A Solid State Density Functional Study of Crystalline Thiophene-Based Oligomers and Polymers

Antonino Famulari,*,[†] Guido Raos,[†] Alberto Baggioli,[†] Mosè Casalegno,[†] Riccardo Po,[‡] and Stefano V. Meille[†]

[†]Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milano, Italy
[‡]Research Center for Non-Conventional Energies, Istituto Donegani, ENI S.p.A, Via Fauser 4, 28100 Novara, Italy

ABSTRACT: We present the results of a molecular modeling study of several thiophene-based oligomers and polymers by solid state density functional theory (DFT) calculations. In particular, we consider two polymers for which limit-ordered crystal structures have been reported by our group, on the basis of powder X-ray data analysis: poly(3-(S)-2-methylbutylthiophene) (P3MBT) and forms I′ and II of poly(3-butylthiophene) (P3BT). The calculations employing the functional by Perdew and Wang (PWC) in conjunction with the double-ζ polarized numerical basis set (DNP) demonstrate that a standard quantum mechanical (QM) approach for solid phases can provide a balanced description of the overall structure and energetics of thiophene-based oligomers and polymers maintaining a moderate computational cost. In addition, the results compare well with those provided by specific force field parametrization developed by our group. In many cases, PWC/DNP models show even closer agreement with experimental crystal structures, making it the method of choice for computationally accessible problems. Finally, solid state DFT minimizations confirm that the reported crystal structures of P3MBT and P3BT correspond to well-defined energy minima.
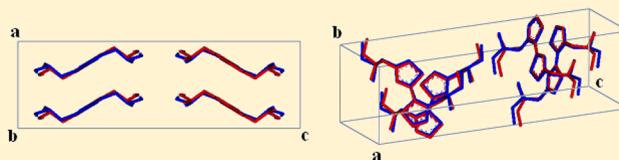
1. INTRODUCTION

Thiophene-based oligomers and polymers are widely employed as organic semiconducting materials.[1−7] In particular, due to the combination of high charge mobility, luminescence, environmental stability, and processability, poly(3-alkylthiophene)s (P3ATs) are being widely employed in a number of electronic devices such as thin film transistors,[8] light-emitting diodes,[9] chemical or biological sensors,[10] and organic solar cells.[11] The performance of these devices is significantly affected by the structural organization of the component materials at the nanoscale. Therefore, the definition of detailed models of the molecular structure and intermolecular packing represents a key step to get a better understanding of the physical processes underlying device behavior. The determination of polymer crystal structures involves the quantitative analysis of experimental data such as X-ray and electron diffraction patterns, which in the case of P3ATs are often of very limited quality. Indeed, in the past few years, several atomistic simulation approaches were applied to poly(3-hexylthiophene) (P3HT) and other P3ATs to resolve ambiguities and allow the definition of well-defined atomistic models consistent with both diffraction data and energetic constraints.[12−17]

Molecular modeling on these systems relies on molecular mechanics (MM), molecular dynamics (MD), and quantum mechanical approaches (QM). QM methods specific for crystalline solids have become available in the last couple of decades.[18] The importance of these methods stems from various considerations. First of all, a knowledge of their electronic structure is fundamental to get a better insight into the properties of these materials. Second, *ab initio* and QM methods can be used synergically with experimental and MM and MD methods. In this regard, in addition, the possibility to approach these systems without the introduction of empirical parameters can be extremely important to complement and validate force field methods.

The present article is a development of previous work (experimental and molecular modeling) on the same systems.[19−25] We present the results of a thorough molecular modeling study of several thiophene-based oligomers and polymers (also including alkyl substituted systems) by solid state density functional theory (DFT) calculations. In particular, we test DFT approaches in the local density approximation (LDA) on the description of well-defined polymer and oligomer crystal structures. Among standard DFT methods, the LDA *ansatz* has recently been indicated as the best choice in the study of structures and energies of the thiophene dimer.[17] This approach was shown to give good results without requiring the optimization of empirical parameters. Limit-ordered polymer crystal structures based on powder X-ray studies have been investigated: P3MBT and forms I′ and II of P3BT. The analysis of these crystal structures is a rather severe test for the quality of the molecular modeling approach. The oligomer structures are a selection among those reported in ref 25 to compare our calculations with the experimental sublimation energies available in the literature and

also to include an oligomeric system with side alkyl chains. The investigation of thiophene oligomers is important in its own right (some of these are employed in organic electronic devices prepared by sublimation or molecular beam deposition techniques) and as well-defined systems for testing both computational and structural analysis methods.

