16. Конгрес на хемичарите и технолозите на Македонија, Скопје, 28-30 октомври, 1999

FOURIER TRANSFORM INFRARED AND COMPUTATIONAL STUDY OF SOME *O*-SUBSTITUTED *S*-PHENYL THIOBENZOATES

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Abstract. A combined experimental and theoretical study of two members of the series of *o*-substituted *S*-phenyl thiobenzoates: *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate was performed. Room and low-temperature solid-state Fourier-transform infrared spectra of the mentioned compounds were recorded and tentative empirical assignment of the most important bands was proposed. The geometries of the two molecules were optimized at Hartree-Fock level of theory, with the 3-21G(d,p) basis set, using Berny's optimization algorithm (computing the energy derivatives analytically). Numerical harmonic vibrational analyses were performed for the optimized geometries, confirming that they corresponded to real minima on the potential energy hypersurfaces. The computed structural parameters were compared to those obtained crystallographically. The obtained scaled harmonic vibrational frequencies are in a very good agreement with the experimental ones, confirming the applicability of HF/3-21G(d,p) scaled harmonic force field for a study of species with more than 12 atoms.

Key words: *S*-phenyl *o*-chlorothiobenzoate, *S*-phenyl *o*-bromothiobenzoate, Fourier-Transform infrared spectra, *ab initio* force field, computational chemistry.

1. Introduction

The *o*-substituted *S*-phenyl thiobenzoates were studied a lot, with an emphasis on both structural and spectroscopic aspects. Structural characteristics of the mentioned compounds dissolved in different solvents were studied employing various techniques, including infrared spectroscopy [1], polarographic methods [2], as well as dipole moment measurements [1]. The crystal structures of *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate were solved using single crystal X-ray diffractometry [3]. However, very few data have been reported on the *solid-state infrared spectra* of these species [2].

In the present work, we report on a systematic solid-state Fourier-transform infrared spectroscopic study of *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate, combined with an *ab initio* HF SCF geometry optimization and subsequent force field calculation.

Theoretical HF SCF harmonic vibrational analysis was used as a basis for a more exact assignment of IR spectral bands.

2. Experimental

Both compounds, *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate were prepared according to the method reported by Prangova *et al.* [2], by mixing of equimolar quantities of pyridine solution of thiophenol and corresponding *o*-substituted benzoyl chloride in the presence of nitrogen. Elemental analysis was employed in order to check the purity of the obtained compounds.

Solid-state Fourier-transform infrared spectra of the mentioned compounds were recorded on a Perkin-Elmer System 2000 interferometer, at both room (RT) and liquid nitrogen boiling temperature (LNT). A Graseby Specac variable temperature cell was used for the low-temperature measurements.

3. Computational details

The geometries of *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate molecules were optimised at the uncorrelated HF SCF level of theory, using Berny's optimization algorithm [4, 5], and an initial guess of the second-derivative matrix. The standard 3-21G(d,p) basis set [6-11] was used for orbital expansion. Although being rather small, the employed basis set has been shown to be sufficient for a harmonic vibrational analysis of species containing more than 12 atoms in the structure [12]. It has been verified that often very little is gained by the usage of larger 6-31G or 6-31G(d,p) bases, especially when computation of harmonic vibrational force field is in question [13-15].

The stationary points found on the molecular potential energy hypersurfaces were characterized by numerical harmonic vibrational analysis. The absence of imaginary frequencies, as well as of the negative eigenvalues of the second-derivative matrix confirmed that they correspond to real minima (instead of being saddle points).

All quantum-chemical calculations were performed with the Gaussian94w series of programs [16].

4. Results and Discussion

The most important structural parameters for *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate molecules calculated at HF/3-21G(d,p) level of theory together with the crystallographically obtained data are presented in Table 1.

Table 1. The HF/3-21G(d,p) optimized structural parameters for *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate molecules together with the single-crystal X-ray data

Parameter	*S*-phenyl *o*-chlorothiobenzoate		*S*-phenyl *o*-bromothiobenzoate	
	HF/3-21G(d,p)	Experimental	HF/3-21G(d,p)	Experimental
R(C–Cl)/Å	1.744	1.754	-	-
R(C–Br)/Å	-	-	1.922	1.888
R(C–O)/Å	1.203	1.164	1.203	1.190
R(C–S)/Å	1.792	1.786	1.791	1.772
R(S–C$_{ring}$)/Å	1.774	1.774	1.774	1.776
R(CO–C)/Å	1.497	1.528	1.497	1.516

As can be seen from Table 1, the HF/3-21G(d,p) level of theory predicts only a subtle geometric change in the other part of the molecule upon the replacement of chlorine with bromine. However, the overall agreement with experimental data is good, having in mind that they refer to a solid state sample, while *ab initio* data refer to a free molecular system.

The computed HF/3-21G(d,p) harmonic vibrational frequencies, together with the solid state LNT FT-IR data are summarized in Table 2. Theoretical vibrational frequencies were scaled by a constant factor of 0.9, in order to account for systematic errors at the HF theoretical levels due to the neglect of the dynamical electron correlation effects, as well as the basis set truncation errors.

Table 2. The HF/3-21G(d,p) harmonic vibrational frequencies (in cm^{-1}, scaled by a constant factor of 0.9) for *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate molecules together with the LNT FT-IR data

Mode	*S*-phenyl *o*-chlorothiobenzoate		*S*-phenyl *o*-bromothiobenzoate	
	HF/3-21G(d,p)	Experimental	HF/3-21G(d,p)	Experimental
$\nu(\mathrm{CO})$	1697.6	1687	1700.0	1687
$\nu(\mathrm{CO\text{-}C_{ring}})$	1168.5	1177	1173.1	1177
$\nu(\mathrm{S\text{-}C_{ring}})$	1090.0	1091	1090.3	1093
$\nu(\mathrm{CO\text{-}S})+\gamma(\mathrm{PhH})$	887.4	882	891.1	879
$\nu(\mathrm{CO\text{-}S})+\gamma(\mathrm{PhH})$	886.8			
$\nu(\mathrm{C\text{-}Cl})$	715.6	715	-	-
$\nu(\mathrm{C\text{-}Br})$	-	-	710.4	708
$\delta(\mathrm{OCS})$	578.5	578	579.8	577

According to Table 2, the agreement between theoretical and experimental frequencies is quite satisfactory. This further supports the statement that the HF/3-21G(d,p) harmonic force field is sufficient for analyzing molecular systems with more than 12 atoms.

Апстракт. Изведена е комбинирана експериментална и теориска студија на два члена од серијата *о*-супституирани *С*-фенил тиобензоати: *С*-фенил *о*-хлоротиобензоат и *С*-фенил *о*-бромотиобензоат. Снимени се фуриетрансформни инфрацрвеи спектри на примероци од споменатите соединенија во цврста фаза на собна и ниска температура, и предложена е емпириска асигнација на најважните ленти. Геометриите на двете молекули се оптимизирани на Хартри-Фок ниво на теоријата, со 3-21Г(д,п) базисниот сет, користејќи го Берниевиот оптимизационен алгоритам. Нумерички хармониски вибрациони анализи се изведени за оптимизираните геометрии. Пресметаните структурни параметри се споредени со оние добиени кристалографски. Добиените скалирани вибрациони фреквенции се во многу дорба согласност со експерименталните, потврдувајќи ја применливоста на скалираното ХФ/3-21Г(д,п) силово поле за молекули со повеќе од 12 атоми.

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