Magnetic and Conductive Properties of Quinoidal Oligothiophenes

G. Zotti,* S. Zecchin, and B. Vercelli

Istituto CNR per l’ Energetica e le Interfasi, c/o Stati Uniti 4, 35127 Padova, Italy

A. Berlin

Istituto CNR di Scienze e Tecnologie Molecolari, via C. Golgi 19, 20133 Milano, Italy

J. Casado, V. Hernández, R. P. Ortiz, and J. T. López Navarrete

Departamento de Química Física, Universidad de Málaga, 29071 Málaga, Spain

E. Ortí, P. M. Viruela, and B. Milián

Institut de Ciència Molecular, Universitat de València, Doctor Moliner 50, Burjassot 46100, Spain

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The magnetic and conductive properties of a series of quinoidal oligothiophenes, that is, bis(dicyanomethylene)oligothiophenes (TrCN4, \( n = 2 \rightarrow 4 \)), have been investigated in the solid state and (for magnetic analysis) in solution, and the results have been compared with those from density functional theory (DFT) calculations. Solution electron spin resonance (ESR) spectra of radical cations and anions are characterized by hyperfine structures due to coupling with nitrogen and thiophene hydrogen atoms. Neutral solutions are ESR active, indicating a significant presence of diradical species with no hyperfine structure. ESR spectra of powder samples at room temperature give a concentration of radical species up to 1 mol % (T3CN4), that is, 0.5% of the compound exists in a diradical state. The percentage decreases dramatically from T3CN4 to T2CN4, as a result of the decreased number of aromatic rings. The diradical concentration increases with temperature according to activation energies which are higher for the shorter members and in very good agreement with DFT calculations. Tetrahexyl-substituted T4CN4 is redox conducting at the neutral-polaron mixed oxidation level with a maximum conductivity of 0.03 S cm\(^{-1}\), about two orders of magnitude higher in comparison with an aromatic tetrahexyl-substituted octathiophene.

1. Introduction

Oligothiophenes have attracted considerable attention over the past few years for their use as the active component in many organic device technologies, particularly in organic field effect transistors (OFETs). Quinoid oligothiophenes, such as bis(dicyanomethylene)oligothiophenes (TrCN4), display a smaller highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap than usual for aromatic oligothiophenes, thus making ambipolar or dual (both p- and n-type) charge transport more likely because smaller gate voltages are required to populate the HOMO and LUMO levels (valence and conduction bands) with charge carriers.\(^2\)–\(^4\)

A recent paper\(^5\) has summarized results on different ter- and tetrathiophenes of the TrCN4 type. Electronic properties, such as the HOMO–LUMO optical band gap, are correlated with the crystal packing parameter. It was previously reported\(^6\) that vapor- and solution-deposited films function as n-channel semiconductors with improved n-channel mobilities or ambipolar (n-channel and p-channel depending on the sign of the gate bias) behavior. The unique electronic structure of the quinoid thiophene molecules allows them to function simultaneously as donors and acceptors.

Beside the conductive properties, this class of organic semiconductors may display novel magnetic properties. In fact their quinoid structure may allow the existence of diradicals by the stabilization of the relevant aromatic structure.\(^6\) However, no magnetic investigation was performed on such compounds. Only very recently\(^7\) the synthesis and characterization of a series of substituted TnCN4 (\( n = 1 \rightarrow 6 \)) soluble oligomers have been evidenced for \( n = 5 \) and 6 unpaired-electron species in solution, identified as diradi-

\(^{*}\) To whom correspondence should be addressed: tel. (39)049-829-5868, fax (39)049-829-5853, e-mail g.zotti@ieni.cnr.it.


(7) Magnetic and Conductive Properties of Quinoidal Oligothiophenes
Chart 1

2.1. Chemicals and Reagents. Acetonitrile was reagent grade (Uvasol, Merck) with a water content < 0.01%. TCNQ (98% from Fluka) was recrystallized from acetonitrile. The supporting electrolyte tetrabutylammonium perchlorate (Bu4NClO4) and all other chemicals were reagent grade and used as received.

