Vibrational Spectroscopic Study of a Series of α,α′-Diethyl End-Capped Oligothiophenes with Different Chain Lengths in the Neutral State

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In this paper, we investigate the vibrational FT-IR and FT-Raman spectra of a series of α,α′-diethyl substituted oligothiophenes with variable chain lengths (from trimer to hexamer) in the neutral state. The experimental data support the existence of an effective intramolecular delocalization of the π electrons. Ab initio quadratic force field calculations, at the RHF/6-31G** level, have been carried out for each oligomer, with the chain length dependence of the Raman spectra being simulated with remarkable accuracy.

I. Introduction

Conjugated organic polymers attract considerable attention because of their interesting properties. (i) Upon chemical doping or photoexcitation, these materials encompass a wide range of conductivities, from an insulator to a metallic-like electronic conductor.[1,2] (ii) Both oligomers and polymers show fast nonlinear optical responses.[3] (iii) Some of these materials are electroluminiscent.[4] These molecular and physical properties make conjugated polymers (and especially well-sized oligomers) good candidates for electronic and optical technologies.[5,6]

Conjugated polymers have, however, the complexities of the "real" polymers, such as their low solubilities, high contents of structural defects, broad distribution of molecular weights, etc. Semiconducting oligomers whose conjugation length can be exactly controlled are being investigated nowadays extensively as model systems to establish the charge transport mechanism in conducting polymers.[7,8]

Among the oligomeric materials, oligothiophenes usually show a well-defined crystal structure in their neutral and oxidized forms, which allows for high anisotropic electronic responses. In addition, the strategy of encapsulating the end α-positions has proved as a useful procedure to enhance chemical stability and crystallinity, without damaging the electronic properties of the material.[9,10] This blocking of the π skeleton further prevents undesidered polymerization reactions upon doping at the terminal units, with the resulting doped samples standing stable for a long time.

In this scenario, experimental studies about the chain length dependence of the optical and electronic properties of these oligothiophenes are crucial to elucidate the microscopic mechanisms responsible for the peculiar properties of polythiophene. In this regard, a number of vibrational spectroscopic studies on different families of α-linked oligothiophenes have been published so far.[11−13]

Current quantum chemical methods are in the position to give reliable information about the molecular structure and vibrational properties of the different classes of polyconjugated systems. The ability to calculate molecular force fields and geometries is likely one of the most important developments in computational chemistry over the past decade. Most current calculations are performed within the ab initio restricted Hartree−Fock (RHF) scheme. At this level, the calculated harmonic force constants and vibrational frequencies are usually higher than the corresponding experimental quantities, due to a combination of electron correlation effects and basis set deficiencies. Nonetheless, as the errors of these calculations are largely systematic, they can be corrected after inclusion of appropriate scaling factors.[14] Over the years, spectroscopists have used the scaled RHF method very successfully in assignments of vibrational spectra of many stable closed-shell organic molecules.[15]

In this paper, we report on the experimental size dependence of the infrared, and Raman-active modes of a series of neutral α,α′-diethyloligothiophenes in the solid state at room temperature. A full vibrational assignment is proposed on the basis of molecular symmetry considerations, spectroscopic correlations for related systems,[12,16] and lattice dynamics calculations for polythiophenes.[17,18] As support for the analysis of the experimental Raman spectra, we also present the main results of a quantum chemical study performed on a series of α,α′-dimethyloligothiophenes. The comparison of the experimental and theoretical spectra reveals that the size of the α-alkyl chains plays a minor role in determining the Raman activity of the π-conjugated backbone, which may be sufficiently simulated by a methyl group.

II. Experiment and Computational Details

The chemical structures of the α,α′-diethyloligothiophenes studied in this work are shown in Figure 1. The details of the synthesis and purification methods are described elsewhere.[9] Infrared absorption spectra were recorded with a Perkin-Elmer model 1760 X FT-IR spectrometer purged with dry argon. Raman scattering spectra were obtained on a Bruker FRA106/S FT-Raman spectrometer in a backscattering configuration.

Infrared spectra were recorded as solid samples embedded in pressed KBr pellets. The means of 20 scans, with a 2 cm^{-1} spectral resolution, were accumulated in all the experiments.

