

Theoretical and Experimental Investigations of Spectroscopic Properties of 2-Thiophenecarbonyl chloride

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Abstract. Molecular structure and vibrational wave numbers for 2-Thiophenecarbonyl chloride have been computed using the B3LYP method with the 6-311++G (d, p) basis set. The computation reveals that the title compound has two minimal conformers (gauche and syn). The conformational energy difference between the syn and gauche is very small, indicating that the syn conformer coexists with the gauche conformer. FT-IR and FT-Raman spectra of 2-Thiophenecarbonyl chloride were recorded and analysed in the range 3500-400 and 3500-200cm⁻¹, respectively. The HOMO-LUMO energy gap of the two conformers have been also calculated for comparison of their chemical activities.

1. Introduction

Theophany is a five membered heterocyclic compounds that contain sulfur. The sulfur atom in this theophany ring acts as an electron donating heteroatom, and theophany is thus considered to be an electron-rich heterocyclic [1]. 2-Thiophenecarbonyl chloride is an organochlorine compound and a slightly yellowish crystal. It is an organic photoelectric material and can also be used to make solar cells. 2-Thiophenecarbonyl chloride is theophany derivatives with the chemical formula (C₅H₃OSCl). It contains the -C (O) Cl group substituted in position 2 to the carbon atom of a theophany ring. The rotation of the -C(O)Cl group on the theophany rings of the title compound leads to two equilibrium isomers. Thus, 2-Thiophenecarbonyl chloride can exist as two geometrical isomers, whereby the carbonyl oxygen and ring sulfur can be either OS-syn or OS-gauche.

Vibrational spectroscopy is an analytical tool for providing information about the structure and composition of molecules [2-4]. Many studies on conformational analysis of acyl chloride group have been made. For example, Aarset and Hagen [5] investigated the structure and conformation of the phenyl acetyl chloride and revealed the existence of its two conformers in the gas phase. To the best of our knowledge, neither experimental nor computational vibrational spectrum study for the 2-Thiophenecarbonyl chloride have been published in the literature up to now. Considering the industrial and biological importance of the 2-Thiophenecarbonyl chloride, we carried out theoretical and experimental studies on it. In order to get more information about this molecule, HOMO-LUMO analysis was also included.



2. Experimental details

2-Thiophenecarbonyl chloride was purchased from a commercial company with more than 98% purity. The FT-IR spectrum was recorded for data collection using a Nicolet Nexus FT-IR spectrometer. The FT-Raman spectrum was collected at about 400 mw by using 1064 nm line of an Nd: YAG laser on a Raman module of the Nexus spectrometer. Both FT-IR and FT-Raman experiments were done at room temperature.

3. Experimental details

Due to the rotations of the -C (O) Cl group, 2-Thiophenecarbonyl chloride leads to two different conformers. The geometry optimization and energy evaluation for two conformers were performed by using Gaussian 09 [6] program package with DFT/B3LYP/6-311++G (d, p) methods. The positive wavenumbers of all normal modes confirmed the stability of the two conformers. HOMO and LUMO energies were calculated and plotted for the two conformers by using the Gaussian 09 and Gauss View programs [7].

4. Results and discussions

4.1. Conformational analysis

The title compound may have two conformations because the rotations of the -C (O) Cl group. The carbonyl oxygen and ring sulfur can be either OS-syn or OS-gauche. Therefore, we calculated the conformational structures and energies of the two conformers in the gas phase by the density functional theory (DFT) method with B3LYP/6-311++G (d, p) level. The atomic numbering scheme was given in Fig. 1.

