Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Polymer 47 (2006) 6692–6697
polymer
www.elsevier.com/locate/polymer

Theoretical investigation of the electronic and optical properties of oligothiophenes upon methyl, thiol, and thiomethyl substitutions

Francesca Costanzo [a,b,*], Domenica Tonelli [a], Giovanni Scalmani [c], Jérôme Cornil [b]

[a] Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy
[b] Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, 20 Place du Parc, 7000 Mons, Belgium
[c] Gaussian, Inc. 340 Quinnipiac Street, Building 40, Wallingford, CT 06492, USA

Received 29 April 2006; received in revised form 6 July 2006; accepted 10 July 2006

Abstract

The geometric, electronic, and optical properties of oligothiophenes of 2, 4, 6 and 8 units of head-to-head–tail-to-tail (HH–TT) regioselectivity and substituted by methyl, thiol, and thiomethyl groups have been characterized in their neutral and p-doped states with quantum-chemical calculations derived from semiempirical Hartree–Fock approaches and with the nonempirical valence effective Hamiltonian (VEH) method. Such calculations provide a good insight into the electronic properties measured for electropolymerized chains.

Keywords: Conducting polymers; Quantum-chemical calculations; Oligothiophenes

1. Introduction

In the last 20 years, considerable attention has been devoted to organic conducting polymers as a new class of electronic materials [1]. In part, this interest is based on the observation that materials with a wide range of electronic properties could be obtained through tailored synthesis of new polymers. Due to their large increase in electrical conductivity upon doping [2,3], conducting polymers are promising materials for use in electrochromic devices, sensors, smart-windows, artificial muscles, and photonic devices [1,4].

The electrical, optical, and mechanical properties of conjugated chains critically depend on the chemical structure of their building blocks; the reactivity of the monomer units is also an important factor governing the properties of the resulting polymer and is considerably influenced by the steric and electronic properties of the substituents [5,6]. The impact of steric effects on the structural properties of oligomers and polymers is generally well understood whereas the impact on the electronic properties is often more difficult to assess [7].

In this context, theoretical studies prove successful to allow a better understanding of the electropolymerization mechanisms and of the role played by various experimental parameters; calculations are also helpful to relate the variation of a given parameter to the changes expected in the experimental measurements. It is thus of interest to investigate the changes in the geometric, electronic, and optical properties of conjugated systems when going from the neutral to the oxidized states, and especially the way these properties are affected by various substitution patterns.

Polythiophene (PT) and substituted derivatives represent an important class of conducting polymers [1]. The synthesis of polythiophenes is generally achieved by electrochemical or chemical oxidation of suitable monomers [1]. These polymers are characterized by a high processability achieved via the introduction of substituents in the 3 position [8,9] (see Fig. 1). Among the various derivatives, alkyl-substituted polythiophenes are very attractive materials for the development of high-performance solution processible electronic polymers

---

* Corresponding author. Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy. Tel.: +39 051 2093710; fax: +39 051 2093690.
E-mail address: costanzo@ms.fci.unibo.it (F. Costanzo).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.07.016

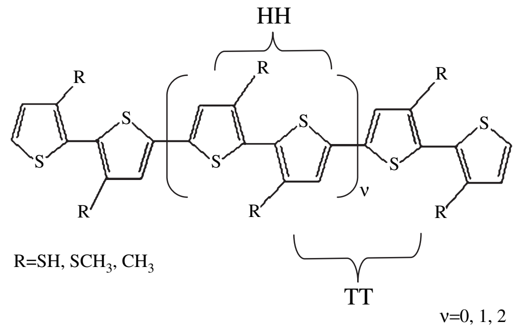


Fig. 1. Molecular structure of the oligothiophenes investigated in this work.

[10,11]. In polyalkylthiophenes, the regiochemistry control is an important factor to be considered since the nature of the coupling controls the structural and electronic properties of the chains. The substituted thiophene rings can be connected via a tail-to-tail (TT) or head-to-head (HH) coupling (see Fig. 1).

