

Scientific paper

# Computational Thermo-chemical Study of Enthalpies of formation of $\beta$ -Alkylthiophenes Using *Ab Initio* and DFT Calculations

Hossein Nikoofard

Faculty of Chemistry, Shahrood University, Shahrood 36199-95161, Iran

\* Corresponding author: E-mail: hnikoofard@shahroodut.ac.ir  
Tel.: +98 23 3239 5441; Fax: +98 23 3239 5441

Received: 07-05-2015

## Abstract

The values for the standard molar enthalpies of formation of a series of the  $\beta$ -ring position alkyl-substituted thiophenes are calculated at 298.15 K using the Hartree-Fock (HF) and density functional theory (DFT) calculations. The results obtained are discussed in terms of the substituent effect on the structural, electronic, and energetics of the titled molecules. In the atomization energy route, the values for the standard enthalpies of formation of these compounds in the gas phase,  $\Delta H_{f,298}^{\circ}$ , obtained using the B3LYP/6-31G(d,p) level of theory, can be successfully correlated to the substituent length via an excellent linear dependence. However, the  $\Delta H_{f,298}^{\circ}$  (g) values (g) obtained using the HF/6-31G(d,p) level of theory are not able to predict the experimental behavior of the alkyl thiophenes (ATs). In the formation reaction route, both the DFT and HF calculations reveal the same trend for the predicted values for the standard enthalpies of formation of these compounds in the condensed phase. It could be anticipated that the proposed method can be extended to estimate the relative thermodynamic stabilities of the oligomers and polymers consisting of these building blocks.

**Keywords:** Computational thermo-chemical study; Standard molar enthalpies of formation; Atomization energy; Hess's law;  $\beta$ -alkylthiophenes.

## 1. Introduction

During the past decade, the thiophene-based compounds have been extensively used in modern drug design, biochemistry, opto-electronic devices, and electrically conductive polymers. Their applications have received a great deal of attention from both the academic and industrial research centers.<sup>1-4</sup> The ease in the chemical modification of the structures of these materials can potentially allow us to fine-tune their optical and electronic properties.<sup>5-9</sup> These properties strongly depend upon the degree of the electronic delocalization present in such materials, effective conjugated length, and introduction of substituents at specific positions. However, a significant drawback of thiophene-based compounds is their low fluorescence and poor stability with respect to those consisting of substituted derivatives.<sup>10</sup>

Conducting polythiophenes with modified solubilities in some industrially important solvents have recently been synthesized by introducing proper substituents on

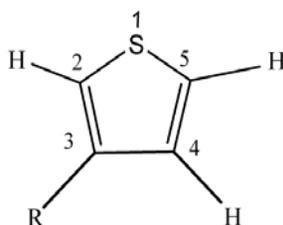
the monomer rings.<sup>11,12</sup> The substituents at the  $\beta$ -position of the monomer rings prevent the undesirable  $\alpha$ - $\beta$  couplings that decrease the conjugated length and solubility of the polymers, and also, the substitution plays an important role in the electrical and electro-optical properties of the polymers.<sup>13</sup> It is clear that the electronic and structural properties of a substituent contribute to the delocalization of the polymer  $\pi$ -conjugate system. However, the introduction of an electron-donating substituent at the  $\beta$ -position of a thiophene ring might be an interesting strategy to prevent defects, and withhold or even surpass the desirable properties of the polymers.<sup>14-18</sup> The alkyl group (*R*) is one of the most common substituents found in natural products. This group, as an electron donor one, has been of great use in studying the reaction mechanisms of the thiophene-based conductive polymers. More specifically, poly( $\beta$ -alkylthiophenes) combine chemical stability, good melting, and solution processability with the electronic and optical properties. They are also used as active materials in the light emitting diodes (LEDs), and have useful

physical properties such as electrical conductivity and electro-luminescence.<sup>19</sup>