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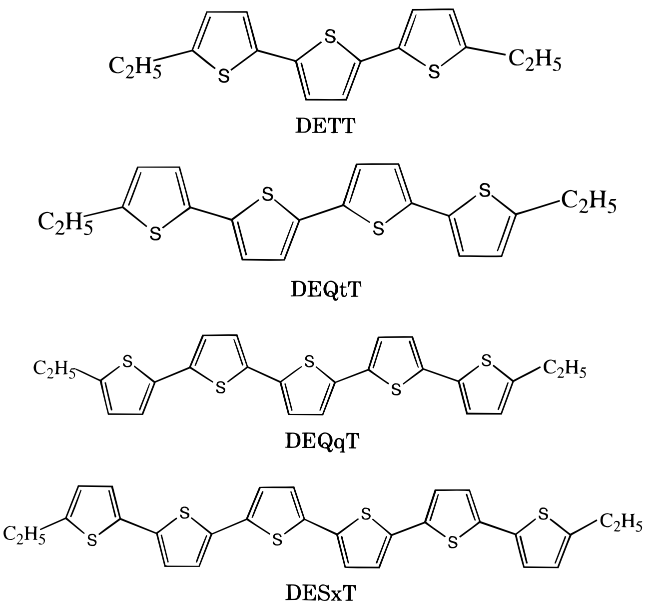


DETT

DEQtT

DEQqT

DESxT

Figure 1. Chemical structures of the series of α,α′-diethyl end-capped oligothiophenes. The nomenclature denotes DETT (α,α′-diethylterthiophene), DEQtT (α,α′-diethylquaterthiophene), DEQqT (α,α′-diethylquinquethiophene), and DESxT (α,α′-diethylsexithiophene).

Raman spectra were collected at room temperature for pure solids in sealed capillaries. We used a radiation excitation of 1064 nm from an Nd:YAG laser with the power adjusted to 100 mW. To increase the signal/noise ratio, 500 scans with a 2 cm^{-1} spectral resolution were added.

Ab initio calculations, at the restricted Hartree–Fock (RHF) level of theory, were carried out with the Gaussian 94 program[19] using SGI Origin 2000 and CRAY-YMP supercomputers. We used the 6-31G** basis set,[20] which includes a set of six second-order (d-type) Gaussian primitive functions for the description of each heavy atom and a single set of Gaussian p-polarization functions for the hydrogens.

The methyl end-capped oligothiophenes theoretically investigated contained 2–5 units. Geometry optimizations were performed on isolated entities. Because of the large cost of the calculations, only the all-anti planar conformations were treated throughout. Cartesian force constants were evaluated analitically within the same theoretical scheme used for the geometry optimization. We used the often-practiced adjustment of the theoretical force fields to experiments in which the frequencies are scaled down uniformly by a factor of 0.9, which has been recommended recently by Scott and Radom.[21] This approach is very attractive in large-scale studies because it avoids the fairly complex procedure of defining internal coordinates. The accuracy of the method is often enough to disentangle serious experimental misassignments. All quoted vibrational frequencies reported throughout the paper are thus the scaled values.

III. Results and Discussion

A. Molecular Structure and Selection Rules. No experimental X-ray or electron diffraction data are available for the α,α′-diethyloligothiophenes. Supposedly, as shown by the X-ray structures of some related compounds (such as the unsubstituted α-oligothiophenes[22] and the α,α′-dimethyl end-capped tetrathiophene[9]), it can be assumed that sulfur atoms are located in an all-anti configuration with respect to the long molecular axis and that the whole molecule retains a coplanar conformation of the aromatic units. With such a structure, the α,α′-diethyloligothiophenes with an odd number of rings belong to the C_{2v} symmetry point group, while those having an even number of rings belong to the C_{2h} symmetry point group. The corresponding normal modes distributions and optical selection rules are summarized in Tables 1 and 2, respectively. Probably, the thiophene rings at both ends of the oligomer chain display a sligtht bend relative to the inner rings least-squares plane (of about 3.5° in α,α′-dimethyl end-capped quaterthiophene).[9] Thus, the strict C_{2h} or C_{2v} molecular symmetries may be partially broken. However, in what follows, we will assume that the whole series of molecules displays internal symmetry in the solid state.