Hadziioannou and co-workers synthesized a number of alkylated polythiophenes and showed photoluminescence and electroluminescence color tuning through the variation of the length of the HT sequences between HH connections [12]. They reported blue shifts in absorption larger than 100 nm when increasing the steric hindrance in the polymer backbone. The energies of the absorption and emission maxima were found to scale linearly as a function of the inverse number of thiophene units ($1/n$) between two consecutive HH links. These results clearly demonstrate that the effective conjugation length is limited by the HH links along the polymer backbone. The presence of HH coupling in PTs induces an increase in the torsion angle between the thiophene rings due to steric effects and a loss of conjugation that leads to an increased bandgap (i.e., a blue shift in the absorption and emission spectra) and a reduced electrical conductivity. Regioregularity can thus be exploited as a tool to tune the luminescence properties of PT-based light-emitting diodes [13].

In electropolymerization, the stability of the radical cations generated upon monomer oxidation plays a crucial role in conditioning the degree of polymerization, and hence the length of the π-conjugated backbone. The polymerization can be hampered by: (i) the high reactivity of the radical cations which may undergo rapid reactions with solvent or electrolyte species to yield low molecular weight products rather than to polymerize in chain propagation reactions [14]; and (ii) the high stability of the reacted species which can diffuse away from the electrode to form oligomers in solution.

Unsubstituted thiophene and 3-alkylthiophene yield sufficiently reactive radical cations to form highly conjugated polymers; the synthesis should be further facilitated by the introduction of π-electron donating groups such as alkoxy and thioalkyl substituents that decrease the oxidation potential of the monomer units, thus increasing the energy of their highest occupied molecular orbital (HOMO) level. However, alkoxy and thioalkyl-substituted thiophenes cannot be easily electropolymerized and are usually obtained by chemical polymerization [15]. High-quality polymers were obtained only when 4-4′-dialkoxy-2-2′-bithiophene or 4-4′-dimethylthio-2-2′-bithiophene were used as starting monomers [16]. In a previous paper, we have reported the successful synthesis of poly[4-4′-bis(butylsulphanil)-2-2′-bithiophene] starting from a dimer unit both by chemical and electrochemical methods [17,18] (see the chemical structure in Fig. 1). In addition to the thermochromic, solvatochromic, and electrical properties [18], the electrochemical properties of the electrogenerated polymers were investigated in depth, with a particular attention paid to the charge–discharge processes and to p- and n-doped states via spectroelectrochemistry [17].

According to the generally accepted model, charges injected in conjugated polymers with a nondegenerate ground state relax under the form of self-localized polarons, which may couple to yield spinless bipolarons [19,20]. The terminology of polarons and bipolarons used in solid-state physics corresponds in chemical terms to radical cations and dications, respectively; they can be generated upon chemical [21,22], photochemical [23], and electrochemical oxidation/reduction [24] of the neutral molecules. The properties of long conjugated chains can be derived in the very first approximation from linear extrapolation to infinite chain length of the data obtained for the corresponding oligomers [25]. The formation of charged defects (polarons and bipolarons) in nondegenerate ground-state polymers deeply modifies their one-electron structure; electronic levels move inside the forbidden gap and induce the appearance of new subgap absorption features in the optical absorption spectra. Two subgap transitions are observed for isolated polarons while a single peak prevails in the presence of isolated bipolarons [26].

As a follow-up of the electrochemical study previously performed [17], the present work aims at investigating at the theoretical level the modifications upon p-doping in the geometric and optical properties of oligothiophenes built by repeating from 2 to 4 bithiophene units in an HH configuration (see Fig. 1). The impact of substitution by thiol and thiomethyl groups has been also investigated in comparison to methyl substituents.