Knowledge of the thermo-chemical properties of thiophene derivatives is essential not only in the development and understanding the structure-energetic relationships but also in the rationalization of their applications. The influence of substituents on the structure and reactivity of the thiophenes-based compounds is one of the most widely studied issues in physical organic chemistry. A development in understanding the structural effects on the thermodynamic stabilities of such compounds is reflected in their gas-phase enthalpies of formation. Over the past years, theoretical calculations based on the *ab initio* and DFT calculations have been employed to investigate the different aspects related to the molecular and electronic structures of thiophene and its substituted derivatives.<sup>20–27</sup>

Theoretical investigations carried out on a series of substituted thiophenes are, thereby, desirable for designing novel functional materials, and this is the main purpose of the current work. In the previous works,<sup>28–31</sup> we have studied a series of substituted pyrroles and thiophenes as potential monomers for the synthesis of conductive polymers and the corresponding oligomers with modified physical and electrical characteristics. In this work, we carried out a thermodynamic study of  $\beta$ -alkylthiophenes (ATs), whose structural formulas are depicted in Scheme 1. We predicted the values for the standard molar enthalpies of formation of ATs in the gas phase at 298.15 K (in brief, 298 K). The atomization and formation reaction routes were used as the selected approach. Both the HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory allowed estimation of the  $\Delta H_{f,298}^\circ$  values for ATs, which were then compared with the experimental values available in the literature. We focused mainly on the energetic differences between the AT derivatives containing different alkyl groups ( $R: C_nH_{2n+1}$ ; with  $n = 0–8$ ), and the substituent effect in ATs relative to thiophene.

T: Thiophene  
MeT: Methylthiophene  
EtT: Ethylthiophene  
PrT: Propylthiophene  
BuT: Butylthiophene  
PnT: Pentylthiophene  
HxT: Hexylthiophene  
HpT: Heptylthiophene  
OcT: Octylthiophene



**Scheme 1.** Structural and numbering scheme used for  $\beta$ -alkylthiophenes.

## 2. Computational Details

The ground-state geometry of each molecule studied in this work was fully optimized using the gradient procedure at both the Hartree-Fock and hybrid density function-

nal B3LYP techniques, together with the 6-31G(d,p) basis set, as implemented in the Gaussian 09 program package.<sup>32–35</sup> The optimized structures were confirmed to be the real minima by performing the frequency calculations. The absolute enthalpies were then obtained at 298.15 K and 1.0 atm by considering the corresponding thermal calculations obtained from the calculated harmonic vibrational frequencies.

## 3. Results and Discussion

### 3.1. Structural and Electronic Properties

The detailed values for the geometrical properties of each optimized structure, calculated by means of both the HF and DFT levels of theory, are given in Tables S1 and S2 of the supporting information. Several important structural parameters at the HF calculations are collected in Table 1. One of these parameters related to the extent of the aromaticity of the thiophene derivatives is the molecular planarity that can be reflected by the torsional angle,  $D_{ijkl}$ , where  $i, j, k$ , and  $l$  are the atom numbers, as defined in Scheme 1. According to Table 1, the dihedral angles defining the torsion between the alkyl group and thiophene ring ( $D_{R345}$ ) and the torsion between the carbon atoms contained in the thiophene ring ( $D_{2345}$ ) indicate that all ATs have planar structures. It is interesting that the influence of alkyl substituents on the structure of ATs does not cause increase in their torsion angles relative to the thiophene molecule (Table 1).

**Table 1.** Calculated torsion angles (in degree) and bond lengths (in angstrom) for studied species at HF/6-31G(d,p) level of theory.

ATs	$D_{R345}$	$D_{2345}$	$C_R-C_3$	$C_3-C_4$	$S_1-C_2$
T	–	0.00	–	1.3451	1.7254
MeT	0.00	0.00	1.5041	1.3462	1.7249
EtT	0.00	0.02	1.5099	1.3469	1.7246
PrT	0.00	0.00	1.5100	1.3471	1.7245
BuT	0.00	0.01	1.5102	1.3470	1.7245
PnT	0.00	0.01	1.5101	1.3470	1.7245
HxT	0.02	0.02	1.5114	1.3471	1.7245
HpT	0.01	0.01	1.5102	1.3470	1.7245
OcT	0.02	0.02	1.5101	1.3471	1.7245

