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Vibrational Analysis of 3-Glycidoxypropyltrimethoxysilane Polymer

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Summary: In this work 3-glycidoxypropyltrimethoxysilane polymer with inorganic SiOSi bonds was prepared by a sol-gel process. The structure of polymer was characterized by vibrational spectroscopy (Raman and IR). The interpretation of vibrational spectra is supported by the normal coordinate analysis based on density functional theory (DFT) calculations. A conformational and vibrational analysis of lowest energy dimer structure has been carried out by DFT calculations using Becke's three-parameter exchange functional in combination with the Lee-Young-Parr correlation functional (B3-LYP) and standard 6–311 + G(d,p) basis set.The comparison of theoretical spectra with the experimental data enabled us to extract the characteristic vibrational bands of polymer structure. The inorganic polymerization gives rise to siloxane network with SiOSi stretchings at 1030 and 1134 cm^{-1} suggesting the ladder-type structure of GPTMS polymer.

Keywords: DFT; force-field calc; 3-glycidoxypropyltrimethoxysilane; IR; Raman spectroscopy

Introduction

Organosilanes have been the subject of intensive studies because they are important for the preparation of novel hybrid organic-inorganic materials.[1–6] The general formula R-$(CH_2)_n$-Si-X_3 of organosilanes shows two classes of functionality. R is organofunctional group capable for specific chemical reactions and X is hydrolyzabile group. One of the most widely used organofunctional alkoxysilane for the preparation of hybrid materials is 3-glycidoxypropyltrimethoxysilane (GPTMS). GPTMS molecule possesses epoxy and silicon alkoxide functionality, enabling thus the formation of interlinked organic -inorganic networks. Inorganic polymerization is performed by hydrolysis and condensation of alkoxy groups. Hydrolysis of methoxy groups gives silanol groups which can subsequently condense to form the siloxane network. The epoxy rings can be opened and polymerized to form organic network. The formation of the hybrid network structure of GPTMS is determined by the relative rates of formation of organic and inorganic parts and the linkages between them. Important applications have been reported for organic-inorganic hybrids derived from GPTMS prepared using sol–gel process.[7,8]

GPTMS has been studied and applied in the pretreatment of metal surfaces and functionalization of nanoparticles. When the hydrolysed GPTMS is applied over the metal surface to be coated, silanol groups can react with metal hydroxyls and form Si-O-metal bonds.[9,10] Therefore, the investigation of the hydrolysis and condensation behaviors of GPTMS is a key point for a variety of applications. Several studies have reported the influence of temperature[11] and catalyst[12] on the hydrolysis behavior of GPTMS. Increase in temperature accelerates hydrolysis and condensation reactions accompanied with the opening of epoxy ring.[11] In acid-catalysed systems the hydrolysis and formation of silanol groups is favored, while in base-catalysed systems

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hydrolysis proccedes simultaneously with condensation.[12] In our previous paper we performed density functional theory (DFT) calculation of structure and vibrational dynamics of GPTMS molecule.[13] Main interest of this work is the vibrational analysis of the GPTMS polymer obtained by inorganic polymerization which was performed by direct mixing of water and GPTMS without any catalyst. The analysis of Raman and IR spectra is supported by DFT calculation of structure and vibrational dynamics of GPTMS dimer.

Experimental Part

98% GPTMS was purchased from ABCR company and used without further purification. Pure GPTMS was mixed with water (weight ratio 1:3) and left at laboratory conditions. After 48 h a gel (GPTMS-gel) was formed and after another 24 h a hard transparent polymer GPTMS was obtained.

Raman spectra of liquid sample were recorded in a glass capilary on DILOR model Z24 triple monochromator using standard 90^0 scattering geometry. Micro Raman spectra of GPTMS polymer were recorded on Horiba Jobin Yvon T64000 instrument equipped with the Olympus open microscope stage and CCD Symphony detector. Spectrometer was operating in triple subtractive mode during the acquisition of spectra. A green line of 514.5 nm from a COHERENT argon-ion laser model Innova-165 was used for excitation. Raman spectra were recorded from 10 cm^{-1} to 1700 cm^{-1} and from 2500 cm^{-1} to 3500 cm^{-1}.

The FTIR spectrum of liquid sample was recorded in the frequency range from 500 to 4000 cm^{-1} using a Brucker Equinox 55 FT-IR spectrometer equipped with a tungsten halogen lamp as a source and a germanium diode as a detector. The spectral resolution was 4 cm^{-1}.

