Infrared and Raman Spectra of a $\pi$-conjugated Methylene-bridged Oligothiophene

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The Fourier transform FT infrared and FT-Raman spectra of a $\pi$-conjugated thiophene-based oligomer were studied. The compound has a well–barrier–well structure, where the well parts are two bithiophene end moieties and the barrier part is a methylene fragment with a larger energy gap. Characteristic vibrational features are compared with those obtained on series of unsubstituted $\pi$-linked oligothiophenes and of $\alpha,\alpha'$-dimethyl end-capped oligothiophenes, in order to estimate the effective conjugation length of this compound in the solid state. Vibrational assignments are also proposed for the main bands over the whole spectral range. © 1998 John Wiley & Sons, Ltd.

INTRODUCTION

Conjugated organic polymers have a promising future as materials for technological applications such as nonlinear optics devices, field-effect transistors and light-emitting diodes. Among them, polythiophene has attracted great attention because of its interesting electronic properties and excellent chemical stability. The unique optical and electronic properties of these materials result from the delocalization of the conjugated electrons along the one-dimensional polymer backbone.

More recently, oligomers of well defined chemical structure and with short chain lengths have been regarded as model compounds to study in a more detailed way the relationship between the structure and properties of these polymers. One of the major advantages of this strategy is that the chain length dependence of physical properties can be systematically investigated.

Kanemitsu et al. recently studied luminescence properties of soluble thiophene-based oligomers. This family compounds had a well–barrier–well structure, where the well parts were $\pi$-linked oligothiophenes with different conjugation lengths connected through a bridge of a non-visibly luminescent material with a larger energy gap. The electronic properties of the $\alpha$-bridged oligothiophenes are not controlled by the difference between the energy gaps of the well and barrier parts only, and are strongly affected by the efficiency of the $\pi$-electron delocalization.

From the beginning of research on these new materials, vibrational Raman scattering has been used as a powerful probe of their structure. In particular, the softening of the resonantly enhanced Raman modes with increasing conjugation length (which does not necessarily coincide with the actual chain length) has been successfully applied to measure the effective delocalization length of $\pi$-electrons in real samples.

We have recently investigated the vibrational properties of a series of $\alpha,\alpha'$-dimethyl end-capped oligothiophenes. The oligomers were studied in relation to their conjugation length in the solid state and solution. The data were consistent with the existence of efficient $\pi$-electron delocalization. In addition, the spectra of the oligomers in solution supported the coexistence of several molecular conformations. However, since the spectral differences from solids to solutions were not too drastic, we concluded that $\pi$-conjugation is the driving force which determines that conformational distortions from planarity of the rings are not too large.

In this paper, we focus on the Fourier transform (FT) IR and FT-Raman spectra of a $\pi$-conjugated oligomer constituted of two bithiophene well parts connected through a methylene bridge ($T_2MT_2$). The problem we addressed in this work was to assess by means of vibrational spectroscopy the effective conjugation length of this system in the neutral state as a solid.

EXPERIMENTAL

The structure of the $T_2MT_2$ thiophene-based oligomer is shown in Fig. 1. The synthesis and purification methods have been described elsewhere. Solvents

Figure 1. Structure of the $T_2MT_2$ oligomer.
(carbon disulfide and chloroform) of analytical grade were supplied by Aldrich. Saturated solutions were prepared just before recording the spectra to avoid solvent evaporation.

Infrared absorption spectra were recorded over probe energies of 400–4000 cm$^{-1}$ to be collected at room temperature on a Perkin-Elmer Model 1760 X FT-IR spectrometer, purged with dry Ar gas. Raman scattering spectra were obtained with a Bruker Model RFS 100 FT-Raman spectrometer in a backscattering geometry.

Infrared spectra were recorded in solution and in the solid state (as a pressed KBr pellet). A demountable cell for liquids with potassium bromide windows was used to record the solution spectra. The mean of 50 scans with a 2 cm$^{-1}$ spectral resolution were accumulated in all the experiments. Raman spectra were recorded for the solid compound in a sealed capillary. Radiation of 1064 nm from a Nd:YAG laser, with the power adjusted to 100 mW, was used for excitation in the FT-IR spectrum of solid is shown in Fig. 2. Infrared absorption spectra over probe energies of 4000 cm$^{-1}$ were collected at room temperature on a series of straight non-substituted organic compounds, concluding that the hydrogen along the longitudinal periphery of the molecule (e.g. those bonded to the C$_g$ atoms for the T$_2$MT$_2$ molecule) play the main role in the stabilization of the solid-state structure.