TABLE 1: Distribution of the Normal Modes in the Various Symmetry Species for the Oligomers with an Odd Number of Thiophene Rings

mode symmetry	optical activity	DETT	DEQqT
	In-Plane Modes		
A_1	(IR, Raman pol.)	32	46
B_1	(IR, Raman dep.)	18	25
	Out-of-Plane Modes		
A_2	(Raman dep.)	18	25
B_2	(IR, Raman dep.)	31	45

TABLE 2: Distribution of the Normal Modes in the Various Symmetry Species for the Oligomers with an Even Number of Thiophene Rings

mode symmetry	optical activity	DEQtT	DESxT
	In-Plane Modes		
Ag	(Raman pol.)	39	53
Bu	(IR)	38	52
	Out-of-Plane Modes		
Au	(IR)	22	29
Bg	(Raman dep.)	21	28

Although the optical selection rules predict a very large population of bands in the infrared and Raman spectra, the actual spectra are fairly simple. This seeming discrepancy between theoretical predictions and experimental observations needs to be accounted for.

(i) Since the two end-caps at the α,α′-positions are relatively far apart, no mechanical coupling is expected to occur between their characteristic vibrational modes. Therefore, we expect that both in-plane and out-of-plane motions are degenerate and do not show any splitting in the spectra.

(ii) Local vibrational modes could also be scarcely coupled with their neighbors. Thus, the wavenumbers should be rather independent of the phase angle and approximately equal to that of an isolated oscillator. This is expected to be the case for the stretching and bending modes of the C–H bonds.

(iii) Some normal vibrations of the outermost rings may be topologically highly localized and fully decoupled from the motions of the inner rings so that their wavenumbers should coalesce.

(iv) As resonance is approached,[23] only a few Raman modes should gain appreciable intensity relative to the remaining Raman-active vibrations (i.e., those modes having a nonvanishing projection along the deformation coordinate describing the equilibrium geometry changes in going from the ground to the excited electronic state involved in resonant excitation). When the molecular symmetry does not change from the ground to the excited state, only totally symmetric vibrations are resonantly enhanced.

B. Infrared Spectra. The FT-IR spectra of the α,α′-diethyloligothiophenes are shown in Figures 2 and 3; while Table 3 summarizes the wavenumbers and relative intensities measured in the IR spectra, together with their tentative full assignments.

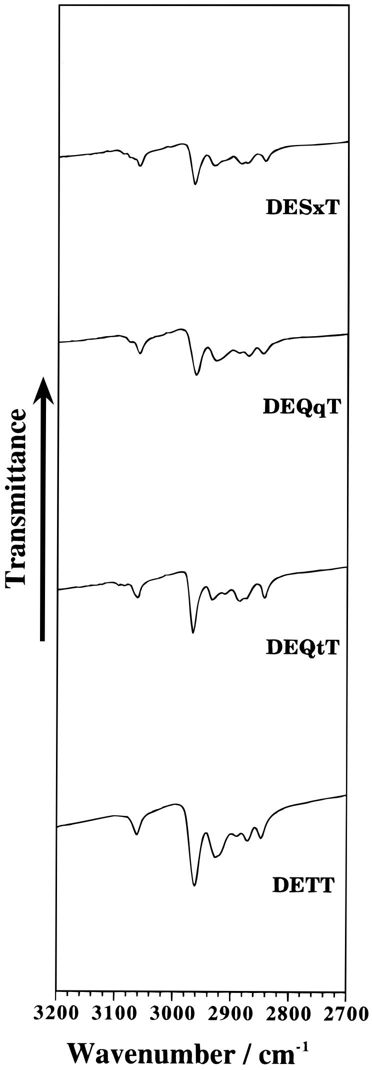


Figure 2. FT-IR spectra over probe energies of 3200−2700 cm^{-1} of neutral α,α′-diethyloligothiophenes.

From the observation of the spectra, there are good reasons to think that the oligomers certainly have a nearly planar conformation in the solid state. Evidence for twisted structures can only be derived from the IR/Raman spectra when the torsion is large.[24]

In the high-energy region, all the oligomers show characteristic bands about 3080−3060 cm^{-1}, assignable to the aromatic ν(C−H) stretchings, and five well resolved peaks below 3000 cm^{-1}, corresponding to the aliphatic ν(C−H) stretching modes. The intensities of the bands due to the aromatic ν(C−H) modes monotonically increase with respect to the aliphatic ones as the number of oscillators augments.

The single and broad absorption at 3061 (DETT), 3062 (DEQtT), 3059 (DEQqT), and 3060 cm^{-1} (DESxT) is due to the stretchings of the C−H bonds attached at the β-positions of the inner rings. The longer oligomers of the series show different multiplets at the high-energy side of this band, which are assignable to ν(C$_\beta$−H) vibrations with different phases and mostly localized on the outermost rings.

