

27 June 2002

Chemical Physics Letters 359 (2002) 466-472



www.elsevier.com/locate/cplett

# Theoretical investigation of the nature of the ground state in the low-bandgap conjugated polymer, poly(3,4-ethylenedioxythiophene)

A. Dkhissi <sup>a,1</sup>, F. Louwet <sup>b</sup>, L. Groenendaal <sup>b</sup>, D. Beljonne <sup>a,c</sup>, R. Lazzaroni <sup>a,c</sup>, J.L. Brédas <sup>a,c,\*</sup>

<sup>a</sup> Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, 20 Place du Parc, B-7000 Mons, Belgium <sup>b</sup> Agfa-Gevaert, N. V, Mortsel B-2640, Belgium

<sup>c</sup> Department of Chemistry, The University of Arizona, 1306 E. University Blvd., Tucson, AZ 85721-0041, USA

Received 22 February 2002; in final form 16 April 2002

### Abstract

Quantum-chemical calculations are performed to study the geometric and electronic structures of poly(3,4-ethylenedioxythiophene) – PEDOT. The relative stability of the two possible structures for PEDOT (aromatic-like and quinoid-like) has been evaluated on oligomers of increasing size. The results obtained on PEDOT are compared to those collected on polythiophene and polyisothianaphthene, i.e., two parent conjugated polymers that are known to possess an aromatic and quinoid ground state, respectively. The vibrational spectra of both forms of PEDOT have also been calculated and compared with recent experimental data. The calculations indicate that the ground state of neutral PEDOT is aromatic-like. © 2002 Elsevier Science B.V. All rights reserved.

# 1. Introduction

One key feature of organic semiconductors, including  $\pi$ -conjugated polymers, is the possibility to tuning their electronic properties via chemical substitution along the backbone. This approach has been widely exploited to modify the ionization

Corresponding author. Fax: +32-16-32-7992.

(oxidation) potential, the electron affinity (reduction potential), or the bandgap (hence, the energy of optical absorption and emission) in polyphenylenes, polythiophenes, and polyphenylene vinylenes [1,2].

A very interesting example of such 'molecular engineering' has been the design of low-bandgap conjugated polymers [3]. Upon doping, the valence to conduction band transition is strongly depleted in favor of lower energy transitions, which basically makes these materials transparent in the visible part of the spectrum (and electrically conductive). The search for low-bandgap polymers was pioneered in the mid-1980's by Wudl et al. [4]

*E-mail addresses:* ahmed.dkhissi@chem.kuleuven.ac.be (A. Dkhissi), jlbredas@u.arizona.edu (J.L. Brédas).

<sup>&</sup>lt;sup>1</sup> Present address: Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium. Also corresponding author. Fax: +1-520-621-8407.

with the synthesis of polyisothianaphthene (PITN) (Scheme 1). The rationale behind the grafting of a benzene ring onto the thiophene ring was to bring some quinoid character to the conjugated backbone. The electronic pattern of the HOMO of polythiophene is aromatic (bonding interactions between  $\alpha$  and  $\beta$  sites and antibonding interactions between  $\beta$  sites and between  $\alpha$  sites) while the LUMO is quinoid (antibonding interactions between  $\alpha$  and  $\beta$  sites and bonding interactions between  $\alpha$  sites and between  $\beta$  sites) [5]. Therefore, driving the backbone towards a quinoid structure would destabilize the HOMO and stabilize the LUMO, i.e., reduce the bandgap. It turns out that the effect of benzene grafting is so strong that the ground-state geometric and electronic structure display in fact a quinoid character (the HOMO and LUMO levels having exchanged their bonding-antibonding pattern with respect to polythiophene). This was first proposed on the basis of theoretical calculations [6,7] and later confirmed with a joint experimental and theoretical investigation of the polymer and model oligomers [8].

For practical applications, another transparent, conductive polymer has been recently very much exploited: poly(3,4-ethylenedioxythiophene), PE-DOT (Scheme 1). The most interesting aspects related to the synthesis and the characterization of that polymer have been reviewed recently [9]. The accessability of the monomer and, especially the possibility of producing the conducting material as a water dispersion by using a water-soluble polymeric counterion, have made PEDOT a successful commercial product. It is extensively used as an antistatic coating on photographic films and as an electrode layer in flexible displays and organic light-emitting devices.

