Vibrational dynamics study of the effect of the substituents on the π-conjugation of different bithiophene molecules

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Received 6 September 2004; accepted 11 October 2004
Available online 9 December 2004

Abstract

We report on the FT-Raman spectroscopic study, aided by DFT model chemistry calculations, of three different classes of π-conjugated oligomers: (i) a dicyanomethylene end-capped bithiophene with a quinoidal chemical structure, (ii) a symmetrically dimethyl-substituted system bearing a non-polar aromatic structure in its ground electronic state and (iii) a highly polarized push–pull system with an electron-donor dimethylamino and an electron-acceptor cyano groups attached to its end α,ω-positions. We have optimized the molecular geometries of these three bithienyls at the DFT//B3LYP/6-31G** level, and compared the main skeletal bond lengths of the π-conjugated backbone in terms of the so-called bond-length-alternation (BLA) parameter. The overall summations of the B3LYP/6-31G** atomic charges for the thienyl rings and the various types of end α,ω-substituents have also been compared along the bunch of compounds. Finally we make use of the well-known effective conjugation coordinate (ECC) theory to assess useful information about the π-conjugation, computing the B3LYP/6-31G** value of the force constant associated to the collective ECC vibrational normal mode.

Keywords: Oligothiophenes; π-Conjugated materials; FT-Raman spectroscopy; DFT calculations

1. Introduction

Organic semiconductors are currently receiving significant attention as new functional materials to be used in organic field-effect transitions (OFETs) [1], organic light emitting diodes (OLEDs) [2], photodiodes [3], and capacitors [4]. At present, OLED displays are being brought to the marketplace, and OFETs are strong candidates for switching devices for OLED, electronic paper and flat-panel liquid-crystal displays [5]. Additionally, low-cost ‘smart cards’, radio-frequency ID tags and printable transistors are under active investigation [6].

p-Type organic semiconductors such as oligothiophenes, acenes, phthalocyanines and poly-3-alkylthiophenes, in which holes are the main carriers, have been extensively studied over the last years. However, there are not many n-type organic semiconductors compared to p-types ones. High performance n-type molecular materials will enable the fabrication of p–n junction devices and complementary logic circuits. Recently, n-type thioephene-based compounds such as fluorocarbon and fluorophenyl-substituted oligothiophenes [7] and some dicyanomethylene-substituted quinoidal oligothiophenes [8] have been reported as high performance electron-transporting materials. These n-type materials were obtained by modifying known p-type ‘cores’ with strong electron-withdrawing substituents.

Vis-NIR electronic absorption and IR and Raman vibrational spectroscopies are among the early techniques most widely used over the last 15 years to study very many classes of electrically conducting polymers and π-conjugated oligomers. Raman spectroscopy has been shown to be particularly useful in: (i) estimating the degree of π-conjugation in neutral state [9–11], (ii) characterizing different types of conjugational defects in doped materials [12], and (iii) analyzing the efficiency of the intramolecular charge transfer in push–pull π-conjugated NLO-phores [13,14]. The usual observation of rather a few and overwhelmingly strong Raman scatterings, even for molecular materials with complex chemical structures, has been successfully explained, in the framework of the effective...
conjugation coordinate (ECC) theory [15], in terms of the occurrence in these quasi one-dimensional systems of a rather effective electron-phonon coupling taking place over the whole \( \pi \)-backbone path. In polyaromatic and polyheteroaromatic \( \pi \)-conjugated systems, the so-termed as collective ECC vibrational coordinate can be analytically defined as the linear combination of skeletal C=CC=CC stretching oscillations mostly pointing towards the structural evolution occurring in the system in passing from the benzenoid form (usually that of the ground state) to the quinonoid form (namely, that corresponding to the electronically excited state or the charged species), ECC theory states that, upon increasing conjugation length (CL), totally symmetric vibrational normal modes of the neutral system largely involved in the lattice dynamics of the ECC coordinate (namely, those giving rise to the few selectively enhanced Raman scatterings experimentally observed) undergo sizeable dispersions both in frequency and intensity. Thus, changes in the peak positions and relative intensities of the Raman features with increasing chain length are particularly useful in evaluating the mean conjugation length for the members of a given homologous series of neutral oligomers. On the other hand, when \( \pi \)-conjugated \( z \)-linked oligomers, and particularly aromatic non-polar oligothiophenes, become oxidized (either chemically or electrochemically), various types of quinonoid-like charged defects are created [16]. These structural modifications also induce a significant redshift of the Raman lines associated to the \( \pi \)-conjugated backbone (i.e. due the softening of the C=C bonds). Thus, the Raman spectral changes between the neutral and doped forms of a given system can provide valuable information to elucidate the nature of the charged carriers induced by chemical or electrochemical doping [9–12].

