



Synthesis and characterization of three new fluorovanadate complexes: $N(C_2H_5)_4^+[VOF_4]^-$, $N(CH_3)_4^+[VOF_3Cl]^-$, $N(C_4H_9)_4^+[VOF_3Br]^-$ and theoretical calculations of VOF_4^- , VOF_3Cl^- and VOF_3Br^- ions

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ABSTRACT

The reaction of VOF_3 with $(C_2H_5)_4NF$, $(CH_3)_4NCl$ and $(C_4H_9)_4NBr$ salts in anhydrous CH_3CN produced new complexes with the anion general formula $[VOF_3X]^-$ in that $(X = F^-, Cl^-, Br^-)$. These were characterized by elemental analysis, IR, UV/Visible and ^{19}F NMR spectroscopy. The optimized geometries and frequencies of the stationary point are calculated at the B3LYP/6-311G level of theory. Theoretical results showed that the V–X ($X = F, Cl, Br$) bond length values for the $[VOF_3X]^-$ in compounds 1–3 are 1.8247, 2.4031 and 2.5595 Å, respectively. Also, the V–F₅ bond length values in $[VOF_3X]^-$ are 1.824, 1.812 and 1.802 Å, respectively. These results reveal that the bond order for V–X bonds decrease from compounds 1 to 3, while for V–F₅ bonds, the bond orders increase. It can be concluded that the decrease of V–X bonds lengths and the increase of V–F₅ bond lengths in compounds 1–3 result from the increase of the hyperconjugation from compounds 1 to 3. Harmonic vibrational frequencies and infrared intensities for VOF_4^- , VOF_3Cl^- and VOF_3Br^- are studied by means of theoretical and experimental methods. The calculated frequencies are in reasonable agreement with the experiment values. These data can be used in models of phosphoryl transfer enzymes because vanadate can often bind to phosphoryl transfer enzymes to form a trigonal-bipyramidal structure at the active site.

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1. Introduction

The interest in coordination chemistry of vanadium has increased in the last decades because of its catalytic and medicinal importance [1–4]. A wide range of structural variations associated with their diverse reactivity are also making them the center of continuous research activities [5]. An application of oxovanadium (IV) compounds as oxidation catalysts was first discovered by Sharpless in the case of the regioselective epoxidation of allylic alcohols [6]. The vanadium coordination compounds play an important role in nitrogen activation, fixation and other biologically important reactions [7,8]. Vanadium complexes with organic ligands are often less toxic and can have improved aqueous solubility and lipophilicity [9]. The most

important oxidation states of vanadium are +3, +4, and +5 and the V(IV) compounds are the most commonly observed in the form of compounds of the vanadyl ion, VO^{2+} [10]. The investigation of the structures and properties of these compounds and their similarities are interested. In this work, we report on the synthesis and characterization of new complexes of type $[VOF_3X]^-$ ($X = F^-, Cl^-, Br^-$) obtained directly from VOF_3 and tetraalkylammonium salts. These vanadium compounds–adducts are actually model structures for phosphorolysis reactions and related analogs have been investigated in that vanadate can often bind to phosphoryl transfer enzymes to form a trigonal-bipyramidal structure at the active site [11]. During this study we report the optimized geometries and infrared spectral measurements; assignments and electronic structure calculations for compounds. The structures of compounds have been optimized by the density functional theory (DFT)-based method at B3LYP/6-311G levels of theory, using the Gaussian 03 package of programs [12–14]. The comparison between theory and experiment is made.

