

FOURIER TRANSFORM INFRARED AND COMPUTATIONAL STUDY OF TWO *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, afterwards verified by *ab initio* results. The geometries of the two molecules were optimized at Hartree-Fock level of theory with the 3-21G(d,p) basis set, and subsequently numerical harmonic vibrational analyses were performed. The computed structural parameters agree well with the crystallographically obtained values. Except for the reminiscent of the benzene ν_{14} vibrational mode (the "Kekule" type vibration), the scaled theoretical 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.

INTRODUCTION

The *o*-substituted *S*-phenyl thiobenzoates were studied widely, with an emphasis on both structural and spectroscopic aspects. Structural characteristics of the mentioned compounds dissolved in different solvents have been 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 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 harmonic force field calculation. Theoretical HF SCF harmonic vibrational analysis was used as a basis for a more exact assignment of the IR spectral bands.

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.

COMPUTATIONAL DETAILS

The geometries of *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate molecules were fully optimized at the uncorrelated HF SCF level of theory, using Schlegel's gradient optimization algorithm [4, 5] (computing the second derivatives of the energy with respect to nuclear coordinates analytically), employing 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 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 (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 Gaussian 94w series of programs [16].

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. The optimized geometries of the two compounds are presented in Fig. 1.

TABLE 1. Selected 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	<i>S</i> -phenyl <i>o</i> -chlorothiobenzoate		<i>S</i> -phenyl <i>o</i> -bromothiobenzoate	
	HF/3-21G(d,p)	Experimental	HF/3-21G(d,p)	Experimental
$R(\text{C-Cl}) / \text{\AA}$	1.744	1.754	-	-
$R(\text{C-Br}) / \text{\AA}$	-	-	1.922	1.888
$R(\text{C-O}) / \text{\AA}$	1.203	1.164	1.203	1.190
$R(\text{C-S}) / \text{\AA}$	1.792	1.786	1.791	1.772
$R(\text{S-C}_{\text{ring}}) / \text{\AA}$	1.774	1.774	1.774	1.776
$R(\text{C}_{\text{CO}}-\text{C}) / \text{\AA}$	1.497	1.528	1.497	1.516
$R(\text{C}_{\text{CX}}-\text{C}) / \text{\AA}$	1.382	1.374	1.378	1.393
$R(\text{C}_{\text{CX}}-\text{C}_{(\text{CO})}) / \text{\AA}$	1.389	1.375	1.384	1.372
$\angle(\text{XCC}_{(\text{CO})}) / ^\circ$	122.2	120.2	122.7	120.7
$\angle(\text{XCC}) / ^\circ$	117.2	118.0	117.0	118.4
$\angle(\text{OCC}) / ^\circ$	124.3	125.7	124.5	125.0
$\angle(\text{SC}(\text{O})\text{C}) / ^\circ$	112.7	109.3	112.4	109.7
$\angle(\text{OCS}) / ^\circ$	122.9	125.0	123.0	125.3

As can be seen from Table 1, the HF/3-21G(d,p) level of theory predicts only a subtle geometry changes 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.

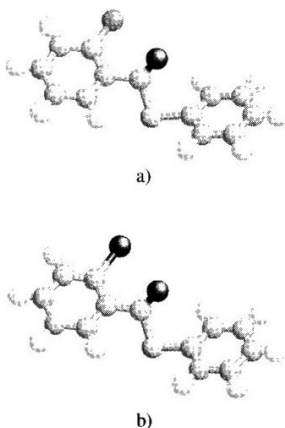


FIGURE 1. The HF/3-21G(d,p) optimized geometries of *S*-phenyl *o*-chlorothiobenzoate (a) and *S*-phenyl *o*-bromothiobenzoate (b).