We report herein on a comparative study, by means of FT-Raman spectroscopy and DFT quantum chemical calculations, of three different types of oligothiophenes: (i) a p-type 5,5'-dimethyl end-capped bithiophene (DMBT), (ii) a n-type 5,5'-bis(dicyanomethylene)-5,5'-dihydro-2,2'-bithiophene (Th2CN4) and (iii) a push–pull 5-dimethylamino-5'-cyano-2,2'-bithiophene (Me2N–T2–CN) NLO-phore. The main aim of this work is to derive useful information about the conjugational properties of these systems from their Raman features with the help of DFT\textsubscript{B3LYP}/6-31G** molecular dynamics calculations and upon the light of the concepts developed in the ECC theory.

2. Experimental and computational details

FT-Raman spectra were recorded on pure solids in sealed capillaries in a back scattering configuration with the FRA 106/S modulus of a Bruker Equinox 55 FT-IR interferometer, operating upon a 1064 nm Raman excitation from an infrared diode pumped Nd-YAG laser. Signal detection was carried out by means of a germanium detector working at liquid nitrogen temperature.

DFT calculations were performed with the GAUSSIAN 98 program [17] running on a SGI Origin 2000 supercomputer. Molecular geometry optimizations were performed with the B3LYP functional and the 6-31G** standard basis set [18,19]. All geometrical parameters were allowed to vary independently apart from planarity of the rings. Symmetry constraints were imposed for the two non-polar end-capped molecules (i.e. DMBT and Th2CN4). On the resulting ground-state minimum-energy structures, we also computed analytically with the B3LYP functional the harmonic force fields from which normal vibrational frequencies, intensities and the corresponding vibrational atomic displacements in the 3M Cartesian coordinates are derived. In molecular dynamics calculations it is customary to use however internal vibrational coordinates \( R \), were \( R \) represents a set of bond stretching, angle bending or torsional coordinates [20–23]. For finite molecules local (three branches) and cyclic redundancies usually occur and can be completely removed by defining a new set of 3N-6 symmetry or group coordinates \( S \) orthogonal to the redundancy conditions. In this paper we follow the method proposed by Pulay et al. [24] to remove systematically all redundancies occurring in our systems.

In matrix notation the linear transformations between coordinates are \( R = Bx \) and \( S = UR \). Then the potential energy in Cartesian coordinates:

\[ 2V = x^tF_xx \]

can be re-expressed in terms of the \( S \) coordinates as:

\[ 2V = S^tU^{-1}F_sB^{-1}U^{-1}S \]

For the solution of the vibrational problem for finite molecules we follow the Wilson’s method [25] and solve the eigenvalue equation:

\[ G_sF_sL_s = \lambda_sA \]

Where \( G_s \) is the kinetic energy matrix, and contains information about the atoms which constitute the molecule and their equilibrium positions, \( F_s \) is the matrix of the Puley force constants, \( L_s \) is the matrix of the vibrational amplitudes and \( A \) is the diagonal eigenvalue matrix. The normal frequencies \( \lambda_n \), in \( \text{cm}^{-1} \), can be obtained from eigenvalues, \( \lambda_n \), through the relation \( \nu_n = (\lambda_n/4\pi^2c^2)^{1/2} \).

It is known that semiempirical or ab initio quantum chemical methods overestimate the vibrational frequencies and force constants, especially the diagonal stretching terms. It is customary to introduce a set of scaling factors, acting on the force constants, to reduce the discrepancies between calculated and experimental data. We have made use in the past [25] of the scaling method of harmonic force fields proposed by Pulay et al. [26], but in the present work force constants were not scaled. Nonetheless, to improve the comparison between the experimental and theoretical
Raman spectral profiles, and as a first and quite easy correction of the rather systematic trends of overestimation of vibrational frequencies by part of the DFT approach, we adopted the nowadays rather usual adjustment of quantum chemical force fields in which all the 6-31G** vibrational frequencies (i.e. and not force constants) obtained for a molecule are uniformly scaled down by the same factor, 0.96, as recommended by Scott and Radom [27]. This simple scaling procedure is often accurate enough to disentangle serious experimental misassignments. All quoted DFT//B3LYP/6-31G** frequencies reported along the paper are thus the scaled ones. Theoretical spectra were plotted by convoluting the scaled frequencies with Gaussian functions (10 cm\(^{-1}\) width at the half-height). The relative heights of the various Gaussians were determined from the corresponding DFT//B3LYP/6-31G** Raman activities.