In the solid state, packing forces overcome steric hindrance and force the molecule to be coplanar. As for other oligomers with relatively long chains, it has been suggested that also in the oligothiophenes the molecular symmetry is a determinant factor of the crystal structure. In this regard, Gavezzotti and co-workers have reported a comprehensive crystallographic study of a series of straight non-substituted organic compounds, concluding that the hydrogen along the longitudinal periphery of the molecule (e.g. those bonded to the C$_g$ atoms for the T$_2$MT$_2$ molecule) play the main role in the stabilization of the solid-state structure.

If the torsional potential in a molecule is rather flat, equilibrium conformations in solution may differ from that in the solid state. Two factors may determine such conformational distortions: (i) intermolecular forces between oligomeric chains are switched off in solution and (ii) polar solvents could preferentially stabilize twisted syn conformers (i.e. those conformers having a permanent dipole moment).

RESULTS AND DISCUSSION

Criteria in vibrational analysis

Since no experimental x-ray or electron diffraction data are available for solid T$_2$MT$_2$ (see Table 1), extrapolation of experimentally observed data for solid $x,x'$-dimethyltetraethylthiophene, we could assume an ideal structure in which sulfur atoms of both bithiophene end-moieties are located in an anti-coplanar conformation (see Fig. 1) and that the molecule as a whole displays internal mirror symmetry in the solid state. This assumption of planarity is based on the low barrier heights for rotation around the inter-ring single bonds (of the order of a few kJ mol$^{-1}$), calculated by using ab initio quantum chemical methods, on a series of methyl-substituted bithiophenes. With such an ideal mirror symmetry molecular structure, T$_2$MT$_2$ belongs to the C$_{2v}$ point group and to the C$_1$ point group if twisted. The 93 vibrational normal modes are distributed in the various symmetry species as shown in Table 1.

The degree of intramolecular delocalization of the $\pi$ electrons in five-membered heteroaromatic chains depends on the extent of the overlapping of the $p_z$ orbitals of the C atoms in the $z$-positions. Such overlapping is modulated by the structural conditions of the molecule (i.e. the chemical structure and conformation). Minimal energy conformation in $\pi$-conjugated systems results from the competition of two major effects: steric hindrance (favouring $\theta = 90^\circ$, clinal conformations) and $\pi$-delocalization forces (favoring $\theta = 0^\circ$, syn conformations, $\theta = 180^\circ$, anti conformations).

In the solid state, packing forces overcome steric hindrance and force the molecule to be coplanar. As for other oligomers with relatively long chains, it has been suggested that also in the oligothiophenes the molecular symmetry is a determinant factor of the crystal structure. In this regard, Gavezzotti and co-workers have reported a comprehensive crystallographic study of a series of straight non-substituted organic compounds, concluding that the hydrogen along the longitudinal periphery of the molecule (e.g. those bonded to the C$_g$ atoms for the T$_2$MT$_2$ molecule) play the main role in the stabilization of the solid-state structure.

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IR AND RAMAN SPECTRA OF A \( \pi \)-CONJUGATED METHYLENE-BRIDGED OLIGOTHIOPHENE

Figure 2. FT-IR spectrum of \( T_2MT_2 \) (KBr pressed pellet) between (a) 3200 and 2800 cm\(^{-1} \) and (b) 1600 and 400 cm\(^{-1} \).

lowest (1418 cm\(^{-1} \)) wavenumbers to an antisymmetric \( v_{as}(C=C) \) and a symmetric \( v_{s}(C=C) \) stretching vibrations, respectively. The band at 1424 cm\(^{-1} \), which is also observed in the Raman spectrum at 1425 cm\(^{-1} \), comes from a totally symmetric mode which shows a characteristic chain length dependence in the \( \alpha,\omega \)-end-capped oligothiophenes\(^{15} \) (see the Raman spectrum section).