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 0.89375, 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. Experimental solid state FT IR spectra of the studied compounds are shown in Fig. 2. According to Table 2, the overall agreement between theoretical and experimental frequencies is quite satisfactory. However, one notable exception is the well recognized multiconfigurational vibrational problem present in the vibrational analysis of benzenoid rings. Namely, it is particularly interesting to study the performances of the uncorrelated HF methodology in predicting the frequencies of the reminiscent of the ν_{14} mode in benzene (according to Wilson's notation) [17]. The ν_{14} (B_{2u}) mode is the so-called "Kekule" type vibration [18, 19], recognized in the language of electronic structure theory as a multiconfigurational problem [20-22]. From a computational aspect, in the case of benzene and some of its substituted derivatives, the mentioned mode has been shown to be particularly sensitive to electron

correlation effects as well as to the basis set size [17, 20, 22]. Even the MP2 methodology using the standard 6-31G(d,p) basis fails to describe it correctly [17]. Rather large basis sets of the TZ2P + *f* quality are required for successful treatment of this problem [17]. On the other hand, the density functional BLYP methodology has been shown to be capable of handling this vibration with sufficient accuracy even with a DZP quality basis set [20], implying a correct description of the correlated density provided by this gradient-corrected DFT method. In the present case, the HF/3-21G(d,p) methodology predicts values of 1103.4 and 1102.6 cm^{-1} (for *S*-phenyl *o*-chlorothiobenzoate), while 1107.1 and 1103.2 cm^{-1} (*S*-phenyl *o*-bromothiobenzoate) for the harmonic vibrational frequency of the multireference ν_{14} ring modes. These values are some 200 cm^{-1} lower than the value measured for benzene.

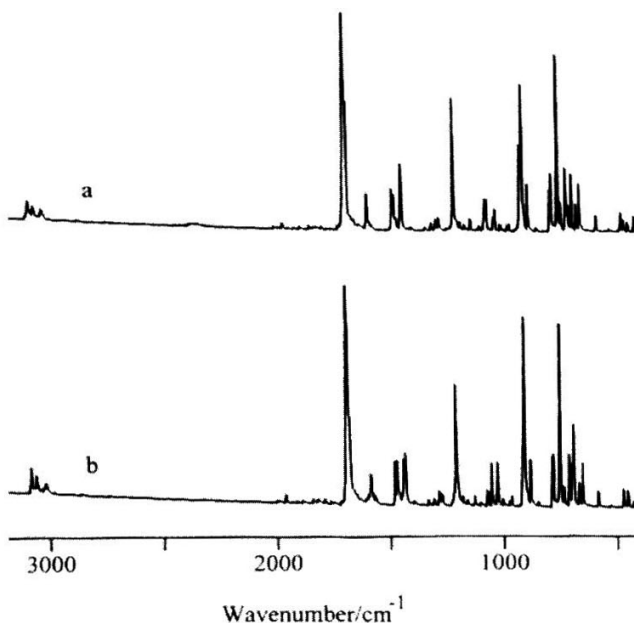


FIGURE 2. Low temperature solid-state FT-IR spectra of *S*-phenyl *o*-chlorothiobenzoate (a) and *S*-phenyl *o*-bromothiobenzoate (b).

Since the frequency of this mode is not expected to be such significantly affected upon substitution [18, 21], one is lead to a conclusion that the HF/3-21G(d,p) force field does not allow an accurate description of this vibration for the present cases. It is unfortunately not possible to make an unambiguous assignment of this mode in the vibrational spectra of the studied compounds, but however, it seems that the predicted frequency is significantly lower than it could be expected. However, the general conclusion on the inadequacy of the single-determinant HF theory in prediction of the harmonic vibrational frequencies for such multi-reference modes is supported according to the presented results. We have recently examined the performances of the HF SCF methodology in predicting the “Kekule” mode frequencies in the case of benzenesulfonate anion, and arrived at very similar conclusions [23].

It is further worth noting (Table 2) that practically all of the higher-frequency modes (above 500 cm^{-1}) are highly localized within the particular aromatic rings of the investigated compounds. The halogen substitution affects only slightly the other vibrational motions. The overall agreement of the HF/3-21G(d,p) values with the experimental data 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.