3. Results and discussion

3.1. Experimental FT-Raman and FT-IR spectra

The chemical structures and notation of the three \(\alpha,\omega\)-disubstituted bithiophenes studied in this paper are depicted in Fig. 1, whereas Fig. 2 shows a comparison between their FT-Raman spectral profiles in the 1700–700 cm\(^{-1}\) frequency range. As aforementioned in the introductory section, Raman spectroscopy can provide valuable information regarding the conjugational properties of either non-polar symmetrically end-capped \(\pi\)-conjugated oligomers or highly polar push–pull chromophores bearing a \(\pi\)-center as electron relay. Some vibrational spectroscopic characteristics which differentiate both classes of systems are the following:

1. Raman spectra of non-polar \(\pi\)-conjugated chain compounds display an unexpected simple appearance, and only three or four lines, associated to particular totally symmetric skeletal CC stretching vibrations, among the very huge number or Raman-active vibrational normal modes predicted by the optical selection rules, are recorded with an overwhelming intensity in the 1600–1000 cm\(^{-1}\) region, as a result of the strong electron-phonon coupling occurring in these systems due to their quasi one-dimensional structure. This characteristic is again clearly evidenced by the Raman spectra of DMBT and Th2CN4 (Fig. 2). The enlarged Raman scattering profile of DMBT plotted in Fig. 3 serves to illustrate more precisely the selective enhancement of rather a few skeletal \(\nu(C=\text{C})\) stretchings of the \(\pi\)-conjugated path. Furthermore, along a given homologous series of oligomers, the Raman bands undergo changes in peak positions and relative intensities with the chain length [9–11].

2. On the contrary, a greater number of strong Raman lines are commonly seen in the spectra of the push–pull \(\pi\)-conjugated dyes due, among other factors, to the lowering of the molecular symmetry. These additional Raman scatterings usually arise from the vibrational
coupling of the $\nu$(CC) stretching vibrations of the $\pi$-conjugated electron relay with those of the donor/acceptor end groups.

(3) The large molecular dipole moment directed from the acceptor to the donor makes the same vibrational normal modes of the $\pi$-conjugated backbone giving rise to the Raman lines experimentally observed to gain also an extra-large IR-activity due to the sizeable fluxes of charge induced along the strongly polarized alternating sequence of double/single CC bonds (compare the FT-Raman and FT-IR spectra of Me$_2$N–T$_2$–CN in Fig. 4). This is not the situation for the centrosymmetric non-polar oligothiophenes, for which the mutual exclusion principle holds due to the existence of an inversion center in the middle of the molecule, so that Raman-active vibrations are almost undetectable in the IR spectrum, and vice-versa. Furthermore, usually the out-of-plane $\gamma$(CH) bending vibrations, appearing around 800 cm$^{-1}$, are by far the strongest IR absorptions for the non-polar oligothiophenes (compare the FT-Raman and FT-IR spectra of DMBT in Fig. 4). Thus, for push–pull $\pi$-conjugated chromophores, a great resemblance between the IR and Raman spectral profiles must be considered as a first indication of the occurrence of a rather effective intramolecular charge transfer [13,14].

### 3.2. Optimized geometries

To gain a deeper insight into the changes on the molecular structures and equilibrium charge distribution induced by the attachment of the various types of end groups at the $\alpha,\omega$-positions of the $\pi$-conjugated backbone, we have performed geometry optimizations, within the framework of the density functional theory, for DMBT, Th$_2$CN$_4$ and Me$_2$N–T$_2$–CN by using ab initio B3LYP/6-31G** model chemistry (the main skeletal bond lengths for the three compounds are summarized in Fig. 5).