In the Me-(Th)\(_n\)-Me series,\(^{15} \) we found that the IR-active band due to the \( v_{as}(C=C) \) mode around 1530 cm\(^{-1} \) showed a sizeable downward shift with increasing chain length (i.e. we measured a \( \Delta \nu \) of 28 cm\(^{-1} \) on going from DMBT to DMS\(_x\)T), indicating a large wavenumber dispersion throughout the Brillouin zone for the related bulk mode in the infinite polymer lattice. In contrast to the large wavenumber dispersion of this \( v_{as}(C=C) \) vibration, the band position of the \( v_{s}(C=C) \) mode was found to be almost independent on the molecular size (i.e. 1445 cm\(^{-1} \) in DMTT and 1443 cm\(^{-1} \) in DMS\(_x\)T). Similar chain length-dependent wavenumber dispersions have been also reported for the unsubstituted \( \alpha \)-oligothiophenes\(^{24,25} \) The spectral differences between \( T_2MT_2 \) and the two series of \( \alpha \)-linked oligothiophenes prove the existence of a vibrational coupling between the aromatic C=C stretchings and those of the methylene bridge.

After solution of the \( T_2MT_2 \) in chloroform (Fig. 3), we observe that the band assigned to the \( v_{as}(C=C) \)
vibration is now recorded at 1519 cm\(^{-1}\). The upward shift by 5 cm\(^{-1}\) of this molecular size-dependent mode relative to the solid state indicates that the effective π-conjugation length of the T\(_2\)MT\(_2\) compound is reduced in solution as a result of the conformational distortions from planarity of the thiophene rings.

A very weak absorption is observed at 1375 cm\(^{-1}\) in the spectrum of T\(_2\)MT\(_2\). This band is generally found to be very stable in position and to be unaffected by substitution of the two hydrogens atoms bonded at both end \(x\)-positions. Similar bands have been recorded in the infrared spectra of DMBT (1376 cm\(^{-1}\))\(^{26}\) and DMTT (1373 cm\(^{-1}\)).\(^{15}\) We attribute this weak band to an aromatic \(ν_{as}(C–C)\) mode.\(^{27–29}\) Furthermore, we believe that the peaks at 1354, 1344 and 1322 cm\(^{-1}\) must also be ascribed to \(ν(C–C)\) modes with different phases.

The four fundamental \(δ(CH)\) in-plane bending modes of thiophene monomer were reported by Rico \textit{et al.}\(^{30}\) at 1250, 1085, 1080 and 1036 cm\(^{-1}\), where the second one

Table 2. Experimental wavenumbers (\(ν\)) and proposed assignments for bands measured in the infrared and Raman spectra of T\(_2\)MT\(_2\)

<table>
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*\(f\) (intensities): w = weak; m = medium; s = strong; v = very; b = broad.
*\(\nu\) Data from Ref. 22.
*\(\nu\) = Stretching; \(\delta\) = in-plane bending; \(ω\) = wagging; \(γ\) = out-of-plane bending; \(s\) = symmetric; \(as\) = antisymmetric.”
is calculated from the isotopic product rule on nine deuterated derivatives. This spectroscopic study also indicated that the two \( \delta(C_\beta H) \) modes had to be assigned to the bands at 1250 and 1080 cm\(^{-1} \) in the infrared spectrum of liquid thiophene. From these experimental data and a number of quantum-mechanical force field calculations for 3-methylthiophene,\(^{27} \) \( \alpha \)-oligothiophenes\(^{28} \) and poly(3-methylthiophene),\(^{29} \) we assigned the bands at 1290, 1247, 1213, 1096, 1082, 1073, 1048 and 1030 cm\(^{-1} \) to \( \delta(CH) \) bending modes. The antisymmetric and symmetric vibrational modes roughly correspond to the higher and lower wavenumber values, respectively.

