Density functional study on the structures and vibrational spectra of
the radical cation and dication of
\(\alpha,\alpha'-\text{bis(aminomethyl)quaterthiophene}\)

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Abstract

This paper reports results of a theoretical study about the effect of ionization on the infrared and Raman spectra of \(\alpha,\alpha'-\text{bis(aminomethyl)quaterthiophene}\) with the objective of obtaining a deeper insight into the geometry and spectral changes occurring upon doping of the oligothiophenes and polythiophene. For these purposes, we determine the structures, vibrational frequencies and infrared intensities of the neutral compound and of its radical cation and dication. Ab initio calculations, at the B3LYP/6-31G and RHF/6-31G levels of theory, are employed to assess the structural and spectral information for the neutral and charged states. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Density functional calculations; Infrared spectroscopy and Raman spectroscopies; Oligothiophenes; Charged defects

1. Introduction

\(\pi\)-conjugated polymers are low bandgap systems having attractive optical and electrical properties [1]. Although the polymer properties can be influenced and tailored by the variation of monomeric building blocks, precise predictions about structure–property relationships are not possible because of the interruption of the conjugated backbone of the polymer by mislinkages and other defects. The controlled synthesis and investigation of oligomers with well-defined substitution patterns and chain lengths is therefore receiving considerable attention since it constitutes the most straightforward procedure to gain insight in the peculiar features of the corresponding polymers [2].

Much work has been devoted in past years to \(\beta\)-substituted oligothiophenes to obtain soluble materials easy to characterize and process [3–8]. However, steric interactions between \(\beta\)-substituents, particularly in head-to-head orientations, prevent the backbone of aromatic rings from full conjugation, often diminishing the electronic and optical features of the oligomer in solution. In addition, bulky \(\beta\)-groups also lead to increased steric hindrance between conjugated backbones, thus reducing \(\pi\)–\(\pi\) interactions between molecular arrays in solid state.

In contrast to \(\beta\)-substitution, disubstitution at the end \(\alpha,\alpha'-\text{positions}\) [9–13] has the advantage of preserving the conjugation and, therefore, the electronic properties of the neutral oligomers. Moreover, this synthetic strategy facilitates the investigation of
long stable and soluble radical cationic and dicationic model systems, which can provide an insight into the doping and conducting mechanism of polythiophene. In the classes of unsubstituted or \( \beta \)-substituted oligothiophenes, the research of charges species is only possible for longer members, since shorter oligomers are inherently reactive and undergo follow-up reactions. Due to their structural variability and chemical stability end-capped oligothiophenes connected in \( \alpha \)-positions seem to be ideal materials for technological applications. It has been previously demonstrated that the amino groups at both molecular ends constitute a suitable functionalization of the \( p \) \-conjugated backbone to fabricate thin films by direct evaporation of the oligomer onto the substrate [14,15].

To fully understand the properties of all these systems, a detailed knowledge of the their structure and of their electronic and dynamical properties is of primary importance. In particular, the vibrational properties as revealed by their infrared and Raman spectra, have been extensively exploited as valuable probes of their structures and of the distance of interaction between the successive chemical units.

Charged defects generated on the \( \pi \)-conjugated skeleton either by chemical ionization or photoexcitation are characterized by the appearance in the infrared and Raman spectra of several bands with exceedingly large intensities. These bands are associated with the normal vibrations of a variety of self-localized excitations (i.e. polarons, bipolarons or others), whose spatial extensions along the chain in the case of a real polymer are, in principle, unknown. Zerbi and co-workers have proposed the Effective Conjugation Coordinate (ECC) theory [16] to interpret doping- and photo-induced infrared absorptions in conjugated polymers, including polythiophene [17,18]. The electronic nature of the conjugal defects is strictly related to the number and peak positions of the subgap bands, which arise upon doping in the NIR region [19,20].