TABLE 2. *Ab initio* HF/ 3-21G(d,p) harmonic vibrational frequencies (scaled by a constant factor of 0.89375), IR intensities and approximate description of normal modes, together with the experimental solid-state FT IR data for *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate.

<i>S</i> -phenyl <i>o</i> -chlorothiobenzoate				
HF/3-21G(d,p)		Exp.		Approximate description
ν / cm^{-1}	$I / \text{km mol}^{-1}$	ν / cm^{-1}		
3110.0	3.9	3080		ν_{PhH} (Ph)
3110.0	1.7	3071		ν_{PhH} (Ph-Cl)
3104.8	1.6	3056		ν_{PhH} (Ph-Cl)
3098.0	13.1	3050		ν_{PhH} (Ph)
3094.1	7.3	3039		ν_{PhH} (Ph-Cl)
3089.8	13.0	3031		ν_{PhH} (Ph)
3082.0	0.8	3019		ν_{PhH} (Ph-Cl)
3081.2	4.6	3010		ν_{PhH} (Ph)
3072.1	0.1			ν_{PhH} (Ph)

TABLE 2. (continued)

1685.8	155.2	1687	v_{Co}
1569.0	17.7	1587	$v_{\text{CC}}(\text{Ph-Cl})$
1566.5	0.9	1576	$v_{\text{CC}}(\text{Ph})$
1552.3	1.0	1567	$v_{\text{CC}}(\text{Ph})$
1543.3	14.6		$v_{\text{CC}}(\text{Ph-Cl})$
1469.5	19.3	1477	$\delta_{\text{PhH}}(\text{Ph})$
1456.9	29.3	1469	$\delta_{\text{PhH}}(\text{Ph-Cl})$
1424.3	20.2	1436	$\delta_{\text{PhH}}(\text{Ph})$
1421.7	21.5		$\delta_{\text{PhH}}(\text{Ph-Cl})$
1322.4	4.5	1304	$\delta_{\text{PhH}}(\text{Ph})$
1266.4	8.1	1271	$\delta_{\text{PhH}}(\text{Ph-Cl})$
1195.1	36.4	1208	$\delta_{\text{PhH}}(\text{Ph-Cl})$
1192.7	0.7		$\delta_{\text{PhH}}(\text{Ph})$
1177.1	1.1	1177	$\delta_{\text{PhH}}(\text{Ph})$
1160.4	97.9	1156	$v_{\text{C(OC)}} + \delta_{\text{CCC}}(\text{Ph-Cl})$
1115.6	11.9	1131	$v_{\text{CC}} + \delta_{\text{PhH}}(\text{Ph-Cl})$
1103.4	0.7		$v_{\text{CC}}(\text{KEKULE})(\text{Ph})$
1102.6	17.7		$v_{\text{CC}}(\text{KEKULE})(\text{Ph-Cl})$
1082.4	2.1	1091	$v_{\text{CS}} + \delta_{\text{CCC}}(\text{Ph})$
1059.0	27.0	1067	$\delta_{\text{CCC}}(\text{Ph-Cl})$
1056.2	0.3	1061	$\gamma_{\text{PhH}}(\text{Ph-Cl})$
1053.3	0.4		$\gamma_{\text{PhH}}(\text{Ph})$
1051.6	1.6		$\delta_{\text{CCC}}(\text{Ph})$
1027.5	0.4	1030	$\gamma_{\text{PhH}}(\text{Ph})$
1021.3	1.8	1023	$\gamma_{\text{PhH}}(\text{Ph-Cl})$
1017.1	6.5	1000	$\delta_{\text{CCC}}(\text{Ph})$
1012.6	7.6		$\delta_{\text{CCC}}(\text{Ph-Cl})$
982.1	0.1	991	$\delta_{\text{CCC}}(\text{Ph})$
977.8	0.8	970	$\gamma_{\text{PhH}}(\text{Ph})$
936.7	7.9	962	$\gamma_{\text{PhH}}(\text{Ph-Cl})$
881.2	133.0	915	$\gamma_{\text{PhH}}(\text{Ph}) + \delta_{\text{CCO}}$
880.6*	102.8	906	$\gamma_{\text{PhH}}(\text{Ph})$
3111.1	5.0	3078	$v_{\text{PhH}}(\text{Ph-Br})$
3109.6	2.3	3066	$v_{\text{PhH}}(\text{Ph})$