The absorption around 1226 cm\(^{-1} \) is probably due to an inter-ring \( \nu(C_\alpha-C_\beta) \) mode.\(^{27}-29 \) A similar band at 1225 cm\(^{-1} \) has been reported by Furukawa and co-workers\(^{24} \) for solid tertithiophene (3T) and quaterthiophene (4T), whose assignment was supported by the large \(^{13}C \) downward shift (ca. 25 cm\(^{-1} \)) and a small D downward shift (ca. 8 cm\(^{-1} \)). The 1180 and 1143 cm\(^{-1} \) bands should also contain large contributions from inter-ring \( \nu(C_\alpha-C_\beta) \) motions.

The assignment of the bands at 1205 and 1192 cm\(^{-1} \) cannot be resolved with certainty without the experimental support of \(^{13}C \) or D shift data. The infrared spectrum of DMBT showed a sharp absorption near 1203 cm\(^{-1} \), the intensity of which readily decreased in DMTT.\(^{15} \) This band was assigned as the \( \nu_{a}(C_\alpha-CH_3) \) of both end-caps. Although the magnitude of its wavenumber seems too high for such an assignment, in \( \pi \)-conjugated chain compounds the substituents in the \( \alpha \)-position are involved in the quinoid canonical structure which stabilizes the ground state.\(^{14} \) As a consequence, the charge distribution of the \( \sigma \)-bonds in the alkyl side-chains may suffer a certain degree of polarization. In this case, the \( \nu(C-C) \), which in the absence of inductive effects show a very weak intensity in the infrared, may become very strong.\(^{31} \) From this discussion, we believe it reasonable to assign the bands at 1205 and 1192 cm\(^{-1} \) as due to \( \nu(C_\alpha-CH_2) \) modes, probably also being coupled with \( \nu(C=C)_{ring} \) modes.

Below 1000 cm\(^{-1} \) the infrared spectrum is more complex because one can distinguish in-plane and out-of-plane modes simultaneously, and the assignment is delicate. On the basis of the lattice dynamics calculations for polythiophene,\(^{23} \) we have assigned the bands at 885, 842, 819, 757 and 743 cm\(^{-1} \) to different \( \nu_{a}(C-S) \) or \( \nu_{l}(C-S) \) modes. Similar bands at almost the same positions have been measured in \( \alpha \)-oligothiophenes\(^{24,25} \) and the Me-(Th)\(_n\)-Me series.\(^{15} \)

The \( \gamma(C-H) \) out-of-plane bending vibrations, the wavenumbers of which are characteristic of the positions of substitution, appear in the 900–600 cm\(^{-1} \) region as very strong absorptions.\(^{32} \) The 802 cm\(^{-1} \) band has no counterpart in the infrared spectrum of bithiophene whereas it is observed in all the longer oligomers\(^{33,34} \) and polythiophene.\(^{24} \) We assign this strong band to highly localized \( \gamma(C_\beta-H) \) modes of the two inner thiophene rings. On the other hand, the bands at 697 and 678 cm\(^{-1} \) are due to \( \gamma(C-H) \) modes of the two end-thiophene rings, without distinction between \( \alpha \) and \( \beta \)-positions.

The most relevant information derived from the spectral pattern of \( T_3MT_2 \) in carbon disulfide solution (Fig. 4) is that the solid-state bands around 697 and 678 cm\(^{-1} \) coalesce into a single sharp peak at 690 cm\(^{-1} \). The effect of the dissolution process on the \( \gamma(C-H) \) modes can be explained in molecular dynamics terms. Within the harmonic approximation theory, the in-plane motions of fully coplanar polynconjugated systems are strictly orthogonal to the out-of-plane modes, and no coupling between them can take place. On going from coplanar to twisted structures, the \( \pi \) delocalization decreases, thus changing the molecular vibrational potential. As a result, the diagonal force constants.

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**Figure 3.** Comparison between (a) the IR bands in chloroform solution and (b) the corresponding solid-state spectral pattern of \( T_3MT_2 \) in the aromatic \( C=C \) stretching region.
associated with the $\gamma$(C–H) modes change as a function of the inter-ring torsion angle. The observed wavenumber shifts are then evidence of the changes of the dynamics of the $T_2$MT$_2$ molecule from the coplanar structure in the solid state to tilted structures in solution.

