Raman spectra and conformational properties of hexyl- and methylsulphanyl-substituted oligothiophenes

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Abstract

A Raman study on bithiophenes β-functionalized with hexyl and methylsulphanyl (SCH3) groups and a quaterthiophene β-functionalized with methylsulphanyl groups is reported. MM2 calculations were carried out on the hexyl derivatives and the results compared to those derived from Raman data. Evidence was obtained of the fact that the conformational preferences of alkyl bithiophenes are the same both in dilute solution and as pure liquids. Raman data confirm the efficiency of the SCH3 group in compensating the loss of π conjugation. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Oligo- and polythiophenes are important molecules in the field of organic materials due to their small energy gap, good environmental stability and easy functionalization [1]. The energy gap, which governs many of the properties of conjugated materials, strongly depends on the mean deviation of the system from planarity and on the mesomeric effect of the substituents [1].

Introduction of alkyl substituents, which is often required to improve processability, decreases the inter-ring coplanarity and increases the energy gap. Substituents which mesomerically interact with the aromatic thiophene system can counterbalance this effect [2]. The knowledge of the degree of distortion induced by the substituents is however of great importance, since different regiochemistry may affect the physical properties of the material in a way which is difficult to predict. In a recent work on the functionalization of oligothiophenes with electron-donating methylsulphanyl groups [3], it was reported that 3,3'-, 3',4'- and 4,4'-dihexyl-2,2'-bithiophenes (I–III) which are characterized by three different inter-ring junction types (head-to-head, head-to-tail and tail-to-tail) whose distortion is affected only by the steric effect. As it is known that molecular mechanics calculations give a satisfactory description of the conformational preferences of bithiophenes [9,2], MM2 calculations on I–III are reported and compared with Raman data. A Raman study is carried out also on 3,3'-bis(methylsulphanyl)-2,2'-bithiophene (IV) and 3, 4',3''-tetra(methylsulphanyl)-2,2':5':5',2''-quaterthiophene (V) with the aim of getting information on the mesomeric effect of the SCH3 group and to deepen the
knowledge of the tetramer structure. MM2 calculations on the conformation of 3,3-bis(methylsulphonyl)-2,2'-bithiophene were already carried out [2]. Structure and numbering scheme are given in Scheme 1.

2. Experimental

The synthesis of all the compounds has already been described: I–II [10], III [11], IV [12], V [3]. All compounds except IV are viscous oils.

Molecular mechanics calculations were performed using Allinger’s MM2(91) program [13] on a Microvax 3500. UV transitions were calculated by a single point ZINDO/S-CI (4 × 4) calculation on previously optimized PM3 geometries [14].

FT-Raman spectra were measured at room temperature using the FT-Raman accessory kit FRA106-S of a Brucker Equinox 55 FT-IR interferometer. A continuous-wave Nd:YAG laser working at 1064 nm was employed for Raman excitation. A Germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a backscattering configuration with a spectral resolution of 4 cm⁻¹. In order to avoid possible damage upon laser irradiation, the laser beam was loosely focused on the sample and its power was kept at a level lower than 50 mW.

3. Results and discussion

3.1. MM2 calculations

The MM2 calculated conformational energies of I–III for two different values of the dielectric constant 1.5 and 5 are reported in Table 1. The value of 5 for the dielectric constant was chosen to simulate the effect of the chloroform. Table 1 also gives the calculated inter-ring dihedral angles (ω°) and relative populations (p) of the conformational minima, together with the value of the maximum UV absorption (λmax) measured in chloroform [11].

In all cases, the preferred conformation of the alkyl chain is that in which the carbon atom of the second methylene group from the ring forms a dihedral angle of 90° with the thiophene double bond and the remaining fragment adopts a trans planar conformation. For all compounds, the preferred conformation of the inter-ring junction at a low dielectric constant is trans-gauche and the degree of distortion increases progressively on going from tail-to-tail to head-to-head substitution. The increase of the dielectric constant stabilizes the syn forms, but leads to the reversal of the conformational preference only in the case of III. The experimental λmax measured in chloroform are in agreement with the theoretical results (cf. λmax = 306–315 nm measured for fixed syn-planar bithiophenes [15]).

It is interesting to observe that the theoretical calculations and the experimental UV maxima are the same as those found for the corresponding methyl derivatives [9]. This indicates that, in the case of dialkyl-substituted bithiophenes, it is the relative position and not the length of the alkyl chain that affects the distortion of the inter-ring junction.