Five minor absorptions are still observable in this energy range. Among them, the bands measured around 2960 and 2930 cm^{-1} have been assigned to the antisymmetric stretchings of the two methyl groups, ν_a(CH$_3$). The corresponding symmetric mode, ν_s(CH$_3$), has been attributed to the absorption at 2915 cm^{-1}. We also believe that the peaks at 2885 and 2845 cm^{-1} arise from the antisymmetric and symmetric stretching modes of the methylene groups, ν_a(CH$_2$) and ν_s(CH$_2$), respectively. Finally, the band around 2870 cm^{-1} must be assigned to the g-type first overtone of the antisymmetric in-plane bendings of the methyl groups.[25]

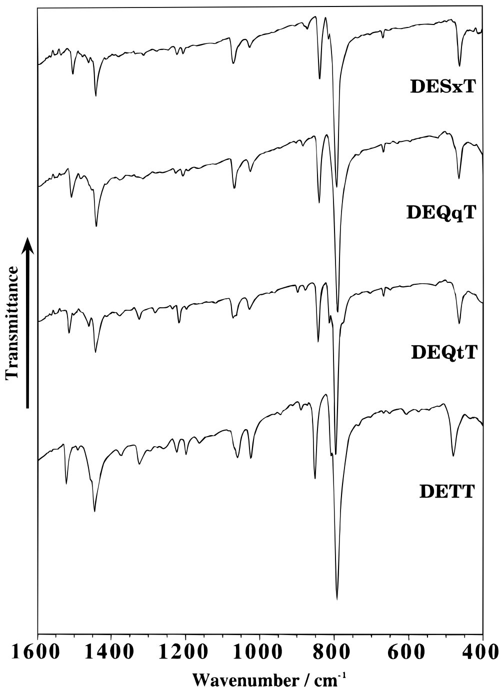


Figure 3. FT-IR spectra over probe energies of 1600−400 cm^{-1} of neutral α,α′-diethyloligothiophenes.

The 1550−1350 cm^{-1} region is overwhelmingly dominated by two sharp bands at about 1525−1500 and 1445 cm^{-1}. These infrared absorptions have been assigned to the antisymmetric and the symmetric stretching modes of the aromatic C=C bonds, ν_a(C=C) and ν_s(C=C), respectively.[12,13,17] The wavenumbers measured for the ν_a(C=C) mode are as follows: 1521 (DETT), 1514 (DEQtT), 1508 (DEQqT), and 1504 cm^{-1} (DESxT). Thus, we observe that this normal mode largely downshifts as the chain length increases. The chain length dispersion for the ν_s(C=C) mode is however much more modest: 1446 (DETT), 1443 (DEQtT), 1441 (DEQqT), and 1441 cm^{-1} (DESxT). We have also identified in this energy region a few weak absorptions, assignable to ν_s(C=C) modes with different phases, at the following positions: 1490 and 1456 cm^{-1} (DETT), 1489 and 1459 cm^{-1} (DEQtT), 1455 cm^{-1} (DEQqT), and 1458 cm^{-1} (DESxT).[13]

The infrared spectra of the shorter compounds display a weak peak around 1375 cm^{-1}, which becomes almost undetectable for the longer members of the series. This band probably arises from an antisymmetric ν(C−C)$_{\text{ring}}$ mode.[11−13,17,25] On the other hand, the absorptions measured at 1325 cm^{-1} (DETT), 1326 cm^{-1} (DEQtT), 1316 cm^{-1} (DEQqT), and 1314 cm^{-1} (DESxT), whose intensity largely decreases with increasing chain length, have been assigned to the wagging vibration of the CH$_2$ groups, ω(CH$_2$).