At first sight, PEDOT appears to be a simply substituted polythiophene; the reduction in bandgap relative to polythiophene being thought to originate from the influence of the electron-donor ethylene dioxy groups on the energies of the frontier levels of the  $\pi$  system [10]. Therefore, the ground-state geometric structure of neutral PE-DOT is expected to be aromatic. However, in a recent study, Lapkowski and Pron [11] have proposed, from spectroscopic data, that the ground state of PEDOT is quinoid. This hypothesis is based on the observation that the Raman peak corresponding to the stretching of the  $C_{\alpha}$ - $C_{\beta}$ bonds shifts to higher wavenumbers upon doping; this suggests that the electron density increases,

hence that the character of the bond evolves from single to double. Similarly, the peak assigned to the  $C_{\alpha}$ - $C_{\alpha}$  bond connecting the EDOT units shifts to lower wavenumbers. This raises the question of the nature of ground state of neutral PEDOT, as a low-bandgap conjugated polymer.

To address this question, we have carried out a theoretical investigation along two lines. On one hand, we have calculated the relative stability of the aromatic and guinoid forms of PEDOT (Scheme 1) and compared the results to those obtained on unsubstituted polythiophene (PTH) (as a reference for an aromatic system) and PITN (as a reference for a quinoid system). This approach has been successfully used previously [8] to determine the nature of the ground state in PITN. It is based on the evaluation of the energy per repeat unit  $(E_{pru})$  of the two forms, from quantumchemical calculations on a series of oligomers of increasing size. On the other hand, the vibrational spectra of the two forms have been calculated and compared to the experimental spectra recorded by Kvarnström et al. [12,13].

PITN



PEDOT

Scheme 1.

## 2. Theoretical methodology

The ground-state geometric structures of PTH, PITN and PEDOT oligomers (where the terminal a-carbons carry a single hydrogen atom Scheme 2, left), ranging in size from 1 to 10 repeat units (1-6 for PITN), were calculated at the restricted Hartree-Fock (RHF) and a hybrid density functional theory (DFT)/B3LYP levels. In the DFT calculations, we adopted Becke's three-parameter exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) [14,15]; such a choice of functionals has been found adequate for the description of the geometric and electronic structure of extended  $\pi$ conjugated structures. Both RHF and DFT calculations were performed using the standard 6-31 G basis set by means of the GAUSSIAN 98 package [16].

Full geometry optimization in the ground state leads to an aromatic structure for all the molecules investigated. In order to force the molecules to adopt a quinoid form, the structural parameters of related compounds wherein the terminal  $\alpha$  carbons bear two hydrogen atoms and are thus in an sp<sup>3</sup> configuration (Scheme 2, right) were optimized at the same level of theory [8]. Note that, for such a starting configuration, switching back to an aromatic form would require the formation of a biradical, which is a highly energetic and hence unlikely scenario. As output of these two sets of calculations, the total energies in the two possible valence-bond isomer forms (aromatic and quinoid) of the conjugated backbones were obtained. The relative stability between the two forms can then be estimated on the basis of the energy per repeat unit  $(E_{pru})$ , derived from the total energies; without zero-point energy (ZPE) correction,  $E_{pru}$  is defined as [8,17]

$$E_{\rm pru}(N) = E(N-1) - E(N),$$
 (1)

where *N* corresponds to the number of repeat units in the oligomer. It has been shown that, for conjugated systems, Eq. (1) provides good estimates of  $E_{pru}$ , even when short oligomers are considered [8,18]. This is due to the fast convergence of this energy with the oligomer size.

On the basis of the optimized aromatic and quinoid structures of the PEDOT pentamer, the vibrational spectra were simulated with the DFT method, since this method is known to provide accurate vibrational frequencies in organic compounds [19–21]. The accuracy of the method lies in part in the fact that correlation effects are included in the DFT approach, in contrast to uncorrelated HF methods that always provide vibrational frequencies overestimated with respect to experiment data.

# 3. Results and discussion

In the first set of calculations, conjugated chains with all carbon atoms being sp<sup>2</sup>-hybridized are considered. To force the quinoid structure, chainend defects, under the form of substitution of the external carbon atoms with two hydrogen atoms (Scheme 2), are introduced in a second set of calculations.