2.2. Apparatus and Procedure. Experiments were performed at room temperature under nitrogen in three electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs saturated calomel electrode). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry (CV) was a platinum minidisk electrode (0.003 cm2). For electronic spectroscopy, a 0.8 x 2.5 cm indium tin oxide sheet (ca. 20 Ω/square resistance, from Balzers, Liechtenstein) was used.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer.

Electron spin resonance (ESR) spectra were taken on a Bruker ER 100D following the procedure previously described. Absolute spin calibration was performed with VOSO4·5H2O or 2,2-diphenyl-1-picrylhydrazyl (DPPH) crystals, g-value calibration with thin films of DPPH (g = 2.0036). Temperatures in the range 100−350 K were obtained with a Bruker ER 4111 VT variable temperature unit.

The apparatus and procedures used for the in situ conductivity experiments were previously described in detail. The electrode for conductivity measurements was a microband array platinum electrode (5 μm bandwidth, 100 nm thick) with interband spacing of 5 μm. The deposit was thick enough to ensure minimum resistance, under which condition the conductivity is given by \( \sigma = k(R - R_0) \), where \( R \) is the measured resistance, \( R_0 \) is the lead resistance, and \( k \) is the cell constant.

2.3. Theoretical Calculations. DFT calculations were performed using the B3LYP functional and the 6-31G** basis set as implemented in Gaussian 03. The equilibrium geometries of the neutral molecules were computed both for the ground state (closed-shell singlet) and for the lowest-energy triplet state (T1).

The geometries of the cation and anion species were also optimized for selected compounds. Spin-unrestricted UB3LYP spin functions were used to calculate the T1 state and the charged species.

which one obtains two subsequent one-electron reductions, by a strong absorption, attributable to the HOMO–LUMO structure with maximum absorption at 660 nm (Figure 1), between the one-electron processes is 60 mV, from which one obtains two subsequent one-electron reductions and predicts that the one-electron reduction product, namely, the radical anion, is appreciably stable. Considering the oxidation, whereas H4T4CN4 gives a low-potential one-electron oxidation and a stable radical cation, T3CN4, TETCN4, and T2CN4 produce a radical cation species labile in the electrolysis time scale.

Compared with T3CN4, TETCN4 shows a negative shift of both the reduction and the oxidation potentials (particularly oxidation) due to the electron-donor properties of the EDOT unit.

3. Results and Discussion

3.1. Optical and Electrochemical Properties. A thorough structural investigation on a series of alkyl-substituted T3CN4 and T4CN4 oligomers, which also includes optical and electrochemical results, has recently appeared in the literature. The optical and electrochemical parameters of the TnCN4 here investigated are summarized in Table 1.

The UV–vis spectrum of these compounds is dominated by a strong absorption, attributable to the HOMO–LUMO electronic transition. The electronic spectrum of TETCN4, the recently produced trimer, shows the usual vibronic structure with maximum absorption at 660 nm (Figure 1), slightly higher than that for T3CN4 (645 nm).

Table 1. TnCN4 Oxidation ($E_{ox}^n$) and Reduction ($E_{red}^n$) Potentials in CH2Cl2 versus Ag/Ag+, Energy Gap (Maximum Absorption) in CH2Cl2 ($E_g$), and Calculated Energy Gap ($E_g$ (calcld)).

<table>
<thead>
<tr>
<th>compound</th>
<th>$E_{ox}^n$, V</th>
<th>$E_{red}^n$, V</th>
<th>$E_g$ (nm)</th>
<th>$E_g$ (calcld), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4T4CN4</td>
<td>0.58</td>
<td>−0.31</td>
<td>1.57 (790)</td>
<td>1.35</td>
</tr>
<tr>
<td>T4CN4</td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T3CN4</td>
<td>1.05</td>
<td>−0.37, −0.43</td>
<td>1.92 (645)</td>
<td>1.62</td>
</tr>
<tr>
<td>T2CN4</td>
<td>1.55</td>
<td>−0.37, −0.60</td>
<td>2.26 (550)</td>
<td>2.12</td>
</tr>
<tr>
<td>TETCN4</td>
<td>0.85</td>
<td>−0.49, −0.57</td>
<td>1.88 (660)</td>
<td>1.63</td>
</tr>
</tbody>
</table>

a: Scarcely reversible. b: Irreversible (peak potential, $E_p$).

