

Magnetic and Conductive Properties of Quinoidal Oligothiophenes

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The magnetic and conductive properties of a series of quinoidal oligothiophenes, that is, bis-(dicyanomethylene)oligothiophenes (T_nCN_4 , $n = 2-4$), 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 % (T_3CN_4), that is, 0.5% of the compound exists in a diradical state. The percentage decreases dramatically from T_3CN_4 to T_2CN_4 , 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 T_4CN_4 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).¹ Quinoid oligothiophenes, such as bis(dicyanomethylene)oligothiophenes (T_nCN_4), 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 paper⁵ has summarized results on different ter- and tetrathiophenes of the T_nCN_4 type. Electronic properties,

such as the HOMO–LUMO optical band gap, are correlated with the crystal packing parameter. It was previously reported³ 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 recently⁷ the synthesis and characterization of a series of substituted T_nCN_4 ($n = 1-6$) soluble oligomers have been evidenced for $n = 5$ and 6 unpaired-electron species in solution, identified as diradi-

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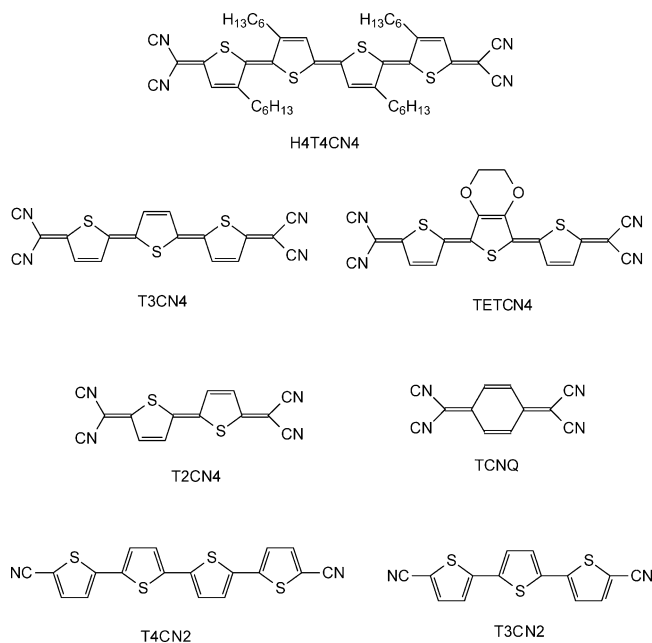
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Chart 1



cal, but no evidence for such species was obtained for the lower members. The thermal generation of magnetic responses in such molecules may be useful for both fundamental knowledge and applications, for example, in organic magnetic devices.

Here we report on the magnetic and conductive properties of a $T_n\text{CN}_4$ series ($n = 2-4$, Chart 1). The investigated oligothiophenes comprise a novel terthiophene-based quinodimethane bearing an electron rich 3,4-ethylenedioxythiophene (EDOT) central unit (TETCN4). We have undertaken the study of the magnetic properties of neutral materials in the solid state, compared with those of neutral (undoped) and positively and negatively doped (cationic and anionic) materials in solution and the conductive properties of thin solid films. Density functional theory (DFT) calculations have also been performed to correlate energy gaps and thermally activated magnetic responses. This investigation parallels the electronic and vibrational spectroscopic investigation performed previously on hexyl-substituted bis(dicyanomethylene)terthiophene and -tetrathiophene.³

2. Experimental Section

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 (Bu_4NClO_4) and all other chemicals were reagent grade and used as received.

5,5''-Bis(dicyanomethylene)-3,3',3'''-tetrahexyl-5,5''-dihydro-2,2':5',2'':5'''-quaterthiophene (H4T4CN4),⁴ 5,5''-bis(dicyanomethylene)-5,5''-dihydro-2,2':5',2''-terthiophene (T3CN4),⁸ 5,5''-bis(dicyanomethylene)-5,5''-dihydro-2,2'-bithiophene (T2CN4),⁸ 5,5''-bis(dicyanomethylene)-3',4'-ethylenedioxy-5,5''-dihydro-2,2':5',2''-terthiophene (TETCN4),⁹ 5,5''-dicyano-2,2':5',2'':5'''-quater-

thiophene (T4CN2),⁹ and 5,5''-dicyano-2,2':5',2''-terthiophene (T3CN2)¹⁰ were prepared as in the literature.