Fig. 1 shows the evolution along the conjugated chain of the degree of bond-length alternation (BLA), defined as the difference between alternating carbon–carbon single and double bonds, as obtained at the HF and DFT levels for the



Scheme 2.



Fig. 1. Evolution of the bond-length alternation, BLA (in Å), along the PEDOT decamer.

aromatic and quinoid forms of the ten-unit PEDOT oligomer. Comparison beween the aromatic form and the quinoid form shows similar patterns, with a change in sign consistent with the bond-length modifications sketched in Scheme 1. Note that: (i) smaller deformations are predicted when going from the aromatic to the quinoid form by the DFT calculations; this can be easily rationalized by the fact that electron correlation effects included in the DFT formalism tend to delocalize the electronic structure and, hence, reduce BLA in both the aromatic and quinoid structures; and (ii) both methods lead to an optimal torsion angle between rings close to 0° [22].

The energies per repeat unit and the relative energies between the aromatic and quinoid forms of PEDOT oligomers are collected in Table 1. Fig. 2 displays the evolution of  $E_{pru}$  as a function of oligomer size. A positive value means that the aromatic structure is more stable than the quinoid structure. It is seen that  $E_{pru}$  converges quickly as the chain gets longer, especially at the RHF level  $(E_{pru}$  remains essentially unchanged after the tetramer). Most importantly, both the RHF and DFT calculations indicate that the aromatic form is more stable than the quinoid form, by 4.9 and 2.4 kcal/mol (repeat unit), respectively. Since this energy difference is large with respect to the thermal energy at room temperature, we conclude that PEDOT adopts an aromatic structure in the neutral ground state. This is in marked contrast with the conclusion drawn by Lapkowski and Pron [11] on the basis of Raman spectroscopic studies on the polymer.

In order to check whether our approach is appropriate to distinguish between the two possible forms of thiophene-based polymers, we have also applied it to PTH and PITN, for which the nature of the electronic ground state is well known both experimentally and theoretically. The chain-length dependences of  $E_{pru}$  are shown in Figs. 3 and 4. In the case of unsubstituted polythiophene, both methods indicate that the aromatic form is more stable than the quinoid form, by 5.5 and 3.1 kcal/ mol (repeat unit) at the RHF and DFT levels, respectively. These results are in reasonable agreement with an AM1 semiempirical study,

Table 1

Energy per repeat unit (in atomic units; 1 a.u. of energy = 627.51 kcal/mol) and relative energy (in kcal/mol) of the neutral PEDOT oligomers, calculated at the HF/6-31G and DFT/B3-LYP/6-31G levels for the aromatic and quinoid structures

6								
Aromatic $E_{pru}^{a}$	1	2	3	4	5	6	8	10
HF DFT	_	776.530084 779.502655	776.530498 779.503579	776.530545 779.503904	776.530564 779.503899	776.530544 779.503920	776. 530532 779. 503962	776.530530 779.503952
$\begin{array}{c} \text{Quinoid} \\ E_{\text{pru}}{}^{\text{a}} \end{array}$								
HF	-	776.519946	776.522342	776.522707	776.522707	776.522756	776. 522743	776.522731
DFT	-	779.492955	779.496919	779.498527	779.498879	779.499522	779. 499856	779.500112
$\Delta E^{\rm b}$								
HF	_	6.36	5.12	4.92	4.93	4.89	4.89	4.89
DFT	-	6.09	4.18	3.37	3.15	2.76	2.58	2.41

 ${}^{a}E_{pru} = E(N-1) - E(N)$ , where E(N) is the total energy of the oligomer containing N repeat units.

<sup>b</sup> $\Delta E = E_{pru}(aromatic) - E_{pru}(quinoid)$ . A positive value means that the aromatic structure is more stable than the quinoid structure.