T4CN4, and H4T4CN4 were calculated under $C_{2v}$ symmetry constraints, while the $C_{6v}$ and $C_{2v}$ symmetries were imposed for T3CN4 and TETCN4, respectively.

3.2. Theoretical Electronic Structure. The values calculated for the HOMO–LUMO energy gap in the TnCN4 series (see Table 1) are much smaller than those obtained for aromatic oligothiophenes Tn (e.g., 1.62 eV for T3CN4 vs 3.45 eV for T3) and are due to the quinoid structure of the molecule which reverses the topologies of the HOMO and the LUMO and narrows the gap.

The first consequence of the reduction of the energy gap is that these molecules present a very intense, low energy electronic transition in the visible region as observed in the absorption spectra. Table 1 shows that the theoretical trend calculated for the HOMO–LUMO gap follows the experimental results.

The second consequence is that the $T_1$ state, resulting from the excitation of an electron from the HOMO to the LUMO, appears at very low energies (see Table 3). At the B3LYP/6-31G** level, the adiabatic energy difference between $S_0$ and $T_1$ ($\Delta E_{ST}$) is of only 0.64 eV for T2CN4, decreases to 0.31 eV for T3CN4, and is almost negligible for T4CN4 (0.07 eV). Moreover, calculations show that $\Delta E_{ST}$ increases from 0.07 to 0.19 eV when T4CN4 is substituted with hexyl groups. The small values calculated for $\Delta E_{ST}$ suggest that the $T_1$ state could be populated at room temperature and that the population should increase with temperature and as the size of the oligomer increases. Thus the spin concentration is expected to increase from the dimer to the tetramer, although the presence of alkyl groups could influence this trend. These predictions are evidenced by ESR investigations at different temperatures (see below).

Figure 3 displays the equilibrium bond lengths calculated for TETCN4 both in the ground state and in the lowest-energy triplet state $T_1$. The $S_0$ state presents a quinoid...
structure, in which the shortest carbon–carbon (CC) distances correspond to the \(C_\beta-C_\beta\) bonds of the thiophene rings (1.36–1.38 Å), to the inter-ring \(C_\alpha-C_\alpha\) bonds (1.38 Å), and to the bonds connecting the oligothiophene spacer to the C(CN)\(_2\) groups (1.39 Å). On passing to \(T_1\), the central thiophene ring reverses the \(C=\equiv C=\equiv C\) bond-length alternation pattern and the outer thiophene rings exhibit almost no alternation. The inter-ring \(C_\alpha-C_\alpha\) bonds lengthen from 1.38 Å in \(S_0\) to 1.43 Å in \(T_1\). Thus, the molecular structure in \(T_1\) is more aromatic than quinoid and, according to the values calculated for the atomic spin densities, it corresponds to a superposition of the resonant structures sketched in Figure 4.

The molecular structures of the cation and anion of the \(T3CN4\) and \(TETCN4\) trimers were also optimized at the B3LYP/6-31G** level. Both oxidation and reduction produce a partial aromatization of the terthiophene skeleton. Upon oxidation, electrons are mainly extracted from the thiophene backbone which for \(TETCN4\) supports charges of \(+0.40e\) on the central EDOT unit and of \(+0.37e\) on the outer thiophene rings. Upon reduction, electrons are mainly introduced on the C(CN)\(_2\) groups which accumulate charges of \(-0.51e\) in \(TETCN4\). Compared to \(T3CN4\), the electron-releasing effect of the ethylenedioxy group in \(TETCN4\) is evidenced by the adiabatic values calculated for the ionization energy (IE) and the electron affinity (EA). Both the IE (7.12 and 6.82 eV) and the EA (3.37 and 3.12 eV) decrease in passing from \(T3CN4\) to \(TETCN4\) in agreement with the stronger electron donor and the poorer electron acceptor abilities electrochemically observed for \(TETCN4\).

