

The theoretical research of the medium effect on the vibrational spectrum and the energy of intramolecular coordination $=O \rightarrow Si$ in (benzoyloxymethyl)trifluorosilane molecule

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Abstract

The characteristics of (benzoyloxymethyl)trifluorosilane $C_6H_5C(=O)OCH_2SiF_3$ containing a five-membered heterocycle closed by intramolecular coordination $=O \rightarrow Si$ bond (**Ia**) and its most stable acyclic isomer (**Ib**) have been calculated by HF, MP2(Full) non-empirical methods, and DFT(B3LYP) using 6-311G(d) and 6-311 + G(2d,p) basis sets. The (C_8H_{18} , C_6H_6 , $(C_4H_9)_2O$, $CHCl_3$, $(CH_2)_4O$, CH_2Cl_2 , CH_3CN) medium effect on the energy and structural characteristics, dipole moments, and vibrational spectra of **Ia** and **Ib** isomers was calculated by the DFT(B3LYP)/6-311 + G(2d,p) method in the Onsager SCRF model approximation. The DFT(B3LYP)/6-311 + G(2d,p) calculation reasonably reproduces the medium effect on coordination energy, geometry, dipole moments, and band frequencies in the vibrational spectrum of **Ia**.

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1. Introduction

In the modern chemistry of pentacoordinate silicon organic derivatives special attention is given to (aroyloxymethyl)trifluorosilanes $XArC(=O)OCH_2SiF_3$ (AFS), named dragonoids [1]. The initial member of this series is represented by (benzoyloxymethyl)trifluorosilane $C_6H_5C(=O)OCH_2SiF_3$ (BFS). For more than 20 years, the nature of valence expansion of the central silicon atom caused by the $=O \rightarrow Si$ intramolecular coordination $=O \rightarrow Si$ bond formation was studied by different physical–chemical and theoretical methods [1–4]. The AFS molecular structure has been studied by X-ray diffraction method [5,6]. The high sensitivity of AFS vibrational

spectra to the medium effect allowed the development of the spectral procedures in the research of such interaction type [2,3]. However, the AFS vibration spectra were not exhaustively studied and interpreted until now.

Previously the present authors conducted HF/6-31G(d), MP2(FC)/6-31G(d) non-empirical and AM1 semi-empirical studies of isolated AFS molecules, including BFS isomers **Ia** and **Ib** [4]. The $=O \rightarrow Si$ energy coordination, dipole moments and structural parameters have been calculated. In harmonic approximation using standard valence-force field a direct vibrational problem has been solved for model (formylloxymethyl)trifluorosilane $H-C(=O)OCH_2SiF_3$ [7] and the 1-hydrosilatrane $HSi(OCH_2CH_2)_3N$ [8] molecules containing coordination bonds $=O \rightarrow Si$ and $N \rightarrow Si$, respectively. The vibrational spectrum, geometry and electronic structure of diverse isolated conformers of

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(acetoxymethyl)trifluorosilane $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{SiF}_3$ were examined using the HF/6-31G(d) method [9]. The BFS molecule geometry was calculated by non-empirical methods HF and MP2 with 6-31G(d), 6-311G(d), 6- and 311 + G(d,p) basis sets [4,10]. An attempt has been made at estimating the medium effect (DMPPhA) on the BFS geometry by HF/6-31G(d) with the help of the Onsager reaction field and Tomasi's polarized continuum (PCM) models [10]. Quantum-chemical examinations of the medium effect on the AFS and BFS vibration spectra as the vibration spectrum calculation of BFS have never been undertaken before.

The goal of the present work is comprehensive quantum-chemical investigation of medium effect on peculiar variations of the coordinate $=\text{O} \rightarrow \text{Si}$ bond, vibrational spectrum, total energy, dipole moment, and electronic structure of BFS.

2. Calculation procedure, results and discussion

The quantum-chemical calculations were performed by non-empirical MP2(Full), HF, and DFT(B3LYP) methods with 6-311 + G(2d,p) basis set (in some cases for the DFT(B3LYP) method with 6-311G(d) basis set) using standard program complex GAUSSIAN-03W [11]. The vibrational spectra, total energies, zero-point energies, dipole moments, and structural characteristics of two stable BFS isomers of C_s symmetry were calculated. One of them contains the intramolecular coordinate $=\text{O} \rightarrow \text{Si}$ bond closing the pentacoordinate heterocycle (**1a**). The other most stable isomer does not possess the coordinate $=\text{O} \rightarrow \text{Si}$ bond and has an acyclic structure with *trans-trans* orientation of $\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{SiF}_3$ chain (**1b**). The **1b** isomer exists exclusively in a gas phase at the temperature above 420 K [12]. The optimized geometries of these two stable structures are presented in Fig. 1. Coordination energy was estimated as the difference between total energies of **1a** and **1b** isomers. In the calculation no BSSE correction was taken into account, since for extended basis sets it cannot affect much the results [13].