On the basis of previous assignments for parent molecules, we believe that the infrared absorptions at 686, 666 and 631 cm$^{-1}$, all of which have a counterpart in the Raman spectrum, arise from in-plane ring deformation $\delta_{\text{ring}}$ modes with different phases.

The weak bands near 525 and 515 cm$^{-1}$ should be correlated with the Raman line of $A_1$ symmetry measured at 608 cm$^{-1}$ for thiophene(in-plane $\delta_{\text{ring}}$), which becomes active in the infrared spectrum due to the symmetry lowering. In the case of 3-methylthiophene, the two in-plane $\delta_{\text{ring}}$ modes were assigned, on the basis of an ab initio quadratic force field calculation, to lower wavenumbers (i.e. 659 and 542 cm$^{-1}$) than for the unsubstituted molecule$^{30,34}$ (i.e. 751 and 608 cm$^{-1}$). The downward shifts were attributed to the dynamic effects of the $\beta$-methyl substitution on both the kinetic energy matrix ($G_K$) and the force constant matrix ($F_K$). In the case of the $T_2$MT$_2$ molecule, we should expect that the dynamic effects of the different types of $\alpha$-substitutions with respect to thiophene monomer will translate into downward shifts of the in-plane $\delta_{\text{ring}}$ modes similar to those of 3-methylthiophene.

Finally, the strong band measured near 467 cm$^{-1}$ arises from an out-of-plane ring-folding vibration, $\gamma_{\text{ring}}$. For thiophene monomer, the related vibration of $B_2$ species was undoubtedly assigned to an infrared band with a pronounced $C$-type structure at 452 cm$^{-1}$. The vibrational assignment for thiophene together with a series of quadratic force fields calculations on a few oligothiophenes and polythiophene$^{28}$ also support the assignment of the bands observed at 586 and 563 cm$^{-1}$ as $\gamma_{\text{ring}}$ modes with different phases.

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**Figure 4.** IR absorptions for the out-of-plane C–H bending modes around 800 and 700 cm$^{-1}$ of $T_2$MT$_2$ (a) in carbon disulfide solution and (b) in the solid state.

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**Raman spectrum**

Raman spectra of $\pi$-conjugated polymers are very simple, even for systems having complex chemical structures. The spectra are constituted by a few strong lines in the 1650–1450 cm$^{-1}$ range, which show pronounced wavenumber and intensity dispersions with chain length. For short chains, however, additional weak lines are also observed. In most cases, they must be ascribed to end-group modes owing to their negligible size dependence and rapid disappearance with increasing number of chemical units.$^{35}$

Raman spectra of $\pi$-conjugated compounds are generally recorded in near-resonance conditions.$^{36}$ As the resonance Raman state is approached, only a few modes (those with a large projection along the deformation coordinate which describes the evolution of the molecular geometry from the ground to the excited states) should gain appreciably intensity.$^{36}$

However, resonance Raman conditions alone cannot fully account for the whole spectroscopic features of $\pi$-conjugated systems. For example, it has been found that even the Raman spectra of very short oligomers, whose energy gaps are well above the energies of the usual exciting laser radiations, have a simple appearance.$^{37}$ Conversely, the pattern of the Raman spectra of a few oligofurans excited with 1064 nm radiation$^{35}$ (which is well below the energy gaps of these materials) almost resembles the Raman spectra of the polymer recorded in near-resonance conditions.$^{38}$

Some theoretical models which assume the existence of electron–phonon coupling have been proposed to explains these findings.$^{35–41}$ A key assumption for the interpretation of the spectra is that, independent of the fact that the resonance condition is fulfilled, only one strongly dipole-allowed electronic state is relevant for the description of the Raman scattering process (two-state model).$^{42,43}$
The FT-Raman spectrum of solid $T_2MT_2$ in the 1650–100 cm$^{-1}$ range is displayed in Fig. 5. At first sight the characteristic feature of the $\pi$-conjugated materials of exhibiting very few strong Raman lines in the aromatic C=C stretching region is still evident.

In a previous paper on the Me-$\text{(Th)}_n$–Me series, we reported that the Raman spectra exhibited only two main strong bands in the 1600–1400 cm$^{-1}$ range. Furukawa and co-workers have also reported similar data for unsubstituted $\alpha$-oligothiophenes.