Current quantum chemical methods are in the position to give reliable information about the molecular structure and vibrational properties of the different classes of charged defects in doped polyconjugated systems. The ability to calculate molecular force fields and geometries for both closed- and open-shell systems is likely to be one of the most important developments in computational chemistry over the past decade. Most calculations are carried out in the ab inito Hartree–Fock (HF) scheme. HF methods are highly demanding computationally since large basis sets are generally required to obtain reliable results. Moreover, uncorrelated HF methods, even with the largest basis sets, result in systematic overestimation of the normal mode frequencies with the additional problem that the neglect of electron correlation affects the various normal modes differently. The HF scheme fails to give proper qualitative descriptions for systems when nondynamical electron correlation is of primary importance. This category of systems is found among molecules with multiple bonds such as well as open-shell species (a positive ion being one
example for which HF method can fail to yield reasonable frequencies and intensities).

Then, appropriate post-HF methods are required to deal with the electron correlation. As an alternative, Density Functional Theory (DFT) [22,23] may be used, because one of the advantages of DFT lies in its ability to incorporate the electron correlation in treating large systems with computational requirements comparable to those for the HF approach. With the most accurate density functional currently in use, DFT predicts harmonic vibrational frequencies of substantially higher accuracy than obtained via HF calculations and of similar accuracy to the predictions of MP2 calculations [24,25]. Recently, we have pointed out the usefulness of the DFT method for the study of the radical cations of a full series of \(\alpha,\alpha'-\)dimethyloligothiophenes [26]. In the present paper, the geometries and the vibrational spectra of \(\alpha,\alpha'-\)bis(aminomethyl)quaterthiophene (BAMQtT) (see Fig. 1) are theoretically investigated in both neutral and positively charged states. This system was chosen because it contains all the essential features pertinent to the \(\alpha,\alpha'-\)bis(aminomethyl)oligothiophenes studied in another paper of this special issue, still remaining computationally tractable at a reasonable level. The results are then compared with the available experimental vibrational data.

2. Computational details

Ab initio Restricted Hartree–Fock (RHF) and DFT calculations were carried out by means of the Gaussian 94 program [27] running on a SGI Origin 2000 supercomputer. As for the DFT method, we have used Becke’s three-parameter exchange functional combined with the Lee–Yang–Parr (LYP) correlation functional (B3LYP) [28], as implemented in Gaussian 94. This functional is defined in terms of the Dirac–Slater (DS), Hartree–Fock (HF), Lee–Yang–Parr (LYP), Becke (B88) and Vosko–Wilk–Nusair (VWN) functionals [27].

It has been shown in several studies that the B3LYP yields similar geometries for medium-sized molecules as MP2 calculations do with the same basis sets [29,30]. Moreover, the DFT force fields calculated using the B3LYP functional yield infrared absorption spectra in very good agreement with experiments [25,31]. We made use of the 6-31G** basis set [32], which is a split valence and includes a set of six second order (d-type) Gaussian primitive functions to describe each heavy atom and a single set of Gaussian p-polarization functions for hydrogens.

The optimized geometries of the BAMQtT oligomer were determined on isolated entities. As usual, the effect of the doping was mimicked by considering the ionized species of the oligomer alone, without the counterion. We remark, however, that the assumption of an ideal charge transfer between the dopant molecule and the oligomer could affect in some way the comparison with experimental results. The neutral and dicaticionic molecules were treated as closed-shell systems (B3LYP procedure), while for the radical cation, open-shell system, the optimization was carried out by using spin unrestricted wavefunctions (UB3LYP). In the practical application of these methods it has been shown that spin unrestricted HF solutions (UHF) are plagued with contamination of higher spin states [33]. Spin-unrestricted DFT solutions have been found to suffer much less from this problem [34].

The structures of the neutral molecule and its radical cation and dication were optimized under the following constraints: (i) all structures were kept planar; and (ii) only the all-anti conformations of the rings were treated throughout. Under these assumptions, the three systems display \(C_{2h}\) symmetry. In this regard, we would like to emphasize that the crystalline oligothiophenes are found to be nearly planar due to large packing effects [35].