After presenting the details of the computational scheme adopted, the results are discussed and compared with the corresponding experimental models, and with those provided by MM and MD simulations employing the force field parametrization developed by our group.[25] Conclusions follow.

2. COMPUTATIONAL DETAILS

All quantum mechanical calculations were carried out by DFT in the LDA approximation.[26] The LDA-DFT scheme adopted is implemented into the DMol3 numerical-based density-functional module[27] of the Materials Studio 5.5 package from Accelrys Inc.[28] The DFT functional by choice was that developed by Perdew and Wang (PWC),[29] as it proved to be adequate to describe, for example, structures and energies of porphyrin−fullerene C60 complexes,[30] carbon nanotube clusters,[31] thiophene dimers,[17] and supermolecular systems containing charged particles.[32] The PWC functional was used in conjunction with the double-ζ numerical basis set (DNP), which has polarization functions on all atoms.[33] In some cases, the functional by Vosko, Wilk, and Nusair (VWN)[34] was also used showing the same level of accuracy of PWC/DNP calculations. The numerical basis sets of DMol3 are more complete than the corresponding Gaussian basis sets of double-ζ plus polarization quality and are expected to have a small basis set superposition error (BSSE) contribution.[35] A small BSSE was verified by Govind et al.[36a] and Andzelm et al.,[36b] performing calculations on a water dimer. The interaction energy changed by less than 0.5 kcal/mol on going from DNP to a larger basis (i.e., five numerical functions per every valence orbital, supplemented with three sets of polarization diffuse functions) in these calculations, indirectly proving that further basis set extensions have a small BSSE effect on interaction energies.

Energy minimizations were performed on each structure by an "atoms-only" (ao) optimization scheme of the atomic coordinates and keeping the lattice parameters at their experimental values. The values of the RMSD(ao) parameter, which are the root-mean-square displacements of the atoms (excluding hydrogens) from their original experimental positions, were determined. In some cases, starting from the (ao) optimized structure, a second "full cell" (fc) minimization was carried out optimizing both the atomic coordinates and the lattice parameters. All the calculations were performed by an all-electron approach on a unit cell of the crystal. The crystal symmetry specified by the space group is exploited in the initial setup of the calculations, but it is not enforced during the energy minimizations. Nonetheless, in the investigated cases, we never observed a change in crystal symmetry.

The LDA combined with the PWC functional was used with the Harris approximation[37] to reduce the computational time for geometry optimizations. Severe convergence tolerances for geometry optimization were chosen (energy change of 1.0×10^{-5} Ha; maximum force change of 3.8×10^{-3} Ha/a_0, i.e., 2.0×10^{-3} Ha/Å, and maximum displacement of 9.4×10^{-3} a_0, i.e., 5.0×10^{-3} Å), with the global orbital cutoff of 7.6 a_0 (i.e., 4.0 Å). The electron smearing values, when used, were gradually reduced from 5.0×10^{-3} Ha, which is the default in DMol3, to

1.0×10^{-5} Ha, which is the smallest allowed value and finally to zero (Fermi occupation).[31]

The MM and MD results obtained with the force field FF3 developed by Moreno et al.[25] are also reported for comparison. This adopts the standard OPLS-AA functional form,[38] borrowing several OPLS-AA parameters (e.g., Lennard-Jones potentials, bond-stretching, and bending energies) and reoptimizing some others (atomic charges, bond torsion potentials). The Supporting Information for ref 25 contains a full force field parameter file, which may be readily used with the TINKER package.[39]

3. RESULTS AND DISCUSSION

We applied the PWC/DNP approach to the minimization of the crystal forms of a few representative oligo- and polythiophenes, both with and without pendant alkyl chains (see Figure 1 for sketches of the corresponding chemical structures):
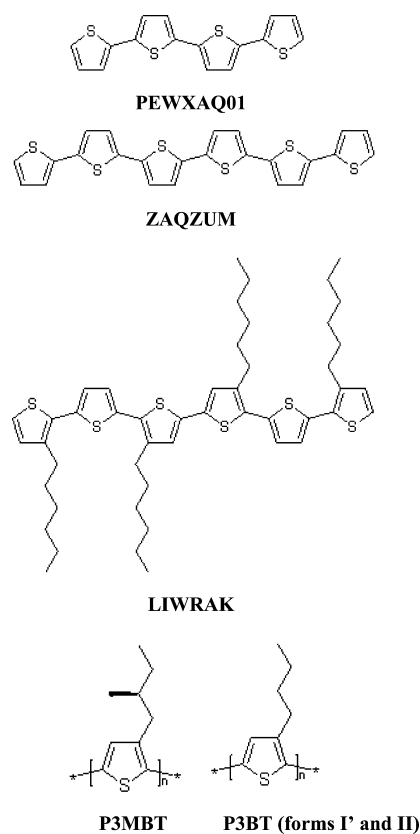

PEWXAQ01

ZAQZUM

LIWRAK

P3MBT   **P3BT (forms I' and II)**

Figure 1. Molecular structures of the investigated thiophene oligomers and polymers.