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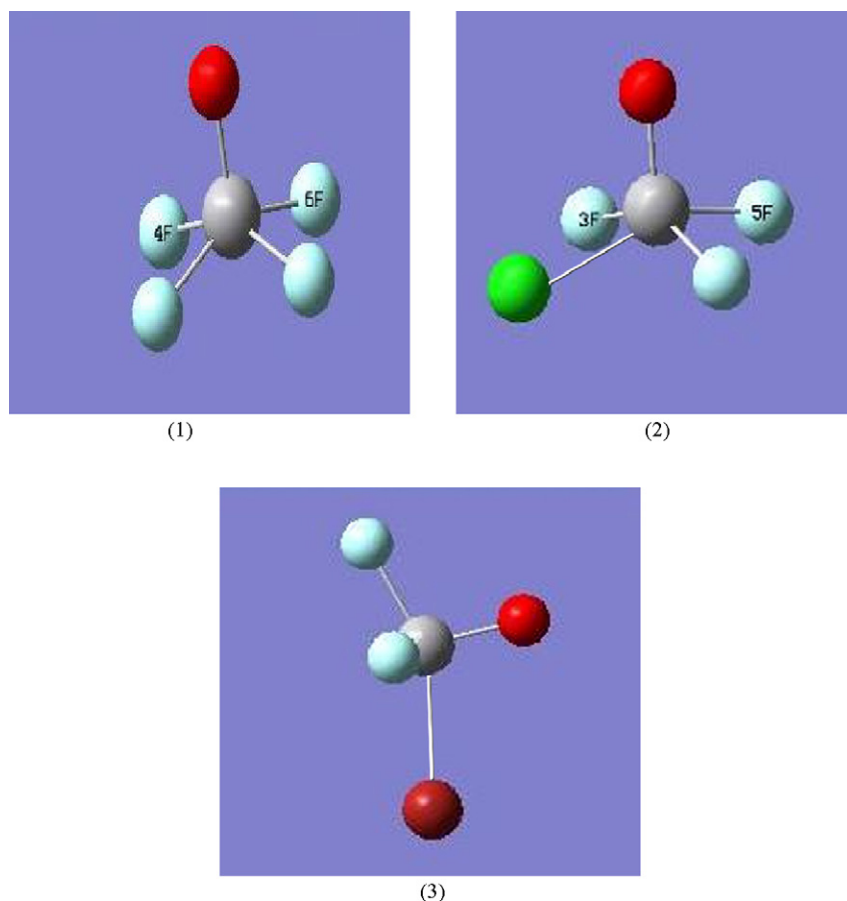


Fig. 1. Optimized geometries of (1) $[\text{VOF}_4]^-$, (2) $[\text{VOF}_3\text{Cl}]^-$, (3) $[\text{VOF}_3\text{Br}]^-$ at B3LYP/6-311G level of theory.

2. Results and discussions

The $(\text{C}_2\text{H}_5)_4\text{N}[\text{VOF}_4]$ complex was obtained by the reaction of $(\text{C}_2\text{H}_5)_4\text{NF}$ with VOF_3 in the acetonitrile solvent (reaction (1)). The reaction of VOF_3 with $(\text{CH}_3)_4\text{NCl}$ in acetonitrile solvent gave $(\text{CH}_3)_4\text{N}[\text{VOF}_3\text{Cl}]$ (reaction (2)). $(\text{C}_4\text{H}_9)_4\text{N}[\text{VOF}_3\text{Br}]$ synthesized by the reaction of VOF_3 with $(\text{C}_4\text{H}_9)_4\text{NBr}$ in acetonitrile (reaction (3)).



The structures of complexes 1, 2 and 3 are shown in Fig. 1. Geometry optimization shows that symmetry for compound 1 is C_{4v} . This is in accordance with the previous theoretical finding that says: all the known $[(d^0\text{-M})\text{X}_4\text{Y}]$ molecules have square-pyramidal structures rather than the expected trigonal-bipyramidal structure. The charge concentration produced by the doubly bonded oxygen is larger than those produced by the singly bonded F ligands. This large charge concentration produced by oxygen is responsible for stabilizing the square pyramidal structure with respect to the trigonal-bipyramidal structure [15].

Geometry optimization shows that symmetry for compounds 2 and 3 are C_s . This is in accordance with the theoretical findings about pentacoordinated heteroleptic systems that identified a coordination arrangement that is close to edge-bridged-tetrahedral (EBT) structure with C_s symmetry [15]. Selected bond distances and angles are reported in Table 1. We could not compare the calculation results given in Table 1 with the experimental data.