Harmonic vibrational frequencies and infrared intensities were computed analytically with the B3LYP functional. We recall however, that Gaussian 94 does not provide the Raman activities for DFT calculations. This is because the Raman spectrum of the neutral oligomer has been calculated by using the RHF approach. In this work we have used the often-practiced adjustment of the theoretical force fields, in which frequencies are uniformly scaled down by a factor of 0.96 for DFT and 0.90 for RHF theoretical values, as has been recommended by Scott and Radom [25]. This approach is very attractive for large-scale studies because it avoids the fairly complex procedure of defining internal coordinates. All quoted vibrational frequencies reported in the paper are thus scaled values.
3. Results and discussion

3.1. Structural properties and atomic charges

The numbering of bonds and atoms of the BAMQtT molecule and its radical cation (BAMQtT\(^{+}\)) and dication (BAMQtT\(^{2+}\)) is shown in Fig. 1. The DFT-optimized geometric structure of the neutral oligomer shows that the bond lengths are characterized by a rather weak degree of CC bond alternation, of the order of 0.04 Å, which slightly differs from that found in the outermost rings due to the end-capped effects. This attenuated CC bond-length alternation is clearly related to a marked aromatic character of the rings.

The B3LYP/6-31G\(^{**}\) optimized geometry of...
BAMQtT$^{2+}$ is consistent with the formation of a positive bipolaron defect localized in the middle of the molecule and extending over the adjacent repeat units. The charged species is characterized by a reversal of the single–double CC bond pattern, while the C–S bond lengths are little affected. The geometry relaxation process thus induces the appearance of a strong quinonoid character within the molecule. The amplitude of the structural modifications progressively decreases when going from the center to the end of the molecule, as illustrated in Fig. 2. However, the region with a genuine quinonoid structure extends over the whole oligomeric chain.

As illustrated in Fig. 3, where the CC bond lengths of both the neutral and the singly oxidized states are plotted, a positive polaron defect localized in the middle of the molecule occurs for BAMQtT$^{+}$. Expectedly, the calculated structural modifications are weaker than in the dication since the quinonoid character is less marked within the rings. The spatial extension of the positive polaron is found to be smaller than for the bipolaron and we estimate the positive polaron to extend over about two rings. It can be concluded that the removal of one or two electrons from the neutral oligomer leads to geometrical changes compatible with the evolution from an aromatic to a quinonoid structure.

Table 1 lists the Mulliken charges (which are viewed approximately as the atomic charges) for half the BAMQtT in the neutral, radical cationic and dicationic states. Sulfur atoms are positively charged in the three situations, showing that sulfur acts as a strong electron donor. Carbon atoms of the $\pi$-conjugated backbone and of the CH$_2$ substituents are negatively charged, mainly due to the polarity of the C–H bonds. The nitrogen atoms of the NH$_2$ substituents carry large negative charges which is mainly withdrawn from the amino hydrogens rather than from the oligothiophene system.

At the bottom of Table 1 the total charge for each aminomethyl (CH$_2$NH$_2$) substituent is shown. In the
neutral oligomer, the whole substituent is slightly positive, 0.04e, and it increases upon passing to the ionized systems. The effects of the removal of one or two electrons from the neutral molecule are felt fundamentally on the sulfur atoms, which increase their strong electron-donor character by increasing their positive charge from 0.26e in BAMQtT up to 0.40e in BAMQtT$^{2+}$.

3.2. Calculated infrared spectra

The vibrational assignment of the FT-IR and FT-Raman of the neutral oligomer have been previously reported [36], whereas the experimental vibrational spectra of the iodine doped material are presented in another paper of this special issue. It is well established that the ionization of the $\alpha,\alpha'$-dialkyloligothiophenes with iodine mainly yields the first oxidized species. As a support to the experimental research, we analyze here the effect of the single positive ionization of the neutral compound on the vibrational frequencies and infrared intensities.

Fig. 4 displays a comparison between the observed infrared spectrum of iodine-doped BAMQtT and the theoretical UB3LYP/6-31G** spectrum computed on the optimized geometry of BAMQtT$.^{+}$.

Fig. 5. Schematic eigenvectors of the most intense infrared-active vibrations of BAMQtT$^{+}$ calculated at the UB3LYP/6-31G** level (all values are in cm$^{-1}$).
also with the relative infrared intensities. The most relevant feature of these plots is that the whole appearance of the spectra of the radical cations is considerably simpler than that of the neutral compounds [36]. Further, one immediately recognizes the emergence of new intensive bands covering the 1500–1000 cm\(^{-1}\) spectral region, with an overall \(B_u\) symmetry. We also observe that the computed infrared intensities are very large, reaching up to 2500 km/mol for the strongest mode of the radical cation.