(1) the "low temperature" form of α-quaterthiophene, 4T (PEWXAQ01[40] code in the Cambridge Structural Database, CSD[41])

(2) the "low temperature" form of α-sexithiophene, 6T (ZAQZUM[42] in the CSD)

(3) the "yellow" form of 3,3″,4‴,3″″‴-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2″″:5″″:2″″‴-sexithiophene (LI-WRAK[43] in the CSD)

(4) the I' form of regioregular poly(3-butylthiophene) (P3BT form I')[21]

B

dx.doi.org/10.1021/jp310066q | *J. Phys. Chem. B* XXXX, XXX, XXX−XXX

(5) the II form of regioregular poly(3-butylthiophene) (P3BT form II)[22]

(6) the crystalline regioregular poly(3-S-methylbutylthiophene) (P3MBT)[20]

Figures 2−8 contain views of all the crystal structures, providing a qualitative idea of the structural motifs encountered
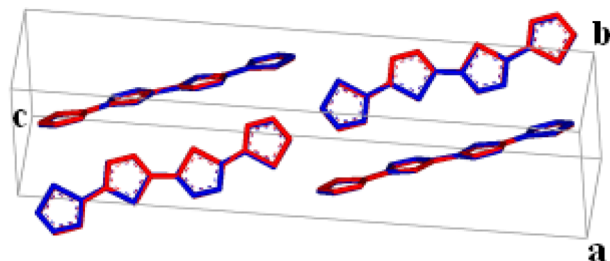

Figure 2. A view of a unit cell of PEWXAQ01 (quaterthiophene). The experimental structure is shown in blue, while the calculated structure is shown in red (PWC/DNP minimization with fixed lattice parameters). Hydrogens have been omitted for clarity.
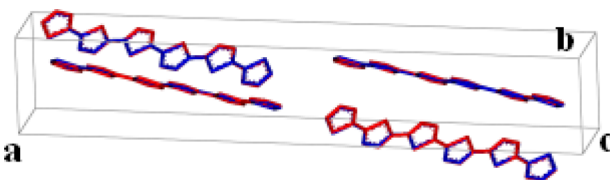

Figure 3. A view of sexithiophene in the ZAQZUM unit cell. The experimental structure is shown in blue, while the calculated structure is shown in red (PWC/DNP minimization with fixed lattice parameters). Hydrogens have been omitted for clarity.

Figure 4. A view of a unit cell of LIWRAK. The experimental structure is shown in blue, while the calculated structure is shown in red (PWC/DNP minimization with fixed lattice parameters). Hydrogens have been omitted for clarity.
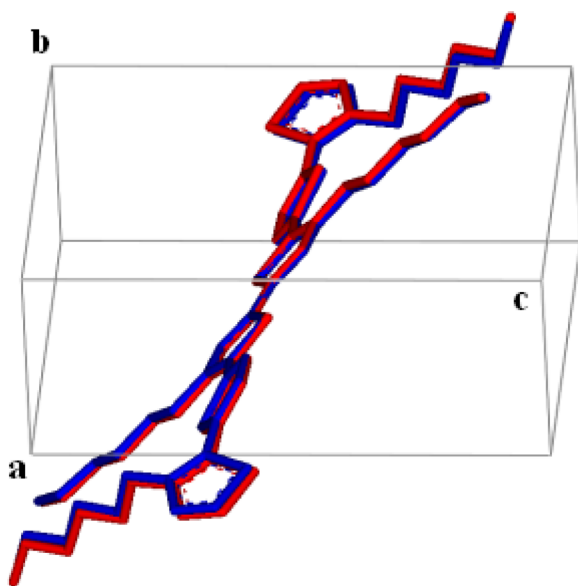
in these systems and of the overall quality of the final results. Table 1 contains a summary of the PWC/DNP minimization results for the systems under investigation.