However, the alkyl substituents are slightly away from the thiophene ring due to their steric hindrance, although with increase in the number of carbon atoms in the substituent ( $n$ ) no significant increase was observed in the  $C_R-C_3$  bond distance relative to the methyl group ( $n = 1$ ). It has been known that a substituent has a tendency to exchange  $p$ -electrons with the thiophene ring. An alkyl group donates a electron density to the ring. This stabilizing electronic transfer is favored by the planar arrangement of the substituent relative to the thiophene ring. This prefe-

rence is indeed observed for all molecules with the substituents being coplanar with the thiophene ring. It is clear that the electrical properties of the conducting polymers are affected by the planarity of their building blocks. The crystalline oligothiophenes have been found to be nearly planar as a result of a more favorable crystal packing.<sup>36</sup> The optimized structures obtained by the DFT calculations are in good agreement with the HF-optimized geometries.

Furthermore, compared to the thiophene molecule, the presence of alkyl groups as the  $\beta$ -substituents could improve the electron delocalization along the molecular structure. Delocalization of the  $\pi$ -electrons onto the molecular structure leads to satisfactory resonance systems and improved stabilization of the AT species. It has been shown that an extended aromatic structure may correspond to the narrow gap for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).<sup>37,38</sup> It is useful to examine HOMO and the lowest virtual orbitals for these molecules since the relative ordering of the occupied and virtual orbitals provides a reasonable qualitative indication of the excitation properties and of the ability of electron or hole transport.<sup>39</sup> Since the first dipole-allowed electron transitions as well as the strongest electron transitions with the largest oscillator strength correspond almost exclusively to the promotion of an electron from the HOMO level to the LUMO one, we calculated the HOMO-LUMO gaps (HLGs) and electric dipole moments for all the studied molecules, the results of which were tabulated in Table 2.

**Table 2.** Calculated HOMO-LUMO gaps (eV) and electrical dipole moments (Debye) for studied species.

ATs	B3LYP/6-31G(d,p) <sub>d</sub>		HF/6-31G(d,p)	
	$\mu$	HLG	$\mu$	HLG
T	0.62	0.2249	0.90	0.4657
MeT	0.98	0.2238	1.24	0.4641
EtT	1.07	0.2248	1.32	0.4653
PrT	1.06	0.2246	1.31	0.4650
BuT	1.12	0.2246	1.37	0.4650
PnT	1.09	0.2246	1.33	0.4650
HxT	1.14	0.2246	1.39	0.4649
HpT	1.11	0.2245	1.35	0.4650
OcT	1.15	0.2246	1.39	0.4649

As it can be seen in Table 2, the HLG values for the AT species are less than that for the thiophene molecule. The calculated results show that closing the  $\beta$ -positions of the thiophene rings by alkyl groups destabilizes both the HOMO and LUMO levels. The results obtained show favorably an increase in the HOMO level and a decrease in the LUMO level after closing the  $\beta$ -positions of the rings by alkyl groups, which provide reductions in the HOMO-LUMO gaps. It is known that the orientation of the elec-

tric dipole moment vectors of the thiophene monomers with respect to the direction of their oligomer chains determines the electro-chemical characteristics of polythiophene on the electrode surface. In addition, the quantities of the electric dipole moment vectors of the monomers and their interactions with the solvent and support electrolyte have key roles in their selection for the electropolymerization process.<sup>40</sup> The calculated values for the electric dipole moments of ATs are listed in Table 2. A comparative study of the dipole moments of all ATs showed that their values were larger than those for the thiophene monomers, and, therefore, the oligomers consisting of ATs are expected to be more soluble in polar solvents with respect to those consisting of thiophene.