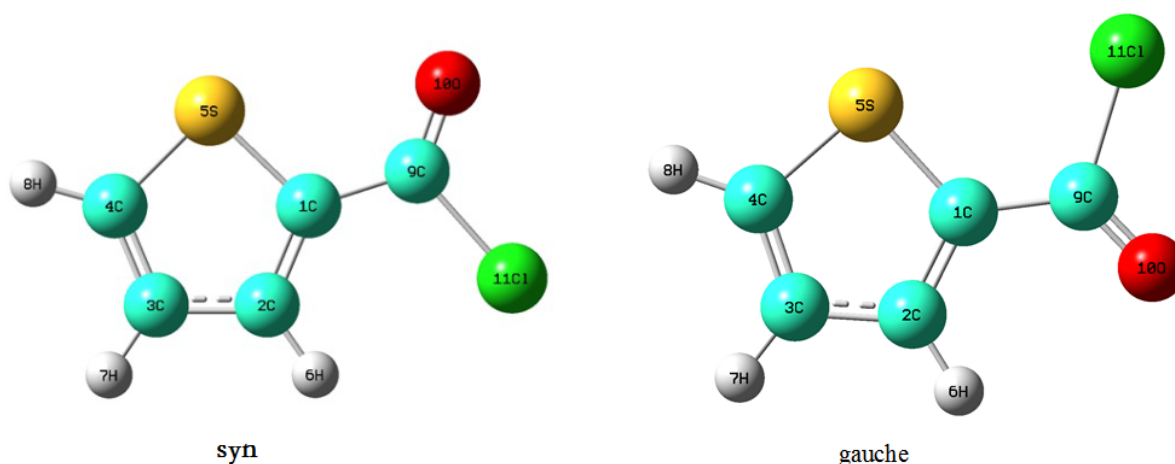


Figure 1. The atomic numbering scheme of 2-Thiophenecarbonyl chloride

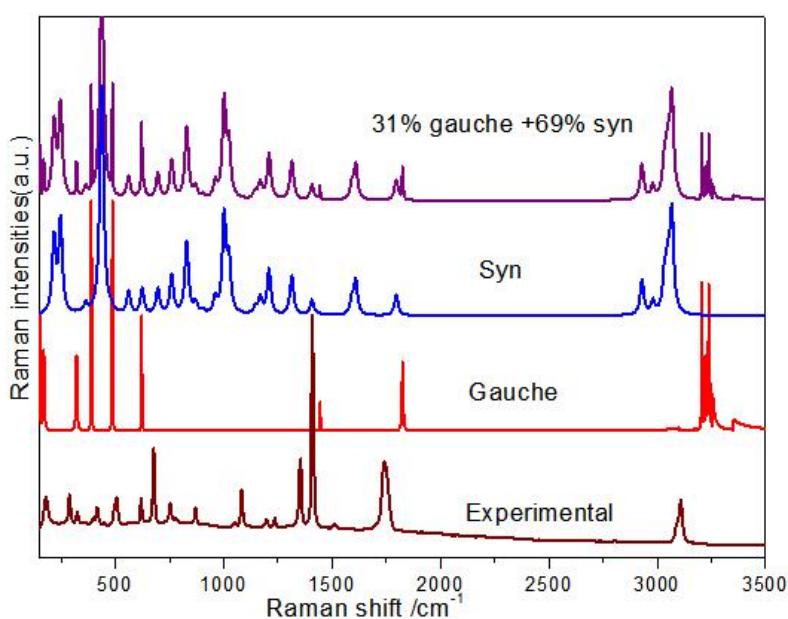
Via theoretical calculations, we found two stable conformers with zero imaginary frequencies. The energy difference between the gauche and syn conformers is very small (Table 1), indicating that 2-Thiophenecarbonyl chloride existed as a mixture of the two conformers. Therefore, it was significant to estimate percent of population for two conformations, which can be calculated based on Gibbs free energies by utilizing Boltzmann distribution law [8]. The Gibbs free energies and corresponding percent of the population for two conformers were shown in Table 1. From the Table it can be seen that the population composition of 69% syn and 31% gauche at room temperature. The electron diffraction analyses have shown the existence of the syn or gauche rotational isomers as a mixture in the gas state with the syn conformer as the most stable species [9]. They are consistent. For both the conformers, the thiophene ring was calculated to be nearly coplanar with the acetyl chloride group.

Table 1. Calculating percent of the population for two conformers of 2-Thiophenecarbonyl chloride based on Boltzmann distribution law.

Parameters	gauche	syn
Gibbs free energies(a.u.)	-1125.99636	-1125.99733
$\Delta E = E_{\text{gauche}} - E_{\text{syn}}$ (kcal/mol)	0.609	
Percent of population	31%	69%

4.2. Analysis of vibrational spectra

The title compound has 11 atoms with 27 normal modes of vibrations. The molecular geometry does not exhibit symmetry and hence belongs to the C1 point group. Visual comparison of the observed and scaled Raman and IR spectra for the two conformers of the 2-Thiophenecarbonyl chloride were shown in Fig. 2 and Fig. 3, respectively. These figures clearly show the spectral characteristics of the title molecule. Since the proportion of conformation gauche was 69%, which was absolutely dominant, the average spectrum of weights was also similar to the conformation gauche as a whole. As it is known, conformational interconversion leads to changes in wavenumbers, line shapes and relative intensities of molecular vibrations, so it is relatively easy to distinguish different conformations by means of vibrational spectroscopy [10]. At room temperature, most of observed IR and Raman bands of two conformers were overlapping. Only a few observed bands possibly belong to either the gauche conformer or the syn conformer.