Because the crystal structure of the title compound is not available till now. B3LYP/6-311G results showed that the V–X (X = F, Cl, Br) bond length values for the $[\text{VOF}_3\text{X}]^-$ in compounds 1–3 are 1.8247, 2.4031 and 2.5595 Å, respectively. Also, the V–F₅ bond length values in $[\text{VOF}_3\text{X}]^-$ are 1.824, 1.812 and 1.802 Å, respectively. These results reveal that the bond order for V–X bonds decrease from compounds 1 to 3, while for V–F₅ bonds, the bond orders increase. It can be concluded that the decrease of V–X bonds lengths and the increase of V–F₅ bond lengths in compounds 1–3 result from the increase of the hyperconjugation from compounds 1 to 3. Besides, the $\theta_{\text{O}_2\text{-V}_1\text{-X}_6}$ bond angle values in compounds 1–3 are 105.36, 102.01 and 101.63, respectively (see Table 1). These angles amounts are in accordance with VSEPR explanation that said “a doubly bonded ligand such as oxygen distorts the metal

Table 1

Geometrical parameters optimized of compounds 1–3, bond length (Å) and angle (°)

	B3LYP/6-311G		
	$[\text{VOF}_4]^-$	$[\text{VOF}_3\text{Cl}]^-$	$[\text{VOF}_3\text{Br}]^-$
Bond lengths (Å)			
V ₁ –O ₂	1.5934	1.586	1.5862
V ₁ –F ₃	1.825	1.8032	1.8107
V ₁ –F ₄	1.825	1.8032	1.8028
V ₁ –F ₅	1.8247	1.812	1.8028
V ₁ –X ₆	1.8247	2.4031	2.5595
Bond angles (°)			
O ₂ –V ₁ –F ₃	105.1693	106.5635	105.0957
O ₂ –V ₁ –F ₅	105.3697	104.3509	106.3908
O ₂ –V ₁ –X ₆	105.3697	102.0133	101.6371