The FTIR spectrum of polymer was recorded with an ABB Bomem MB 102 spectrometer using Single Reflection ATR System. The spectrum was collected with a resolution of 2 cm^{-1} by co-adding the results of 10 scans.

Computational Method

In this research we have employed a gradient-corrected DFT method to support the interpretation of the measured spectroscopic data. The calculations were performed with the Gaussian 03 software package.[14] The standard 6–311 + G(d,p) basis set was applied to carry out the DFT calculations using B3LYP exchange-correlation functional that gives very good results in calculations of molecular geometry and vibrational wavenumbers of organosilanes.[13,15,16] That approach was used to optimize the structures, predict the energies, calculate force fields, vibrational frequencies, Raman activities and IR intensities. Calculated vibrational frequencies of all investigated structures showed that all optimized geometries correspond to the local minima of the potential energy surface.

In order to obtain a complete description of the molecular motion involved in the normal modes, the force constant matrix in Cartesian coordinates from DFT calculation was transformed into the system of internal coordinates. The force field was scaled with scaling factors presented in Table 1, taken from the recently

Table 1.
Scaling factors for the internal coordinates.[13,15,16]

Internal coordinate	Scaling factor
CC stretching	0.970
SiC stretching	0.970
SiO stretching	0.920
CH stretching	0.920
OH stretching	0.920
CO stretching	0.970
SiCC deformation	0.990
CCC deformation	0.990
SiOH deformation	0.990
OCC bending	0.990
CH_2 bending	0.915
SiO_3 bending	0.990
SiOH tors	1.000
Tors	1.100

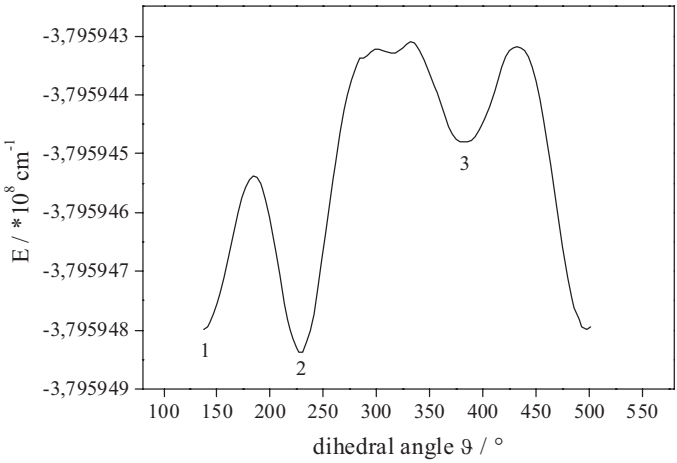

Figure 1.
Potential energy of GPTMS dimer as a function of CSiOSi dihedral angle.

investigated molecules[13,15,16] which contain similar molecular groups.

Dimer is the smallest and simplest structure with siloxane bond formed in the process of polymerization so we performed DFT calculations of the possible dimer structures.

Conformational Analysis

The possible conformers of GPTMS dimer are determined using a potential energy (PE) scan calculation. The scan was done by minimizing the potential energy in all geometrical parameters by varying the CSiOSi dihedral angle from 0° to 360° in 3.6 degrees increments. The shape of PE curve in dependence of the CSiOSi dihedral angle is presented in Figure 1.

The calculated PE curve exhibits three distinct minima. This calculation gives three starting structures for three separated DFT calculations. Minimization of potential energy in all variables, gave us optimized structures. The calculations of force field and vibrational frequencies confirmed that all structures correspond to the minimum energy conformations without imaginary frequencies. Those calculations gave more accurate energies for all three conformations. Energies are given in Table 2. The molecular geometries of calculated GPTMS dimers are presented in Figure 2 with the numeration of atoms.

The lowest energy dimer **2** has CSiOSi dihedral angle at 219.2°. The local minima observed at 137.1° and 79.2°correspond to conformers **1** and **3**, respectively. Most of the geometrical parameters calculated for

Table 2.
Differences in geometry parameters of conformers and their energy.

