Theoretical description of the Raman spectrum of a vinylene-bridged quaterthiophene oligomer

Pedro M. Viruelaa, Rafael Viruelaa, Enrique Ortı´ *,a, Juan Casadob, Victor Hernándezb, Juan T. López Navarreteb,*

aInstitut de Ciència Molecular, Universitat de València, E-46100 Burjassot, València, Spain
bDepartamento de Química Física, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain

Received 3 September 2002; accepted 26 September 2002

Abstract

The Raman spectrum of a quaterthiophene oligomer incorporating a central vinylene spacer has been investigated using density functional theory B3LYP/6-31G** calculations. The spectrum has been fully assigned with the aid of the calculations and in comparison with unsubstituted quaterthiophene. The spectrum preserves most of the vibrational features of linear oligothiophenes. The vibrations of the vinylene spacer are clearly differentiated from those of the rest of the chain. The vinylene spacer increases the conjugation length of the molecule and induces a frequency downshift of <20 cm⁻¹ for the normal modes associated with the νₛ(C=C) and νₐ(C=C) vibrations of the thiophene rings. The molecule is predicted to have a structure in which both the thiophene rings and the vinylene spacer are in an all-anti conformation.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Conjugated oligomers; Oligothiophenes; Raman spectrum; Density functional theory calculations; Normal modes

1. Introduction

Conjugated polymers and oligomers are the focus of an intense research activity as functional materials for a variety of electronic applications [1]. Polymeric materials however, present a number of characteristics (polydispersity, low crystallinity and solubility, chemical defects, etc.) that makes difficult to establish a precise relationship between structure and electronic properties. In this sense, conjugated oligomers with perfectly controlled chemical structures have acquired a growing importance both as model compounds for the parent polymers and as a novel class of molecular materials [2,3].

The unique electronic properties of conjugated polymers and oligomers originate from the delocalization of the π-electrons. For systems involving aromatic units such as oligophenylenes (nP) and oligothiophenes (nTs), the effectiveness of delocalization along the conjugated chain is limited by the resonance energy of the aromatic rings and the rotations around the inter-ring single bonds [4]. These two factors tend to confine the π-electrons within the rings. To reduce the effect of these two factors, vinylene groups are incorporated bridging...
the aromatic rings as in oligophenylenevinylene 
(\(n\)PVs) [5] and oligothienylenevinylene 
(\(n\)TVs) [6]. The presence of these groups produces at the same 
time a decrease of the overall aromatic character of 
the conjugated system and the suppression of the 
rotational disorder. \(n\)PVs, \(n\)TVs and their respective 
polymers (PPV and PTV) are among the most studied 
compounds as linear \(p\)-conjugated systems.

In this paper, we focus on T2VT2 (Fig. 1) a 
cooligomer formed by two bithienylene (T2) units 
connected through a vinylene bridge (V). T2VT2 can 
be viewed as a quaterthiophene (T4) analogue bearing 
a central vinylene spacer. Our goal is to investigate 
how the spacer influences the conjugated structure by 
performing a detailed study of the Raman spectrum. 
Raman spectroscopy has been shown to be a useful 
tool to derive information about the extent of 
\(p\)-electron delocalization in polyconjugated com-
ounds [7–14]. The Raman spectrum of T2VT2 has 
been recently recorded for both neutral and cation 
species [15,16]. The analysis of the Raman spectrum 
has been performed on the basis of density functional 
theory (DFT) calculations and in comparison with T4. 
DFT calculations using hybrid functionals have been 
shown to predict vibrational frequencies in very good 
accord with experimental values [17–20]. The Raman 
spectrum of T4 was previously reported by two 
different groups [21,22].

2. Computational details

DFT calculations were carried out using the A.7 
revision of the GAUSSIAN98 program package [23] 
running on SGI Origin 2000 computers and IBM 
RS/6000 workstations. All the calculations were 
performed on isolated systems using the Becke’s 
three-parameter B3LYP exchange-correlation func-
tional [24], together with Pople’s 6-31G** basis 
set [25]. The calculated harmonic vibrational fre-
quencies were scaled down uniformly by a factor of 
0.96 as recommended by Scott and Radom [18]. All 
the theoretical vibrational data quoted in the text are 
thus scaled values. The theoretical Raman spectra 
were obtained by convoluting the scaled frequencies 
with Gaussian functions (10 cm\(^{-1}\) width at the half-
maximum). The height of the Gaussians was 
determined from the Raman scattering activities 
calculated for the Raman-active normal modes.