### 3. 2. Thermo-chemical Properties

The absolute thermo-chemical properties of the studied species including the values for the standard gas-phase molar energy ( $E^\circ$ ), enthalpy ( $H^\circ$ ), entropy ( $S^\circ$ ), Gibbs energy ( $G^\circ$ ), and heat capacity ( $C_p^\circ$ ) were obtained at 298.15 K for the optimized structures by means of both the HF and DFT levels of theory (Tables S3 and S4). A comparative study of the relative Gibbs energies of ATs,  $\Delta G_{rel,298}^\circ(ATs)$ , defined as

$$\begin{aligned} \Delta G_{rel,298}^\circ(ATs) &= G_{298}^\circ(ATs) - G_{298}^\circ(T) \\ &= [H_{298}^\circ(ATs) - H_{298}^\circ(T)] - \\ &\quad - 298.15[S_{298}^\circ(ATs) - S_{298}^\circ(T)] \end{aligned} \quad (1)$$

was carried out to show (Table S5) that the insertion of an alkyl group on a thiophene ring creates a thermodynamic stabilization, which corresponds to the number of carbon atoms in the substituent via an excellent straight line (correlation coefficients,  $r^2 = 1.0000$ ), with the following equations:

$$\Delta G_{rel,298}^\circ(ATs) = -3.12 * 10^{-3} - 39.22 n; \quad (2)$$

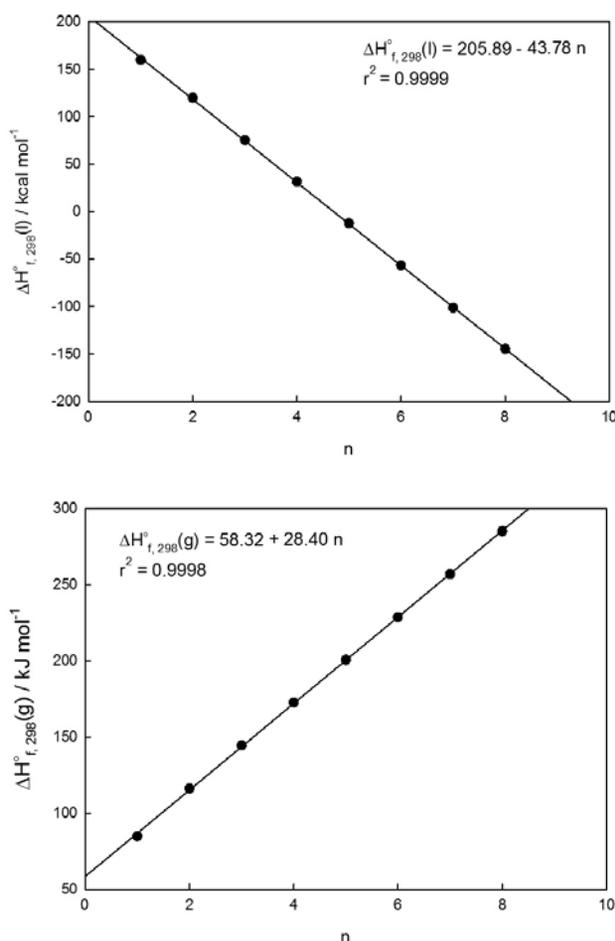
B3LYP/6-31G(d,p)

$$\Delta G_{rel,298}^\circ(ATs) = -2.55 * 10^{-3} - 39.01 n; \quad (3)$$

HF/6-31G(d,p)

However, the observed behavior for  $\Delta G_{rel,298}^\circ(ATs)$ , which was completely expected, was identical for both the B3LYP/6-31G(d,p) and HF /6-31G(d,p) levels of theory, although the former was slightly lower than the latter.

The values for the gas-phase standard molar enthalpies of formation at 298 K,  $\Delta H_{f,298}^\circ(g)$ , for ATs were estimated through the atomization procedure.<sup>41,42</sup> The calculation procedure and detailed description of the route have been reported in the literature.<sup>43</sup> The calculated values for  $\Delta H_{f,298}^\circ(g)$  at both the HF and DFT levels of theory are demonstrated in Figure 1.



**Figure 1.** Plot of gas-phase standard molar enthalpies of formation vs. number of carbon atoms in alkyl group for ATs at 298 K, obtained using atomization reaction route at B3LYP/6-31G(d,p) and HF/6-31G(d,p) levels of theory (up and down, respectively).