First of all, we performed "atoms-only" (ao) optimizations. The results have been summarized in Table 1 by the RMSD(ao) parameter. In selected cases, starting from ao-optimized structures, "full cell" (fc) minimizations were carried out. The results are summarized in Tables 2 and 3 (PEWXAQ01 and P3MBT systems, respectively) by the values of the final lattice parameters in comparison with available experimental values and with those corresponding to the force field FF3 developed by Moreno et al.[25] Finally, Table 4 contains the heats of sublimation for the PEWXAQ01 and LIWRAK systems calculated at the PWC/DNP level together with available experimental data[44] and the corresponding values obtained by Moreno et al.[25]

In the following discussion, we shall start from the oligomer structures and then move on to consider the two polymers. According to the results in Table 1, PWC/DNP minimized structures of oligomers compare very well with experimental crystal structures, giving results very close to those provided by the FF3 force field. In the cases of PEWXAQ01 and ZAQZUM, PWC/DNP models show even closer agreement with experimental structure data, with root-mean-square displacements of non-hydrogen atoms of a few hundredths of Å. When considering the prediction of the unit cell parameters (see PEWXAQ01 in Table 2), it should be noted that experimental data are collected at room temperature while calculated cell parameters refer to 0 K. For all oligomers, RMSD(ao) values are lower than 0.2 Å with the higher value pertaining to the LIWRAK system (RMSD(ao) = 0.19 Å) containing an alkyl side chain that could be affected by disorder and thus be responsible for the higher disagreement of the predictions. Visual inspection of the structures in Figures 2−4 demonstrates that the approach here adopted reproduces fairly well the conformation of both the conjugated main chains and of the alkyl side chains of the systems under investigation (see again Table 1 for the corresponding RMSD values of the calculated structures).

In the cases of the PEWXAQ01 and ZAQZUM crystal structures, the calculations evidenced that 4T and 6T molecules adopt herringbone packing arrangements along the *b* axes generating improper blue-shifting hydrogen bonds[45] by the interaction of C−H moieties of a ring with π electrons of adjacent molecules also including C−H···S specific interactions.[24] Because of these interactions, the C−H bonds are shortened by about 0.01 Å with respect to isolated gas phase molecules. Work is in progress in our group to characterize these intermolecular interactions (energies, structures, and electron density topology) by high level first principle calculations on model systems.[46]

We now turn to the discussion of crystal structures of the two polymers, namely, forms I′ and II of P3BT and P3MBT.[20−22] We started with the P3BT system, and we studied isolated chain conformations that can be considered the most plausible from previous calculations on polymers and from oligomer crystal structures. PWC/DNP calculations confirmed the three energy minima (see Figure 5) all characterized by a planar or quasi-planar thiophene backbone conformation. The *glide* plane conformation and the helical conformation with side chain plane approximately orthogonal to the thiophene backbone plane are very close in energy, differing by about 0.10 kcal/mol/(monomeric unit). In particular, whereas the latter has an essentially planar main chain, the former (the more stable conformation) has a slight deviation from the planarity (inter-ring angle of about 8° along
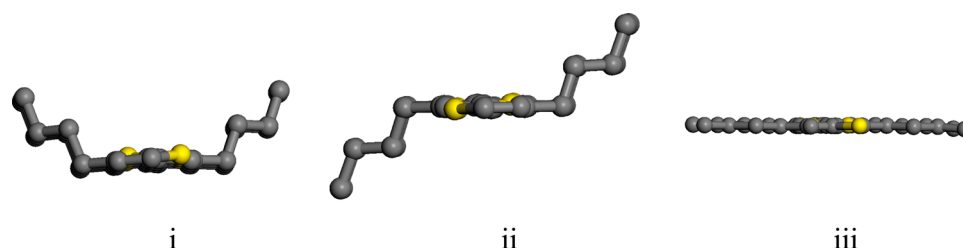
Figure 5. A view along the backbone axes of minimized P3BT isolated chains. Three main families of planar conformations were investigated: (i) p_c *glide*, (ii) $p2_1$ helix with side chains orthogonal to thiophene rings plane, and (iii) $p2_{1/c}$ planar conformation with side chains in the plane of thiophene rings. Hydrogens have been omitted for clarity.
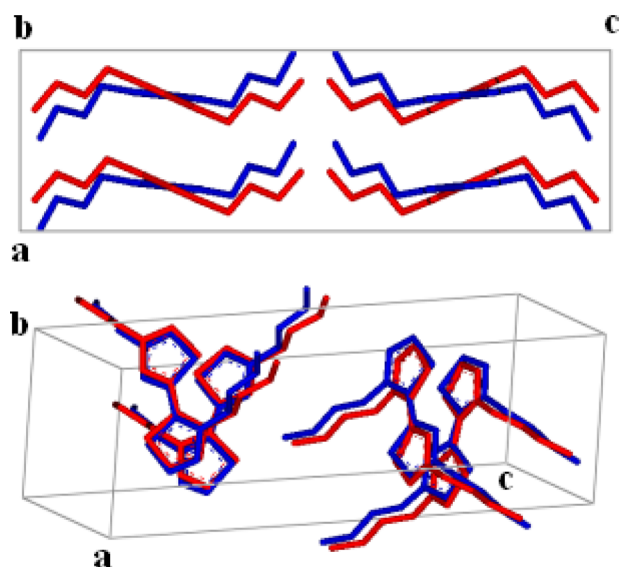