**Table 2. Oligothiophene ESR \(g\) Values and Spin Concentrations in the Solid State.**

<table>
<thead>
<tr>
<th>compound</th>
<th>(g)</th>
<th>S, spin mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4T4CN4</td>
<td>2.0029</td>
<td>(3 \times 10^{-3})</td>
</tr>
<tr>
<td>T3CN4</td>
<td>2.0040</td>
<td>(10 \times 10^{-3})</td>
</tr>
<tr>
<td>T2CN4</td>
<td>2.0037</td>
<td>(0.2 \times 10^{-3})</td>
</tr>
<tr>
<td>TETCN4</td>
<td>2.0031</td>
<td>(0.3 \times 10^{-3})</td>
</tr>
<tr>
<td>TCNQ</td>
<td>2.0028</td>
<td>(2 \times 10^{-5})</td>
</tr>
<tr>
<td>T4CN2</td>
<td>2.0038</td>
<td>(3 \times 10^{-7})</td>
</tr>
<tr>
<td>T3CN2</td>
<td>2.0037</td>
<td>(2 \times 10^{-6})</td>
</tr>
</tbody>
</table>

### 3.3. Solid-State ESR. 3.3.1. Room-Temperature Analysis.

The X-band ESR spectrum recorded for powder samples of \(TETCN4\) at room temperature gives symmetrical signals at the \(g\) values shown in Table 2. Spin-quantification experiments show high concentrations of unpaired-electron species \((3 \times 10^{-4} \text{ to } 10^{-3} \text{ molar fraction of unpaired electrons})\), see Table 2). For comparison, crystalline TCNQ displays a much lower spin concentration \((\text{ca. } 10^{-5} \text{ molar fraction})\). Crystalline samples of the \(\alpha,\alpha\)-dicyano-oligothiophenes, for which a diradical formulation is much unfavored, show even weaker ESR signals \((10^{-6} \text{ to } 10^{-7} \text{ molar fraction})\), see Table 2). Thus, the signals of the \(TsCN4\) compounds here investigated are not attributable to impurities.

Also, the possibility that the ESR responses are due to radical anion and cation couples produced by disproportionation of two neutral molecules is not acceptable. The electrochemical stability in solution (0.9 V or higher, see Table 1) gives these radical species an upper limit of \(10^{-8}\) molar fraction to their concentration, which is five orders of magnitude lower than the measured values. On this basis we attribute the measured magnetic responses to diradicals.

For \(H4T4CN4\) the value of concentration is 0.3 mol % of radical species; that is, approximately 0.15% of the compound exists in a diradical state. The percentage is higher but in fact comparable for \(T3CN4\) (see Table 2). Instead it decreases dramatically from \(T3CN4\) to \(T2CN4\), which may be attributed to the decreased number of aromatic rings. The lower value for \(H4T4CN4\) compared with \(T3CN4\), despite the higher number of rings, may be accounted for by hyperconjugation with the alkyl substituents, which destabilizes the aromatic forms. Spin-quantification experiments for \(TETCN4\) show a molar fraction of radical species comparable with the value found for \(T2CN4\) (see Table 2); that is, the presence of the electron rich substituent destabilizes the diradical form, probably via resonance of the alkoxy moiety.

### 3.3.2. \(g\) Values

In the unpaired-electron species of the unsubstituted compounds \(T2CN4\) and \(T3CN4\) (the synthesis of the \(T4CN4\) tetramer was unsuccessful),\(^2c\) the \(g\) values fall in the range \(2.0037 \text{ to } 2.0040\), that is, with a substantial increase from the free electron value \((2.0023)\). It must be noticed that the same values are measured in powders of \(\alpha,\alpha\)-dicyano-oligothiophenes.