3. Molecular structure

The molecular geometries of T2VT2 and T4 were 
optimized assuming planar \(C_{2h}\) structures and \(anti\) 
arrangements of adjacent thiophene rings. These 
geometrical restrictions were adopted on the basis of 
the all-\(anti\) planar structures observed for unsubstit-
tuted and end-substituted oligothiophenes in the solid 
state [26] and, in particular, for T4 [27,28]. No 
structural data are available for the T2VT2 oligomer. 
Two \(C_{2h}\) conformations were actually considered for 
T2VT2. The conformation depicted in Fig. 1, for 
which the vinylene \(C_1\)=\(C_1'\) double bond is in an \(anti\) 
disposition with respect to the \(C_2\)=\(C_3\) bonds of the 
neighboring thiophene rings, and a second confor-
mation for which the vinylene \(C=\)\(C\) double bond is in 
a \(syn\) orientation. The \(anti\) conformation was calcu-
lated to be 2.51 kcal/mol more stable than the \(syn\) 
conformation and the data discussed below refer, if no 
other indication is made, to the former.

Fig. 2 shows the optimized bond lengths of the 
carbon–carbon (CC) bonds defining the conjugated 
pathway for \(\pi\)-delocalization in T2VT2 and T4. Both 
molecules present highly delocalized structures with 
small differences among the CC bond lengths. The 
shortest bond distance corresponds to the vinylene 
\(C_1\)=\(C_1'\) bridge (1.357 Å) in T2VT2, and the longest 
distances are those connecting the thiophene rings 
(1.443–1.446 Å). The degree of bond length alter-
nation (BLA), calculated as the difference between the 
average lengths of the \(C=\)\(C\) and \(C=\)\(C\) bonds, can be 
taken as a measure of the effectiveness of delocaliza-
tion [29]. For T2VT2, the BLA amounts to 0.031 Å for 
the inner thiophene rings and to 0.048 Å for the
outer rings. For T4, these values slightly increase to 0.034 and 0.049 Å, respectively. The BLA calculated at the B3LYP/6-31G** level for the thiophene molecule is 0.062 Å. These trends indicate that π-conjugation is more effective in the centre of the molecule and weakness in going to the outer rings. Furthermore, the lower BLA values obtained for T2VT2 suggest that the vinylene bridge is effectively conjugated with the bithienylene moieties giving rise to a more delocalized system. The HOMO–LUMO energy gap in linear π-conjugated systems is a consequence of the degree of BLA [29]. It has a value of 2.77 eV for T2VT2 significantly smaller than that calculated for T4 (3.03 eV), thus supporting a higher degree of delocalization for the former.

4. Raman spectrum

The Raman spectrum calculated for T2VT2 is depicted in Fig. 3 together with the experimental spectrum recorded in the solid state [15]. The Raman frequencies are collected in Table 1 together with those obtained for T4. The theoretical eigenvectors (atomic vibrational displacements) associated with the most intense Raman bands of T2VT2 and T4 are plotted in Figs. 4 and 5. The Raman spectra of thiophene (T1), bithiophene (T2) and terthiophene (T3) were also calculated for comparison purposes.

The Raman spectrum of T2VT2 shows the simplicity already observed for nonpolar oligothiophenes [9–12,21,22], for which the spectrum only presents a few, very strong bands in the C=C

---

**Table 1**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>T4</th>
<th>T2VT2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
<td>Theory</td>
</tr>
<tr>
<td>υ(C=C) vinylene</td>
<td>1601</td>
<td>1600</td>
</tr>
<tr>
<td>υ(C=C) thiophenes</td>
<td>1560</td>
<td>1514</td>
</tr>
<tr>
<td>υ(C=C) thiophenes</td>
<td>1458</td>
<td>1458</td>
</tr>
<tr>
<td>δ(CH) vinylene</td>
<td>1296</td>
<td>1230</td>
</tr>
<tr>
<td>δ(CH) thiophenes</td>
<td>1052</td>
<td>1045</td>
</tr>
<tr>
<td>δ(CH) thiophenes</td>
<td>1045</td>
<td>1034</td>
</tr>
</tbody>
</table>

*a* $\nu =$ Stretching, $\delta =$ in-plane deformation.

