev, F. E.; Wang, Y. A.; MacLachlan, M. J. *J. Org. Chem.* **2005**, *70*, 7936-7946.
[32]. Salehzadeh, S.; Bayat, M. *J. Chinese Chem. Soc.* **2007**, *54*, 1145-1150.
[33]. Khanmohammadi, H.; Erfantalab, M. *Spectrochim. Acta A* **2010**, *75*, 127-133.
[34]. Sheikhshoaie, I.; Saheb, V. *Spectrochim. Acta A* **2010**, *77*, 1069-1076.
[35]. Infante-Castillo, R. *J. Mol. Struct. (Theochem)* **2010**, *940*, 124-128.
[36]. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
[37]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Menucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ciolowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Jonhson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Repogle, E. S.; Pople, J. A., Gaussian 03, Gaussian Inc., 2003, Pittsburgh, PA, USA.
[38]. Cheeseman, J. R. Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497-5509.
[39]. Hyper Chem. Released on May 2nd; Hypercube, INC: Gainesville 1997.
[40]. Keypour, H.; Rezaeivala, M.; Fall, Y.; Dehghani-Firouzabadi, A. A. *Arkivoc* **2009**, *10*, 292-301.
[41]. Larkins, H. L.; Hamilton, A. D. *Tetrahedron Lett.* **1986**, *27*, 2721-2724.
[42]. Hubin, T. J.; McComick, J. M.; Collinson, S. R.; Buchalova, M.; Perkins, C. M.; Alcock, N. W.; Kahol, P. K.; Raghunathan, A.; Busch, D. H. *J. Am. Chem. Soc.* **2000**, *122*, 2512-2522.
[43]. Keypour, H.; Rezaeivala, M.; Valencia, L.; Salehzadeh, S.; Perez-Lourido, P.; Khavasi, H. R. *Polyhedron* **2009**, *28*, 3533-3541.
[44]. Boiocchi, M.; Bonizzoni, M.; Fabbrizzi, L.; Foti, F.; Licchelli, M.; Taglietti, A.; Zema, M. *J. Chem. Soc. Dalton Trans.* **2004**, 2616-2620.