2. Theoretical methodology

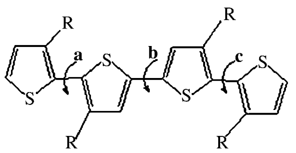
The geometries of neutral and charged oligomers containing 4, 6, and 8 rings have been optimized with the semiempirical Hartree–Fock Austin Model 1 (AM1) method [27], which is parameterized to reproduce the geometry and heat of formation of organic molecules in their ground state. The AM1 approach has also been shown to provide a good description of the torsional potential energy curve in bithiophene compared to that obtained with sophisticated *ab initio* calculations [28,29]. The geometry optimizations are performed on isolated molecules, thus neglecting the effect of counter-ions for charged oligomers (both singly and doubly oxidized molecules). The restricted open shell Hartree–Fock (ROHF) formalism has been adopted in the case of singly charged oligomers, as in earlier works [30,31]. The calculations have been carried out on oligothiophenes containing 4, 6, and 8 rings (denoted as 4T, 6T, and 8T in the following) substituted by SH, SCH_3, and CH_3 groups with an alternated HH and TT coupling, as shown in Fig. 1. In all calculations, the substituents are located in the same plane as the thiophene rings, as expected from packing effects, with the hydrogen pointing towards the ring (see Fig. 1).

The transition energies and associated oscillator strengths have been calculated for the neutral and oxidized compounds by means of the valence effective Hamiltonian method (VEH) [32,33], as reported in Tables 3–5, which was shown to provide values in good agreement with the experimental data in the case of the α-sexithienyl molecule [26]. The VEH technique does not deal explicitly with electron correlation effects and is parameterized to reproduce the energies of the occupied levels provided by *ab initio* calculations with molecular orbitals expanded in a double ζ basis set.

3. Geometric structure

We report in Tables 1 and 2 the torsion angles between adjacent rings, as calculated at the AM1 level, in 4T and 6T in the neutral and both singly and doubly oxidized states. Similar trends are observed for 8T. The results indicate that the neutral unsubstituted oligomers are characterized by torsion angles on the order of 25°, in agreement with *ab initio* calculations [29,31]. The substitution by thiol and thioalkyl substituents leads to a planarization of the backbone between the rings involved in the head-to-head coupling, in full consistency with the *ab initio* calculations performed on SCH_3-substituted oligothiophenes [15,34]. In contrast, large torsion angles are calculated between the thiophene units upon methyl substitution due to the large steric hindrance induced by the substituents. Our results are different from those reported by Dos Santos et al. who have reported an optimized twist angle of 90° for the head-to-head coupling at the AM1 level [35]. The structure reported for the corresponding 4T oligomer substituted by CH_3 groups in CH_3Cl solution is actually characterized by a *cis–trans–cis* conformation, with a torsion between the two central rings on the order of 40°, in agreement with our calculated values [36]. We stress that packing effects tend to make the conjugated backbone more planar, as revealed by the X-ray structure of tetrathiophene substituted by methyl groups which is characterized by a quasi-planar conformation, with slight torsions of the terminal rings [36].

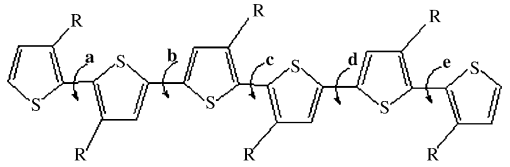
Table 1
Torsion angles in the oligothiophene containing four rings with different substituents in the neutral and doped states



Substituent	R = H	R = SH	R = SCH_3	R = CH_3	Torsion angle
4T	154.15	179.78	179.75	66.00	*a*
	156.15	150.27	149.8	154.00	*b*
	153.82	179.92	179.78	66.00	*c*
4T + 1	179.99	179.87	179.00	58.91	*a*
	180.00	180.00	175.00	178.00	*b*
	180.00	179.92	179.00	56.80	*c*
4T + 2	179.98	176.34	179.00	38.90	*a*
	179.99	179.96	180.00	177.02	*b*
	179.98	176.34	179.00	38.00	*c*

All calculations are performed at the AM1 level. A torsion of 180° implies that the two adjacent rings are coplanar and point in opposite directions.