According to Figure 1(up), correlation of  $\Delta H_{f,298}^{\circ}(g)$  with the number of carbon atoms in the alkyl group gives an excellent straight line, with the following equation:

$$\Delta H_{f,298}^{\circ}(g) = 552.89 - 112.27 n; \quad r^2 = 1.0000 \quad (4)$$

B3LYP/6-31G(d,p)

This equation shows this well-known fact that the energetic increment for the increase of a carbon atom in the alkyl group is  $-112.27 \text{ kJ mol}^{-1}$ . Figure 1(down) reveals a similar kind of correlation, with a straight line but with an opposite sign in the slope:

$$\Delta H_{f,298}^{\circ}(g) = 58.32 + 28.40 n; \quad r^2 = 0.9998 \quad (5)$$

HF/6-31G(d,p)

Eq. (5) shows that the thermodynamic stability of the studied molecules decreases by  $+28.40 \text{ kJ mol}^{-1}$  for the entrance of a carbon atom in the alkyl group. The values for the experimental gas-phase molar enthalpies of formation at 298 K for the butyl-, hexyl-, and octylthiophenes

were tabulated in Table 3,<sup>44</sup> for which, the correlation equation can be reported as:

$$\Delta H_{f,298}^{\circ}(g) = 249.71 - 123.56 n; \quad r^2 = 0.9969 \quad (6)$$

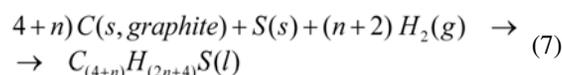
(for experiment)

**Table 3.** Experimental values for standard molar enthalpies of formation ( $\text{kJ mol}^{-1}$ ) for thiophene derivatives at 298 K.<sup>44</sup>

Condensed phase	Gaseous phase	Species
Butylthiophene	$17.31 \pm 2.59$	$28.97 \pm 5.02$
Hexylthiophene	$32.69 \pm 3.39$	$88.11 \pm 6.69$
Octylthiophene	$82.68 \pm 2.22$	$147.30 \pm 4.6$

The  $\Delta H_{f,298}^{\circ}(g)$  values for ATs calculated by the DFT level of theory in the atomization reaction route (Eq. 4) have the same trend as the experimental ones (Eq. 6). However, the  $\Delta H_{f,298}^{\circ}(g)$  values calculated using the HF approach in the atomization reaction route (Eq. 5) are not able to estimate the experimental trend for the  $\Delta H_{f,298}^{\circ}(g)$  values. It was found that the enthalpy variation for Eq. (4) amounts to  $-26.86 \text{ kJ mol}^{-1}$ , indicating an interesting stabilization, while for Eq. (5), real instabilization of the studied molecules was found. It should be pointed out here that the calculated Hartree-Fock energy is necessarily always larger (i.e. less negative) than the exact ground state energy due to neglecting the correlation energies through the HF scheme. The electron correlation is mainly caused by the instantaneous repulsion of the electrons, which are not covered by the effective HF potential.<sup>45</sup> However, the standard post-HF levels for including the correlation effect such as MP4, CCSD(T), and QCISD(T) or multi-level  $G_n$  methods are the most accurate ones, although they are the most expensive computational methods. Therefore, the observed behavior of the  $\Delta H_{f,298}^{\circ}(g)$  value, calculated by the B3LYP/6-31G(d,p) level of theory, appears to be reliable, and can be used to investigate the alkyl substituent effect on the stabilization of ATs by means of the atomization reaction route.

Furthermore, the values for the condensed-phase standard molar enthalpies of formation,  $\Delta H_{f,298}^{\circ}(l)$ , for ATs were estimated based on the formation reaction route through the following generalized formation reaction:

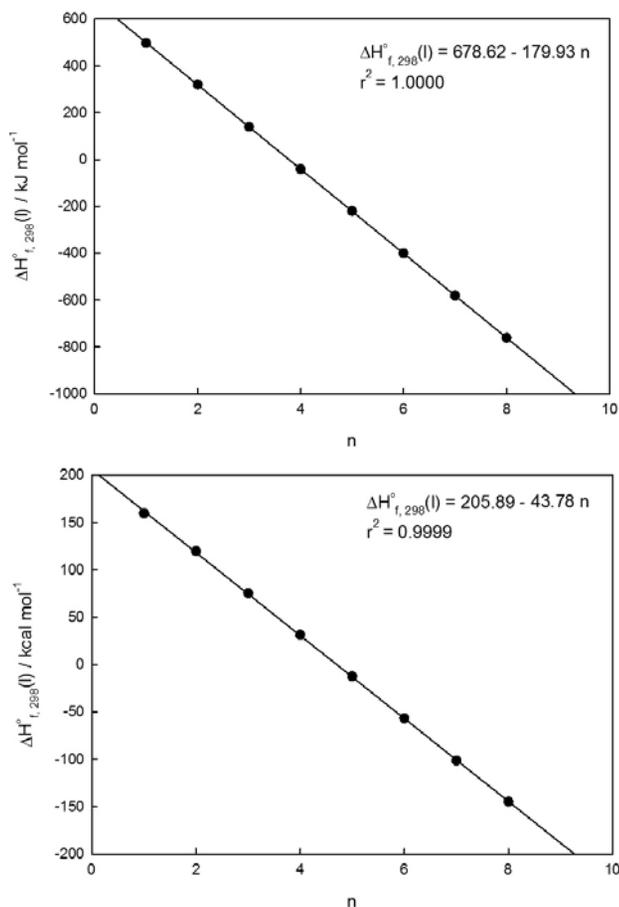


where  $n$  is the number of carbon atoms in the substituent. The reaction always forms one mole of the target substance in its standard state. To calculate the values for the standard molar enthalpies of formation (Eq. 7), we needed to use the following relationship for the enthalpies of reaction,  $\Delta H_{r,298}^{\circ}$ , as:

$$\Delta H_{r,298}^{\circ} = \sum_{\text{prod}} \Delta H_{f,298}^{\circ}(\text{prod}) - \sum_{\text{react}} \Delta H_{f,298}^{\circ}(\text{react}) \quad (8)$$

The  $\Delta H_{f,298}^{\circ}(l)$  values for ATs in Eq. (7) can be determined using the Hess's law<sup>46</sup> for the enthalpies of reaction (Eq. 8). All of the thermodynamic quantities for the stable forms of the constituting elements in Eq. (7) were calculated at the same level of theory, except for the C(s, graphite) and S(s) atoms, which were taken from the literature.<sup>47</sup> The calculated results for  $\Delta H_{f,298}^{\circ}(l)$  from the formation reaction route at both the HF and DFT computational approaches are depicted in Figure 2.

The results obtained show that attachment of alkyl groups to the thiophene ring leads to an evident reduction in the standard molar enthalpies of formation, and then an increase in the thermodynamic stabilization. It was found that both the HF and DFT calculations (Figure 2) show the same trend, in which, as the fraction of methylene group in the substituent increases, the  $\Delta H_{f,298}^{\circ}(l)$  values decrease fully linearly, which corresponds to the improvement in the stability of ATs. However, the thermodynamic stabilizations predicted by means of the DFT calculations are



**Figure 2.** Plot of condensed-phase standard molar enthalpies of formation vs. number of carbon atoms in alkyl group for ATs at 298 K, obtained using formation reaction route at B3LYP/6-31G(d,p) and HF/6-31G(d,p) levels of theory (up and down, respectively).

more than those predicted by means of the HF calculations. In general, it may be concluded that the relationships obtained between the standard molar enthalpies of formation and the length of the alkyl group helps us to predict the relative thermodynamic stability of alkyl-substituted compounds, for which the respective experimental determination was not performed.

## 4. Conclusion

In the current work, the influence of alkyl substituents on the structure-energetics of  $\beta$ -alkylthiophenes was investigated by means of the two different DFT and HF computational studies. The results obtained indicated that the electron donating groups in the alkyl substituents play fine-tune effects on the structures, electronics, and thermodynamic stabilities of ATs. The calculations carried out on the thiophene derivatives showed that alkyl substitution in thiophene created more satisfactory characteristics for the conducting polymers. Comparison of the available experimental  $\Delta H_{f,298}^{\circ}(g)$  values for ATs with those calculated in the atomization energy route showed that the B3LYP/6-31G(d,p) level of theory can establish linear correlations of  $\Delta H_{f,298}^{\circ}(g)$  with the number of carbon atoms in the alkyl group. In the atomization energy route, large discrepancies were found for the  $\Delta H_{f,298}^{\circ}(g)$  values calculated using the HF/6-31G(d,p) level of theory. However, the calculated standard molar enthalpies of formation in the condensed phase,  $\Delta H_{f,298}^{\circ}(l)$ , through the general formation reaction route, indicated that both the HF and B3LYP/6-31G(d,p) levels of theory were successful to predict the values for the relative thermodynamic stabilization of ATs, which were in good agreement with their correlation observed from the experimental measurements. The results obtained reveal that with increase in the substituent chain length, the values for the standard molar enthalpies of formation tend towards large negative values, corresponding to higher thermodynamic stabilization, which is also in agreement with the values predicted by the structural and electronic studies.