3.2. Raman spectra

The Raman spectra of low band gap polyconjugated materials are usually recorded in resonance or near resonance conditions [16]. As resonance is approached, only few Raman-active vibrations, i.e., those modes having a non-vanishing projection along the deformation coordinate
describing the equilibrium geometry changes from the ground to the excited electronic state involved in resonance should increase appreciably in intensity relative to all other Raman lines. The symmetry point group of the molecule in the excited state determines which symmetry species are selectively enhanced upon resonance. When the molecular symmetry does not change from the ground to the excited state, only totally symmetric modes are resonance enhanced.

However, resonance Raman enhancement itself cannot fully account for the spectroscopic behavior of \( \pi \)-conjugated systems. For example, very short conjugated molecules, having a energy gap well above the energies of the commonly used optical lasers, also show a strong conventional Raman spectrum with very few bands [17]. On the contrary, the FT-Raman spectra of \( \pi \)-conjugated compounds, recorded with an excitation energy of 1064 nm which is well below the energy gap of the material [18], show almost the same spectral pattern as that of the fully resonant Raman spectra [19]. The key assumption for the right interpretation of the spectra is that, independently that the resonance Raman condition is fulfilled, only one strongly dipole-allowed electronic state is relevant for the description of the Raman process [20–22]. Thus, this strong Raman enhancement is associated with the existence of an electron–phonon coupling when atoms move along one or a few specific vibrational normal modes.

The FT-Raman spectra of compounds I–V are given in Figs. 1 and 2, in the 1700–100 cm\(^{-1}\) spectral range.

It can be observed that all the materials show the characteristic vibrational feature of many other classes of \( \pi \)-conjugated organic compounds [4]: the Raman spectra are rather simple, in spite of the complex chemical structures. Another particularity of these systems is that, of the usually large population of Raman-active modes predicted by the optical selection rules, the very few ones experimentally observed are overwhelmingly strong in the aromatic C=C stretching region.

In Table 2, we summarize the wavenumbers of the two main Raman lines recorded in the C=C stretching energy region (denoted as lines A and B, respectively), on which we will restrict our further discussion along this section. Data for unsubstituted bithiophene (T2) and tetrathiophene (T4) are added for the sake of comparison [23].

Line A shows a large dispersion toward lower wavenumbers when the \( \pi \)-skeleton length increases. Along with this downward shift, its relative intensity quickly weakens and becomes almost unobservable for long oligomers (e.g., sexithiophene) [5]. Line B however is always very strong and dominates the Raman spectrum. For the class of the oligothiophenes, this strong line appears at somewhat different wavenumbers from one chemical series to another, but within each series of compounds.

Fig. 1. FT-Raman spectra of the hexyl-substituted oligothiophenes in the 1700–100 cm\(^{-1}\) spectral range: (a) I, (b) II, and (c) III. The excitation wavelength was 1064 nm.

Fig. 2. FT-Raman spectra of the methylsulphanyl-substituted oligothiophenes in the 1700–100 cm\(^{-1}\) spectral range: (a) IV and (b) V. The excitation wavelength was 1064 nm.
it is only slightly shifted with the π-skeleton length [4–6]. In addition, line B is experimentally found to occur at higher wavenumber values in oligothiophenes bearing electronically inert substituents at either π-skeleton end [4–6].

Theoretical normal modes DFT calculations recently performed on the series of α,α′-dimethyl end-capped oligothiophenes [24] have shown that line A originates from the in-phase ν_{sym}(C=C) vibration of the thiophene rings at either end of the π-skeleton, coupled to a large extent with an in-phase combination of stretchings of the inter-ring C–C bonds joining the inner thiophene rings. These calculations also point out that the strongest Raman line B originates from the totally symmetric in-phase ν_{sym}(C=C) vibration of the “bulk” thiophene rings [24]. The collective stretchings of the CC bonds are necessarily coupled with the in-plane bending of the C–H bonds, in which the H atoms recoil with a large displacement which opposes that of the C atoms. This normal mode corresponds to the so-called Π coordinate in the ECC model [7,8].