Table 2
Torsion angles in the oligothiophene containing six rings with different substituents in the neutral and doped states



Substituent	R = H	R = SH	R = SCH_3	R = CH_3	Torsion angle
6T	152.98	180.00	179.00	65.84	*a*
	154.05	147.22	149.00	154.84	*b*
	154.06	179.68	179.00	66.13	*c*
	154.15	146.97	148.00	156.23	*d*
	153.11	179.88	179.00	66.00	*e*
6T + 1	179.96	179.89	179.00	65.74	*a*
	180.00	179.91	173.00	177.19	*b*
	179.99	179.92	179.00	30.75	*c*
	179.99	179.67	172.00	177.87	*d*
	179.88	179.90	179.00	65.68	*e*
6T + 2	180.00	179.99	177.00	179.00	*a*
	180.00	179.97	179.00	178.98	*b*
	180.00	179.87	179.00	15.00	*c*
	179.99	179.89	179.00	178.00	*d*
	179.99	179.78	177.00	179.00	*e*

All calculations are performed at the AM1 level. A torsion of 180° implies that the two adjacent rings are coplanar and point in opposite directions.

The AM1-optimized geometry of the unsubstituted oligomers in the singly charged state, assumed here to be fully planar, shows that the polaron is mostly located at the center of the molecule [26,37]. The semi-quinoid geometry induced upon doping mostly affects the four central rings [38,17] and is not affected by an increase in the chain length. The largest change in the C–C bond length (Δr) when going from the neutral to the singly charged state is ±0.04 Å, as illustrated in Fig. 2 for 8T. We report in the same figure the charge distribution per site (defined as a carbon atom plus the attached hydrogen atom if present) in the singly charged eight-ring oligomer, as calculated with a Mulliken population analysis. The results show that the carbon atoms of the two central rings present a marked decrease in electron-density upon doping, which is consistent with the observation that most of the positive charge is localized in the central portion of the oligomer. The withdrawal of a second electron to form bipolarons gives rise to a geometry relaxation process which induces a strong quinoid character and a strong charge depletion in the central part of the chain regardless of the chain length. On the basis of the AM1 results, we estimate that the charge distribution and

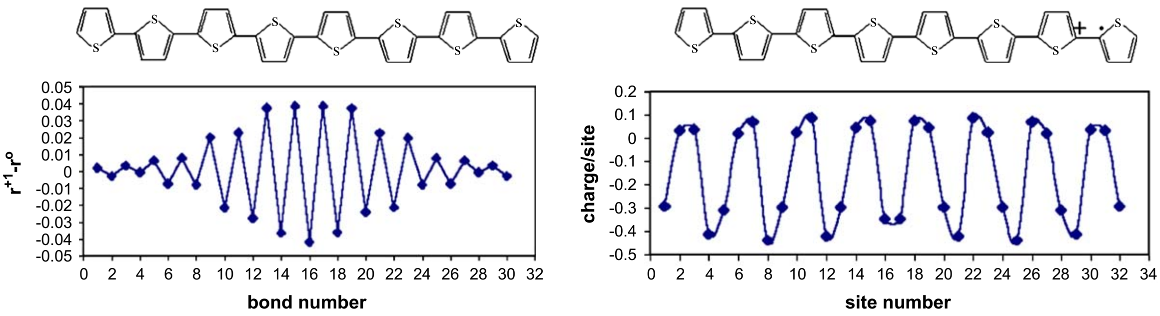


Fig. 2. Left: differences in the AM1-optimized C–C bond lengths (in Å) of 8T (a neutral molecule is reported on the top of the graphic) going from the neutral to the singly charged state. Right: charge per each site (C–H atoms) in the singly charged 8T (a singly charged molecule is reported on the top of the graphic), as obtained from a Mulliken population analysis. Charges on the sulfur atoms are not reported in the figure.

geometric distortions associated to the polaron (bipolaron) mostly spread over three (four) thiophene rings, with the two central rings being the most affected (Δr value on the order of ±0.08 Å, see Fig. 3).

When no constraints of planarity are imposed, the AM1-optimized geometry of the oxidized oligomers shows a tendency towards the planarization of the chain segments affected by the lattice distortions; however, we note that the large torsion angles (>50°) prevailing in the neutral oligomers substituted by CH_3 groups are progressively attenuated upon single and double oxidation, without reaching the fully planar conformation. The extent of the charged defect in the substituted derivatives is found to be slightly reduced with respect to that in the corresponding unsubstituted oligomers.