TABLE 2. (continued)

3105.2	1.9	3054	$\nu_{\text{PhH}} (\text{Ph-Br})$
3097.9	13.3	3049	$\nu_{\text{PhH}} (\text{Ph})$
3094.0	7.3	3038	$\nu_{\text{PhH}} (\text{Ph-Br})$
3089.6	13.0	3026	$\nu_{\text{PhH}} (\text{Ph})$
3081.9	0.7	3020	$\nu_{\text{PhH}} (\text{Ph-Br})$
3081.1	4.6	3013	$\nu_{\text{PhH}} (\text{Ph})$
3071.9	0.1		$\nu_{\text{PhH}} (\text{Ph})$
1688.2	155.1	1687	ν_{CO}
1571.7	18.4	1582	$\nu_{\text{CC}} (\text{Ph-Br})$
1566.6	1.0	1562	$\nu_{\text{CC}} (\text{Ph})$
1552.3	1.0		$\nu_{\text{CC}} (\text{Ph})$
1545.4	13.5		$\nu_{\text{CC}} (\text{Ph-Br})$
1469.6	19.3	1477	$\delta_{\text{PhH}} (\text{Ph})$
1462.4	30.1	1466	$\delta_{\text{PhH}} (\text{Ph-Br})$
1424.4	26.8	1438	$\delta_{\text{PhH}} (\text{Ph})$
1423.6	8.4	1430	$\delta_{\text{PhH}} (\text{Ph-Br})$
1322.5	4.4	1303	$\delta_{\text{PhH}} (\text{Ph})$
1272.3	8.6	1281	$\delta_{\text{PhH}} (\text{Ph-Br})$
1200.1	43.2	1208	$\delta_{\text{PhH}} (\text{Ph-Br})$
1192.5	0.7		$\delta_{\text{PhH}} (\text{Ph})$
1177.1	1.0	1177	$\delta_{\text{PhH}} (\text{Ph})$
1164.9	81.4	1156	$\nu_{\text{C(OC)}} + \delta_{\text{CCC}} (\text{Ph-Br})$
1115.7	7.4	1123	$\nu_{\text{CC}} + \delta_{\text{PhH}} (\text{Ph-Br})$
1107.1	12.4		$\nu_{\text{CC (KEKULE)}} (\text{Ph-Br})$
1103.2	4.8		$\nu_{\text{CC (KEKULE)}} (\text{Ph})$
1082.7	1.7		$\nu_{\text{CS}} + \delta_{\text{CCC}} (\text{Ph})$
1077.0	0.9	1068	$\gamma_{\text{PhH}} (\text{Ph-Br})$
1061.7	23.4	1050	$\delta_{\text{CCC}} (\text{Ph-Br})$
1053.3	0.4		$\gamma_{\text{PhH}} (\text{Ph})$
1051.6	1.7		$\delta_{\text{CCC}} (\text{Ph}) + \delta_{\text{PhH}} (\text{Ph})$
1036.3	1.9	1023	$\gamma_{\text{PhH}} (\text{Ph-Br})$
1027.5	0.4		$\gamma_{\text{PhH}} (\text{Ph})$
1017.1	6.1	1000	$\delta_{\text{CCC}} (\text{Ph})$
1013.6	7.2	990	$\delta_{\text{CCC}} (\text{Ph-Br})$
982.1	0.1		$\delta_{\text{CCC}} (\text{Ph})$
977.6	0.8		$\gamma_{\text{PhH}} (\text{Ph})$
960.0	8.9		$\gamma_{\text{PhH}} (\text{Ph-Br})$
884.9	228.9	907	$\delta_{\text{CCC}} (\text{Ph-Br}) + \delta_{\text{CCO}}$
880.8*	2.5	879	$\gamma_{\text{PhH}} (\text{Ph})$