**Figure 2.** Experimental and calculated FT-Raman spectra of 2-Thiophenecarbonyl chloride

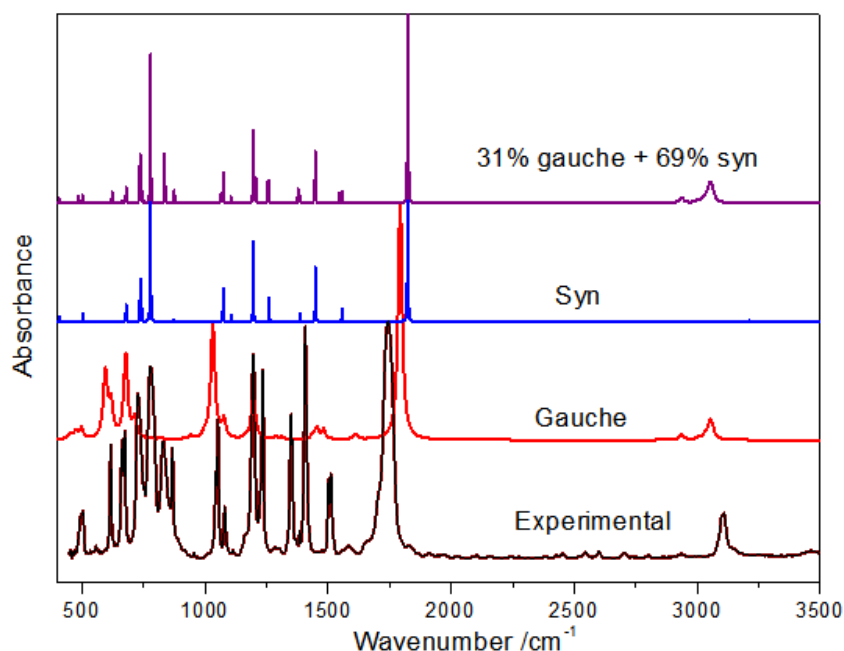


Figure 3. Experimental and calculated FT-IR spectra of 2-Thiophenecarbonyl chloride

4.3. Analysis of molecular orbital

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) play an important role in molecular electric and optical properties [11]. The HOMO represents the ability to donate an electron, and the LUMO represents the ability to accept an electron. Thus, the energy of the HOMO is directly related to the ionization potential, while the LUMO energy is directly related to electron affinity, and the energy gap between HOMO and LUMO characterizes chemical reactivity of a molecule [12].

The HOMO and LUMO energies for the two conformers were calculated at the B3LYP/6-311++G (d, p) level of theory. The 3D plots of the HOMO and LUMO from the calculations were shown in Fig. 4. The results contain 37 occupied molecular orbitals and 175 virtual molecular orbitals. As seen from Fig. 4, the HOMO is localized on the C-C bonds (C3-C4 and C1-C2) and O, Cl atoms, there is no contribution from S atom. The LUMO mainly comes from the skeleton of the thiophen ring and the -C (O) Cl group. The HOMO and LUMO energy of the gauche conformer was -7.576 and -2.642eV, respectively, the HOMO and LUMO energy of the syn conformer was -7.596 and -2.660eV, respectively. The energy gaps were shown in Fig. 4. HOMO-LUMO energy gaps were found to be 4.934 and 4.936 eV for the gauche and syn conformer, respectively. 2-Thiophenecarbonyl chloride has a large HOMO-LUMO gap, and this is generally associated with less chemical reactivity, less polarizability, high kinetic stability, and can be termed as chemically stable molecule.

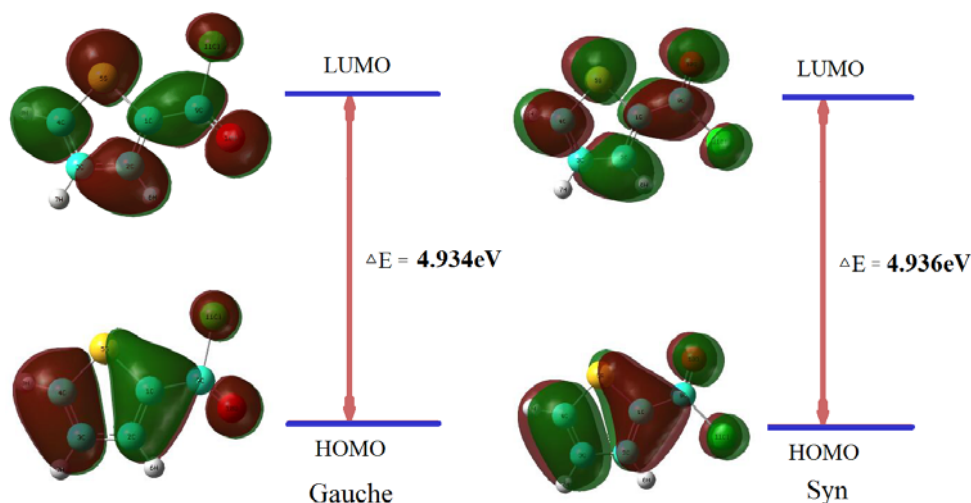


Figure 4. Contour plots of the HOMO, LUMO molecular orbitals for 2-Thiophenecarbonyl chloride

5. Conclusion

In this work, the molecular structure, energy, conformation and vibrational spectra of 2-Thiophenecarbonyl chloride were obtained by density functional theory (DFT) calculations. The theoretical calculations indicate that the molecule exists as a mixture of syn and gauche conformers. The experimental and theoretical analyses on the spectra of the two conformers are reported. Most of the observed IR and Raman bands belong to both the two conformers, whereas a few weak Raman and IR bands only present in the syn conformer; in the meantime, a few weak the Raman bands and IR bands only belong to the gauche conformer. The difference between the experimentally observed and theoretically evaluated wavenumbers of the fundamentals is minimal. Furthermore, the HOMO-LUMO gap of 2-Thiophenecarbonyl chloride was determined, it showed low chemical reactivity. We believe this study will be useful to gain better understanding of the structure, molecular properties, vibrational spectra of 2-Thiophenecarbonyl chloride and related compounds.

Acknowledgments

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