4. Electronic structure and optical properties

4.1. Neutral molecules

We focus here on the one-electron structure obtained at VEH level in order to analyze how the energies of the HOMO and LUMO levels of 4T are affected by the different substitution patterns; this is illustrated in Fig. 4 where we have also reported the VEH-calculated lowest transition energy of the oligomers associated to the HOMO–LUMO transition. The results show that the breaking of the conjugation induced upon introducing CH_3 substituents leads to a significant blue shift of the lowest optical transition; in the other cases (R = SCH_3, SH), a red shift prevails due to the joint effects of the charge transfer between the substituents and the thiophene rings and of the concomitant planarization of the backbone. The SCH_3 substitutions give rise to the lowest optical transition and oxidation potential (when estimated as the opposite energy of the HOMO level within Koopmans' approximation) among the various derivatives. A linear relationship is observed between the VEH-calculated optical transition energies for the unsubstituted and substituted chains (see Table 3 for unsubstituted and SH-substituted oligomers) and the inverse chain size, as found for many other conjugated organic systems [37]; this is explained by the delocalized nature of the HOMO and LUMO wavefunctions.

The VEH-calculated lowest transition energy is estimated to be 1.77 eV for the SH-substituted octathiophene, which is expected to be a good representative of the corresponding polymer. This has to be compared to the experimental value of 2.38 eV reported for the corresponding polymer in acetonitrile [17]. The lowest band maximum is red-shifted with respect to that typically measured for unsubstituted polythiophene chains in solution (2.87 eV) [39], in agreement with the trends provided by the VEH calculations. This evolution is primarily driven by the planarization of the chain upon thiol or thioalkyl substitution. This demonstrates that the study of oligomers is a good strategy to shed light into the properties of the parent polymers. In contrast, the CH_3 substituent efficiently breaks the conjugation. This behaviour could be utilized for tuning optical properties, as achieved by

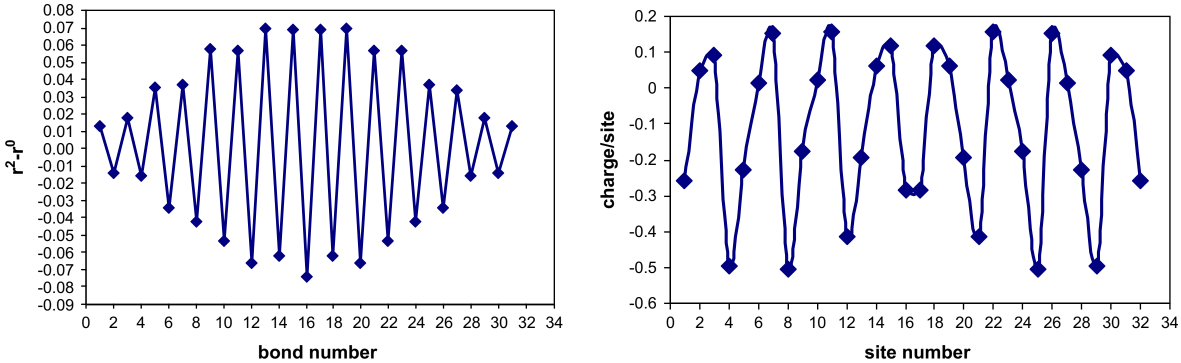
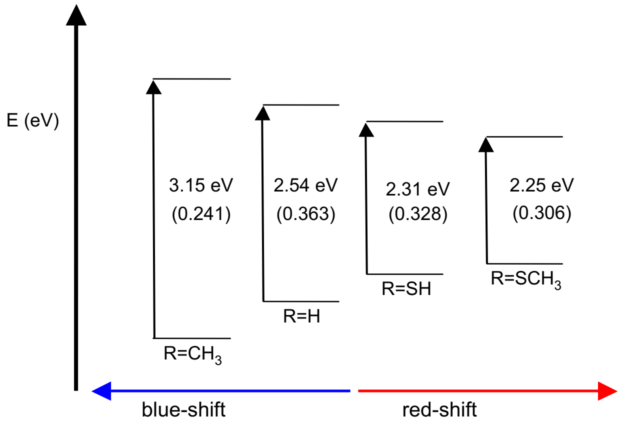


