Theoretical and Experimental Studies on a Metallorganic Complex of (Isopropylxanthato)(Phenyl)Mercury(I) [Hg(I)(C₆H₅)(C₄H₇OS₂)]

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The title compound, (isopropylxanthato)(phenyl)mercury(I), was synthesized and characterized by elemental analysis, IR and thermogravimetric analysis. Density functional theory (DFT) method calculations were performed at B3LYP/CEP-121G and B3LYP/CEP-31G levels of theory, respectively. Vibrational frequencies were predicted, assigned, compared with the experimental values, and they are supported each other. The calculated results show that the strength of bond Hg—C is stronger than that of Hg—S, which is good agreement with the experimental data. The calculations of the second order optical nonlinearity and electronic absorption spectra are also performed.

KEY WORDS: Organomercury (I); DFT; vibrational frequency; TG; second-order optical nonlinearity.

INTRODUCTION

With the vast development of computational chemistry in the past decade, theoretical modeling of transition metal chemistry becomes much more mature than ever. Many important chemical and physical properties of the chemical systems can be predicted from the first principles by various computational techniques [1]. Among numerous calculated methods, density functional theory (DFT) has long been recognized as a better alternative tool in the study of transition metal chemical systems than traditional Hartree–Fock (HF) or Möller–Plesset perturbation theory at the second-order (MP2) methods [2, 3] due to the fact that it is computationally less demanding for inclusion of electron correlation, and gives better and more reliable descriptions of the geometries, dipole moment, and vibrational frequency. Phenylmercury compounds used as fungicides have been studied for a long time [4]. Recently, coordination complexes containing phenylmercury have attracted considerable interesting due to the linear organomercury compounds exhibit second-order nonlinear optical properties [5, 6]. However, the direct theoretical efforts on studying mercury complexes based on high-level quantum chemical investigations are relatively scarce. We synthesized the linear (isopropylxanthato)(phenyl)mercury(I) and performed DFT calculations for it at CEP-121G and CEP-31G basis sets, respectively. The second-order optical nonlinearity of the title compound has also been studied using MOPAC program package. Herein, we report the experiments as well as the calculational results.

EXPERIMENT AND COMPUTATIONAL METHODS

Physical Measurements

Elemental analyses for carbon, hydrogen and nitrogen were performed using a Perkin-Elmer 240C elemental instrument. The IR spectra were recorded in the 4000-400 cm⁻¹ region using KBr pellets on a Nicolet 170SX spectrophotometer. Thermal gravity (TG) and differential analysis (DTA) were recorded on a SDT 2980 simultaneously for the samples of ca. 10 mg under a nitrogen atmosphere (150 mL/min) at a heating rate of 20 °C/min.
Synthesis

All chemicals were obtained from a commercial source and used without further purification.

The title compound was prepared according to the literature procedure [7]. The products were collected and brown crystals were obtained by recrystallizing from EtOH. Found: C, 29.01; H, 2.85%. Calc. for C_{10}H_{12}HgOS_{2}: C, 29.09; H, 2.93%.

Computational Methods

DFT calculations with a hybrid Functional B3LYP (Becke’s Three Parameter Hybrid Functional Using the LYP Correlation Functional) at basis set CEP-121G and CEP-31G by the Berny method [8] were performed with the Gaussian 03 software package [9]. The vibrational frequencies calculated proved that the structure is stable (no imaginary frequencies). The thermodynamic properties of the title compound at different temperature have been obtained according to the vibrational analyses. Natural Bond Orbital (NBO) analyses and the time–dependent density functional theory (TD-DFT) [10–13] calculations of electronic absorption spectra were performed on the optimized structure.

On the basis of the MNDO Hamiltonian [14] and PM3 parametrization [15] with the MOPAC [16] program package, the molecular hyperpolarisability value was also calculated.

All calculations were performed on a Pentium IV computer using the default convergence criteria.

RESULTS AND DISCUSSION

Optimized Geometries

Figure 1 shows the molecular structure of the title compound with atomic numbering scheme. The selected optimized geometric parameters are listed in Table I along with the experimental data. Although the crystal structure of (isopropylxanthato)(phenyl) mercury(I) has been reported by Tiekink in 1987 [17], the available information about it, such as FTIR spectra and bond lengths and bond angles of the crystal structure, is not complete. So, in the following discussion, we use our own crystal data of the title compound, where the bond lengths and bond angles are almost the same as those reported earlier. (The detail information about the crystal sturcture, see CCDC number 254302.)

It can be found from Table I that the calculated bond lengths are all longer than those of experimental data due to that the theoretical values belong to the molecule in gas-phase and the experimental values are attributed to the molecule in solid state. Comparing the differences of bond distances in calculations with those in experiment indicates the calculational precision of the B3LYP/CEP-121G method are better than that of B3LYP/CEP-31G. The differences in former are all smaller than the differences in later except the bond distance of Hg(1)—C(6). In view of the bond angles, both of the two calculational methods give comparable values to the experimental data, revealing their fine calculational precisions. To sum up, the optimized geometries by two methods exhibit good similarity with the X-ray structure on the whole, which are the basis for our below discussion, such as vibrational frequencies and thermodynamic properties.

Vibrational Frequencies

Harmonic vibrations of the title compound were predicted by using DFT method at B3LYP/CEP-121G and B3LYP/CEP-31G levels of theory, respectively. The frequencies obtained from calculations have been scaled by 0.96, which is typical scaling factor for B3LYP frequencies [18]. The simulated infrared (IR) spectra, where

Fig. 1. Molecular structure with the atomic numbering scheme for the title compound.