*b* Solid-state experimental data.

*c* Data from Ref. [22].

*d* B3LYP/6-31G** scaled data for all-anti conformations.

*e* Data from Ref. [15].

*f* Weak band detected about 1560 cm$^{-1}$. 
stretching region. These bands are selectively enhanced with respect to the remainder Raman-active normal modes, due to the strong electron–phonon coupling that takes place along the conjugated CC pathway [30–32], and show pronounced dispersions, both in wavenumber and intensity, with chain length.

The Raman lines observed at 1601 and 1296 cm\(^{-1}\) for T2VT2 are calculated at 1600 and 1279 cm\(^{-1}\), respectively. These bands do not appear in the spectrum of T4 and are characteristic of the vinylene spacer. As depicted in Fig. 4, the line at 1601 cm\(^{-1}\) almost purely corresponds to the C–C stretching of the spacer and the line at 1296 cm\(^{-1}\) is associated with the in-plane symmetric bending of the C–H bonds attached to the spacer. The appearance of these two bands suggests that the vinylene bridge preserves its structural identity. However, the downshift of 17 cm\(^{-1}\) that the C–C stretching undergoes in passing from 1,2-bis(thienylene)vinylene (TVT, 1618 cm\(^{-1}\)) [33] to T2VT2 (1601 cm\(^{-1}\) indicates that the vinylene spacer is actively involved in the conjugation path. The value calculated for the C1=C1' bond length slightly increases from TVT (1.353 Å) to T2VT2 (1.357 Å) showing the effect of extending the conjugated system.

The Raman spectra of oligothiophenes over the range 1550–1400 cm\(^{-1}\) are dominated by two peaks due to the antisymmetric [\(\nu_{as}(C=\overline{C})\)] and symmetric [\(\nu_{s}(C=C)\)] stretchings of the thiophene rings [9–12, 21,22]. The line corresponding to the \(\nu_{as}(C=\overline{C})\) vibration (termed as line A for \(\alpha,\alpha'-\)dimethyloligothiophenes [9–12]) appears at higher frequencies and undergoes a sizeable redshift and a continuous loss of intensity as the length of the oligomer increases (T2: 1552 cm\(^{-1}\); T3: 1524 cm\(^{-1}\); T4: 1514 cm\(^{-1}\)) [22,34]. This trend is perfectly reproduced by B3LYP/6-31G** calculations (T2: 1544 cm\(^{-1}\); T3: 1523 cm\(^{-1}\); T4: 1511 cm\(^{-1}\)). The dispersion observed for this line can be taken as a measure of the extent of conjugation along the series.

For T2VT2, the \(\nu_{as}(C=\overline{C})\) line is observed at 1539 cm\(^{-1}\) and calculated at 1533 cm\(^{-1}\). These values are intermediate between those obtained for T2 and T3 and suggest that the extent of conjugation in T2VT2 is significantly smaller than for T4. However, a careful look to the normal modes reveals that there are two \(\nu_{as}(C=\overline{C})\) Raman-active modes both for T2VT2 (1533 and 1493 cm\(^{-1}\)) and for T4 (1553 and 1511 cm\(^{-1}\)) (see Fig. 5). The displacement patterns of these two modes are the same for the two molecules and correspond to out-of-phase and in-phase vibrations of adjacent thiophene rings, respectively. The difference between the two molecules is the relative intensity of the respective modes. For T2VT2, the higher frequency mode at 1533 cm\(^{-1}\) is 138 times more intense than the mode at 1493 cm\(^{-1}\) and this mode is not observed in the spectrum. For T4, the lower frequency mode at 1511 cm\(^{-1}\) is the most intense (16:1) and the mode at 1553 cm\(^{-1}\) is observed as a weak peak at \(<560\) cm\(^{-1}\) [22]. The vinylene bridge therefore changes the intensity of the Raman-active modes and, as a consequence, the \(\nu_{as}(C=\overline{C})\) line observed in the spectrum of T2VT2 and T4 originates in different normal modes separated by \(<40\) cm\(^{-1}\).