The \(g\) values of organic radicals are related to the orbital participation of carbon, sulfur, nitrogen, and oxygen atoms according to the equation

\[
\Delta g = g - g_e \propto \lambda/E_g
\]

where \(g_e\) is the free-electron \(g\) value \((2.0023)\), \(\lambda\) is the spin–
At low T this way we see that an almost constancy of the temperature and then starts increasing (Figure 5a).

The evolution of S with T for the TETCN4 powders is better described by the product S × T versus T (Figure 5b). In this way we see that an almost constancy of the S × T value at low T (suggested Curie behavior) passes to a steep exponential increase. The exponential behavior is a well-known feature of the dimer model for radicals. A better inspection reveals that the plots are in fact constituted by a sigmoid curve so that a double exponential plot (eq 2) was applied with successful fitting.

\[ S \times T = A \exp(-E_A/T) + B \exp(-E_B/T) \] (2)

The double exponential indicates two different diradical orbit coupling parameters (29 cm\(^{-1}\) for C\(_{2p}\), 382 cm\(^{-1}\) for S\(_{3p}\), 76 cm\(^{-1}\) for N\(_{2p}\), and 151 cm\(^{-1}\) for O\(_{2p}\), and \(E_g\) is the band gap.\(^{20}\) As a consequence, the \(g\) values would be higher than the free-electron value. Thus, the results may be attributed to a strong participation of the CN nitrogen atoms to the unpaired electron. Exceptions are the tetralkyl-substituted H4T4CN4 and the ethylenedioxy-substituted TETCN4 with values (2.0029–2.0031) closer to those of simple oligothiophenes, due to hyperconjugation and conjugation of alkoxy substituents, respectively.

### 3.3.3. Variable Temperature Analysis

Our hypothesis about the presence of unpaired-electron species considers the thermal population of diradical excited states bearing an aromatic structure. Theory effectively accounts for the existence of these excited states very close in energy to the ground electronic state.

The intensity of the ESR signal \(S\) was, therefore, followed at different temperatures \(T\). It was found that the intensity of the signal of solid TnCN4 decreases with increasing temperature and then starts increasing (Figure 5a).

The reason no such accord is found for TETCN4 is not clear at the moment, though the experimentally lower activation energy may be possibly due to a specific stabilization through the 3,4-ethylenedioxy side chain.\(^{22}\)

### Table 3. Experimental and Calculated \(S_0-T_1\) Activation Energies \(\Delta E_{ST}\) for TnCN4 Oligomers

<table>
<thead>
<tr>
<th>compound</th>
<th>(\Delta E_{ST(expl)}), eV</th>
<th>(\Delta E_{ST(calcd)}), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4T4CN4</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>T4CN4</td>
<td>0.07</td>
<td>0.18</td>
</tr>
<tr>
<td>T3CN4</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>T2CN4</td>
<td>0.64</td>
<td>0.44</td>
</tr>
<tr>
<td>TETCN4</td>
<td>0.18</td>
<td>0.36</td>
</tr>
</tbody>
</table>

\(\Delta E_{ST}\) increases as the number of thiophene rings is decreased. In the case of TETCN4 the activation energy for B is high (16 kJ mol\(^{-1}\)), comparable with that measured for H4T4CN4. It is possible that the two diradical forms, A and B, are a self-interacting (e.g., dimeric) and an isolated species, respectively.