In view of the theoretical data, one observes that the mean single-double CC bond length alternation pattern (BLA) of the thienyl units amounts to $+0.052$ Å for DMBT and $-0.077$ Å for Th$_2$CN$_4$, in full agreement with the aromatic-like and quinoid-like patterns of their $\pi$-conjugated spines, respectively. The situation is somewhat different for Me$_2$N–T$_2$–CN: the conjugated C=C/C–C bonds of the acceptor subunit are mainly affected by the interaction with the electron-withdrawing cyano end group, whereas those of the donor subunit are less affected by the interaction with the electron-donating dimethylamino group. The BLA values reported here, related to the difference between the average lengths of single and double CC bonds, can be compared with the $\approx0.07$ Å usually found from experiments for the innermost rings of the neutral non-polar oligothiophenes [28]. The quinoidization of the thiophene ring covalently attached to the nitrile is not however as large as previously found for other thiophene-based NLO-phores bearing nitro or malonitrile acceptor groups [13,14].

The actual electronic structure of a push–pull $\pi$-conjugated molecule can be considered, at first glance, to result from a linear combination of two limiting resonant structures: (i) a non-polar form, for which the net charges over the donor and acceptor end groups should be equal to

![Fig. 3. Enlarged FT-Raman profile recorded for DMBT, which clearly shows the selective enhancement of the lines appearing in the 1600–1400 cm$^{-1}$ region, associated to the skeletal $\nu$(CC) stretchings of the $\pi$-conjugated path, with respect to the remainder Raman-active vibrations predicted by the optical selection rules.](image1)

![Fig. 4. Comparison between the FT-IR and FT-Raman spectra of DMBT, Me$_2$N–T$_2$–CN and Th$_2$CN$_4$.](image2)
zero, and (ii) a charge-separated (zwitterionic) form, for which one electron should be fully transferred from the donor to the acceptor. The relative stability of the latter with respect to the former determines their weights into the linear combination describing the ground-state structure of the NLO-phore. The B3LYP/6-31G** geometry optimization of $\text{Me}_2\text{N}^\text{–} \text{T}_2^- \text{CN}$ reveals again a result which is in contrast with the rather simple chemical point of view of the balance between the aforementioned two limiting resonant or canonical forms: the occurrence in the push–pull $\pi$-conjugated systems of an intramolecular charge transfer from the donor to the acceptor translates into a larger perturbation of the acceptor subunit than that of the donor subunit, thus generating two different molecular domains within the $\pi$-conjugating spacer (one of them bearing a partial quinonoid character, while the other still retains a partial aromatic character). The structural modifications induced by the attachment of strong electron withdrawing groups are expected to extend towards the middle of the $\pi$-conjugated electron relay as its chain length becomes longer, due to the increasing molecular polarizability [13,14].

Fig. 6 shows the B3LYP/6-31G** Mulliken atomic charges over the various types of z,ω-substituents and each thiophene ring. As for $\text{Me}_2\text{N}^\text{–} \text{T}_2^- \text{CN}$, DFT/B3LYP/6-31G** model chemistry reveals another difference with respect to the hypothetic charge distribution associated to the Zwitterionic canonical form. Thus, the net charge over the cyano acceptor end group is larger than that of the dimethylamino donor group, being the $\pi$-electron relay largely polarized since it bears a sizeable amount of positive charge.

As for the symmetrically end-capped bithiophenes, B3LYP/6-31G** calculations predict an overall Mulliken charge over each thiophene ring (with hydrogens summed into heavy atoms) of $+0.248e$ in $\text{Th}_2\text{CN}_4$ and $-0.021e$ in DMBT. In the former case, the coexistence in a same molecule of a central electron-rich bithiophene moiety and two electron deficient dicyanomethylene end caps is expected to cause intramolecular charge transfer [29]. This DFT/B3LYP/6-31G** 0.25 of intramolecular charge transfer, $\rho$, agrees well with the $=0.28$ value estimated from the linear relationship between $\rho$ and the frequencies.

Fig. 5. Selected B3LYP/6-31G** skeletal bond lengths for DMBT, $\text{Th}_2\text{CN}_4$ and $\text{Me}_2\text{N}^\text{–} \text{T}_2^- \text{CN}$, together with the computed BLA values for the thiienyl rings of each $\pi$-conjugated system.