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 cm^2). For electronic spectroscopy, a $0.8 \times 2.5 \text{ cm}$ indium tin oxide sheet (ca. $20 \Omega/\text{square}$ 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.¹¹ Absolute spin calibration was performed with $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ or 2,2-diphenyl-1-picrylhydrazyl (DPPH) crystals, g -value calibration with thin films of DPPH ($g = 2.0036$).¹² 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.^{13,14} The electrode for conductivity measurements was a microband array platinum electrode ($5 \mu\text{m}$ bandwidth, 100 nm thick) with interband spacing of $5 \mu\text{m}$. The deposit was thick enough to ensure minimum resistance, under which condition the conductivity σ 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 functional¹⁵ and the 6-31G** basis set¹⁶ as implemented in Gaussian 03.¹⁷ The equilibrium geometries of the neutral molecules were computed both for the ground state (closed-shell singlet) and for the lowest-energy triplet state (T_1). The geometries of the cation and anion species were also optimized for selected compounds. Spin-unrestricted UB3LYP spin functions were used to calculate the T_1 state and the charged species. T2CN4,

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Table 1. $TnCN4$ Oxidation (E_{ox}^0) and Reduction (E_{red}^0) Potentials in CH_2Cl_2 versus Ag/Ag^+ , Energy Gap (Maximum Absorption) in CH_2Cl_2 ($E_g(\lambda)$), and Calculated Energy Gap ($E_g(\text{calcd})$)

compound	E_{ox}^0 , V	E_{red}^0 , V	$E_g(\lambda)$, eV (nm)	$E_g(\text{calcd})$, eV
H4T4CN4 ⁴	0.58, 1.12	-0.31	1.57 (790)	1.35
T4CN4				1.27
T3CN4 ⁸	1.05 ^a	-0.37, -0.43	1.92 (645)	1.62
T2CN4 ⁸	1.55 ^b	-0.37, -0.60	2.26 (550)	2.12
TETCN4 ⁹	0.85	-0.49, -0.57	1.88 (660)	1.63

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

T4CN4, and H4T4CN4 were calculated under C_{2h} symmetry constraints, while the C_{2v} and C_2 symmetries were imposed for T3CN4 and TETCN4, respectively.

3. Results and Discussion

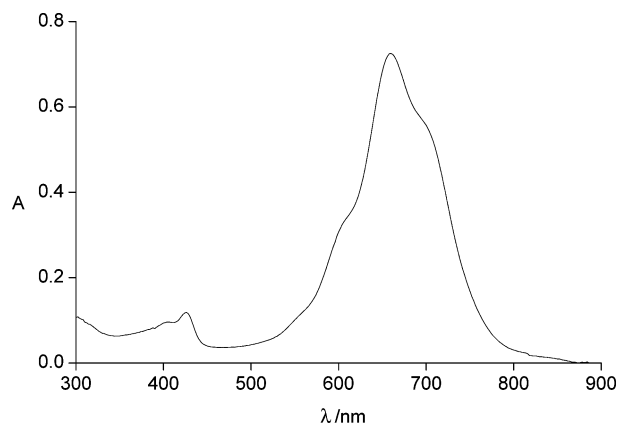
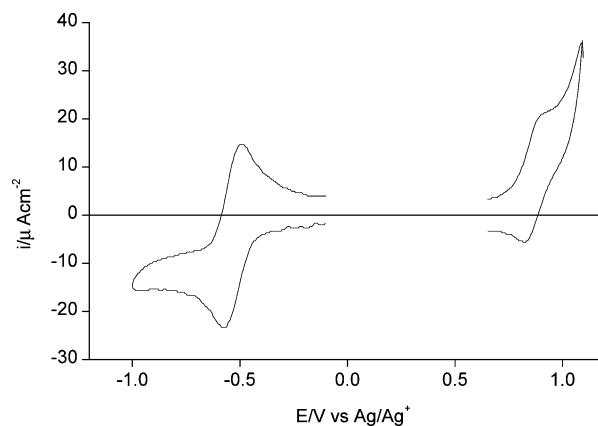
3.1. Optical and Electrochemical Properties. A thorough structural investigation on a series of alkyl-substituted T3CN4 and T4CN4 oligomers, which also includes optical and electrochemical results, has recently appeared in the literature.⁵ The optical and electrochemical parameters of the $TnCN4$ here 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,⁹ shows the usual vibronic structure with maximum absorption at 660 nm (Figure 1), slightly higher than that for T3CN4 (645 nm).