The bands appearing between 1280 and 1230 cm^{-1} have been assigned as antisymmetric in-plane δ_a(C−H) deformations.[11−13] In view of the spectra, we can conclude that these normal modes display a very weak infrared activity for all the oligomers studied. The corresponding symmetric δ_s(C−H) modes have been measured between 1070 and 1020 cm^{-1}.[11−13,17,25,26] The precise wavenumbers for each oligomer are as follows: 1069, 1061, and 1024 cm^{-1} (DETT); 1071, 1065, and 1028 cm^{-1}

TABLE 3: Wavenumbers Correlation between the Infrared Absorption Bands in the High- and Medium−Low-Energy Regions of Neutral α,α′-Diethyloligothiophenes in the Solid State

DETT	DEQtT	DEQqT	DESxT	description[a]
		High-Energy Region		
	3095		3087	
	3084		3076	$\nu(C\beta{-}H)$
	3067	3075	3069	
3061	3062	3059	3060	
2961	2966	2961	2964	$\nu_a(CH_3)$
2926	2933	2926	2930	$\nu_a(CH_3)$
2917	2911	2919	2910	$\nu_s(CH_3)$
2889	2887	2886	2884	$\nu_a(CH_2)$
2871	2875	2870	2874	overtone ($\delta_a CH_3$)
2848	2843	2846	2842	$\nu_s(CH_2)$
		Medium−Low-Energy Region		
1521	1514	1508	1504	$\nu_a(C{=}C)$
1490	1489			
1456	1459	1455	1458	
1446	1443	1441	1441	$\nu_s(C{=}C)$
	1376	1375	1375	$\nu_a(C{-}C)_{ring}$
	1363	1340	1337	$\nu_s(C{-}C)_{ring}$
1325	1326	1316	1314	$\omega(CH_2)$
1296				
1280	1283	1280	1275	
1261		1261		$\delta_a(C{-}H)$
1249	1236		1245	
1224	1218	1226	1222	
1199	1198	1207	1205	$\nu(C{-}C)_{inter-ring}$
		1193	1194	
1163	1164	1164	1165	
1069	1071	1069	1070	
1061	1065			$\delta_s(C{-}H)$
1024	1028	1025	1026	
889	898	903	905	
	878	884	871	$\nu(C{-}S)$
852	844	840	838	
808	813		814	
792	796	791	792	$\gamma(C{-}H)$
667	669	669	669	δ_{ring}
481	469	466	462	γ_{ring}

[a] a = antisymmetric; s = symmetric; ν = stretching; δ = in-plane deformation; γ = out-plane deformation; w = wagging.

(DEQtT); 1069 and 1025 cm^{-1} (DEQqT); 1070 and 1026 cm^{-1} (DESxT). Contrary to the $\delta_a(C{-}H)$ vibrations, the $\delta_s(C{-}H)$ modes display an intensity comparable to that of the $\nu_a(C{=}C)$ vibration.

The multiplets of bands at 1224, 1199, and 1163 cm^{-1} (DETT); 1218, 1198, and 1164 cm^{-1} (DEQtT); 1226, 1207, 1193 and 1164 cm^{-1} (DEQqT); 1222, 1205, 1194 (sh), and 1165 cm^{-1} (DESxT) are mainly due to inter-ring $\nu(C{-}C)$ stretchings with different phase angles.[11] Quite similar absorptions were observed in the series of neutral α,α′-dimethyloligothiophenes.[12,27]

The bands recorded at 889 and 852 cm^{-1} (DETT); 898, 878, and 844 cm^{-1} (DEQtT); 903, 884, and 840 cm^{-1} (DEQqT); and 905, 871, and 838 cm^{-1} (DESxT) are thought to be due to the aromatic antisymmetric or symmetric $\nu(C{-}S)$ stretchings.[11−13,25,26] Among these modes, that located around 840 cm^{-1} is the strongest one along the whole series of compounds.

The out-of-plane $\gamma(C{-}H)$ bending vibrations, the wavenumbers of which are characteristic of the substitution pattern,[26] appear in the 900−600 cm^{-1} region. We have easily identified the $\gamma(C{-}H)$ normal modes of the 2,5-disubstituted thiophene rings as the very strong peak near 795 cm^{-1}. The band is not however splitted into different components, thus indicating that the diethyl end-substitution of the oligothiophenes generates a loss of crystal packing and the disappearance of the factor group splitting previously observed for DMTT and DMQtT.[12,27]