The modeling of the effect of the medium polarity (C_8H_{18} , C_6H_6 , $(\text{C}_4\text{H}_9)_2\text{O}$, CHCl_3 , $(\text{CH}_2)_4\text{O}$, CH_2Cl_2 , CH_3CN) on the energy and structural characteristics, dipole moments, and vibrational spectra of isomers **1a** and **1b** was carried out by DFT(B3LYP)/6-311 + G(2d,p) in the Onsager self-consistent reaction field (SCRFF+Dipole) model approximation. Taking into account the optimized geometry, the radiuses of spherical cavity were determined as: 545.0 pm for **1a** and 580.0 pm for **1b**.

At the present time, the nature of intramolecular coordinate $=\text{O} \rightarrow \text{Si}$ bond in AFS molecules [14] is theoretically described within Masher's hypervalence scheme [15] that was developed for pentacoordinate sil-

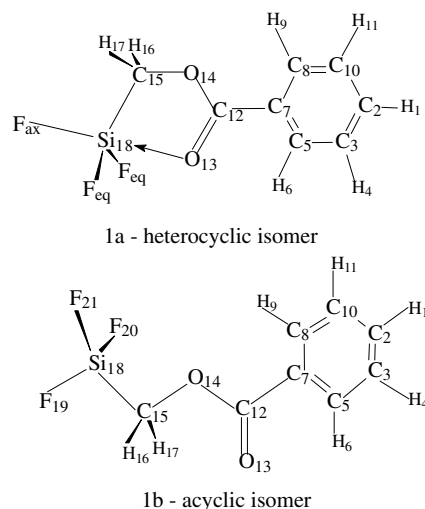


Fig. 1. Electronic structure of stable BSR according to DFT(B3LYP)/6-311 + G(2d,p) calculations: **1a**, heterocyclic isomer containing a $=\text{O} \rightarrow \text{Si}$ coordinate bond; **1b**, acyclic isomer containing a tetracoordinate silicon atom.

icon compounds [16,17]. Experimental examination of medium effect on the energy and spectral characteristics of BFS it was determined that their variation follows the model of three-center, 4-electron ($3c-4e$) binding for the $\text{C}=\text{O} \rightarrow \text{Si}-\text{F}_{\text{ax}}$ fragment, and depends exclusively on the medium polarity. Herewith, the observed strengthening of intramolecular coordinate interaction, increase of the BFS dipole moment, and variation of fundamental frequencies in IR spectrum are mostly described by the function of medium polarity $(\epsilon - 1)/(2\epsilon + 1)$ with a small contribution from the dispersion member $(n^2 - 1)/(2n^2 + 1)$ [2]. This all determined the choice of solvation Onsager SCRFF model.

The IR absorption spectra of the BFS in the 400–4000 cm^{-1} region were measured by IFS-25 Fourier spectrometer in tablets with KBr and in CCl_4 and CH_3CN solutions ($d = 0.003$ cm, $c = 0.01$ mol/l). The Raman spectrum of solid sample in the 200–2000 cm^{-1} region was recorded on Cary-81 Raman spectrometer with excited line at 4880 Å for a 1-Wt Ar laser.

2.1. The coordination energy

Table 1 shows calculated total energy of **1a** and **1b** structures of BFS, E_{tot} , total energy with zero-point energy corrections, E_{ZPE} (a.u.), coordination energy, E_{coord} (kJ/mol) in different mediums, and available literature data.

A distinguished feature of **1a** isomer structure is the presence of intramolecular coordinate bond $=\text{O} \rightarrow \text{Si}$. The quantum-chemical evaluation of energy of this type of interaction (25.3 kJ/mol), that was calculated by MP2(FC) non-empirical method with 6-31G(d) standard basis set [4], is considered in the literature as most concerted with the experimental value $E_{\text{coord}} = -28.5$

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