Fig. 3. Left: differences in the AM1-optimized C–C bond lengths (in Å) of 8T going from the neutral to the doubly charged state. Right: charge per each site (C–H atoms) in the doubly charged 8T, as obtained from a Mulliken population analysis. Charges on the sulfur atoms are not reported in the figure.



substituent	E_{HOMO}(eV)	E_{LUMO}(eV)
R=CH_3	–7.67	–4.52
R=H	–7.49	–4.95
R=SH	–7.37	–5.06
R=SCH_3	–7.36	–5.11

Fig. 4. Evolution of the electronic structure of 4T upon substitution and relative oscillator strength (in parenthesis), as obtained at the VEH level. The corresponding energy of the HOMO and LUMO levels is collected in the table above.

Hadziioannou and co-workers [12]. In their case, they have studied structures in which the conjugation of the polymer main chain is regularly interrupted to generate blue emitting compounds.

4.2. Singly oxidized molecules

We primarily focus hereafter for the charged systems only on the unsubstituted and thiol-substituted oligomers. The VEH calculations indicate that the formation of polarons leads to the appearance of two subgap absorption features. The lowest energy absorption feature corresponds to a transition between the HOMO level and the lower polaronic level, while the second absorption originates from an excitation between the two polaron levels within the gap (POL1–POL2). The transition energies calculated for the unsubstituted and thiol-substituted oligomers are reported in Table 4. A linear relationship is observed between the calculated transition energies and the inverse chain size. According to the calculated oscillator strengths, the most intense transition occurs between HOMO and POL1; note, however, that the relative intensities might be changed when dealing with quantum-chemical approaches going beyond the one-electron picture. The calculations also show that all the substitution patterns lead to a substantial decrease in the intensity of the two polaronic transitions. Interestingly, the lowest polaronic transition calculated at 0.62 eV for the SH-substituted 8T oligomer closely matches with the absorption peak observed at 0.64 eV in the experimental absorption spectrum of the oxidized polymer [17]. The second subgap feature predicted at 1.24 eV by the VEH results cannot be unambiguously distinguished in the experimental spectrum, thus suggesting that this second feature has not a strong one-electron character. This is consistent with the trends calculated with configuration interaction (CI) calculations in phenylene-vinylene oligomers [40].

Table 3
VEH-calculated transition energy and oscillator strength for the lowest optical transition of neutral oligothiophenes without substituents and substituted by thiol groups

Number of rings	Substituent	Transition energy (eV)	Oscillator strength
4	R = H	2.53	0.36
	R = SH	2.30	0.33
6	R = H	2.22	0.47
	R = SH	1.91	0.41
8	R = H	2.02	0.56
	R = SH	1.77	0.49

Table 4
VEH-calculated transition energy and oscillator strength for the lowest two optical transitions of singly charged oligothiophenes without substituents and substituted by thiol groups

Number of rings	Substituent	Transition energy (eV)	Oscillator strength	Transition energy (eV)	Oscillator strength
4	R = H	1.39	0.49	1.82	0.42
	R = SH	1.11	0.27	1.72	0.36
6	R = H	0.93	0.67	1.48	0.59
	R = SH	0.77	0.57	1.40	0.51
8	R = H	0.71	0.81	1.31	0.72
	R = SH	0.62	0.72	1.24	0.64

The third column corresponds to a transition between the HOMO level and the lower polaronic level, while the fifth column corresponds to the second absorption that originates from an excitation between the two polaron levels within the gap.

The transition described at the one-electron level by an excitation between the lower polaronic level and the LUMO level (or between the HOMO level and the upper polaronic level) has often been considered to provide a third subgap feature in the absorption spectra [30]. However, this transition has a very low intensity due to the selection rules imposed by the C_{2h} or quasi-C_{2h} symmetry of the chain segments supporting the charged defect [38]. We emphasize that the intensity of the absorption originating from the HOMO → POL2 or POL1 → LUMO transitions would remain negligible if the symmetry is slightly lowered, for instance by small torsions leading to a departure of planarity.