Considering the electrochemical properties (potentials are also given in Table 1), the compounds are reversibly reduced in two one-electron reduction processes which are separate for T2CN4 but merged into a single two-electron reduction process for the other $TnCN4$ members ($n > 2$), TETCN4 included (Figure 2). In the latter cases the potential separation between the one-electron processes is 60–80 mV, from which one obtains two subsequent one-electron reductions¹⁸ 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.

**Figure 1.** UV-vis spectrum of TETCN4 in $CHCl_3$ solution.**Figure 2.** CV of 2×10^{-4} M TETCN4 in CH_2Cl_2 solution.

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 (ΔE_{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).¹⁹ Moreover, calculations show that ΔE_{ST} increases from 0.07 to 0.19 eV when T4CN4 is substituted with hexyl groups. The small values calculated for ΔE_{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

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(19) The diradical species was also computed as a singlet state within the spin-unrestricted approach using the mixed spin state option (GUESS = MIX) of Gaussian 03. This option builds, as the initial guess wave function, a 1:1 mixture of the singlet and triplet states with a spin-squared expectation value $\langle S^2 \rangle = 1$ and has been shown to provide reliable geometries and energies for singlet-state diradicals even though the spin density it provides is fully wrong (Davidson, E. R. *Int. J. Quantum Chem.* **1998**, *69*, 241. Lahti, P. M.; Ichimura, A. S.; Sanborn, J. A. *J. Phys. Chem. A* **2001**, *105*, 251). For T2CN4, T3CN4, and T4CN4, the UB3LYP/GUESS = MIX calculations did not provide a reliable description of the singlet-state diradical and mostly converged to the closed-shell 1A_g (dimer and tetramer) or 1A_1 (trimer) state. The expectation values obtained for S^2 are significantly lower than 1. For instance, the values calculated for $\langle S^2 \rangle$ in T3CN4 are 0.20 and 0.02 before and after annihilation of the first spin contaminant, respectively.

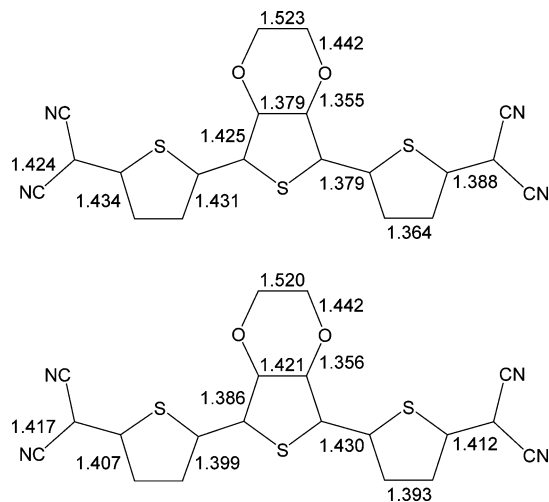


Figure 3. B3LYP/6-31G**-optimized bond lengths (Å) for TETCN4 (C_2 symmetry) in the S_0 ground state (top) and in the T_1 state (bottom).

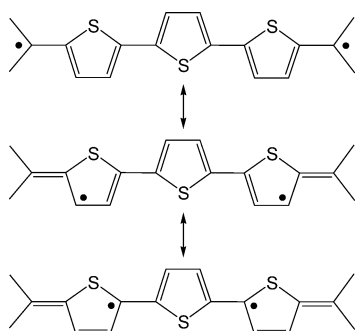


Figure 4. Resonant forms proposed to represent the T_1 state of TETCN4.

structure, in which the shortest carbon–carbon (CC) distances correspond to the C_β – C_β bonds of the thiophene rings (1.36–1.38 Å), to the inter-ring C_α – C_α 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 $C=C/C-C$ bond-length alternation pattern and the outer thiophene rings exhibit almost no alternation. The inter-ring C_α – C_α 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 terthiophene 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.