Fig. 2. Evolution of  $E_{pru}$  for PEDOT oligomers as a function of the number of repeat units, as calculated at the RHF and DFT levels. The energy scale has been shifted arbitrarily for the sake of clarity, in order to avoid displaying the large numbers mentioned in Table 1.

indicating a  $\sim 8.7$  kcal/mol (repeat unit) gain in energy when switching from the quinoid to the aromatic form [8]. Most importantly, they are also consistent with a number of experimental data and the expectations based on chemical intuition. For PITN, the situation is completely different: the quinoid geometry is found to be more stable than the aromatic one; the energy difference between the two forms amounting to 7.0 and 3.5 kcal/mol (repeat unit), from RHF and DFT calculations,



Fig. 3. Evolution of  $E_{pru}$  for PTH oligomers as a function of the number of repeat units, as calculated at the RHF and DFT levels.



Fig. 4. Evolution of  $E_{pru}$  for PITN oligomers as a function of the number of repeat units, as calculated at the RHF and DFT levels.

respectively. That PITN has a quinoid structure in its ground state has been demonstarted earlier on the basis of experimental and theoretical investigations [6–8]. The driving force towards the quinoid form was identified as the aromatic character of the benzene ring fused to the thiophene unit that forces the conjugated backbone to revert the alternation between single and double C–C bonds with respect to unsubstituted PTH. Note that the value obtained here at the DFT level is close to that predicted from AM1 calculations, 2.4 kcal/ mol (repeat unit) [8].

The results discussed above clearly validate our approach to estimate the relative stabilities of the aromatic and quinoid forms in thiophene-based materials and suggest that the interpretation of the Raman spectra of undoped and doped PEDOT by Lapkowski and Pron [11] should be reconsidered. Quantum-chemical computation of Raman spectra is a highly demanding task for extended structures such as those considered here. In addition, the measured intensity of the Raman bands depends on the laser input frequency, which makes the comparison between theory and experiment and the interpretation of the spectrum quite difficult. We have therefore rather relied on infra-red spectroscopy to support or infirm the conclusions drawn from the energetic aspects described above; IR spectra have indeed been reported recently for electropolymerized neutral PEDOT by Kvarnström et al. [12,13].

DFT frequency calculations have been performed on the PEDOT pentamer (which should be long enough to provide a good representation of the polymer and can be handled at a good level of theory). The frequencies of the most intense bands in the  $400-1650 \text{ cm}^{-1}$  frequency range together with their assignment are reported in Table 2 for the aromatic and quinoid forms and confronted to the experimental values (when available). We stress that the assignment of the calculated vibrational spectra in terms of localized deformations of bonds or angles should only be considered as qualitative since all the computed modes involve collective motions among basically all atoms of the structure. Bearing this in mind, vibrations measured at 1454, 1370, 1183, and 903 cm<sup>-1</sup> originate from the stretching of C-C, C=C and C-S bonds in the thiophene rings, while the mode at 1047 cm<sup>-1</sup> is assigned to breathing of the ethylenedioxy group. The position of all these bands is well reproduced by the DFT calculations assuming an aromatic ground-state structure. Furthermore, a strong band at 1283 cm<sup>-1</sup> is predicted when considering the quinoid form of the PEDOT

pentamer, which is mainly due to intering carboncarbon stretching vibrations. Such a feature is absent or weak in the experimental spectrum and it is computed with a much lower intensity for the aromatic form. Note that similar conclusions apply in the case of  $\alpha$ ,  $\alpha'$ -dimethyloligothiophenes [23]; this indicates that both alkyl- and alkoxysubstituted polythiophenes display an aromatic ground-state structure.

## 4. Conclusions

By applying density functional theory and ab initio Hartree–Fock methods to model oligomers for PEDOT, we have explored the nature of the electronic ground state in the corresponding neutral polymer. Energetic considerations, based on the energy per repeat unit as obtained by both DFT and RHF techniques, lead us to conclude that PEDOT has an aromatic character in the ground state, as is the case for unsubstituted PTH but in contrast to PITN. These conclusions are fully supported by the comparison between the

Table 2

Vibrational frequencies (in cm<sup>-1</sup>) of the PEDOT pentamer in the aromatic and quinoid form

Exp. frequencies	DFT frequencies	Calculated intensities (km/mol)	Assignment
	Aromatic form		
_	1450	175	v(C-C) + v(C=C)
1454	1445	497	v(C-C) + v(C=C)
1370	1388	996	v(C–C)
_	1296	80	Vintering
1183	1197	111	v(C=C)
1047-1052	1063	580	v(COROC) <sup>a</sup>
_	935	228	$v(COROC) + v_{intering}$
_	920	225	v(COROC)
930–943	906	153	v(C–S)
	Quinoid form		
	1606	273	$v(C=C)_{Asy}$
	1368	524	$v(C-C)_{Asy} + v(C=C)_{sy}$
	1336	336	$v(C-C)_{sy}$
	1283	555	Vintering
	1233	393	$v(C=C)_{sy}$
	1146	415	v(COROC)
	1048	392	v(COROC)a
	911	226	v(COROC)
	766	442	v(C–S)

The experimental frequencies are taken from [11,12].