Figure 6. A view of a unit cell of P3BT form I′. The experimental structure is shown in blue, while the calculated structure is shown in red (PWC/DNP minimization with fixed lattice parameters). Hydrogens have been omitted for clarity.
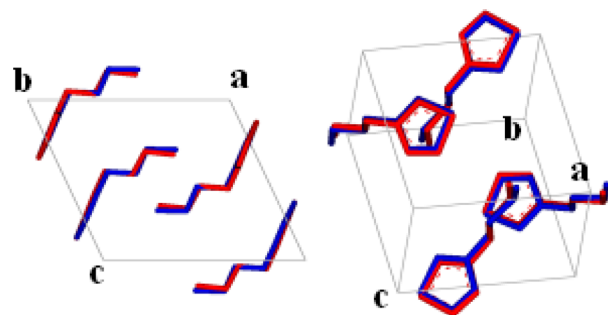
Figure 7. A view of a unit cell of P3BT form II. The experimental structure is shown in blue, while the calculated structure is shown in red (PWC/DNP minimization with fixed lattice parameters). Hydrogens have been omitted for clarity.

Figure 8. A view of a unit cell of P3MBT. The experimental structure is shown in blue, while the calculated structure is shown in red (PWC/DNP minimization with fixed lattice parameters). Hydrogens have been omitted for clarity.

Table 1. Summary of PWC/DNP and FF3[25] "Atoms-Only" Energy Minimizations[a]

crystal phase	RMSD(ao) PWC/DNP	RMSD(ao) FF3[25]
PEWXAQ01	0.06	0.16
ZAQZUM	0.05	0.24
LIWRAK	0.19	0.15
P3MBT	0.34	0.38
P3BT form I′	0.73	0.44
P3BT form II	0.22	0.32

[a]The values of RMSD(ao) parameter, which are the root-mean-square displacements of the atoms (excluding hydrogens) from their experimental positions, are reported (Å).

the backbone). The helical mode presents a side chain that lies at 81° out of plane defined by the thiophene rings. The third structure with side chains coplanar to the main chain has an energy higher by about 0.83 kcal/mol. Concerning the packed P3BT chains, we minimized the structures of form I′ and II (see Table 1 and Figures 6 and 7). According to the results in Table 1, PWC/DNP structures of the two forms compare very well with both experimental crystal structures and FF3 calculations. The form II model shows a better correspondence than the form I′ model. This outcome might be partly due to
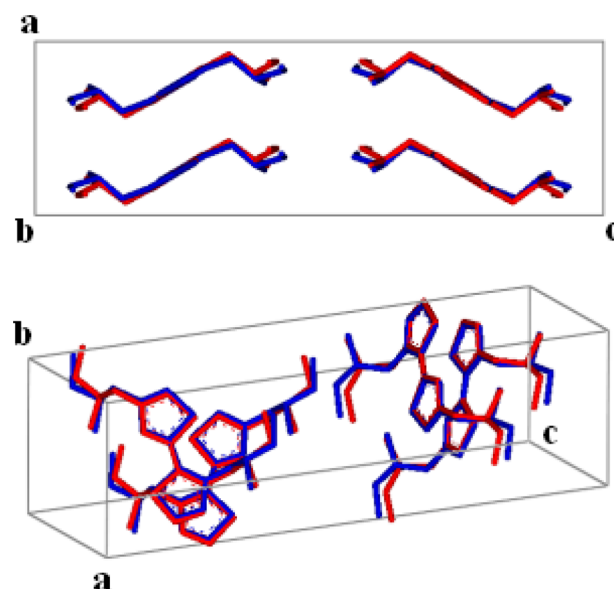
the greater uncertainty about the crystal structure of form I′, which was derived solely on the basis of X-ray powder diffraction (unlike form II, which relied also on the analysis of electron diffraction data). Our previous MD simulations indicate also a larger amplitude of motions in I′ than in II.[25] The more "static" nature of form II might explain the better performance of the DFT calculations. It should be noted that the model proposed for form II is more stable than that proposed for form I′ by about 0.2−0.3 kcal/mol, confirming previous molecular modeling calculations. In form II, side chains are interdigitated and the system presents a higher mass