These results show that the suggestion performed above about the conjugation extent in T2VT2 was wrong because we were correlating different vibrations. They also prevent about the necessity of performing an in-depth analysis of the vibrational properties even when comparing molecules with similar structures. For T2VT2, the introduction of the vinylene bridge downshifts the frequencies of both \(\nu_{as}(C=\overline{C})\) Raman-active vibrations by \(<20\) cm\(^{-1}\).
with respect to T4. This shift is due to the participation of the bridge in the vibrations and cannot be only taken as an indicative of a larger conjugation extent.

The line associated to the $\nu_4(C=\text{C})$ vibration (termed as line B for, $\alpha,\alpha'$-dimethyloligothiophenes [9–12]) is the strongest one and blueshifts with chain length for unsubstituted oligothiophenes meeting saturation for the tetramer (T1: 1405 cm$^{-1}$; T2: 1440 cm$^{-1}$; T3: 1453 cm$^{-1}$; T4: 1458 cm$^{-1}$) [22,34]. The frequencies calculated for this line (T1: 1408 cm$^{-1}$; T2: 1443 cm$^{-1}$; T3: 1450 cm$^{-1}$; T4: 1443 cm$^{-1}$) are in good agreement with the experimental data but for the frequency downshift predicted for T4. This downshift is actually observed for end-capped $\alpha,\alpha'$-dimethyloligothiophenes (T2: 1492 cm$^{-1}$; T3: 1488 cm$^{-1}$; T4: 1482 cm$^{-1}$) [9–12].

The most intense peak in the Raman spectrum of T2VT2 appears at 1433 cm$^{-1}$ and is calculated at 1422 cm$^{-1}$. As depicted in Fig. 5, the associated eigenvector describes a symmetric $\nu_4(C=\text{C})$ vibration.
mainly located on the thiophene rings directly linked to the vinylene spacer. The stretching of the CC bonds is coupled with the in-phase bending of the C–H bonds in which the H atoms move with a large displacement which opposes that of the C atoms. The displacement pattern calculated for T2VT2 exactly matches that obtained for the most intense peak of T4 (observed at 1458 cm\(^{-1}\) [7] and calculated at 1443 cm\(^{-1}\)) showing that the most intense Raman lines of T2VT2 and T4 originate in the same vibration. The introduction of the vinylene spacer causes a downshift of \(\sim 20\) cm\(^{-1}\) for this vibration, similar to that observed for the \(\nu_{\text{sp}}(\text{C–C})\) vibrations.

Theoretical calculations predict the existence of a second Raman-active \(\nu_{\text{as}}(\text{C–C})\) vibration for T2VT2 and T4 (see Fig. 5). The vibration is located on the outer thiophene rings and shows no contribution of the central spacer. This displacement pattern determines that the vibration is calculated at almost the same energy for T2VT2 (1428 cm\(^{-1}\)) and T4 (1429 cm\(^{-1}\)). The Raman intensity of this vibration is much smaller than that calculated for the \(\nu_{\text{sp}}(\text{C–C})\) vibration located on the central rings (intensity ratio \(= 1.13\) for T2VT2 and 1.23 for T4). For T2VT2, the vibration is not observed in the spectrum because it lies under the most intense vibration calculated at 1422 cm\(^{-1}\). For T4, the vibration is observed as a weak peak at 1426 cm\(^{-1}\) well-differentiated from the most intense peak at 1458 cm\(^{-1}\) [22].

DFT calculations therefore predict the existence of two Raman-active normal modes associated with the \(\nu_{\text{as}}(\text{C–C})\) vibrations of the two different types of thiophene rings present in T2VT2 and T4. This description differs from that previously given for T2VT2 and \(\alpha,\alpha'\)-dimethyloligothiophenes [9–12,15] on the basis of HF/6-31G** calculations, for which the most intense Raman line originates in a \(\nu_{\text{sp}}(\text{C–C})\) vibration that spreads over the whole molecule. The fact that this line shows a small dispersion with chain length is however better explained by the DFT description presented here. DFT calculations associates the most intense Raman line to a normal mode localized over the central rings; since the geometry of these rings remains almost unchanged in going beyond the tetramer, the frequency of the normal mode meets saturation. This interpretation is further supported by the results obtained in a previous study for the more extended T3VT3 molecule [20].