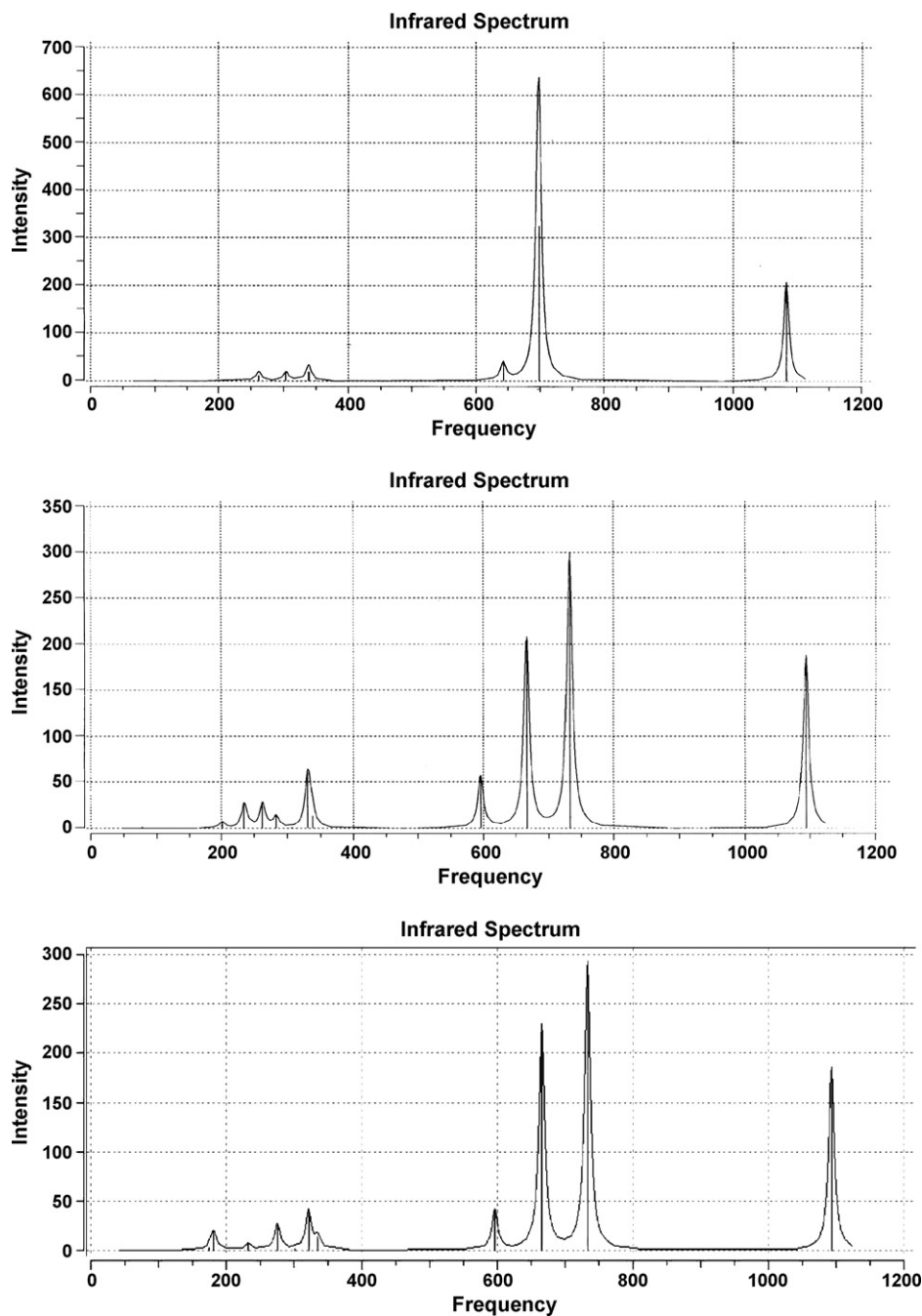


Fig. 2. Calculated infrared spectra of VOF_4^- , VOF_3Cl^- and VOF_3Br^- (top to bottom, frequencies in cm^{-1} , intensities in arbitrary units).

core more than a singly bonded ligand such as fluorine or chlorine” [15]. The decrease of $\theta_{\text{O}_2-\text{V}_1-\text{X}_6}$ bond angle values from compounds 1 to 3, could again, be explained by the increase of the hyperconjugation from compounds 1 to 3. The calculated infrared spectra of three oxovanadium complexes are presented in Fig. 2. The solid-state IR spectra for the complexes 1, 2 and 3 shows $\text{V}=\text{O}$

stretching resonances ($951\text{--}989\text{ cm}^{-1}$) Fig. 3. The harmonic vibrational frequencies of all the stationary points at the B3LYP/6-311G level along with the available experimental data [15–18] presented in Table 2. The compounds structures show the presence of $\text{V}=\text{O}$ stretching vibrations in the region $980 \pm 50\text{ cm}^{-1}$ which is the characteristic region for the ready identification of the $\text{V}=\text{O}$

Table 2

Calculated and experimental frequencies of compounds 1–3 (cm^{-1})

	B3LYP/6-311G	Exptl
$[\text{VOF}_4]^-$	265, 312, 343, 649, 698, 1083	621, 682, 786, 822, 989
$[\text{VOF}_3\text{Cl}]^-$	218, 235, 265, 273, 332, 341, 599, 666, 732, 1093	533, 740, 815, 869, 951, 980
$[\text{VOF}_3\text{Br}]^-$	174, 181, 231, 275, 301, 321, 334, 596, 665, 732, 1093	739, 796, 882, 921, 988