Table 2. Summary of "Full Cell" PWC/DNP Minimization Results for PEWXAQ01[a]

parameter	experimental	PWC/DNP	FF3[25]
RMSD(ao) (Å)		0.06	0.16
a (Å)	6.085	5.943 (−2.33%)	5.902 (−3.00%)
b (Å)	7.858	7.625 (−2.97%)	7.634 (−2.85%)
c (Å)	30.483	30.442 (−0.14%)	31.112 (+2.06%)
β (deg)	91.81	90.42	93.18

[a]Column 3 reports the corresponding results obtained with the force field FF3 developed by Moreno et al.[25]

Table 3. Summary of "Full Cell" PWC/DNP Minimization Results for P3MBT[a]

parameter	EXP[20]	PWC/DNP	FF3[25]
RMSD(ao) (Å)		0.34	0.38
a (Å)	8.242	8.12 (−1.50%)	8.37 (+1.59%)
b (Å)	7.75	7.73 (−0.25%)	7.78 (+0.42%)
c (Å)	27.00	26.32 (−2.52%)	25.29 (−6.36%)

[a]Column 3 reports corresponding results obtained with the force field FF3 developed by Moreno et al.[25]

Table 4. Comparison of the Experimental and Calculated Heats of Sublimation (in kcal/mol) (by PWC/DNP and by Force Field FF3 Developed by Moreno et al.[25]) of α-Quaterthiophene and α-Sexithiophene, from the Atoms-Only Minimizations of the "Low Temperature" Forms

	Exp[44]	PWC/DNP(ao)	FF3(ao)[25]
T4	33.3 ± 1.5	37.1[a]	36.3
T6	50.0 ± 1.0	54.5	53.9

[a]The corresponding value calculated by VWN/DNP minimization is 37.2 kcal/mol. The heat of sublimation obtained by full optimized cell at the PWC/DNP level of calculation is 40.2 kcal/mol.

density and a more stable packing than form I type structures. The relative potential energy of the two families of polymorphs is likely to apply at least to the same extent to P3ATs with longer side chains, such as poly(3-hexylthiophene) and poly(3-octylthiophene) (P3OT).

In the case of P3MBT (see Table 1 and Figure 8), the PWC/DNP minimized structures compare very well with both experimental crystal structures and FF3 calculations. Optimized lattice parameters (see Table 3) show a small deviation also with respect to experimental values. The disagreement is in the range 1−2%, as found by FF3 calculations.[25]

In the case of α-quaterthiophene and α-sexithiophene, the energies obtained from the crystal structure optimizations can also be used to compute their heats of sublimation, which have been measured experimentally.[44] We computed the heats of sublimation as

$$\Delta H^0_{subl} \cong U_{gas} - U_{cr} \qquad (1)$$

where U_{cr} and U_{gas} are potential energies per mole in the crystal and gas phase (the latter from single-molecule optimization). In eq 1, we have neglected the RT ($\approx p\Delta V$) correction to the right-hand side. This is only 0.6 kcal/mol at 300 K, which is comparable with the experimental uncertainties and accounts for a relatively modest 2−5% of the heats of sublimation. We see that PWC/DNP calculations (Table 4) give heats of sublimation in good agreement with experiment and with MM calculations.[25] The results are unchanged when the VWN

functional is adopted, while there is an overestimation of the heat of sublimation when lattice parameters are fully optimized (see footnote of Table 4).

To summarize, our PWC/DNP calculations are all broadly satisfactory in the difficult task of modeling the crystal structures of thiophene-based oligomers and polymers. They reproduce all the crystal structures in our test set, with acceptable deviations from the experimental atomic coordinates and lattice parameters. A detailed comparison with MM calculations allows us to conclude that the adopted PWC/DNP approach shows in many cases even closer agreement with experimental structure parameters than specific force fields. The approach does not require the optimization of empirical parameters.

4. CONCLUSIONS

We have presented the results of a quantum mechanical study of some thiophene-based oligomers and polymers by solid state DFT calculations. In particular, we have considered the crystal structures of two polymers reported by our group, on the basis of powder X-ray Rietveld refinements: P3MBT[20] and forms I′[21] and II[22] of P3BT. The calculations at the PWC/DNP level of the DFT theory demonstrate that a standard QM approach can provide a balanced description of overall structure and energetics of thiophene-based materials without necessarily resorting to the latest-generation density functionals, which may contain a number of empirical parameters. In addition, the results compare well with the specific force field parametrization developed by our group.[25] In many cases, PWC/DNP models show even closer agreement with experimental structure determination results, making it the method of choice for computationally accessible problems. Of course, a DFT-based approach has also the advantage of providing information about band structures and density of states, which may be useful for discussing electronic properties related to charge and energy transport. Finally, DFT minimizations confirm that the reported crystal structures of P3MBT and P3BT correspond to well-defined energetic minima, as shown by our previous MD simulations.[25]