Fig. 6. Net B3LYP/6-31G** Mulliken atomic charges over different molecular domains for DMBT, $\text{Th}_2\text{CN}_4$ and $\text{Me}_2\text{N}^\text{–} \text{T}_2^- \text{CN}$ (values are given in e).
of the IR-active n(C≡N) stretching vibrations for various TCNQ salts, and also with the about 0.4 value obtained for a parent heteroquinonoid terthiophene, Th3CN4 [30,31]. On the other hand, the B3LYP/6-31G** ‘electrostatic picture’ of DMBT also reveals that, even in the pristine state, the two end alkyl side chains are slightly charged positively, while the central bithienyl spine is charged negatively twice the amount, what can be understood in terms of the positive inductive effect by part of the α,ω-dimethyl end-caps.

3.3. Theoretical Raman spectra and vibrational dynamics analysis

The DFT/B3LYP/6-31G** Raman spectra depicted in Fig. 7 compare quite well with the experimental ones, particularly in the case of DMBT and Th2CN4, although for Me2N–T2–CN there are some discrepancies regarding: (i) the intensity of the line measured at 1492 cm\(^{-1}\) and computed at 1473 cm\(^{-1}\) (i.e. whose Raman-activity appears to be stronger than really found in the experiments), and (ii) the peak position of the strongest Raman scattering measured at 1410 cm\(^{-1}\), which is overestimated by around 28 cm\(^{-1}\) in the B3LYP/6-31G** calculations. Anyway, for the three types of bithiophenes, the DFT approach satisfactorily accounts for the selective enhancement of the skeletal n(CC) stretching Raman vibrations appearing in the 1600–1400 cm\(^{-1}\) spectral region.

The comprehensive Raman analysis of many homologous series of non-polar α-linked oligothiophenes (i.e. even with complex chemical structures) has shown that their spectral profiles are dominated by the appearance of only four main lines (usually termed as lines A, B, C and D) whose peak positions and relative intensities are dependent on the chain length of the oligomer [9–11]. Their particular behaviours are as follows: (i) Line A shows a continuous softening and weakening with increasing number of units in the chain; (ii) line B is the strongest Raman scattering, being its position almost independent on the molecular size. Line B experiences a sizeable upshift upon substitution of the α and/or β positions with electronically inert groups; (iii) Line C is only present in the Raman spectra of the α or β-substituted oligothiophenes, but absent in the unsubstituted counterparts. It continuously upshifts and acquires stronger activity with increasing molecular size; (iv) Line D appears in all oligothiophenes as a sharp band (sometimes as a doublet) of medium intensity in the range 1080–1050 cm\(^{-1}\), becoming stronger as the oligomer grows longer.

The B3LYP/6-31G** vibrational eigenvectors depicted in Fig. 8 show that the Raman lines of DMBT at 1560 and 1492 cm\(^{-1}\) are to be correlated with lines A and B, respectively; the former being due to a totally symmetric \(\nu_{\text{asym}}(\text{C}=\text{C})\) stretching vibration, whereas the latter arises from a related fully in-phase \(\nu_{\text{sym}}(\text{C}=\text{C})\) normal mode spreading over the whole \(\pi\)-conjugated path, and it gives rise to the Raman band mostly involved in the molecular dynamics of the ECC coordinate. These two Raman-active vibrations were experimentally found to downshift to 1510 and 1466 cm\(^{-1}\), respectively, in going to Th2CN4 (i.e. upon the attachment at the outermost α-positions of the bithienyl spine of electron-deficient groups instead of electron-releasing alkyl side chains); this ‘vibrational redshift’ can be taken as a measure of the degree of softening of the \(\pi\)-conjugated backbone induced by the electron withdrawing ability of the two dicyanomethylene end caps.

The situation is somewhat more complex for Me2N–T2–CN. B3LYP/6-31G** vibrational analysis confirms that the Raman lines at 1554 and 1492 cm\(^{-1}\) are to be correlated with lines A and B at 1560 and 1492 cm\(^{-1}\) for DMBT, although the atomic vibrational displacements of the \(\pi\)-conjugated path are larger for the donor-subunit than for the acceptor-subunit (i.e. for the molecular domain with a more pronounced heteroaromatic pattern). On the other hand, the Raman scatterings measured at 1515 and 1442 cm\(^{-1}\) arise from similar \(\nu_{\text{asym}}(\text{C}=\text{C})\) and \(\nu_{\text{sym}}(\text{C}=\text{C})\) vibrations, respectively, but this time they are mainly located within the molecular domain bearing a partial heteroquinonoid pattern (i.e. on the acceptor-subunit), what accounts for the downshift of the latter two modes with respect to the former ones. The strong scattering at 1410 cm\(^{-1}\) is due to the strong vibrational mixing of the \(\nu_{\text{sym}}(\text{CH})\) bending of the two methyl groups of the amine with a \(\nu_{\text{sym}}(\text{C}=\text{C})\) vibration of the adjacent thiényl unit. Thus, the attachment of an electron-donor and an electron-acceptor groups at the end α-positions of the oligothienyl chain induces the splitting of the lines A and B of the \(\pi\)-conjugated bridge into two components. One of the components is mostly located on the heteroaromatic-like donor-subunit and the other on the heteroquinonoid-like acceptor-subunit. For each pair of related vibrations, the heteroquinonoid component