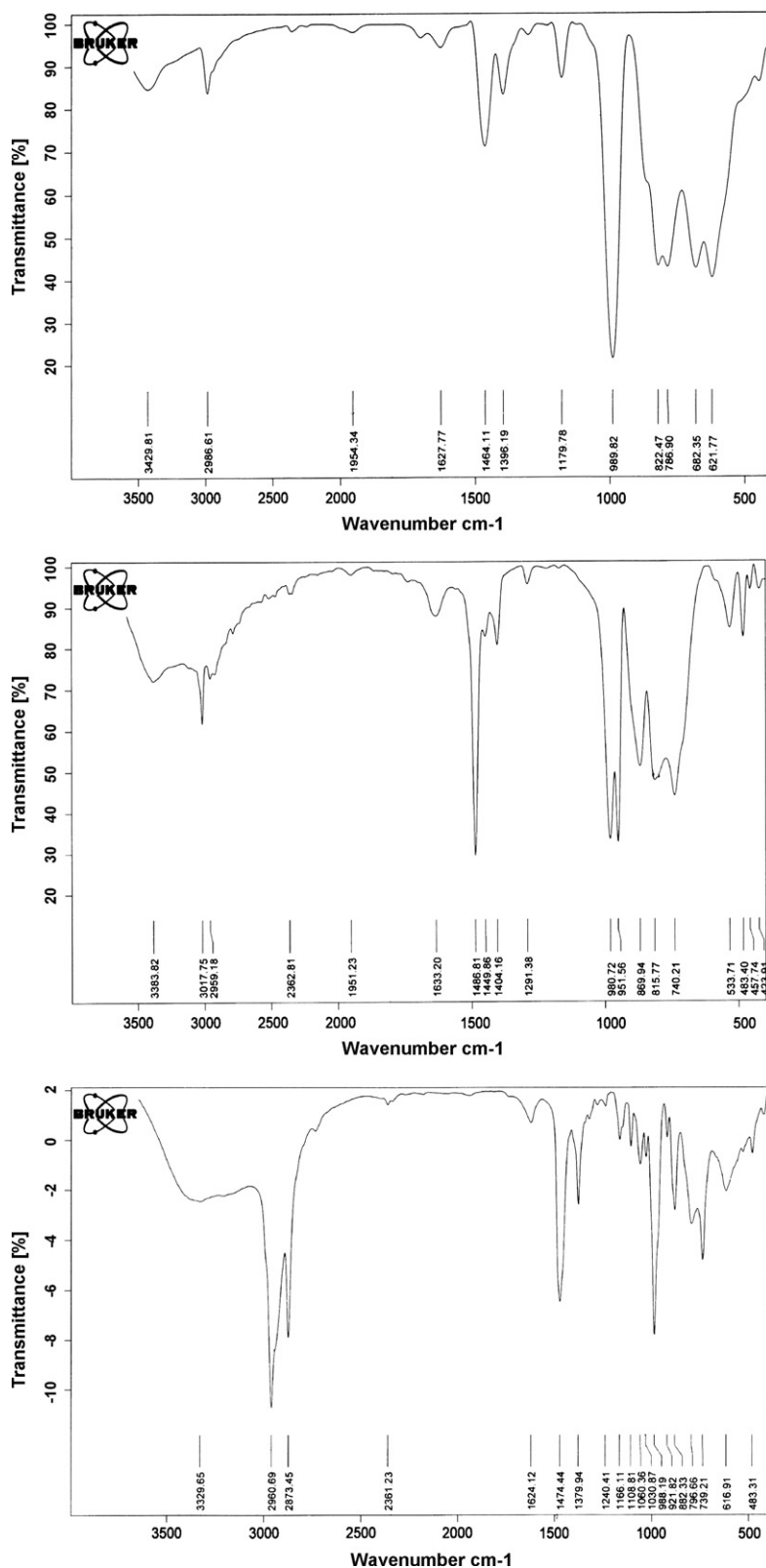


Fig. 3. IR spectra of $(\text{C}_2\text{H}_5)_4\text{N}[\text{VOF}_4]^-$, $(\text{CH}_3)_4\text{N}[\text{VOF}_3\text{Cl}]^-$ and $(\text{C}_4\text{H}_9)_4\text{N}[\text{VOF}_3\text{Br}]^-$ (top to bottom, frequencies in cm^{-1}).

stretching vibrations. Hence, the FT-IR bands at $1035\text{--}950\text{ cm}^{-1}$ in compounds 1–3 have been designated to $\text{V}=\text{O}$ stretching vibration. In general the compounds $\text{V}=\text{O}$ vibrations calculated theoretically are in good agreement with the experimentally reported values [19,20].

3. Conclusions

Three tetraalkylammonium salts of VOF_3 were synthesized in one step and characterized by elemental analysis, IR, UV/Visible

and ^{19}F NMR techniques. Production of these compounds shows the ability of tetraalkylammonium salts in halide addition to transition metal and main group elements compounds and the optimized geometry parameters calculated at B3LYP/6-311G level. The optimized structures are in good agreement with the available experimental results. In the present article, the infrared spectra of the oxovanadium halide complexes were studied using the theoretical and experimental methods. Our theoretical infrared spectra of Compounds 1–3 are in very good agreement compared to our experimental spectra.

4. Experimental

4.1. General

The density functional and ab initio calculation have been performed with the Gaussian program and the basis sets implemented therein [13,21–23].