	Dimer **1**	Dimer **2**	Dimer **3**
$C_3Si_4O_{23}Si_{24}$/°	137.1	219.2	79.2
$C_3Si_4O_{12}H_{46}$/°	158.0	142.7	150.1
$C_3Si_4O_{11}H_{47}$/°	88.3	125.6	86.6
$Si_4O_{23}Si_{24}C_{25}$/°	282.5	253.1	220.1
$O_{23}Si_{24}O_{26}$ H_{49}/°	89.4	172.4	83.3
$O_{23}Si_{24}O_{27}$ H_{48}/°	32.6	310.7	32.4
E/*10^8 cm^{-1}	−3.795826918	−3.795833979	−3.795827026

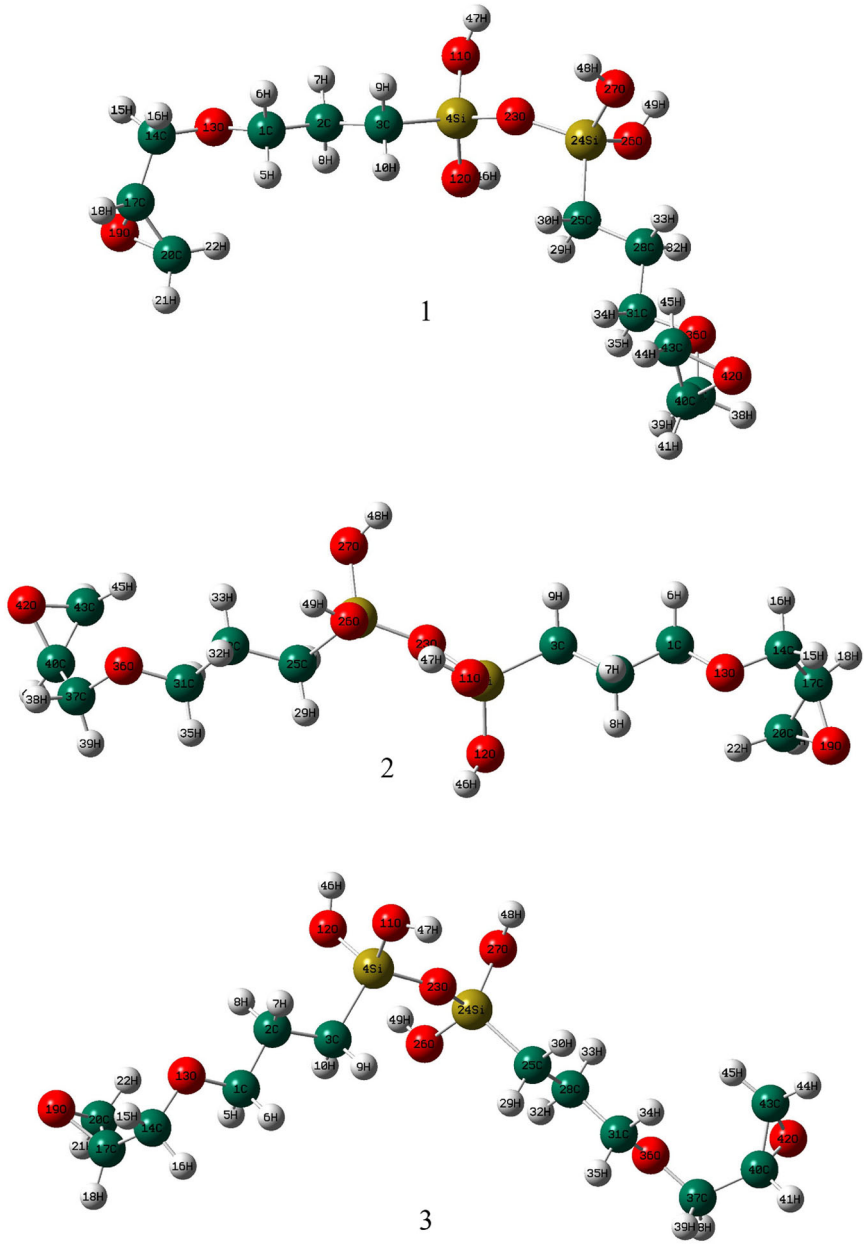

Figure 2.
Conformers **1**, **2** and **3** of GPTMS dimer with atom numeration.

three conformers have nearly equal values. There are differences in dihedral angles which define the orientation between two molecules forming the dimer and they are given in the Table 2 together with the energies of all conformers.