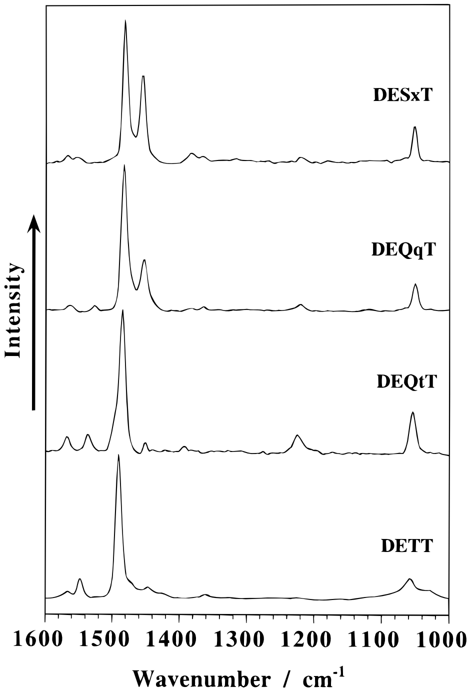


Figure 4. FT-Raman spectra of neutral α,α′-diethyloligothiophenes. The excitation wavelength was 1064 nm.

TABLE 4: Correlation between the Vibrational Raman Spectra of Neutral α,α′-Diethyloligothiophenes in the Solid State

DETT	DEQtT	DEQqT	DESxT	description[a]
1565	1566	1562		$\nu_a(C{=}C)$
1548	1536	1527		line A
1491	1485	1483	1481	line B
1447	1451	1453	1455	line C
	1412			
1360	1361			$\nu_s(C{-}C)_{ring}$
	1338			
1258	1266			
1225	1225			
	1180			
	1072			
1058	1055	1051	1052	line D

[a] a = antisymmetric; s = symmetric; ν = stretching.

The absorptions at 808 (DETT), 813 (DEQtT), and 814 cm^{-1} (DESxT) were not observed in the dimethyl end-capped series.[12,27] This band probably arises also from a $\gamma(C{-}H)$ vibration.

Finally, the weak peak around 668 cm^{-1} and the bands at 481 (DETT), 469 (DEQtT), 466 (DEQqT), and 462 cm^{-1} (DESxT) should be correlated with an in-plane ring deformation, δ_{ring}, and a ring folding mode, γ_{ring}, respectively.[11−13,17,25,26]

C. Raman Spectra. The FT-Raman spectra of the neutral forms of the various α,α′-diethyl end-capped oligothiophenes are shown in Figure 4. Table 4 summarizes the wavenumbers measured for the different Raman lines, together with their tentative assignments. The calculated Raman spectra of the model compounds are displayed in Figure 5, while the calculated eigenvectors for the main Raman-active normal modes (see below) of the pentamer are plotted in Figure 6.

A first observation is that the Raman spectra show very few lines, despite the large population of Raman-active normal modes predicted by the optical selection rules. This is a vibrational feature common to many other classes of conjugated organic polymers and oligomers that has been already abun-

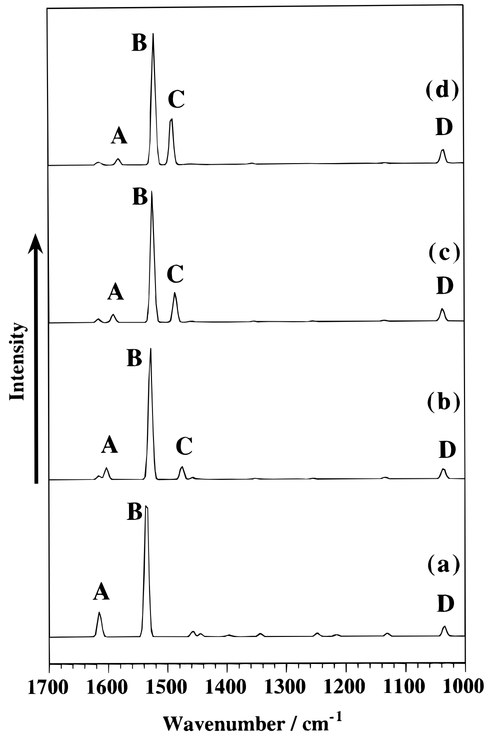


Figure 5. Theoretical Raman spectra of the α,α′-dimethyloligothiophenes in the neutral state at the RHF/6-31G** level: (a) dimer; (b) trimer; (c) tetramer; (d) pentamer.

dantly discussed in the literature.[11,12,18,28−30] Another spectral singularity of the π-conjugated systems is that, from the very few Raman lines experimentally observed, those assignable to the aromatic C═C stretchings are overwhelmingly intense.

Both vibrational features are rather evident in the experimental spectra of Figure 4. In addition, the chain length dependence of the Raman spectral pattern is nicely reproduced by the theoretical RHF/6-31G** calculations (compare Figures 4 and 5). This good agreement let us use the calculated atomic displacements as a guide for the qualitative assignment of the relevant Raman bands.