compound	g	S , spin mol^{-1}
H4T4CN4	2.0029	3×10^{-3}
T3CN4	2.0040	10×10^{-3}
T2CN4	2.0037	0.2×10^{-3}
TETCN4	2.0031	0.3×10^{-3}
TCNQ	2.0028	2×10^{-5}
T4CN2	2.0038	3×10^{-7}
T3CN2	2.0037	2×10^{-6}

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

The X-band ESR spectrum recorded for powder samples of the compounds at room temperature give symmetrical signals at the g values given in Table 2. Spin-quantification experiments show high concentrations of unpaired-electron species (3×10^{-4} to 10^{-2} molar fraction of unpaired electrons, see Table 2). For comparison, crystalline TCNQ displays a much lower spin concentration (ca. 10^{-5} molar fraction). Crystalline samples of the α,ω -dicyano-oligothiophenes, for which a diradical formulation is much unfavored, show even weaker ESR signals (10^{-6} to 10^{-7} molar fraction, see Table 2). Thus, the signals of the T_n CN4 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 2.0037–2.0040, 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 α,ω -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

$$\Delta g = g - g_e \propto \lambda/E_g \quad (1)$$

where g_e is the free-electron g value (2.0023), λ is the spin–

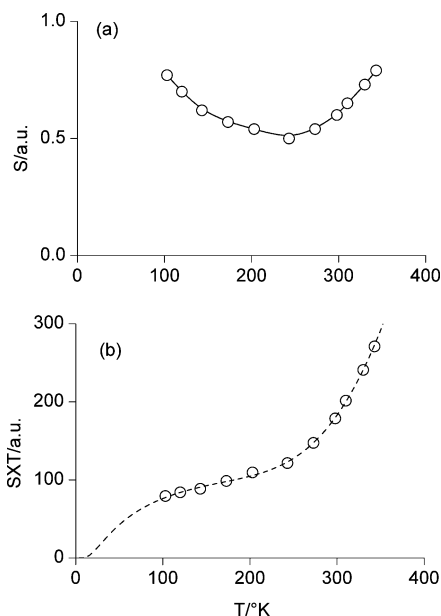


Figure 5. (a) ESR intensity S of TETCN4 powder at different temperatures T (K) and (b) product of ESR intensity S and temperature T vs T (connecting line: fit according to eq 2).

orbit coupling parameter (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 tetraalkyl-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 evolution of S with T for the $TnCN4$ powders is better described by the product $S \times T$ versus T^{21} (Figure 5b). In this way we see that an almost constancy of the $S \times T$ value at low T (suggesting Curie behavior)²¹ passes to a steep exponential increase. The exponential behavior is a well-known feature of the dimer model for radicals.²¹ 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.

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

The double exponential indicates two different diradical

Table 3. Experimental and Calculated S_0-T_1 Activation Energies ΔE_{ST} for $TnCN4$ Oligomers

compound	$\Delta E_{ST}(\text{exptl})$, eV	$\Delta E_{ST}(\text{calcd})$, eV
H4T4CN4	0.18	0.19
T4CN4		0.07
T3CN4	0.29	0.31
T2CN4		0.64
TETCN4	0.18	0.36

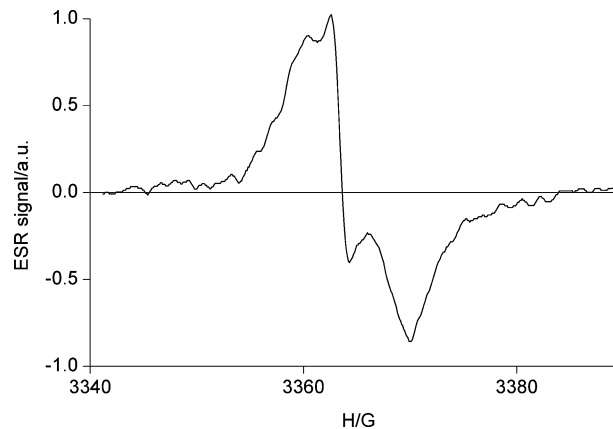


Figure 6. ESR signal of H4T4CN4 in CH_2Cl_2 solution at 298 K.