The energy difference between conformers **1** and **3** is very small and is calculated to be 10.7 cm^{-1} (0.128 $kJmol^{-1}$). The calculated barrier for **2**→**1** and **2**→**3** conformation interchange was found to be around 970 cm^{-1} (11.56 $kJmol^{-1}$) and

1195 cm^{-1} (14.29 $kJmol^{-1}$) respectively. At room temperature thermal energy of 207 cm^{-1} (2.48 $kJmol^{-1}$) is not sufficient for conformation interchange, so we assumed the minimum energy conformation for dimer in further analysis. We also assumed that, for the majority of internal coordinates, the intramolecular force field does not change significantly when the molecule is placed in different surrounding. So the vibrational analysis is based on normal coordinate calculation performed for dimer.

Vibrational Analysis

Vibrational analysis is based on the comparison of spectra of GPTMS molecule, polymer and calculated spectra of hydrolysed dimer. The assignment of characteristic normal modes of dimer based on potential energy distribution (PED) obtained from the scaled force field for minimum energy conformer 2 is given in Table 3.

The proposed structure of dimer (Figure 2.) contains two SiOH groups, therefore in calculated spectra OH stretching vibrations around 3700 cm^{-1} are present.

Raman spectra of GPTMS molecule, polymer and calculated spectrum of dimer are presented in Figure 3. The characteristic vibrational bands of methoxy groups in GPTMS molecule are CH stretching vibrations observed at 2844 cm^{-1} and 2944 cm^{-1}.[13] The two strong bands at 642 and 612 cm^{-1} observed are assigned to SiO stretching vibrations.[13]

During hydrolysis methoxy groups react with water molecules forming SiOH groups. Therefore the intensities of vibrational bands of methoxy groups in polymer are related to the amount of unhydrolysed GPTMS. As can be seen in Figure 3., vibrational bands at 2844 and 2944 cm^{-1} (Figure 3a) as well as bands at 642 and 612 cm^{-1} (Figure 3b) are disappearing in spectra of polymer. The wide band at 246 cm^{-1} assigned to SiOC deformations is also missing in spectra of polymer. Therefore, it can be concluded that all methoxy groups are hydrolysed.

The strong Raman band at 1256 cm^{-1} and band at 910 cm^{-1} are characteristic for epoxy ring vibrations (Table 3, Figure 3). Two bands at 3006 cm^{-1} and 3056 cm^{-1} are CH_2 and CH stretching modes connected to epoxy groups (Table 3, Figure 3). The intensity of vibrational modes of the epoxy ring does not change during hydrolysis.

IR spectra of GPTMS molecule, gel, polymer and calculated spectrum of dimer

Table 3.
Characteristic vibrations of GPTMS dimer.

Observed[a]	Calc-Nsc[b]	Calc-Sc[b]	IR[b]	RA[b]	PED[c]	Group[d]
	3899.7	3741.5	79.6	105.3	OH str	
	3895.5	3737.5	83.1	137.0	OH str	
	3893.2	3735.3	76.4	76.4	OH str	
	3774.4	3621.4	277.4	111.8	OH str	
3056 R	3183.9	3054.8	21.1	57.1	CH_2 str	Epoxy
	3182.1	3053.1	22.1	57.4	CH_2 str	
3006 R	3091.5	2966.5	30.5	260.1	CH_2 str, CH str	Epoxy
	3091.2	2966.1	30.0	234.9	CH_2 str, CH_2str	
1256 R	1291.7	1276.2	2.7	8.3	HCO def, CCH def, CC str	Epoxy
	1291.0	1276.0	5.6	16.5	HCO def, CCH def, CC str	
1050 IR	1066.4	1050.5	862	0.7	SiOSi str	
910 R	945.5	929.6	1.5	1.9	CO str, CC str, CH_2 rock	epoxy
	945.2	929.1	4.1	2.2	CO str, CC str, CH_2 rock	

[a] Abbreviations used: R-observed in Raman spectrum, IR-observed in IR spectrum.
[b] Abbreviations used for calculated values: Nsc-calculated non-scaled frequencies, Sc-scaled frequencies, IR-infrared intensities (km mol^{-1}), RA-Raman activities ($Å^4$ u^{-1}).
[c] Calculated PED contributions are listed if larger than 10% and in descending order.
[d] Characteristic groups included in PED with highest contributions.