As observed above, theory is in accord with the spin concentrations found from ESR measurements. Moreover, the activation energies measured for H4T4CN4 and T3CN4 are in full agreement with those calculated (see Table 3). The reason no such accord is found for TETCN4 is not clear at the moment, though the experimentally lower activation energy may be possibly due to a specific stabilization through the 3,4-ethylenedioxy side chain.\(^{22}\)

### 3.4. Solution ESR of Neutral Quinoid Oligothiophenes

The ESR spectrum of CH\(_2\)Cl\(_2\) solutions of H4T4CN4 (Figure 6) and T3CN4 at 298 K comprises three signals, which can be simulated assuming three \(g\) values (2.0005, 2.004, and 2.006 for H4T4CN4; 2.0005, 2.005, and 2.007 for T3CN4). The anisotropy may be due to the slow tumbling rate...
associated with the size of the rigid-rod molecules or possibly to aggregated forms because solubility is low.

The ESR spectrum of a 10^{-2} M T3CN4 solution in CH2Cl2 at 298 K has an intensity corresponding to 10^{-6} M free spins (10^{-4} molar fraction). Acetonitrile gives the signal with the same intensity as CH2Cl2. In contrast a 10^{-2} M T3CN4 solution in N,N-dimethylformamide (DMF) shows a relative concentration about 10 times higher (0.1% molar fraction).

The maximum signal, with a g value which is the same in the different media, is stable for at least several days. Moreover, because after the ESR analysis in DMF the compound, redissolved in CH2Cl2, recovers the initial signal, the spin-generating reaction in DMF is reversible.

It appears that a higher stability of the diradical is the main reason for the higher ESR signal in DMF, namely, that DMF coordinates better the TnCN4 molecule stabilizing the unpaired-electron form possibly via dipole–dipole interactions.

The ESR signal of T3CN4 increases reversibly (by ca. five times in DMF) from nitrogen-degassed to air-saturated solution. It appears that the increase of the ESR signal, which is not due to dissolved oxygen itself because it gives broad and almost undetectable signals,23 is due to an O2 adduct. This behavior is not specific of T3CN4 because H4T4CN4 and T2CN4 behave similarly. Oxygen increases significantly and reversibly the ESR signal for all compounds. The formation of oxygen adducts of aromatics is not unusual (see, for instance, the formation of adducts with polyconjugated radicals).24 The nature of these adducts is actually under investigation.

3.5. Solution ESR of Electrolyzed Quinoid Oligothiophenes. The ESR spectrum of a solution of H4T4CN4 in CH2Cl2 after one-electron oxidation displays the signal of the stable radical cation (g = 2.0036). The one-electron reduction produces stable radical anions for all the oligothiophenes with g = 2.0026 (T2CN4, T3CN4, and TETCN4) and 2.0028 (H4T4CN4).

The literature reports the chemical oxidation and reduction of 3,4′-dibutyl-T3CN4 to species with featureless signals at g = 2.0035 and 2.0026, respectively.25 The g values we obtained are in agreement with those in the literature. At difference, hyperfine splitting is shown in all cases and is particularly evident for the T2CN4 radical anion (Figure 7). The line width is about 0.3 G for all compounds whereas coupling constants are 0.6 G for T2CN4 and 0.5 G for T3CN4 and TETCN4 radical anions. In the case of H4T4CN4, the values are 0.6 G for the radical anion and 0.5 G for the radical cation.

Computer simulation for the T2CN4 radical anion, assuming coupling with four equivalent nitrogen atoms (0.6 G) and four equivalent hydrogen atoms (0.3 G), gives a substantial agreement with the experimental spectrum.

It must be recalled that the neutral species do not show such hyperfine structures in their ESR spectra, which rules out their anion or cation radical nature and is, therefore, a confirmation of the neutral (diradical) nature of the detected paramagnetic species.

3.6. In Situ Conductivity. H4T4CN4 is reversibly oxidized to the radical cation and reduced to the radical anion and dianion states.3 Thus, in principle we can measure both the p- and n-type conductivities of the materials. The short TnCN4 oligomers, TETCN4 included, are not oxidized to a stable radical cation so that their p-conductivity is not achievable.

The in situ conductivity of the H4T4CN4 film cast from CHCl3 has been measured in acetonitrile (+ 0.1 M Bu4NClO4). Dashed line: CV for comparison.

Figure 7. ESR signal of T2CN4 radical anion in CH2Cl2 solution at 298 K.