The theoretical calculations indicate that the ionization process induces the appearance of several relevant infrared absorption bands, which are calculated at: 1439–1396 (vs), 1344–1324 (s), 1195 (m) and 1093–1082 (m) (cm\(^{-1}\)). Four minor absorptions are also calculated in the low wavenumber range at 869, 787, 702 and 687 cm\(^{-1}\). The experimental observations are that the FT-IR spectrum of the doped tetramer is characterized by the appearance of at least five new rounded features at 1400 (vs), 1346 (s), 1211–1174 (m), 1124 (m) and 1056, whose intensity readily increases with increasing doping level. The resemblance between theoretical and experimental data are compatible with the existence of a polaron-type defect in the iodine doped materials.

Finally, Fig. 5 sketches the atomic vibrational displacements belonging to the most intense infrared absorptions calculated by the UB3LYP methodology for BAMQ\(\text{rT}^+\). Analyzing the data, we find that by far the largest contributions stem from the CC bond stretching along the polyconjugated chain. The most intensive peak, calculated at 1396 cm\(^{-1}\), corresponds to a symmetric stretching of the CC bonds of the two outermost rings of the molecule, for which the vibrational motions of both molecular ends are completely out-of-phase. Similarly, the band calculated at 1093 cm\(^{-1}\) can be associated with a mode involving CC stretchings of the outermost rings alone, i.e. from the transition edges between the benzenoid and the quinonoid structures. The remaining prominent absorptions calculated in the infrared spectra can clearly be assigned to different modes where the CC stretching contributions are delocalized over the whole molecule. Further, we note that the CC stretchings strongly mix with the in-plane CH bendings in most of the calculated eigenvectors and specially for those calculated at 1195 and 1093 cm\(^{-1}\). In this regard, a strong coupling between the intra-ring CC stretchings and the terminal methylene caps is observed for the normal modes calculated at 1435, 1396, 1344 and 1124 cm\(^{-1}\).

3.3. Calculated Raman spectra

Fig. 6 shows a comparison between the FT-Raman scattering spectrum of the neutral form of the BAMQ\(\text{rT}\) and the theoretical RHF/6-31G\(^{**}\) one. We recall that GAUSSIAN 94 does not provide the Raman activities for DFT calculations. This is because, only for the neutral molecule, the Raman spectrum has been calculated by using the RHF methodology.

The main characteristic of the Raman spectrum of a neutral \(\pi\)-conjugated chain compound is its extremely simple appearance, even for systems with complex chemical structures. The spectra usually consist of very few and strong lines, in spite of the large number of vibrational degrees of freedom. This experimental Raman spectral pattern is nicely reproduced by the
Theoretical RHF/6-31G** Raman spectrum plotted in the Fig. 6. This good agreement lets us use the calculated atomic displacements as a guide for the qualitative assignment of the Raman bands. The calculated eigenvectors for the main Raman-active normal modes are sketched in Fig. 7.

The exciting laser lines commonly used to record the Raman spectra of the polyconjugated materials fall within the electronic absorption band due to the $\pi-\pi^*$ transition. When Resonance Raman conditions are fulfilled, only a few Raman-active normal vibrations are known to gain appreciable intensity (i.e. those with a large projection along the deformation coordinate describing the evolution of the molecular geometry from the ground to the excited electronic states involved in the Raman process) [37]. However, it has already been shown that the Resonance Raman condition itself cannot fully account for the whole spectroscopic features of $\pi$-conjugated materials. For instance, even oligomers of very short length, whose energy gaps are well above the energies of the common exciting laser radiations, show Raman spectra of a rather simple appearance [38]. Conversely, the 1064 nm excited-Raman spectra of $\alpha$-terfuran and $\alpha$-quaterfuran [39] (an exciting line well below the energy gaps of these materials), approach that of polyfuran, obtained upon full resonance conditions [40].