## 5. Acknowledgement

The financial support of Shahrood University is gratefully acknowledged.

## 6. References

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, *Nature* **1990**, 347, 539–541. <http://dx.doi.org/10.1038/347539a0>
2. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A.J. Heeger, *Nature* **1992**, 357, 477–479. <http://dx.doi.org/10.1038/357477a0>

3. P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, *Nature* **1992**, 356, 47–49. <http://dx.doi.org/10.1038/356047a0>
4. A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* **1998**, 110, 416–443. [http://dx.doi.org/10.1002/\(SICI\)1521-3757\(19980216\)110:4<416::AID-ANGE416>3.0.CO;2-N](http://dx.doi.org/10.1002/(SICI)1521-3757(19980216)110:4<416::AID-ANGE416>3.0.CO;2-N)
5. D. Fichou (Ed.), *Handbook of Oligo- and Polythiophenes*, Wiley, New York, **1999**.
6. M. Kobayashi, J. Chem, T. C. Chung, F. Moraes, A. J. Heeger, F. Wudl, *Synth. Met.* **1984**, 9, 77–96. [http://dx.doi.org/10.1016/0379-6779\(84\)90044-4](http://dx.doi.org/10.1016/0379-6779(84)90044-4)
7. T. C. Chung, J. H. Kaufman, A. J. Heeger, F. Wudl, *Phys. Rev. B* **1984**, 30, 702–710. <http://dx.doi.org/10.1103/PhysRevB.30.702>
8. S. Hotta, H.S. Nalwa (Ed.): *Molecular conductive materials: polythiophenes and oligothiophenes*, *Handbook of Organic Conductive Molecules and Polymers*, Wiley, Chichester, **1997**, vol. 2, pp. 309–387.
9. C. Ziegler, H.S. Nalwa (Ed.): *Thin film properties of oligothiophenes*, *Handbook of Organic Conductive Molecules and Polymers*, Wiley, Chichester, **1997**, vol. 3.
10. W. Yu, H. Meng, J. Pel, W. Huang, *J. Am. Chem. Soc.* **1998**, 120, 11808–11813. 11. X.-L. Wei, Y. Z. Wang, S. M. Long, C. Bobeczko, A. J. Epstein, *J. Am. Chem. Soc.* **1996**, 118, 2545–2552.
12. M. Tsuchiya, S. Matsui, K. Sano, T. Kojima, *J. Appl. Polym. Sci.* **1998**, 70, 471–475. [http://dx.doi.org/10.1002/\(SICI\)1097-4628\(19981017\)70:3<471::AID-APP7>3.0.CO;2-K](http://dx.doi.org/10.1002/(SICI)1097-4628(19981017)70:3<471::AID-APP7>3.0.CO;2-K)
13. G. Zotti, S. Zecchin, G. Schiavon, B. Vercelli, A. Berlin, S. Grimoldi, *Macromol. Chem. Phys.* **2004**, 205, 2026–2031. <http://dx.doi.org/10.1002/macp.200400151>
14. M. Charton, *J. Am. Chem. Soc.* **1975**, 97, 1552–1556. <http://dx.doi.org/10.1021/ja00839a047>
15. R. W. Taft, *Steric Effects in Organic Chemistry*, Wiley, New York, **1956**, pp. 556–565.
16. R. J. Waltman, J. Bargon, A. F. Diaz, *J. Phys. Chem.* **1983**, 87, 1459–1466. <http://dx.doi.org/10.1021/j100231a035>
17. M. Sato, H. Morii, *Polym. Commun.* **1991**, 32, 42–48.
18. M. Sato, H. Morii, *Macromolecules* **1991**, 24, 1196–1201. <http://dx.doi.org/10.1021/ma00005a035>