![Fig. 7. B3LYP/6-31G** Raman spectra for DMBT, Th2CN4 and Me2N–T2–CN.](image-url)
always appears at lower frequency, in good agreement with the predictions of the ECC formalism and as experimentally found for the doped species of the \( \alpha \)-linked oligothiophenes [12].

As aforementioned in the introductory section, the ECC coordinate describes the vibrational trajectory which best favours C\(=\)C/C–C changes, i.e. which mostly involves the \( \pi \)-electron delocalization along the oligomeric or polymeric one-dimensional chain. The \( \mathfrak{R} \) coordinate can be described as a suited linear combination of internal coordinates (\( \mathbf{R} \) or \( \mathbf{S} \) of Sec. II) that always belongs to the totally symmetric irreducible representation. All the IR/Raman vibrational data collected for many \( \pi \)-conjugated conducting polymers, either in the pristine, doped or photoexcited states, were accounted for some years ago in terms of an unique parameter, \( F_6 \), which represents the symmetry force constant relative to the ECC coordinate [32].

In the present work we have defined two different ECC coordinates (Table 1), one of them only accounts for the \( \pi \)-conjugational properties of the bithienyl spine, whereas the other one includes also the participation of the outermost CC bonds connecting the end groups to the \( \pi \)-center into the overall \( \pi \)-conjugation of the system. Both ECC coordinates, whose analytical forms are provided in Table 1, describe a collective vibrational oscillation of the \( \pi \)-conjugated path in which all double C\(=\)C bonds stretch at the time that all single C–C bonds shrink in-phase, thus describing a structural evolution of the molecule from the heteroaromatic-like pattern to the heteroquinonoid-like pattern.

As expected the highest value of \( F_{\mathfrak{R}1} \) is found for DMBT and the lowest for Th2CN4 (i.e. in agreement with their aromatic and quinonoid structures, respectively), while that for Me\(_2\)N–T\(_2\)–CN is closer to that of DMBT than to that of Th2CN4, what suggests that the degree of quinoidization of the bithienyl spine upon the attachment of the dimethylamino donor group and the cyano acceptor group is still moderate. This also holds if the outermost CC bonds linking the end groups to the \( \pi \)-center are taken into consideration, but now there is not any difference between the \( F_{\mathfrak{R}2} \) values obtained for DMBT and Me\(_2\)N–T\(_2\)–CN.

Table 2 summarises the contributions, in terms of \% PED, of the \( \mathfrak{R}1 \) and \( \mathfrak{R}2 \) coordinates to the normal mode associated to the strongest B3LYP/6-31G** Raman vibration of each of the bithienyl systems studied here. As for DMBT, the dynamical calculations reveal that the band experimentally measured at 1492 cm\(^{-1}\) is the Raman scattering mostly involved in the \( \pi \)-conjugation.

Table 1
Analytical form of the ECC vibrational coordinate (\( \mathfrak{R} \)) and unscaled B3LYP/6-31G** values (in mdyn/Å) of its associated force constant for the systems under study

<table>
<thead>
<tr>
<th></th>
<th>( F_{\mathfrak{R}1} )</th>
<th>( F_{\mathfrak{R}2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMBT</td>
<td>5.80</td>
<td>5.54</td>
</tr>
<tr>
<td>Th2CN4</td>
<td>5.17</td>
<td>5.22</td>
</tr>
<tr>
<td>Me(_2)N–T(_2)–CN</td>
<td>5.62</td>
<td>5.55</td>
</tr>
</tbody>
</table>

\[ \mathfrak{R}1 = R_{2-3} - R_{3-4} + R_{4-5} - R_{5-6} + R_{6-7} - R_{7-8} = R_{8-9} + R_{9-10}; \]
\[ \mathfrak{R}2 = -R_{2-3} + R_{3-4} - R_{4-5} + R_{5-6} - R_{6-7} + R_{7-8} - R_{8-9} + R_{9-10} - R_{10-12}; \]
Table 2
Contribution, in terms of %PED, of the collective ECC coordinate (β) to the strongest B3LYP/6-31G** Raman vibrations of the three bithiophene systems studied here