The theoretical aspects which constitute the basis for the interpretation of these Raman spectra were proposed by Zerbi et al. in the ECC model [16,41]. Over the past few years the ECC model has allowed the analysis of the vibrational spectra of many $\pi$-conjugated polymers: polypyrrole [42,43], polythiophene [17,18], poly($p$-phenylenevinylene) [44,45], polyfuran [40], poly($p$-phenylene) [46], and poly(3-methylthiophene) [47]. The model assumes the existence in these one-dimensional systems of a strong $e-p$ interaction, which is the largest for the normal modes with a large content of the so-called $6$ coordinate (i.e. $6$ is a collective vibrational coordinate, belonging to the totally symmetric irreducible representation of the relevant point group for the system, which defines the in-phase oscillation of the alternating C=C/C=C–C bonds of the $\pi$-conjugated backbone). Theory also shows that normal modes with large contents of $6$ should undergo frequency-softening and intensity-enhancement with the increase of the distance of interaction between the successive repeating units along the chain (i.e. with increasing effective conjugation length).

Let us now inspect the calculated Raman spectrum...
of the BAMQtT (see Fig. 6) in more detail to correlate its vibrational features with data previously collected on related compounds. The comprehensive study of many series of neutral oligothiophenes has shown that the Raman spectrum is universally dominated by the appearance of only three or four lines (depending on the substitution pattern), and that each line shows a characteristic chain-length dependence both in relative intensity and position [48,49], their particular behaviors being as follows:

(a) Line A undergoes a continuous softening and weakening with increasing number of repeat units. The theoretical eigenvector for this mode (see Fig. 7) indicates that it arises from a totally symmetric \( \nu_{as}(C=C) \), mostly laying on the outermost rings, and being mixed to a large extent with stretchings of the inner C=C bonds.

(b) Line B is the strongest one of the spectrum. However, its position is scarcely dependent on the molecular size. The eigenvector depicted in Fig. 7 shows the large contribution from the “bulk” thiophene rings to Line B. This normal mode can be described as a fully in-phase symmetric \( \nu_d(C=C) \) vibration spreading over the whole oligomer chain. In addition, the stretchings of the C=C bonds are extensively mixed with the in-plane bendings of the C–H bonds: along this normal mode the H atoms recoil with a large displacement which opposes that of the C\(_\beta\) atoms.

(c) Line C appears at the lower energy side of Line B only for the \( \alpha \) or \( \beta \) end-capped oligothiophenes [26]. It slightly upshifts, gaining much activity, from increasing molecular size. The eigenvector plotted in Fig. 7 indicates that Line C also arises from a collective symmetric \( \nu_d(C=C) \) stretching, mostly localized on the bulk rings, but whereas opposed to Line B, the motions of the outermost rings take place out-of-phase with respect to the central unit.

(d) Finally, Line D is observed for all classes of oligothiophenes as a sharp band (or a doublet) of medium intensity. In view of the calculated eigenvector for the tetramer, Line D has to be assigned to the fully in-phase symmetric bending of the C–H bonds attached at the various \( \beta \)-positions of the inner part of the chain. Along this normal mode, a slight recoiling of the C\(_\beta\) atoms also occurs. Thus, we can conclude that Lines B and D are directly associated with the dynamics of the 6 collective coordinate. So that, the electron–phonon interaction is particularly large for these two molecular vibrations.

Although HF methodology can be used very reliably and successfully in the assignments of vibrational spectra of stable close-shell molecules, it fails to give proper qualitative descriptions for open-shell species. As aforementioned, GAUSSIAN 94 does not provide the Raman activities for DFT calculations [27]. However, ECC theory shows us that Raman spectra of polyconjugated systems originate only from totally symmetric modes [16,41]. In addition, the ab initio HF calculations carried out on closed-shell oligothiophenes (as neutral [50] or dicationic [51] species) further support that the few Raman lines experimentally observed are exclusively due to totally symmetric vibrations. For these reasons, Table 2 summarizes the scaled DFT frequencies of the totally symmetric normal modes (A\(_g\) symmetry) calculated for BAMQtT\(^+\).

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*Experimental values taken from the another contribution of the group at the University of Málaga to this special issue.
model, at first look there is a satisfactory agreement between the calculated frequencies for the radical cation model system and the location of the experimentally observed Raman bands of the iodine-doped sample of BAMQT (see Table 2). As a result, the softening of the C=C stretching modes upon ionization of the molecule are well reproduced by the calculations. These downshifts are the consequence of the fact that removing one electron from the π-system of the aromatic molecule softens the bondings of its skeleton, which then can vibrate more easily.