Future work will be devoted to the study of new solid phase systems with longer side chains (such as P3HT and P3OT) by DFT approaches, testing also the performance of gradient-corrected (GGA) and dispersion-corrected (DFT-D) methods. We intend to compare and validate experimental structures and force-field simulations. Improvements in our force field parameters will also be attempted, taking into account the results of these calculations. As underlined in the Results and Discussion section, some of the investigated crystal structures of packed oligomers contain improper blue-shifting C−H/π hydrogen bonds[45] and C−H···S specific interactions.[24] Work is also in progress in our group to characterize these interactions (energies, structures, and electron density topology) by high level first principle calculations on model systems.[46]

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: antonino.famulari@polimi.it. Phone: +39-02-2399-3044. Fax: +39-02-23993080.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Roncali, J. *Chem. Rev.* **1997**, *97*, 173−205.

(2) *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(3) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, Germany, 1999.

(4) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571−588.

(5) Mena-Osteritz, E. *Adv. Mater.* **2002**, *14*, 609−616.

(6) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202−1214.

(7) *Handbook of Thiophene-Based Materials*; Perepichka, I. F., Perepichka, D. F., Eds.; Wiley-Blackwell: Chichester, U.K., 2009; Vols. *1* and *2*.

(8) (a) Katz, H. E.; Bao, Z. *J. Phys. Chem. B* **2000**, *104*, 671−678. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99−117.

(9) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402−428. (b) Kohler, A.; Wilson, J. S.; Friend, R. H. *Adv. Mater.* **2002**, *14*, 701−707.

(10) (a) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574. (b) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581−1593.

(11) (a) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324−1338. (b) Thompson, B. C.; Frechet, J.-M. *Angew. Chem., Int. Ed.* **2008**, *47*, 58−77.

(12) Maillard, A.; Rochefort, A. *Phys. Rev. B* **2009**, *79*, 115207.

(13) Northrup, J. E. *Phys. Rev. B* **2007**, *76*, 245202.

(14) Johansson, E.; Larsson, S. *Synth. Met.* **2004**, *144*, 183−191.

(15) Cheung, D. L.; McMahon, D. P.; Troisi, A. *J. Phys. Chem. B* **2009**, *113*, 9393−9401.

(16) Lan, Y.-K.; Huang, C.-I. *J. Phys. Chem. B* **2008**, *113*, 14857−14862.

(17) Melis, C.; Colombo, L.; Mattoni, A. *J. Phys. Chem. C* **2011**, *115*, 576−581.

(18) (a) Pisani, C. *Quantum-Mechanical Ab-initio Calculation of the Properties of Crystalline Materials*; Lecture Notes in Chemistry, Vol. *67*; Spinger Verlag: Heidelberg, Germany, 1996. (b) Dovesi, R.; Civalleri, B.; Orlando, R.; Roetti, C.; Saunders, V. R. *Rev. Comput. Chem.* **2005**, *21*, 1−125. (c) Towler, M. D.; Causà, M.; Zupan, A. *Comput. Phys. Commun.* **1996**, *98*, 181−205.

(19) Catellani, M.; Luzzati, S.; Bertini, F.; Bolognesi, A.; Lebon, F.; Longhi, G.; Abbate, S.; Famulari, A.; Meille, S. V. *Chem. Mater.* **2002**, *14*, 4819−4826.

(20) Arosio, P.; Famulari, A.; Catellani, M.; Luzzati, S.; Torsi, L.; Meille, S. V. *Macromolecules* **2007**, *40*, 3−5.

(21) Arosio, P.; Famulari, A.; Moreno, M.; Raos, G.; Catellani, M.; Meille, S. V. *Chem. Mater.* **2009**, *21*, 78−87.

(22) Buono, A.; Son, N. H.; Raos, G.; Gila, L.; Cominetti, A.; Catellani, M.; Meille, S. V. *Macromolecules* **2010**, *43*, 6772−6781.

(23) Raos, G.; Famulari, A.; Marcon, V. *Chem. Phys. Lett.* **2003**, *379*, 364−372.

(24) Raos, G.; Famulari, A.; Meille, S. V.; Gallazzi, M. C.; Allegra, G. *J. Phys. Chem. A* **2004**, *108*, 691−698.

