Theoretical study of the *syn* and *anti* thiophene-2-aldehyde conformers using density functional theory and normal coordinate analysis

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Abstract

An extensive computational study of thiophene-2-aldehyde conformers *syn* and *anti* has been carried out using density functional (DFT). From these calculations, B3LYP/6-31G(d) has been chosen as it produces results remarkably close in comparison with experimental ones, with less demanding computational time. Data obtained from DFT computation were used to perform a normal coordinate analysis to complement and give insight in the experimental vibrational assignment. Calculated dipole moments and relative stabilities of isomers coherently support experimental statements given in the literature.
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1. Introduction

The use of computational techniques is becoming increasingly common throughout all the various fields of chemistry [1]. This can be largely attributed to the increasing availability of robust energy derivative programs, in which first and second energy derivatives are computed analytically [2], that is, the energy gradient has greatly improved the efficiency and reliability of geometry optimization of ab initio molecular orbital methods. Taking into account that optimization methods that use gradients require an initial estimate of the Hessian or second derivative matrix, underlines the importance of an accurate estimate as it would lead to a more rapid convergence.

The main purpose of this work is to take advantage of the quantum mechanics to support and complement experimental data. In this sense, we have considered the different structural and energetic implications in the study of conformational systems. Thus, the preference between two possible planar conformations in the study of monosubstituted heterocycles such as thiophene is often strongly medium-dependent because of their differing polarities. The conformational preferences of these molecules have, during the last few years, attracted much attention, with virtually the complete armory of physical-organic chemistry being brought to bear the problem. In these circumstances, the conformational preference in the absence of solvent is of some importance. Ab initio molecular orbital theory provides a means of determining intrinsic conformational preferences and is suitable to study physical properties and vibrational characteristics of conformers arising from the molecular structure and conformational equilibrium.

When thermodynamic parameters as well as infrared and Raman spectra of conformers are determined experimentally procedures, the quality of different ab initio methods can be tested by comparison with experimental results. This work was performed to identify a suitable computational method for treating conformers of thiophene derivatives on the basis of experimental data of thiophene-2-aldehyde obtained by electron diffraction and microwave, infrared, Raman and matrix isolation spectroscopy [3]. This work will reveal additional quantitative chemical knowledge of the formation, relative stability, geometry, as well as giving more detailed insight into systematic differences between calculation and experiment in the assignment of vibrational spectra, through the calculated force field and potential energy distribution of the corresponding normal modes.

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Among the distinct ab initio methods, one of the most popular is that concerning to Hartree–Fock calculations, which treat the electrons as individual wave functions. However, electrons do not act independently of each others and to improve results the electron correlation must be taken by mixing in excited state wave functions with ground state wave functions.

Density functional theory (DFT) takes another approach. The interaction system of electrons is approximated by using a function to describe the electron density (a functional) rather than individual wave functions for each of the electrons [4]. That is, DFT relies on the total electron density, with the electron "placed" in non-interacting Kohn–Sham (KS) orbitals [5]. There are some results indicating that the vibrational frequencies and intensities from DFT calculations are better than those obtained from second order Møller–Plesset (MP2) perturbation theory [6]. With the DFT approach it is possible to perform calculations of large molecules because the potential depends on three spatial coordinates rather than 3N degrees of freedom.

On the other hand, application of DFT [7–10] to chemical systems has received much attention recently because of a faster convergence in time than traditional quantum mechanical correlation methods in part, and improvements in the prediction of the molecular force field, vibrational frequencies (and consequently thermodynamic parameters), dipole moments and polarizability data. Therefore, the force field from DFT calculation could be utilized with the spectroscopic data for the assignment of observed frequencies and the refinements of molecular force field under study.