4.3. Doubly oxidized molecules

The generation of bipolarons in oligothiophenes generates the appearance of a single subgap absorption feature that is red-shifted with increasing chain length; this also induces a complete bleaching of the neutral $\pi-\pi^*$ transition, as observed in the experimental spectrum of the doped polymer [17]. The new absorption peak results, at the one-electron level, from an excitation between the HOMO and the lower bipolaronic level (BIP1). As emphasized in earlier works [29], the transition between the HOMO and the upper bipolaronic level is optically forbidden due to selection rules. On the basis of these calculations, we assign the absorption band observed

Table 5
VEH-calculated transition energy and oscillator strength for the lowest two optical transitions of doubly charged oligothiophenes without substituents and substituted by thiol groups

Number of rings	Substituent	Transition energy (eV)	Oscillator strength
4	$R = H$	1.60	0.52
	$R = SH$	1.33	0.34
6	$R = H$	1.13	0.73
	$R = SH$	0.95	0.64
8	$R = H$	0.90	0.93
	$R = SH$	0.78	0.84

at 0.85 eV in the UV–vis–near IR spectrum of the thioalkyl-substituted polymer to the lowest bipolaronic transition estimated at 0.78 by the VEH calculations on the SH-substituted eight-ring oligomer (Table 5). The methyl substitution (data not shown) leads to larger optical transitions than those calculated for the corresponding SCH_3-substituted oligomers (1.46 eV for CH_3-substituted versus 1.14 eV for SCH_3-substituted chains); this can be attributed to the lack of planarity of the chain segment supporting the bipolaron in the CH_3-substituted chains, thereby implying a stronger confinement of the bipolaron that translates into a larger H → BIP1 transition energy.

5. Conclusions

We have investigated by means of quantum-chemical calculations the influence of thiol, thioalkyl, and alkyl ($R = SH$, SCH_3, and CH_3, respectively) groups on the geometric, electronic, and optical properties of oligothiophenes. The SH and SCH_3 substitutions lead to a red shift of the lowest optical transition with respect to the corresponding unsubstituted oligomers. In contrast, alkyl substitutions increase the bandgap of the chains as a result of conjugation breaking driven by steric effects. The role of the conformation effects on the calculated optical properties is attenuated in oxidized chains due to the fact that the relaxation processes tend to planarize the conjugated backbone. The experimental absorption features observed in the spectra of neutral and electrochemically oxidized thioalkyl-substituted polymer chains match very well with the transition energies calculated at the VEH level; in particular, the two dominant subgap peaks observed at 0.64 eV and 0.85 eV have been assigned to the optical signature of the intense polaronic transition and the bipolaronic transition, respectively.

Acknowledgements

The work in Mons was partly supported by the Belgian Federal Government "Interuniversity Attraction Pole in Supramolecular Chemistry and Catalysis", and the Belgian National Fund for Scientific Research (FNRS/FRFC). J.C. is an FNRS Research Associate.

References

[1] Roncali J. Chem Rev 1992;92:711.

[2] Schotheim TA, editor. Handbook of conducting polymers. New York: Dekker M; 1998; Nalwa HS, editor. Organic conductive molecules and polymers. Chichester: Wiley; 1997; Brédas JL, Silbey R. Conjugated polymeric materials: opportunities in electronics, optoelectronics, and molecular electronics. London: Kluwer Academic Publishers; 1989.

[3] Ueno H, Nogami K, Yoshino Y. Phys Rev B 1987;36:8142.

[4] Kofmehl G, Schopf G. Adv Polym Sci 1997;129:1.

[5] Tourillon G, Garnier F. J Electroanal Chem 1984;161:51.

[6] Büchner ML, Garreau R, Hoa HA, Roncali AG. J Electroanal Chem 1990;281:293.

[7] Heinze J. Top Curr Chem 1990;152:1.

[8] Winokur MJ, Chunwachirasiri W. J Polym Sci 2003;41:832.