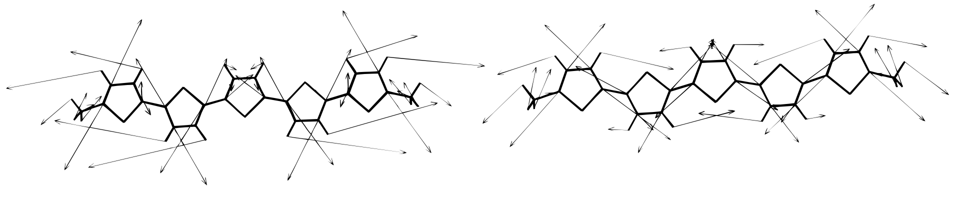
Two main theoretical models have been proposed to account for the seeming simplicity of the Raman spectral pattern of these materials, (i) the amplitude mode (AM) theory proposed by Horovitz et al.,[31] which turned out to be inapplicable to systems with complex structures, and (ii) the effective conjugation coordinate (ECC) theory developed by Zerbi et al.[32−35] The discussion throughout this section will be made following the theoretical foundations of the ECC model.

The Raman enhancement showed by these materials is associated with the existence of an electron−phonon (e/ph) coupling. This e/ph coupling is largest for a specific totally symmetric normal mode, usually termed as Я, which involves the collective stretchings and shrinkings of the alternating C═C and C−C bonds along the conjugated backbone of the molecule. Thus, this mode mimics the geometrical changes occurring in the system when an effective intramolecular delocalization of the π electrons takes place. However, the extent of the interactions between the succesive p_z orbitals, which is directly related to the effective π-delocalization length (ECL) of the molecule, is at first unknown. Theory indicates that molecular vibrations with large contributions by the Я coordinate show sizable wavenumber and intensity dispersions with variable ECL. Experiments carried out on many classes of well-defined oligomers have given further support to the theoretical predictions.[11,12,18,28−30] We refer the reader to the existing literature to get a deeper insight on these issues.

The comprehensive analysis of many homologous series of oligothiophenes[30] has shown that the Raman spectra of these materials are characterized by the appearance of four main bands (denoted as lines A, B, C, and D in Table 4) whose wavenumbers and intensities are functions of the chain length. The general behavior of these Raman lines and the precise data for the compounds studied in this work are as follows.

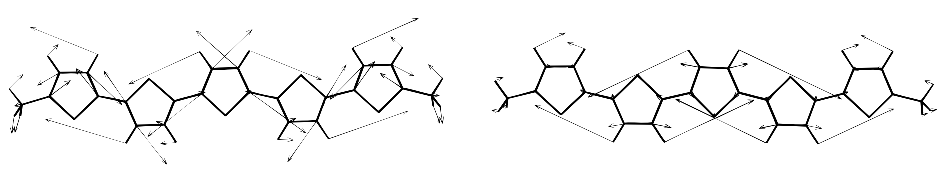
(i) Line A is generally weak and shows an unquestionably dispersion toward lower wavenumbers with increasing conjugation length. In addition, its intensity weakens and becomes almost unobservable for relative long chain lengths (i.e., for the hexamer). For the α,α′-diethyl end-capped oligothiophenes, this band disperses 21 cm^{-1} giving 1548 cm^{-1} (DETT), 1536 cm^{-1} (DEQtT), and 1527 cm^{-1} (DEQqT). The theoretical eigenvector indicates that line A arises from an in-phase antisymmetric ν(C═C) vibration that is mostly localized on the outer rings of the chain (see Figure 6).

(ii) Line B is always very strong and dominates the whole Raman spectrum. While it largely shifts downward in the oligopyrroles and oligofuranes, for the oligothiophenes it is



Line A (1582)

Line B (1522)



Line C (1492)

Line D (1036)

Figure 6. Schematic eigenvectors of the more relevant totally symmetric modes calculated for neutral α,α′-dimethylquinquethiophene at the RHF/6-31G** level (all the values are in cm^{-1}).

almost independent of the chain length and quickly meets saturation.[30] When the end α or β positions of the oligothiophene are substituted by an electronically inert group, the line experiences a sizable upshift. However, within each class of compounds it is almost invariably strong and only slightly shifted. In the case of our end-capped oligothiophenes, line B is measured at 1491 cm^{-1} (DETT), 1485 cm^{-1} (DEQtT), 1483 cm^{-1} (DEQqT), and 1481 cm^{-1} (DESxT), downshifting by 10 cm^{-1} from the trimer to the hexamer. We also observe that the intensity of line B, relative to lines C and D, readily decreases as the chain length grows longer.