Figure 8. In- situ conductivity vs (a) potential and (b) redox charge of H4T4CN4 film in acetonitrile + 0.1 M Bu4NClO4. Dashed line: CV for comparison.

Properties of Quinoidal Oligothiophenes

H4T4CN4 is low-conducting in the neutral and in the one-electron oxidized state through a conducting state (Figure 8a) with a maximum conductivity of 0.03 S cm\(^{-1}\). The maximum is displayed at the potential of the neutral/cation transition, indicating mixed-valence conduction.\(^{26}\) The maximum conductivity occurs at 50% of the redox charge (Figure 8b) as expected for redox conduction.\(^{26}\)

A relatively high value of conductivity is expected for this class of compounds on the basis of their lower gap, given by the quinoid form, compared with that of aromatic analogues. If we in fact consider p-doping conduction as electron hopping from the neutral quinoid to the oxidized aromatic forms, the energy of the activated state for conduction, intermediate between the two forms, is expected to be lower than that for an aromatic oligomer. A homogeneous comparison with aromatic analogues is required, but unfortunately data in the literature are quite scarce. In fact, the measured conductivity is comparable with that of (aromatic) \(\alpha,\alpha\)-dimethyltetraphiophene, for which the maximum conductivity of BF\(_3\) or PF\(_6\)\(^{-}\) chemically doped samples is 0.02–0.04 S cm\(^{-1}\).\(^{27}\) Havinga et al.\(^{28}\) have doped with iodine several dodecyl-substituted oligothiophenes obtaining values in the range 0.01–20 S cm\(^{-1}\) from T5 to T11. Yet all these values are not related to a specific redox state and are possibly those of the more oxidized (and more conducting) polaron–bipolaron redox couple.\(^{29}\) Moreover the dimethyltetraophiene has no substituent so that it is more conducting strongly.

In any case we have recently investigated the in situ conductivity of a tetrahexyl-substituted \(\alpha,\alpha\)-capped octathiophene,\(^{29}\) that is, a longer aromatic oligothiophene with similarly bulky substituents and, therefore, more comparable steric hindrance and interchain spacing. The conductivity of the neutral/cation transition was found to be 3 \(\times\) 10\(^{-4}\) S cm\(^{-1}\), that is, 100 times lower than that of H4T4CN4, so that it appears that the lower gap is in fact a factor which favors conductivity strongly.

Conclusions

The investigation of the magnetic and conductive properties of a whole series of quinoidal oligothiophenes (namely, bis(dicyanomethylene)-end-capped-oligothiophenes; TnCN4 with \(n = 2–4\)), both as pure solids and upon solution, has evidenced for the first time that diradical species are present in a sizable amount in the pristine state of this class of heteroquinodimethanes. This is particularly true for the longer oligomers (i.e., T3CN4 and H4T4CN4), although the attachment of either 3,4-ethylenedioxy or alkyl side chains to the \(\beta\)-positions of the thienyl units partly destabilizes the diradical form as a result of the electron-releasing ability of the former substituent or hyperconjugation.

Two diradical forms seem to coexist; one is a minority species, thermally activated and with activation energies in good correspondence to calculated values about the adiabatic energy difference between the ground electronic state and the first excited triplet state and which has been attributed to the free diradical, whereas the second one, present in concentrations up to 1% in T3CN4 and 0.01% in T2CN4, is a nonactivated stabilized form which may exist also as an oxygen adduct.

The p-type conductivity, which could be measured only for the most stable oxidized form of tetrahexyl-substituted T4CN4, is relatively high and agrees with what could be anticipated from the significantly lower energy gap as compared with those of usual oligothiophenes. As a result, the mobility when acting as p-channels (and likely also as n-channels) in OFETs should be strongly favored.

Finally, the thermally promoted paramagnetic (diradical) responses, with progressively lower activation energies upon elongation of the oligothienoquinonoid core, could open the possibility for future applications of such molecular materials in organic magnetic devices.

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