

Vibrational spectra and *ab initio* DFT calculations of 3,3'- and 4,4'-dimethyl substituted 2,2'-bithiophene.

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Abstract

We present FT-Raman and FT-IR spectra of two β -methyl substituted thiophene dimers. Methylation at β -positions modulates the equilibrium molecular conformation, thus affecting the intramolecular delocalization of π -electrons. *Ab initio* Density Functional Theory (DFT) calculations have been performed to analyze the experimental data.

Keywords: (Infrared and Raman spectroscopy, *Ab initio* quantum chemical methods and calculations, polythiophene and derivatives)

1.- Introduction

Alkyl-thiophene oligomers may show optical and electrical properties comparable to those of the polymer; their use for optical devices and molecular electronics has recently been suggested^[1,2].

The main purpose of the present work is to investigate experimental and theoretically the vibrational spectra of two β -methyl substituted thiophene dimers. We use here FT-IR to probe the fundamental modes of vibrations of 3,3'- and 4,4'-dimethyl-2,2'-bithiophene (referred to as HH and TT hereforth, respectively). Moreover, *ab initio* calculations have been performed by Density Functional Theory (DFT) at the B3LYP/6-31G** level.

2.- Experimental and Computational Details

The details on the synthesis are described elsewhere^[3]. The infrared absorption spectra were recorded with a Perkin Elmer FT-IR spectrometer model 1760 X. DFT calculations were carried with the Gaussian 94 program^[4] using a SGI Origin 2000 supercomputer. All calculations were carried using Becke's three-parameter exchange functional (B3LYP)^[5]. Calculations on the HH and TT were performed assuming that both molecules belong to

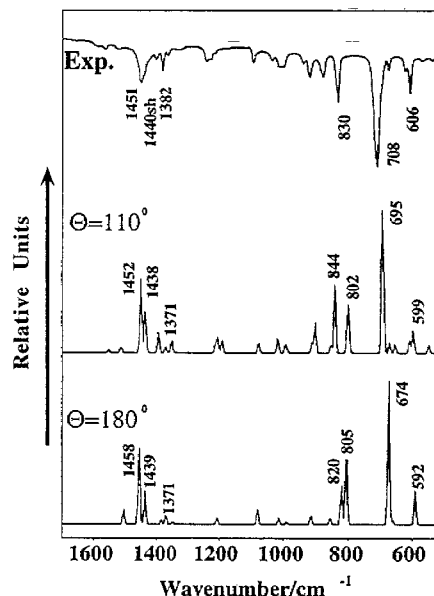


Fig. 1. Experimental and B3LYP/6-31G** calculated spectra (for the *anti* planar and the *twisted* conformations) of 3,3'-dimethyl-2,2'-bithiophene (HH).

the C_{2h} symmetry point group in the *anti* conformations. In the case of the HH molecule, a C_2

symmetry was imposed in the calculations of the twisted conformers.

In this communication we used the often-practiced simple adjustment in which the frequencies are scaled down uniformly by a factor of 0.96, which have been recommended recently by Scott and Radom[6]. All quoted vibrational results are thus the scaled values.

3.- Infrared spectra

The Fourier transform infrared spectra of HH and TT in the solid state are shown in Figures 1 and 2, respectively, which also display the computed B3LYP/6-31G** infrared spectra of the two substituted bithiophenes.

In the TT bithiophene (see Fig.2), the 1550–1350 cm^{-1} region is dominated by three bands at 1537, 1459 (with a shoulder at 1433) and 1404 cm^{-1} . The experimental bands are correlated with the computed B3LYP/6-31G** at 1544 cm^{-1} assigned to the C=C antisymmetric stretching mode, 1455 and 1440 cm^{-1} assigned to the in-plane deformations of the methyl groups, and 1413 assigned to the C=C symmetric stretching mode.

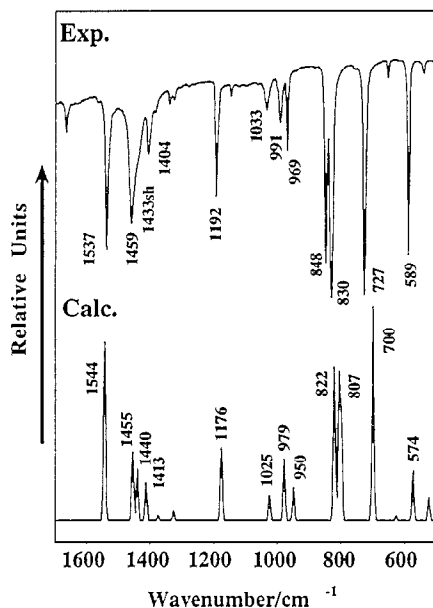


Figure 2. Experimental and B3LYP/6-31G** calculated spectra of 4,4'-dimethyl-2,2'-bithiophene (TT).

The 1300–500 region of the experimental infrared spectrum is dominated by five strong peaks recorded at 1192, 848, 830, 727 and 589 cm^{-1} . In the calculated infrared spectrum of this molecule, the region below 1300 is dominated by also five modes calculated at 1176, 822, 807, 700 and 574 cm^{-1} . Analyzing the corresponding eigenvectors, the band at 1176 cm^{-1} should be assigned to a in-plane CH deformation. We assigned the mode at 822 cm^{-1} $\nu_a(\text{C-S})$; the out-of-plane C–H bending vibrations are calculated at 807 and 700 cm^{-1} for the H_β and

H_α , respectively. Finally, the mode calculated at 574 cm^{-1} correspond to a $\gamma(\text{ring})$ out-of-plane bending mode.

The discussion for the HH bithiophene will be restricted on the changes of the infrared spectrum upon conformational distortions of the rings. Figure 1 displays the experimental IR spectrum together with those calculated for the *anti* coplanar ($\Theta = 180^\circ$) and the minimal energy conformation ($\Theta = 110^\circ$).

The overall appearance of the experimental spectrum is more close to that of the distorted conformer than to the *anti* one. In particular, the vibrations recorded in the middle energy spectral region between 1300–900 cm^{-1} are more accurately reproduced (in both peak positions and relative intensities) by the calculation performed for the *twisted* conformer.

The three main bands calculated in the 1600–1400 cm^{-1} region for the *twisted* model (i.e., 1452, 1438 and 1371 cm^{-1}) are almost coincident with the bands experimentally recorded at 1451, 1440 and 1382 cm^{-1} . In addition, the increasing dynamical decoupling on rotation of the motions of the C=C bonds located of different rings could justify the absence in the experimental spectrum of the band due to the $\nu_{as}(\text{C=C})$ normal vibration (i.e., that calculated at 1507 cm^{-1} with some intensity for the *anti* conformer). Contrarily, this normal mode displays a very large infrared activity for the TT bithiophene.

In the low energy region, the most outstanding feature is the sizeable upshift by 21 cm^{-1} , in going from $\Theta = 180^\circ$ to $\Theta = 110^\circ$, of the absorption around 690 cm^{-1} , which is assignable to an out-of-plane $\gamma(\text{C-H})$ bending mode. The closeness of the calculated value for the *twisted* conformer to the experimental one gives further support to the hypothesis that this compound posses a large tilted conformation.

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