The observed Raman spectrum of $T_2MT_2$ shows, however, up to six bands with appreciable intensity in this region. These spectral differences are caused by two independent factors: (i) the sp$^3$ defect effectively acts as an electronic barrier and the $\pi$-electrons are greatly confined within the bithiophene quantum wells and (ii) the motions of the aromatic C=C bonds show extensive coupling with the stretchings of the $\alpha$-methylene spacer.

Let us now inspect the spectrum of $T_2MT_2$ in more detail, in order to correlate the measured lines with data previously collected on related series of oligothiophenes.

(i) The medium-strong line at 1559 cm$^{-1}$ is almost coincident with the line near 1560 cm$^{-1}$ in the Raman spectrum of $\alpha,\alpha'$-dimethylbithiophene. Its rapid disappearance for the longer oligomers supported the assignment as a $\nu_2$(C=C) mode mostly localized on the two outer thiophene rings.

(ii) It is worth noting that the line of medium-strong intensity at 1515 cm$^{-1}$ and the shoulder at the lower wavenumber side of the line at 1425 cm$^{-1}$ are virtually coincident with the corresponding infrared bands; they do not have counterparts in the Raman spectra of the $\alpha$-oligothiophenes.

For most $\pi$-conjugated chain compounds, the molecular symmetry point group does not change from the ground to the only one strongly dipole-allowed excited state, hence only totally symmetric (TS) vibrations are selectively enhanced in the Raman spectrum. In the case of $T_2MT_2$, however, the sp$^3$ defect makes the intramolecular delocalization along the whole molecule compete with the confinement of $\pi$-electrons within each bithiophene moiety. As a consequence, the selective Raman enhancement of the TS modes is less effective than in $\alpha$-quaterthiophene or in $\alpha,\alpha'$-dimethylquaterthiophene, and modes of different symmetry species are experimentally observed. From these accounts, we believe it reasonable to assign the lines near 1515 and 1418 cm$^{-1}$ to in-plane $B_1$ symmetry modes.

(iii) The line near 1363 cm$^{-1}$ has to be assigned as a $\nu_3$(C=C) mode, probably being mixed with inter-ring $\nu$(C=C) vibrations, although it would be more correct to emphasize its character of a ring vibration. This mode appears at almost the same position as in the Me-$\text{(Th)}_n$–Me series: 1357 cm$^{-1}$ (trimer), 1359 cm$^{-1}$ (tetramer) and 1361 cm$^{-1}$ (pentamer).

(iv) Below 1350 cm$^{-1}$, we can distinguish many weak Raman lines, all of which have a counterpart in the IR spectrum (Table 2). This observation corroborates that the selective enhancement of the TS modes in $T_2MT_2$ is lowered with respect to the fully $\pi$-conjugated oligothiophenes. The assignment of all these weak Raman lines has been thoroughly discussed in the preceding section.

(v) Finally, lines around 1547 (line A), 1471 (line B) and 1425 cm$^{-1}$ (line C) should be correlated with Raman lines at 1546, 1488 and 1445 cm$^{-1}$ in DMTT, 1533, 1482 and 1448 cm$^{-1}$ in DMQrT and 1525, 1481 and 1450 cm$^{-1}$ in DMQqT, respectively.

These lines exhibit a characteristic chain length dependence, which is common to other series of thiophene-based oligomers. (a) line A shows a

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**Figure 5.** 1064 nm excited Raman spectrum of neutral $T_2MT_2$ in the solid state.
considerable downward shift and grows weaker with increasing chain length; (b) the position of the strongest line B is almost independent of the oligomer size; and (c) line C, which is observed only in \( x \)-monosubstituted and \( x,y \)-disubstituted oligothiophenes, shows a noticeable enhancement with increasing chain length.