The most intense line of T3VT3 originates in a normal mode identical to that found here for T2VT2 and appears at 1432 cm\(^{-1}\) almost matching the frequency recorded for T2VT2 (1433 cm\(^{-1}\)).

The Raman spectrum of T2VT2 exhibits three weak peaks around 1200 cm\(^{-1}\) (see Fig. 3 and Table 1) that are due to vibrations associated to \(\delta(\text{CH})\) bendings of the hydrogen atoms and to \(\nu(\text{C–C})\) stretchings of the inter-ring bonds and of the C–C bonds connecting the vinylene spacer to the bithiénylene moieties. The normal modes calculated are actually a mixture of these displacements.

T2VT2 finally presents a medium-intense peak at 1047 cm\(^{-1}\). The peak is also observed for T4 at 1045 cm\(^{-1}\) and is assigned to \(C_{\beta}–H\) bending vibrations [22]. The peak actually involves two vibrations which different intensities. The most intense vibration is calculated at 1034 cm\(^{-1}\) for both T2VT2 and T4 and corresponds to the totally in-phase oscillation depicted in Fig. 5. For the low intense vibration, calculated at 1043 cm\(^{-1}\), the \(C_{\beta}–H\) bonds of the outer rings vibrate out-of-phase with respect to the \(C_{\beta}–H\) bonds of the inner rings. This vibration is observed as a shoulder on the higher frequency side of the experimental peak for both T2VT2 and T4 [22] and appears well-differentiated for shorter oligomers such as TVT [33] and T2 [21,34].

The Raman spectrum was also calculated for the less stable \(\text{syn}\) conformation of T2VT2 and is shown in Fig. 6. The spectrum is very similar to that depicted

![Fig. 6. B3LYP/6-31G** Raman spectrum calculated for T2VT2 in the less stable \(\text{syn}\) conformation.](image-url)
in Fig. 3 for all-anti T2VT2 but present small distinctive features. It exhibits two small peaks at 1497 and 1355 cm\(^{-1}\) that are not observed in the experimental spectrum (see Fig. 3). The peak at 1497 cm\(^{-1}\) corresponds to the vibration calculated at 1493 cm\(^{-1}\) for the anti conformation (see Fig. 5), for which it has almost no intensity. The peak at 1355 cm\(^{-1}\) is due to the in-phase stretching of all the C\(_b\)-C\(_b\) bonds and is observed as an extremely weak peak around 1365 cm\(^{-1}\) for oligothiophenes [22,33]. This normal mode is also active for the anti conformation but it has a negligible intensity. The double peak calculated at 1304–1288 cm\(^{-1}\) for syn T2VT2 has also no correspondence in the experimental spectrum in which only a single peak is observed at 1296 cm\(^{-1}\). These results, together with the good correlation obtained between experiment and theory for anti T2VT2, suggest that the molecule exits in an anti structure in the solid state in agreement with the higher stability calculated for this conformation.

5. Conclusion

The Raman spectrum of the vinylene-bridged quaterthiophene oligomer T2VT2 has been comprehensively assigned on the basis of DFT B3LYP/6-31G** calculations and in comparison with linear unsubstituted oligothiophenes. The T2VT2 molecule is predicted to have an all-anti structure and shows an effective conjugation length that surpasses that of T4. The vinylene spacer contributes to the conjugation pathway but also preserves its structural identity and the vibrations associated to this group appear clearly differentiated in the spectrum. The Raman spectrum of T2VT2 presents most of the vibrational features observed for quaterthiophene (T4), the most intense peak corresponding to a symmetric \(v_s(C=C)\) stretching of the inner thiophene rings. A direct correlation between the lines observed in the spectrum for T2VT2 and T4 is however not always possible because the vinylene bridge strongly affects the intensity of the \(v_{as}(C=C)\) modes and changes the assignment of the lines. Conclusions about the extent of conjugation on systems with similar structures like T2VT2 and T4 based on the comparison of the Raman frequencies observed in the spectra should be taken with care and a detailed analysis of the vibrational normal modes is highly recommended to avoid unreliable correlations.

Acknowledgements

The research at the Universities of Málaga and Valencia was supported by the Ministerio de Ciencia y Tecnología (MCyT) of Spain through the projects BQU2000-1156 and PB98-1447, respectively. The group of Málaga is indebted to the Junta de Andalucía (Spain) for funding their research group (FQM-0159).

References