species (A and B) with different thermal activations. The pre-exponential parameters A and B , which indicate the population of the two states, are such that the B/A ratio is about 10^3 so that given that the absolute diradical concentration corresponding to A is between 10^{-2} and 10^{-3} , it is reasonable to argue that B corresponds to a population of 100%, that is, the absolute majority of the individual molecules. The exponential factor E_A is very low (0.4 – 0.5 kJ mol^{-1}) and indicates a population of stable diradicals A. In contrast E_B is high because 28 and 17 kJ mol^{-1} (0.29 and 0.18 eV) for T3CN4 and H4T4CN4, respectively, are measured (T2CN4 does not allow the evaluation of this parameter at the allowed temperatures). The second population (B) is, therefore, strongly activated, with an energy difference ΔE_{ST} that 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_2Cl_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

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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 CH_2Cl_2 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 CH_2Cl_2 . 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 CH_2Cl_2 , 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 *Tn*CN4 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 O_2 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 CH_2Cl_2 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

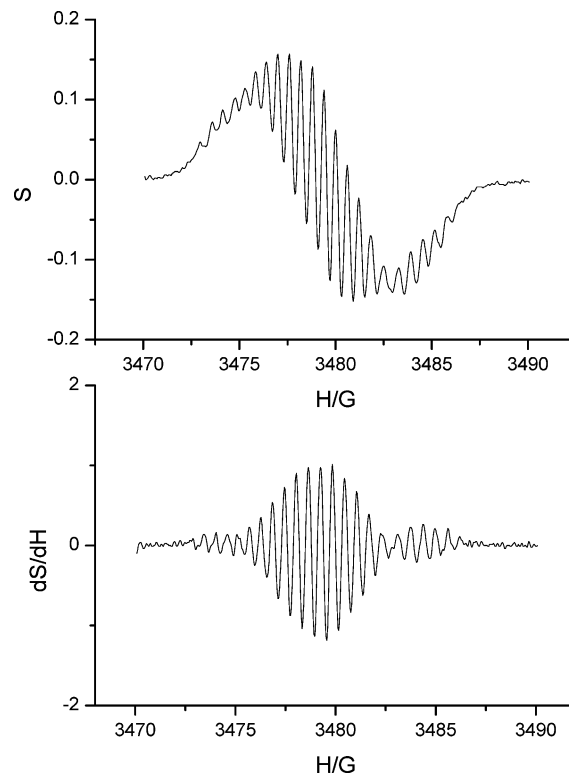


Figure 7. ESR signal of T2CN4 radical anion in CH_2Cl_2 solution at 298 K.

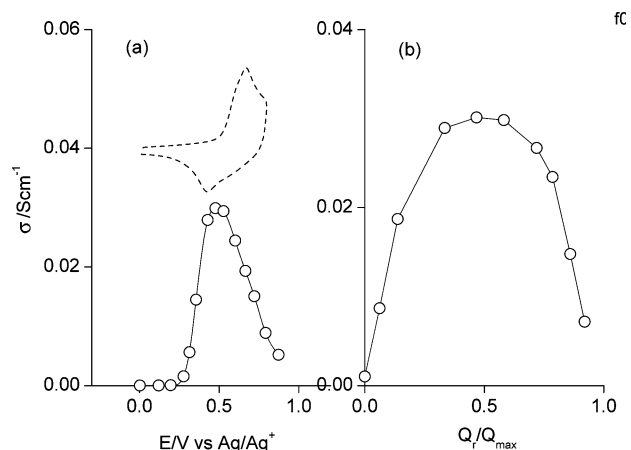


Figure 8. In-situ conductivity vs (a) potential and (b) redox charge of H4T4CN4 film in acetonitrile + 0.1 M Bu_4NClO_4 . Dashed line: CV for comparison.

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 *Tn*CN4 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 CHCl_3 has been measured in acetonitrile (where it is insoluble) as a function of the potential. For p-type conductivity, this has been done going from the oxidized to the neutral state of the materials (Figure 8a) because equilibrium conditions are in this way continuously maintained as

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previously found for polythiophene.¹¹ In contrast no n-type conductivity could be measured because the produced radical anions dissolve into the medium.

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) α,ω -dimethyltetrathiophene, for which the maximum conductivity of BF₄⁻ or PF₆⁻ 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 dimethyltetrathiophene has no substituent so that it is more closely packed than tetrahexyl-substituted H4T4CN4 quinoid tetrathiophene and is probably for this reason more conducting.

In any case we have recently investigated the in situ conductivity of a tetrahexyl-substituted α,ω -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 3×10^{-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; T_nCN4 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 β -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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