2. Computational details

The calculations in this study were performed using the Gaussian '03 suite of programs [11]. Several DFT methods have been evaluated, they consisted of the S-VWN local functional, corresponding to the Slater–Dirac exchange functional (S) [12] with the Vosko–Wilk–Nusair fit for the correlation functional (VWN) [13], the BLYP gradient-corrected functional, corresponding to Becke's gradient corrected exchange functional (B) [14] with the Lee–Yang–Parr fit for the correlation functional (LYP) [15] and two hybrid functional B3LYP and B3PW91, corresponding to Becke's three parameter exchange functional (B3) [16] with the LYP correlation functional and with Perdew and Wang's gradient-corrected correlation functional (PW91) [17]. With respect to geometry and vibrations, only small differences are observed for the different functionals, so that we limit the study to the best-known B3LYP hybrid functional.

Basis set dependence for the density functional was investigated by systematically adding polarization function to split valence basis sets, such as 6-31G(d,p) [18], 6-311G(d,p) and 6-31G(d) [19–21]. Again, no significant differences were observed, so that for subsequent calculations the well-known B3LYP/6-31G(d) level of theory is employed which also gives the best agreement for vibrations with the experimental data.

Results of the other level of calculation are presented in Appendix A (Table A1). The harmonic vibrational frequencies and eigenvectors as well as infrared intensities were subsequently calculated using the analytical second derivatives for ab initio methods and numerical differentiation of analytical gradients for the functionals, while Raman intensities which depend on the square of the polarizabilitiy derivatives require the calculation of the third derivative of the system energy with respect to coordinates and electric field. In order to account for an harmonic behavior, the obtained frequencies are scaled with a factor of 0.9614. This value has been applied to all regions of the spectrum, so it is possible that some vibrations are affected more significantly than others [22].

Those force constants obtained in Cartesian coordinates with Gaussian were transformed into internal force constants through FCART 01, which is a modification of a previous software [23] written to accomplish all the necessary transformation and calculations using the G03 output. It extracts from the G03 archive file the calculated geometry (including atom type and number sequencing), Cartesian force constants, dipole moment and polarizability derivatives to produce the calculated frequencies, intensities, depolarization ratios and statistics. With this program we have also obtained the matrices of the potential energy distribution (PED) which provide a measure of each internal coordinate's contribution to the normal coordinate at the above mentioned theory level.
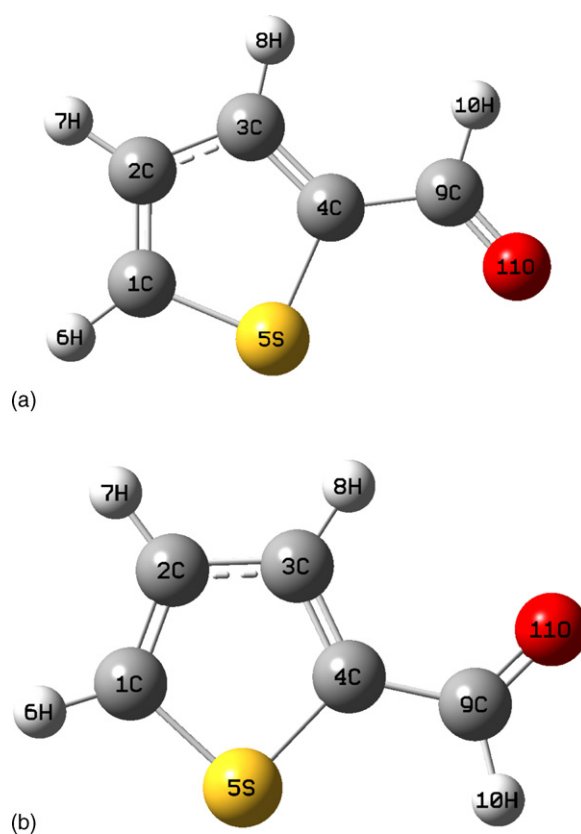

Fig. 1. Diagram of the *syn* (a) and *anti* (b) thiophene-2-aldehyde conformers.