Acetonitrile (Fluka, PA) was distilled several times from phosphorus pentoxide before use, thereby reducing its water content to <4 ppm. VOF_3 (Merck, PA) were used without further purification. Anhydrous $\text{Et}_4\text{N}^+\text{F}^-$ and $\text{Me}_4\text{N}^+\text{F}^-$ were obtained by a drying procedure of the tetrahydrate in high vacuum (d, 130 °C) [24]. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. ^{19}F NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

4.2. Synthesis of tetraethylammonium tetrafluorooxovanadate (V), $[(\text{C}_2\text{H}_5)_4\text{N}][\text{VOF}_4]$ (1)

To a solution of VOF_3 (0.22 g, 1.77 mmol) in MeCN the solid powder tetraethylammonium fluoride (0.30 g, 2.01 mmol) was added under stirring at room temperature until dark orange solid precipitate was formed. After 2 h stirring, the mixture was filtered, washed with ether and dried at room temperature. mp 247.6 °C (dec.). Anal. Calc. for $\text{C}_8\text{H}_{20}\text{NVOF}_4$: C, 35.17; H, 7.32; N, 5.12. Found: C, 35.30; H, 7.42; N, 5.20%. IR (KBr) (cm^{-1}): 3429, 3225, 3028, 2986, 2968, 2780, 2780, 2655, 2458, 1950, 1464, 1396, 1280, 1028, 989, 822, 786, 682, 621, 499, 428. ^{19}F NMR (CDCl_3): δ –28.21 (br w, 4F). UV–Vis in CH_3CN , λ (cm^{-1}): 36,231, 29,761, 21,459.

4.3. Synthesis of tetramethylammonium chlorotrifluorooxovanadate (V), $[(\text{CH}_3)_4\text{N}][\text{VOF}_3\text{Cl}]$ (2)

Solid powder tetramethylammonium chloride (0.25 g, 2.34 mmol) was added to a solution of VOF_3 (0.26 g, 2.13 mmol) in MeCN the under stirring at room temperature until orange solid precipitate was formed. Stirring was continued for 3 h, the mixture was filtered, washed with ether and dried at room temperature. mp 136.8 °C (dec.). Anal. Calc. for $\text{C}_4\text{H}_{12}\text{NVOF}_3\text{Cl}$: C, 20.56; H, 5.14; N, 5.99. Found: C, 20.64; H, 5.23; N, 6.08%. IR (KBr) (cm^{-1}): 3423, 3383, 3017, 2980, 2959, 2780, 2655, 2362, 1951, 1486, 1404, 1291, 980, 951, 869, 815, 740, 533, 483, 423. UV–Vis in CH_3CN , λ (cm^{-1}): 34,246, 26,881, 22,026.

4.4. Synthesis of tetrabutylammonium bromotrifluorooxovanadate (V), $[(\text{C}_4\text{H}_9)_4\text{N}][\text{VOF}_3\text{Br}]$ (3)

To a solution of VOF_3 (0.138 g, 1.11 mmol) in MeCN the solid powder tetrabutylammonium bromide (0.39 g, 1.21 mmol) was

added under stirring at room temperature until green solid precipitate was formed. After 2 h stirring, the mixture was filtered, washed ether, and dried at room temperature. mp 68.5–69.9 °C. Anal. Calc. for $\text{C}_{16}\text{H}_{36}\text{NVOF}_3\text{Br}$: C, 43.05; H, 8.07; N, 3.13. Found: C, 43.13; H, 8.15; N, 3.21%.

IR (KBr) (cm^{-1}): 3329, 3315, 3225, 3010, 2960, 2873, 2765, 2361, 1950, 1474, 1379, 1166, 1030, 988, 921, 882, 796, 739, 483, 453. UV–Vis in CH_3CN , λ (cm^{-1}): 45,248, 37,037.

4.5. Computational methods

Density functional theory calculations were carried out at B3LYP/6-311G levels of theory with the Gaussian 03 package of programs [13,25] which combines the exact Hartree-Fock exchange with Becke's and uses the Lee-Yang-Parr correlation function in order to include the most important correlation effects. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima [26]. Harmonic vibrational frequencies (ν) in cm^{-1} and infrared intensities (int) in kilometer per mole of all compounds were performed at the same level on the respective fully optimized geometries. These compounds and their data are in accordance with recent works on the formation of five coordinate intermediates.

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