The upshift of the line A in the spectrum of the 3,3′-dihexyl-2,2′-bithiophene (I) (1564 cm$^{-1}$) with respect to the unsubstituted compound (1556 cm$^{-1}$) (T2) can be simply accounted for by the more tilted molecular conformation of the alkyl derivative, leading to a less conjugated π-backbone. As a matter of fact, some ab initio calculations have suggested that the alkyl substitution causes rather small changes in the thiophene ring geometry, and only the overall shape of the torsional potentials are dramatically influenced by the steric hindrance [25].

On the contrary, a small distortion from coplanarity of the thiophene rings should be expected for 3,4,3′,4′-dihexyl-2,2′-bithiophene (II), since line A appears almost at the same wavenumber (1559 cm$^{-1}$) than in the unsubstituted pattern molecule (1556 cm$^{-1}$). However, no conclusions on the molecular conformation can be drawn for 4,4′-dihexyl-2,2′-bithiophene (III) from the simple observation of its Raman spectrum. The upward shifts of both lines A (1566 cm$^{-1}$) and B (1475 cm$^{-1}$) with respect to T2 (1556 and 1445 cm$^{-1}$, respectively) are thought to arise mainly from dynamical end-effects. Accurate normal mode calculations should be useful in this case.

Table 2

<table>
<thead>
<tr>
<th>Materials</th>
<th>Line A</th>
<th>Line B</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1564</td>
<td>1448</td>
</tr>
<tr>
<td>II</td>
<td>1559</td>
<td>1458</td>
</tr>
<tr>
<td>III</td>
<td>1566</td>
<td>1475</td>
</tr>
<tr>
<td>IV</td>
<td>1531</td>
<td>1441</td>
</tr>
<tr>
<td>V</td>
<td>1528</td>
<td>1444</td>
</tr>
<tr>
<td>T2*</td>
<td>1556</td>
<td>1445</td>
</tr>
<tr>
<td>T4*</td>
<td>1519</td>
<td>1463</td>
</tr>
</tbody>
</table>

*From Ref. [23].

The Raman results for the dialkyl compounds are in good agreement with the findings from theoretical MM2 calculations and UV data. In particular, experimental evidence is given on the existence of a distorted form for a head-to-head junction also in a pure liquid for a dimer having a dialkyl substitution.

As far as the mesomeric effect of the SCH$_3$ group is concerned, the charge injection by the sulphur atoms of the methylsulphanyl-substituents is nicely reflected by the large red shift of line A in IV (1531 cm$^{-1}$) with respect to T2 (1556 cm$^{-1}$). The downshift of line A could be ascribed to an enhanced intramolecular charge delocalization. In addition, the effect seems to be strong enough to overcome the repulsive steric interactions between the aromatic S atoms and the methylsulphanyl groups.

We observe however that the π-skeleton length downward dispersion of line A in the methylsulphanyl-oligothiophenes studied in this work quickly reaches saturation (e.g., the downshift is only of 3 cm$^{-1}$ in going from the methylsulphanyl-dimer to the tetramer (V), while line A shifted up to 37 cm$^{-1}$ from unsubstituted T2 to unsubstituted T4 [23]).

On the other hand, we know that unsubstituted bi- and quarterthiophene are trans planar solids [26,27]. Thus, the 37 cm$^{-1}$ shift is only the result of a longer π-skeleton. On the contrary, it is probable that V is present in a very tilted conformation. We expect from MM2 calculations of the relative dimers [2] that the central head-to-head junctions in V is 127° tilted, while the two head-to-tail outer junctions can be syn-planar or 136° tilted. Also the value of UV maximum absorption in CHCl solution ($\lambda_{\text{max}} = 395$ nm) [3] is in agreement with a tilted conformation. In fact ZINDO/S///PM3 calculations on V give a $\lambda_{\text{max}} = 460$ nm for a fully planar conformation, a $\lambda_{\text{max}} = 417$ nm for the conformation with the central junction 127° tilted and the outer junctions planar and a $\lambda_{\text{max}} = 387$ nm for the all tilted conformation. This conformation is also in agreement with a X-ray determined structure of a tetramethylated quarterthiophene with the same regiochemistry [28]. The little shift observed on going from IV to V is therefore the evidence that we are in the presence of the balance of two opposing effects, namely, the longer π-skeleton and the increased inter-ring distortion.

In conclusion, Raman data proves to be valuable in determining the efficiency of mesomeric interactions with aromatic thiophene rings, and, together with UV data and theoretical calculations, allows to obtain information on the preferential conformation of a compound also as a pure liquid.

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