*followed by 10 low-frequency modes

The structures and vibrational force fields of *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate were studied on the basis of the solid-state FT IR spectra and *ab initio* HF/3-21G(d,p) calculations. The computed structural parameters of these systems agree well with the crystallographic data. Except for the multireference "Kekule" type vibration of the benzenoid rings, the HF/3-21G(d,p) level of theory leads to a very good overall agreement with the experimental FT IR data, allowing thus a more rigorous basis for band assignments.

REFERENCES

- [1] L. S. Prangova, S. P. Fradkina, I. N. Vasileva, *Zh. Obshch. Khim.*, **1987**, 57, 1853.
- [2] L. Prangova, T. Strellov, J. Voss, *J. Chem. Res.* **1985**, 1401.
- [3] G. Jovanovski, B. Šoptrajanov, B. Kaitner, L. Prangova, *J. Crystallogr. Spectrosc. Res.*, **1993**, 23, 49.
- [4] H. B. Schlegel, *J. Comp. Chem.*, **1982**, 3, 214.
- [5] H. B. Schlegel, in *New Theoretical Concepts for Understanding Organic Reactions*, Ed. J. Bertran, Kluwer Academic: The Netherlands, 1989, 33-53.
- [6] J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **1980**, 102, 939.
- [7] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.*, **1982**, 104, 2797.
- [8] W. J. Pietro, M. M. Francel, W. J. Hehre, D. J. Defrees, J. A. Pople, J. S. Binkley, *J. Am. Chem. Soc.*, **1982**, 104, 5039.
- [9] K. D. Dobbs, W.J. Hehre, *J. Comp. Chem.*, **1986**, 7, 359.
- [10] K. D. Dobbs, W.J. Hehre, *J. Comp. Chem.*, **1987**, 8, 861.
- [11] K. D. Dobbs, W.J. Hehre, *J. Comp. Chem.*, **1987**, 9, 880.
- [12] J. R. Durig, M. J. Lee, H. M. Badawi, J. F. Sullivan, D. I. Durig, *J. Mol. Struct.*, **1992**, 266, 59.
- [13] I. G. Binev, *Spectrochim. Acta*, **1997**, 53A, 1795.
- [14] I. G. Binev, Y. I. Binev, *J. Mol. Struct.*, **1997**, 435, 235.
- [15] I. G. Binev, B. A. Stamboliyska, Y. I. Binev, *J. Mol. Struct.*, **1996**, 378, 189.

- [16] Gaussian 94 (Revision B.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
- [17] P. E. Maslen, N. C. Handy, R. D. Amos, D. Jayatilaka, *J. Chem. Phys.*, **1992**, 97, 4233.
- [18] F. R. Dollish, W. G. Fateley, F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley, New York, 1974, pp. 162-175.
- [19] G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, 1956, pp. 116-118.
- [20] N. C. Handy, C. W. Murray, R. D. Amos, *J. Phys. Chem.*, **1993**, 97, 4392.
- [21] D. Michalska, D. C. Bienko, A. J. Abkowitz-Bienko, Z. Latajka, *J. Phys. Chem.*, **1996**, 100, 17786.
- [22] H. Lampert, W. Mikenda, A. Karpfen, *J. Phys. Chem. A*, **1997**, 101, 2254.
- [23] L. Pejov, M. Ristova, Z. Zdravkovski, B. Soptrajanov, *J. Mol. Struct.*, **2000**, 524, 179.