<sup>a</sup> R corresponds to CH<sub>2</sub>-CH<sub>2</sub>.

infra-red spectra calculated for the aromatic and quinoid structures of a model oligomer and those measured in the polymer. A very good agreement between experiment and theory is obtained when considering the aromatic form in the theoretical simulations. This casts some doubt on the interpretation of the Raman spectra for the neutral and doped polymers, as proposed by Lapkowski and Pron [11]. Further investigations are clearly required to clarify this issue.

#### Acknowledgements

The work in Mons is partly supported by the IWT 'DOTCON' project and the Belgian Federal Government Interuniversity Attraction Pole Program (PAI V/3: Chimie supramoléculaire et Catalyse Supramoléculaire). The work at Arizona is partly supported by the National Science Foundation. D.B. and R.L. are Senior Research Fellows of the Belgian National Fund for Scientific Research (FNRS).

### References

- A. Kraft, A..C. Grimsdale, A.B. Holmes, Angew. Chem. Int. 37 (1998) 402.
- [2] T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Eds.), Handbook of Conducting Polymers, New York, 1998.
- [3] H.A.M. Mullekom, J.A.J.M. Vekemans, E.E.E. Havinga, E.W. Meijer, Mater. Sci. Eng. 32 (2001) 1.

- [4] F. Wudl, M. Kobayashi, A.J. Heeger, J. Org. Chem. 49 (1984) 3382.
- [5] J.L. Brédas, J. Chem. Phys. 82 (1985) 3808.
- [6] K. Nayak, D.S. Marynick, Macromolecules 23 (1990) 2237.
- [7] A. Karpfen, M. Kertesz, J. Phys. Chem. 95 (1991) 7680.
- [8] I. Hoogmartens, P. Adriaensens, D. Vanderzande, J. Gelan, C. Quattrocchi, R. Lazzaroni, J.L. Brédas, Macromolecules 25 (1992) 7347.
- [9] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, R. Reynolds, Adv. Mater. 12 (2000) 481.
- [10] J. Cornil, D.A. dos Santos, D. Beljonne, J.L. Brédas, J. Phys. Chem. 99 (1995) 5604.
- [11] M. Lapkowski, A. Pron, Synth. Met. 110 (2000) 79.
- [12] C. Kvarnström, H. Neugebauer, S. Blomquist, H.J. Ahonen, J. Kankare, A. Ivaska, Electrochim. Acta 44 (1999) 2739.
- [13] C. Kvarnström, H. Neugebauer, A. Ivaska, N.S. Sariciftci, J. Mol. Struct. 521 (2000) 271.
- [14] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [15] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [16] M.J. Frisch et al., GAUSSIAN 98, Revision A 7, Gaussian Inc., Pittsburgh, PA, 1998.
- [17] J. Ciolowski, Chem. Phys. Lett. 153 (1988) 446.
- [18] C.X. Cui, M. Kertesz, Y. Jiang, J. Phys. Chem. 94 (1990) 5172.
- [19] A. Dkhissi, L. Adamowicz, G. Maes, J. Phys. Chem. A. 104 (2000) 2112.
- [20] R. Ramaekers, L. Adamowicz, G. Maes, A. Dkhissi, J. Mol. Struct. 560 (2001) 205.
- [21] R. Vallée, P. Damman, M. Dosière, G. Scalmani, J.L. Brédas, J. Phys. Chem. B. 105 (2001) 6064.
- [22] All structural data for the oligomers can be obtained from the authors.
- [23] V. Hernandez, J. Casado, F.J. Ramirez, G. Zotti, S. Hotta, J.T. Lopez Navarrete, J. Chem. Phys. 104 (1996) 9271.