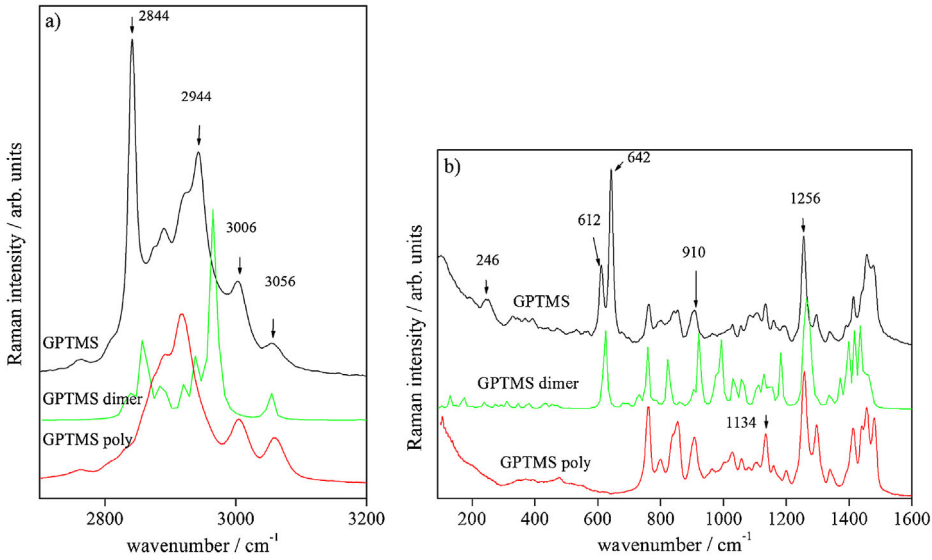

Figure 3.
Comparison of Raman spectra of GPTMS molecule, GPTMS polymer and calculated dimer spectra. a) High frequency spectrum. b) Low frequency spectrum.

are presented in Figure 4. Strong bands in IR spectrum of molecule observed at 1196 cm^{-1} and 1100 cm^{-1} are connected with CH_2 waging vibrations of propyl chain and glycidoxy group, respectively. The intensity of those bands remained unchanged during hydrolysis and condensation.

Hydrolysed GPTMS molecules react and form dimer via condensation reaction between the silanol groups. Further condensation leads to the formation of higher oligomers and inorganic network. In calculated spectrum of dimer (Table 3 and Figure 4), SiOSi stretching vibration is at

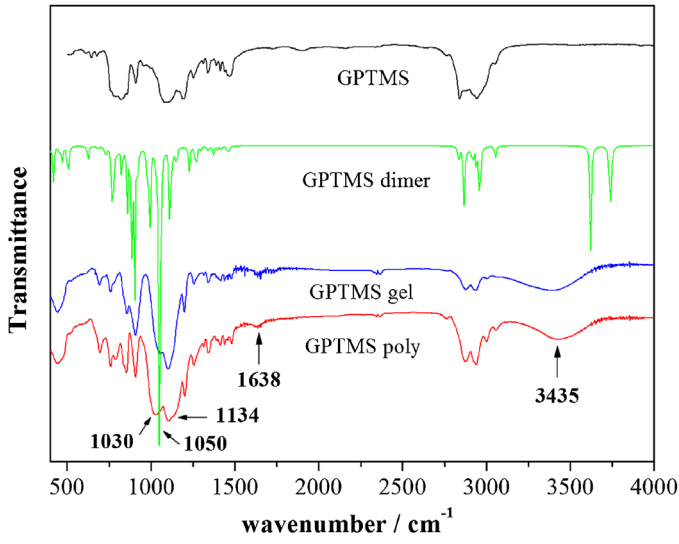

Figure 4.
Comparison of infrared spectra of GPTMS molecule, gel, polymer and calculated dimer spectrum.

1050 cm^{-1}. The appearance of intensive band at 1050 cm^{-1} in IR spectrum of gel indicates the formation of dimers and probably some oligomers. In IR spectrum of polymer SiOSi stretching vibrations are shifted to 1030 cm^{-1} indicating the formation of siloxane network.[17,18] The broad feature centered at ~3435 and band at 1638 cm^{-1} point to the fact that some water is still embedded in polymer matrix.