<table>
<thead>
<tr>
<th></th>
<th>F_{A1}</th>
<th>F_{A2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMBT</td>
<td>73</td>
<td>77</td>
</tr>
<tr>
<td>Th2CN4</td>
<td>29</td>
<td>60</td>
</tr>
<tr>
<td>Me_{2}N-T_{2}–CN</td>
<td>28</td>
<td>33</td>
</tr>
</tbody>
</table>

This is also true for the Raman band of Th2CN4 measured at 1469 cm\(^{-1}\), although for this dimer the noticeably increase of % PED in going from \(\mathbf{R}_1\) to \(\mathbf{R}_2\) evidences the main role played by the electron-withdrawing dicyanomethylene end groups into the overall \(\pi\)-conjugation of the system (i.e. this result could be also anticipated in view of the B3LYP/6-31G** eigenvector associated to theoretical Raman line at 1466 cm\(^{-1}\), depicted in Fig. 8).

As for Me_{2}N-T_{2}–CN, the rather low % PED values obtained in the molecular dynamics analysis for either the \(\mathbf{R}_1\) or \(\mathbf{R}_2\) collective coordinates to the vibrational normal mode giving rise to the strongest Raman line at 1410 cm\(^{-1}\) are in line with the aforementioned splitting of the characteristic Line B into two well-differentiate components, one of them located on the donor-subunit and the other on the acceptor-subunit, so that the assumption of the existence of an unique collective \(\pi(\text{CC})\) stretching oscillation spreading over the whole conjugated backbone and strongly coupled to the \(\pi\)-electron degree of freedom may be not longer adequate at all.

4. Summary and conclusions

In summary, we have performed a joint Raman and infrared spectroscopy and quantum chemical DFT study of three different classes of \(\pi\)-conjugated bithiophene: (i) a dicyanomethylene end-capped bithiophene with a quinoidal chemical structure, (ii) a symmetrically dimethyl-substituted system bearing a non-polar aromatic structure in its ground electronic state and (iii) a highly-polarized push–pull system with an electron-donor dimethylamino and a electron-acceptor cyano groups attached to its end \(\text{Me}_2\text{N}\)-positions. The good comparison between theory and experiments aims us to analyze the molecular structures and charge distributions as deduced by calculations: while DMBT and Th2CN4 are respectively aromatic and quinoid for their thiophene rings, in Me_{2}N-T_{2}–CN the thiophene connected to the donor is aromatic and the other is quinoid, which is consistent with an intramolecular charge transfer from the dimethylamino groups plus the bithiophene spacer to the cyano group. We have found great similarities between the experimental infrared and Raman spectra of Me_{2}N-T_{2}–CN which is a proof of the intramolecular charge transfer.

The Raman spectra have been interpreted in the framework of the ECC theory. In DMBT and Th2CN4, it has been found only one C–C/C=C collective motion according to the ECC statements. For Me_{2}N-T_{2}–CN however the occurrence of an aromatic and a quinoid rings makes the ECC coordinate to split into four Raman lines. As a whole the Raman lines associated to the ECC coordinate experience a frequency downshift on going from the aromatic molecules to the quinoid. This has been numerically accounted for by the decreasing of the force constant values of each Raman vibration associated to the ECC modes on passing from DMBT to Me_{2}N-T_{2}–CN and to Th2CN4.

Acknowledgements

We acknowledge the Dirección General de Enseñanza Superior (DGES, MEC, Spain) for financial support to this investigation through project BQU2003-03194. The research was also supported by the Junta de Andalucía (Spain) under grant FQM-0159. JC, MCRD and RPO thank the Ministerio de Ciencia y Tecnología (MCyT) and MEC of Spain for a ‘Ramón y Cajal’ position of chemistry at the University of Málaga (JC) and personal grants (MCRD and RPO).

References