As can be seen in Figure 6, the corresponding eigenvector demonstrates that the "bulk" rings effectively contribute to this normal mode, which should be described as a fully in-phase symmetric $\nu(C{=}C)$ vibration spreading over the whole oligomeric chain. The motions of the CC bonds are necessarily coupled with the in-plane bending of the C−H bonds, in which the H atoms recoil with a large displacement which opposes that of the C atoms. This normal vibration corresponds to the collective Я coordinate of the ECC Theory.[32−35]

(iii) Line C appears at the lower energy side of line B only for the classes of α or β end-capped oligothiophenes. The wavenumbers for the α-diethyl series are 1447 cm^{-1} (DETT), 1451 cm^{-1} (DEQtT), 1453 cm^{-1} (DEQqT), and 1455 cm^{-1} (DESxT). This line becomes stronger with the molecular size and upshifts by 8 cm^{-1} from the DETT to the DESxT. Thus, we find that lines B and C show a convergent trend as the chain length increases. The eigenvector indicates that this band should be described as a collective symmetric $\nu(C{=}C)$ vibration mostly localized on the "bulk" rings, but where, opposite to line B, the motions of the outest rings take place in out-of-phase with respect to the central unit.

(iv) Line D appears for all the oligothiophenes as a sharp band (sometimes as a doublet) of medium-strong intensity around 1050−1080 cm^{-1}. The wavenumbers for our diethyl end-capped series of oligothiophenes are the following: 1058 cm^{-1} (DETT); 1055 cm^{-1} (DEQtT); 1051 cm^{-1} (DEQqT); 1052 cm^{-1} (DESxT). The integrated intensity of these bands increases on going from the trimer to the hexamer.

In view of the calculated eigenvector, line D has to be assigned to the fully in-phase symmetric bending vibration of the C−H bonds attached to the different β-positions of the inner part of molecule. Along this normal mode, a slight recoiling of the C_β atoms effectively takes place. Thus, we must conclude that lines B and D derive directly from the dynamics associated to the Я coordinate.[32−35]

IV. Conclusions

We have investigated the vibrational properties of a series of medium-sized α,α′-diethyl end-capped oligothiophenes. The FT-IR and FT-Raman spectra of these compounds were studied in relation to their effective conjugation length in the neutral state. Our experimental study evidences that a considerable chain length dependent π-delocalization occurs in this series of model systems; large wavenumber dispersions with chain length (sometimes accompanied by noticeable intensity enhancements) are observed for some Raman and infrared-active normal modes, particularly at the high-energy side of the aromatic C═C stretching spectral region. With a great probability, the π-conjugation extends over several thiophene units and it has not yet reached saturation at the hexamer.

The two most intense Raman-active aromatic $\nu(C{=}C)$ vibrations (lines B and C) show a convergent trend. Furthermore, the line at higher energy readily yields its intensity to the second line as the chain length increases. Thus, the electron−phonon coupling along these two vibrations must be rather large. The theoretical calculations show that the atomic displacements for these two normal modes greatly resemble the molecular geometry changes taking place during the $\pi-\pi^*$ electronic transition.

In addition, we have proposed a tentative assignment of the main spectral features, which is based on molecular symmetry considerations, previous spectroscopic studies, and force field calculations. From our work, the following structural information can be inferred. (i) The intensity ratios of the "bulk" modes vs bands associated with end modes are apparently proportional to the number of oscillators, indicating the existence of a regular ordering along the whole series of oligomers. (ii) The similarity of the spectral patterns for all the compounds and the absence of infrared absorptions due to out-of-plane bendings of C−H attached to the α positions further confirms that the amount of misslinkings is negligible.

In conclusion, these α,α′-diethyloligothiophenes constitute a model series to thoroughly study the saturation with chain length of the nonlinear optical properties, together with the nature of the charge carriers in doped polythiophene. *Furthermore, the results of the present studies will contribute optimizing the electronic or optical device configurations when one intends to apply to those devices similar conjugated organic polymers and oligomers that are potentially useful for the relevant technologies.*

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