It is interesting to comment the vibrational band observed at 1134 cm^{-1} in Raman and IR spectra of polymer. In spectra of GPTMS molecule there is a low intensity vibrational band at 1134 cm^{-1} assigned as CC torsion mixed with CH_2 and CH rocking vibration of glycidoxy group.[13] In spectra of polymer this band gains intensity. Underhill at al. assigned this band in polymer as a silane epoxy linkage obtained from a reaction of silanol group and epoxy group.[10] According to our analysis there is no opening reaction of epoxy group during hydrolysis. In our reported investigation of structure of aminopropylsiloxane polymer[19] the vibrational spectra were calculated for two different conformations of silicooxygen rings:[17,18] ladder and cubic structure. The vibrational spectrum of calculated ladder strucuture contains band at 1134 cm^{-1} assigned as out of-phase Si–O stretching.

Therefore, the increase in intensity of band at 1134 cm^{-1} in spectra of polymer indicates the possibility of polymerization in ladder-type structure.[19]

Conclusion

The comparison of theoretical spectra with the experimental data enabled us to extract the characteristic vibrational bands of polymer structures. GPTMS molecule has characteristic fundamentals at 1256 cm^{-1} (mode of epoxy ring) as well as SiO stretching modes at 642 and at 612 cm^{-1} and CH_3 stretchings at 2944 and 2844 cm^{-1}. The methoxy group vibrations (SiO and CH_3 stretchings) are not evident in spectra of GPTMS polymer, while the epoxy ring modes remain unchanged. This is the evidence of complete hydrolysis of methoxy groups. The absence of OH stretching vibrations of silanol groups in spectra of polymer indicates complete condensation and inorganic SiOSi polymerization. The intense Raman band observed at 1134 cm^{-1} and assigned to the SiOSi stretching vibrations suggests the ladder-type structure of GPTMS polymer.

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[1] F. Beari, M. Brand, P. Jenkner, R. Lehnert, H. J. Metternich, J. Monkiewicz, H. W. Siesler, *J. Organomet. Chem.* **2001**, *625*, 208.
[2] S. R. Davis, A. R. Brough, A. Atkinson, *J. Non-Cryst. Solids* **2003**, *315*, 197.
[3] P. Innocenzi, C. Figus, M. Takahashi, M. Piccinini, L. Malfatti, *J. Phys. Chem. A* **2011**, *115*, 10438.
[4] C. Figus, M. Takahashi, T. Kidchob, T. Yoko, M. Piccinini, M. Casula, P. Innocenzi, *J. Sol-Gel Sci. Technol.* **2009**, *52*, 408.
[5] K. Wojtach, M. Laczka, K. Cholewa-Kowalska, Z. Olejniczak, J. Sokolowska, *J. Non-Cryst. Solids* **2007**, *353*, 2099.
[6] G. Brusatin, G. Della Giustina, M. Guglielmi, M. Casalboni, P. Prosposito, S. Schutzmann, G. Roma, *Mater. Sci. Eng. C* **2007**, *27*, 1022.
[7] G. Schottner, *Chem. Mater.* **2001**, *13*, 3422.
[8] L. Matejka, O. Dukh, J. Brus, W. J. Simonsick, Jr. B. Meissner, *J. Non-Cryst. Solids* **2000**, *270*, 34.
[9] L. Yang, J. Feng, W. Zhang, J. Qu, *Appl. Surf. Sci.* **2010**, *257*, 990.
[10] P. R. Underhill, G. Goring, D. L. DuQuesnay, *Appl. Surf. Sci.* **1998**, *134*, 247.
[11] F. de Buyl, A. Kretschmer, *J. Adhes.* **2008**, *84*, 125.
[12] C. Sanchez, F. Ribot, *New J. Chem.* **1994**, *18*, 1007.
[13] I. Movre Šapić, L. Bistričić, V. Volovšek, V. Dananić, *Spectochim. Acta A* **2009**, *72*, 833.
[14] 03. Gaussian, E01. Revision, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma,

G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT **2004**.

[15] L. Bistričić, V. Volovšek, V. Dananić, I. Movre Šapić, *Spectrochim. Acta A* **2006**, *64*, 327.

[16] L. Bistričić, V. Volovšek, V. Dananić, *J. Mol. Struct.* **2007**, *834-836*, 355.

[17] M. Handke, W. Jastrzębski, *J. Mol. Struct.* **2004**, *704*, 63.

[18] M. Handke, W. Jastrzębski, *J. Mol. Struct.* **2005**, *744-747*, 671.

[19] V. Volovšek, L. Bistričić, V. Dananić, I. Movre Šapić, *J Mol. Struct.* **2007**, *834-836*, 414.