The weak line measured at 1480 cm\(^{-1}\) in the Raman spectrum of iodine-doped BAMQT should be correlated with the mode calculated at 1478 cm\(^{-1}\). The corresponding eigenvector is almost identical to that calculated for Line A in the neutral compound (see Fig. 6). The Raman spectrum of iodine-doped BAMQT exhibit a major band at around 1420 cm\(^{-1}\) with a shoulder near 1435 cm\(^{-1}\). The eigenvector of the band at the lower frequency (which is calculated at 1432 cm\(^{-1}\)) evidences that this normal mode is highly localized on the inner rings (i.e. on those thiophene rings strongly affected by the ionization). From the optimized geometries (see Fig. 3) we observe that the bulk thiophene units of the charged species support an almost pure quinonoid structure. Thus, the band at about 1420 cm\(^{-1}\) is attributable to a collective totally symmetric \(\nu(C=C)\) stretching of the polaronic defect, being clearly related to the vibrational coordinate labeled as 6 in the ECC model [16,41]. This normal vibration describes the geometrical evolution from the quinoid to the aromatic configurations of the nuclei. The shoulder at 1435 cm\(^{-1}\) could be correlated to the

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Fig. 8. Schematic eigenvectors of some of the totally symmetric Raman-active normal modes of BAMQT\(^{+}\) calculated at the UB3LYP/6-31G** level (all values are in cm\(^{-1}\)).
theoretical band at 1440 cm$^{-1}$. The appearance of the corresponding normal mode, plotted in Fig. 8, recall that of Line B of the neutral compound, and it should be described as an in-phase symmetric $\nu$(C=C) stretching having a pronounced collective character, which spreads over the whole oligomeric chain.

We experimentally observe another two bands located near 1227 and 1160–1130 cm$^{-1}$. Calculations indicate that both of them also arise from typical modes of the polaronic defect localized in the middle of the molecule. The band at the lower frequency (which is calculated at 1161 cm$^{-1}$) is due to the anti-symmetric $\delta$(C–H) bending. The one at the higher energy (calculated at 1206 cm$^{-1}$) corresponds to the in-phase symmetric $\delta$(C–H) bending extensively coupled with the in-phase symmetric stretching of the like-single C–C bonds of the ionized thiophene rings (see Fig. 8).

Finally, from the calculations we believe that the band measured at 1060 cm$^{-1}$ arises from the superposition of two different modes: (i) a totally symmetric $\delta$(C–H) bending mode spreading over the entire oligomer chain (whose eigenvector is rather similar to that calculated for Line D in the neutral molecule); and (ii) a totally symmetric $\delta$(C–H) bending mode characteristic of the polaronic defect (see Fig. 8). The calculated frequencies for these two modes are 1049 and 1067 cm$^{-1}$, respectively. Thus, we can conclude that among the few modes which become enhanced in the Raman spectrum upon ionization, the totally symmetric $\delta$(C–H) bending vibration is the only one whose location is slightly affected with respect to the neutral system, in full agreement with the local character of this type of mode.

4. Conclusions

It has been shown that it is possible to thoroughly combine infrared and Raman experiments with DFT calculations to obtain a highly satisfactory description of the vibrations of iodine-doped $\alpha,\alpha'$-bis(amino-methyl) quaterthiophene (BAMQiT). We have performed extensive and systematic calculations of the equilibrium structures and of the vibrational spectra, at the B3LYP/6-31G** and RHF/6-31G** levels, for neutral, radical cation and dication BAMQiT. The optimized geometries for the radical cation and the dication of BAMQiT are consistent with the generation of a conjugal defect localized in the middle of the molecule. This conjugal defect is characterized by the reversal of the single–double CC bonds alternation pattern with respect to the neutral system.

The calculated eigenvectors have also enabled us to identify a variety of IR and Raman-active normal modes, which should be considered as characteristic vibrations of the charged defects generated by the oxidation process. The combination of the DFT calculations with the theoretical formalism of the ECC model has yielded a satisfactory explanation of the changes observed in the FT-Raman spectrum of the doped material with respect to the neutral state.

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