We note another experimental observation: line B shows a sizeable upward shift of up to 30 cm\(^{-1}\) when the \( x \)-positions are substituted (i.e. it is measured around 1461 and 1463 cm\(^{-1}\) in 3T and 4T, respectively, whereas it appears at 1488 and 1482 cm\(^{-1}\) in DMTT and DMQQT, respectively). The spectral differences between the various series of oligothiophenes may be due to changes in the \( G \) and/or \( F \) matrices. However, within each series, line B invariably remains strong and shifts only slightly with increasing chain length. Incidentally, given that lines B and C are very close and belong to the same symmetry species, an intensity borrowing can be observed depending on the oligomer size.

Since the wavenumber dispersion of line A with chain length is large but its intensity is relatively low, we believe that this band arises from an in-phase \( \nu_{as}(C=\equiv C) \) mode mostly localized at the end two rings, although it is probably mixed in some extent with stretchings of the \( \equiv C \equiv C \equiv C \) bonds. We also think that the strong line B has to be assigned to an in-phase \( \nu(C=\equiv C) \) which extends over the whole molecule, say the collective totally symmetric mode mostly localized at the end of the whole molecule, say the collective totally symmetric mode usually termed \( \gamma \) (effective conjugation coordinate). The assignment of line C is not straightforward, however, and we believe that it originates from a complex mixture of \( \nu(C=\equiv C) \) and \( \nu(C=C) \) modes, probably coupled also with stretchings of the methylene spacer.

### Mean conjugation length

It is possible to obtain information on the MCL of the \( T_2 \) oligomer from the experimental chain length-dependent wavenumber dispersions observed for the Me–(TH)–Me series.\(^{1,5}\)

(i) The infrared-active \( \nu_{as}(C=\equiv C) \) mode near 1530 cm\(^{-1}\) shows a substantial downward shift, by 28 cm\(^{-1}\), on going from the dimer to the hexamer: DMBT (1531 cm\(^{-1}\)), DMTT (1518 cm\(^{-1}\)), DMQQT (1513 cm\(^{-1}\)), DMQQT (1508 cm\(^{-1}\)) and DMSxT (1503 cm\(^{-1}\)).

(ii) The strongest Raman line B around 1490 cm\(^{-1}\) also showed a decreasing trend of ca. 15 cm\(^{-1}\):

- DMBT (1492 cm\(^{-1}\)), DMTT (1488 cm\(^{-1}\)), DMQQT (1482 cm\(^{-1}\)), DMQQT (1481 cm\(^{-1}\)) and DMSxT (1477 cm\(^{-1}\)).

(iii) The weak line A above 1500 cm\(^{-1}\) showed a very large dispersion with the chain length for the shorter oligomers: DMTT (1546 cm\(^{-1}\)), DMQQT (1533 cm\(^{-1}\)) and DMQQT (1525 cm\(^{-1}\)).

The infrared and Raman bands of \( T_2 \) to be correlated with the data listed above are the following: 1514 cm\(^{-1}\) (IR), 1547 and 1471 cm\(^{-1}\) (Raman). In view of the spectra, we conclude that the pattern of \( T_2 \) between 1600 and 1400 cm\(^{-1}\) is similar to that of DMTT. Within the reliability of this comparison, we can estimate an MCL for \( T_2 \) in the solid state of around three thiophene rings. This MCL should be the result of a hyperconjugative contribution to the \( \pi \)-conjugation from the methylene spacer, in spite of the sp\(^3\) defect introduced between the two thiophenones.

### CONCLUSIONS

We have investigated the vibrational properties of a thiophene-based oligomer having a well–barrier–well structure. The spectroscopic data have been correlated with the size-dependent IR- and Raman-active modes of a series of \( \pi,\pi' \)-dimethyl end-capped oligothiophenes studied previously.

The appearance of the Raman spectrum of this methylene-bridged oligothiophene suggests that \( \pi \)-polyconjugation is still fairly effective, in spite of the introduction of an sp\(^3\) defect into the oligomer backbone.

The detailed analysis of the FT-IR and FT-Raman spectra indicates that the mean conjugation length of this compound in the solid state is half way between two and three thiophene rings. The study has confirmed that \( \pi \)-electrons are largely confined within each thiophene end-moiety, although hyperconjugative contributions coming from the CH\(_2\) group connecting the two thiophene segments probably further contribute to the increase in the effective conjugation length.

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### REFERENCES


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