(25) Moreno, M.; Casalegno, M.; Raos, G.; Meille, S. V.; Po, R. *J. Phys. Chem. B* **2010**, *114*, 1591−1602.

(26) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford Scientific: Oxford, U.K., 1989. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley VCH: New York, 2001. (c) Jensen, F. *Introduction to Computational Chemistry*; Wiley and Sons: Chichester, U.K., 2007.

(27) (a) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508−517. (b) Delley, B. *J. Phys. Chem.* **1996**, *100*, 6107−6110. (c) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756−7764. (d) Baker, J.; Kessi, A.; Delley, B. *J. Chem. Phys.* **1996**, *105*, 192−212. (e) Andzelm, J.; King-Smith, R. D.; Fitzgerald, G. *Chem. Phys. Lett.* **2001**, *355*, 321−326.

(28) *Materials Studio*; Accelrys, Inc.: San Diego, CA, 2011.

(29) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244−13249.

(30) (a) Kolokoltsev, Y.; Amelines-Sarria, O.; Gromovoy, T. Yu.; Basiuk, V. A. *J. Comput. Theor. Nanosci.* **2010**, *7*, 1095−1103. (b) Amelines-Sarria, O.; Kolokoltsev, Y.; Basiuk, V. A. *J. Comput. Theor. Nanosci.* **2010**, *7*, 1996−2003. (c) Basiuk, V. A.; Amelines-Sarria, O.; Kolokoltsev, Y. *J. Comput. Theor. Nanosci.* **2010**, *7*, 2322−2330.

(31) Basiuk, V. A. *Int. J. Quantum Chem.* **2011**, *15*, 4197−4205.

(32) (a) Yu, G.; Yin, S.; Liu, Y .; Shuai, Z.; Zhu, D. *J. Am. Chem. Soc.* **2003**, *125*, 14816−14824. (b) Maccaroni, E.; Malpezzi, L.; Famulari, A.; Masciocchi, N. *J. Pharm. Biomed. Anal.* **2012**, *60*, 65−70.

(33) Delley, B.; Ellis, D. E.; Freeman, A. J.; Baerends, E. J.; Post, D. *Phys. Rev. B* **1983**, *27*, 2132−2144.

(34) Vosko, S. J.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(35) (a) Simperler, A.; Watt, S. W.; Bonnet, P. A.; Jones, W.; Motherwell, W. D. S. *CrystEngComm* **2006**, *8*, 589−600. (b) Kim, B. G.; Li, X.; Blowers, P. *Langmuir* **2009**, *25*, 2781−2789. (c) Boys, S. F.; Bernanrdi, F. *Mol. Phys.* **1970**, *19*, 553−566. (d) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024−11031. (e) Famulari, A.; Gianinetti, E.; Raimondi, M.; Sironi, M. *Int. J. Quantum Chem.* **1998**, *69*, 151−158. (f) Famulari, A.; Raimondi, M.; Sironi, M.; Gianinetti, E. *Chem. Phys.* **1998**, *232*, 275−287. (g) Famulari, A.; Raimondi, M.; Sironi, M.; Gianinetti, E. *Chem. Phys.* **1998**, *232*, 289−298.

(36) (a) Govind, N.; Andzelm, J.; Reindel, K.; Fitzgerald, G. *Int. J. Mol. Sci.* **2002**, *3*, 423−434. (b) Andzelm, J.; Govind, N.; Fitzgerald, G.; Maiti, A. *Int. J. Quantum Chem.* **2003**, *91*, 467−473.

(37) Harris, J. *Phys. Rev. B* **1984**, *31*, 1770−1779.

(38) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225−11236.

(39) Ponder, J. W. *TINKER: Software Tools for Molecular Design*, 6.1 ed.; Washington University School of Medicine: Saint Louis, MO, 2012.

(40) Siegrist, T.; Kloc, C.; Laudise, R. A.; Katz, H. A.; Haddon, R. C. *Adv. Mater.* **1998**, *10*, 379−382.

(41) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380−388.

(42) Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J. L.; Garnier, F. *Chem. Mater.* **1995**, *7*, 1337−1341.

(43) Destri, S.; Ferro, D. R.; Khotina, I. A.; Porzio, W.; Farina, A. *Macromol. Chem. Phys.* **1998**, *199*, 1973−1979.

(44) Kloc, C.; Laudise, R. A. *J. Cryst. Growth* **1998**, *193*, 563−571.

(45) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253−4264.

(46) Baggioli, A.; et al. Manuscript in preparation, 2012.

F

dx.doi.org/10.1021/jp310066q | *J. Phys. Chem. B* XXXX, XXX, XXX−XXX