[9] Sato M, Tanaka S, Kaeriyama K. J Chem Soc Chem Commun 1986;11: 873.

[10] Hotta S. In: Nalwa HS, editor. Handbook of organic conductive molecules and polymers, vol. 2. New York: J. Wiley and Sons Ltd; 1997. p. 309.

[11] McCullough RD. Adv Mater 1998;10:93.

[12] Malliaras GG, Herrems JK, Wildeman J, Wierings RH, Lampours SS, Hadziioannou G. Adv Mater 1993;5:721; Gill RE, Malliaras GG, Wildeman J, Hadziioannou G. Adv Mater 1994;6:132; Hilberer A, Brouwer H-J, van der Scheer BJ, Wildeman J, Hadziioannou G. Macromolecules 1995;28:4525.

[13] Xu B, Holdcroft S. Macromolecules 1993;34:2522.

[14] Waltman RJ, Bargon J. Can J Chem 1986;64:76.

[15] Smie A, Synowczyk A, Heinze J, Alle R, Tschuncky P, Götz G, et al. J Electroanal Chem 1998;452:87.

[16] Tschunky P, Heinze J. Synth Met 1993;55:1603; Baüerle P, Götz G, Synowczyk A, Heinze J. Liebigs Ann Chem; 1996;279.

[17] Ballarin B, Costanzo F, Mori F, Mucci A, Pigani L, Schenetti L, et al. Electrochim Acta 2001;46:881.

[18] Iarossi D, Mucci A, Goldoni F, Affronte M, Nava F, Schenetti L, et al. Macromolecules 1999;32:1390.

[19] Street GB, Brédas JL. Acc Chem Res 1985;18:309.

[20] Heeger AJ, Kivelson S, Schrieffer JR, Su WP. Rev Mod Phys 1988;60: 781.

[21] (a) Fichou D, Horowitz G, Garnier F. Synth Met 1990;39:125;
(b) Fichou D, Horowitz G, Xu B, Garnier F. Synth Met 1990;39:243.

[22] (a) Guay J, Diaz A, Wu R, Tour JM, Dao LH. Chem Mater 1992;4:254;
(b) Guay J, Kasai P, Diaz A, Wu R, Tour JM, Dao LH. Chem Mater 1992; 4:1097.

[23] Zinger B, Mann KR, Hill MG, Miller LL. Chem Mater 1992;4:1113.

[24] Hapiot P, Audebert P, Monnier K, Pernaut JM, Garcia P. Chem Mater 1994;6:1549.

[25] Nessakh B, Horowitz G, Garnier F, Deloffre F, Srivastava P, Yassar AJ. Electroanal Chem 1995;399:97.

[26] Cornil J, Brédas JL. Adv Mater 1995;7:295.

[27] Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP. J Am Chem Soc 1985; 107:3902.

[28] Quattrocchi C, Lazzaroni R, Brédas JL. Chem Phys Lett 1993;208:120.

[29] Viruela PM, Viruela R, Orti E, Brédas JL. J Am Chem Soc 1997;119: 1360.

[30] Cornil J, Beljonne D, Brédas JL. J Chem Phys 1995;103:842.

[31] Zojer E, Cornil J, Leising G, Brédas JL. Phys Rev B 1999;59:7957.

[32] Brédas JL, Chance RR, Silbey R, Nicolas G, Durand P. J Chem Phys 1982;77:371.

[33] Brédas JL, Chance RR, Silbey R, Nicolas G, Durand P. J Chem Phys 1981;75:255.

[34] Barone V, Lelj F, Russo N, Toscano M. J Chem Soc Perkin Trans II 1986; 6:907.

[35] Giovanni Scalmani. Ph.D Thesis; 1999.

[36] dos Santos DA, Galvão DS, Laks B, dos Santos MC. Chem Phys Lett 1991;184:579.

[37] Brédas JL, Beljonne D, Shuai Z, Toussaint JM. Synth Met 1991;43:3743.

[38] Heinze J, Bilger R, Meerholz K. Ber Bunsenges Phys Chem 1988;92: 1266.