19. M. E. Nicho, H. Hu, C. Lopez-Mata, J. Escalante, *Sol. Energy Mater.* **2004**, 82, 105–118. <http://dx.doi.org/10.1016/j.solmat.2004.01.009>
20. A. Dkhissi, F. Louwet, L. Groenendaal, D. Beljonne, R. Lazzaroni, J. L. Bredas, *Chem. Phys. Lett.* **2002**, 359, 466–472. [http://dx.doi.org/10.1016/S0009-2614\(02\)00651-6](http://dx.doi.org/10.1016/S0009-2614(02)00651-6)
21. A. Dkhissi, D. Beljonne, R. Lazzaroni, F. Louwet, L. Groenendaal, J. L. Bredas, *Int. J. Quantum Chem.* **2002**, 91, 517–523. <http://dx.doi.org/10.1002/qua.10446>
22. C. Aleman, D. Curco, J. Casanovas, *Chem. Phys. Lett.* **2004**, 386, 408–413. <http://dx.doi.org/10.1016/j.cplett.2004.01.095>
23. C. Aleman, J. Casanovas, *J. Phys. Chem.* **2004**, 108, 1440–1447. <http://dx.doi.org/10.1021/jp0369600>
24. Y. Dai, E. Blaisteu-Barojas, *J. Chem. Phys.* **2008**, 129, 164903–8. <http://dx.doi.org/10.1063/1.2996297>
25. S. Suramit, A. piriyagagoon, P. Wolschann, S. Hannongbua, *Theor. Chem. Acc.* **2012**, 131, 1209–1217. <http://dx.doi.org/10.1007/s00214-012-1209-8>
26. U. Salzner, P. G. Pickup, R. A. Poirier, J. B. Lagowski, *J. Phys. Chem. A* **1998**, 102, 2572–2578. <http://dx.doi.org/10.1021/jp9716521>
27. R. Colle, A. Curioni, *J. Am. Chem. Soc.* **1998**, 120, 4832–4837. <http://dx.doi.org/10.1021/ja9735618>
28. H. Sabzyan, H. Nikoofard, *Chem. Phys.* **2004**, 107, 105–113. <http://dx.doi.org/10.1016/j.chemphys.2004.07.025>
29. H. Nikoofard, H. Sabzyan, *J. Fluor. Chem.* **2007**, 128, 668–673.
30. H. Nikoofard, A.H. Amin, M. Khorrami, *C. R. Chimie* **2013**, 16, 1147–1152. <http://dx.doi.org/10.1016/j.crci.2013.07.006>
31. H. Nikoofard, M. Gholami, *C. R. Chimie* **2014**, 17, 1034–1040. <http://dx.doi.org/10.1016/j.crci.2013.11.001>
32. M.J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 09W, Gaussian Inc., Pittsburgh PA, **2009**.
33. A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648–5652. <http://dx.doi.org/10.1063/1.464913>
34. C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1998**, 37, 785–789. <http://dx.doi.org/10.1103/PhysRevB.37.785>
35. R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, 54, 724–728. <http://dx.doi.org/10.1063/1.1674902>
36. G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J.-L. Fave, F. Garnier, *Chem. Mater.* **1995**, 7, 1337–1345. <http://dx.doi.org/10.1021/cm00055a010>
37. G. Zhang, J. Ma, Y. Jiang, *J. Phys. Chem. B* **2005**, 109, 13499–13509. <http://dx.doi.org/10.1021/jp051259c>
38. H. Cao, J. Ma, G. Zhang, Y. Jiang, *Macromolecules* **2005**, 38, 1123–1130. <http://dx.doi.org/10.1021/ma048534y>
39. M. A. De Oliveira, H. Duarte, J. Pernaut, W. B. De Almeida, *J. Phys. Chem. A* **2000**, 104, 8256–8262. <http://dx.doi.org/10.1021/jp001252p>
40. W. H. Meyer, H. Kiess, B. Binggeli, E. Meier, G. Harbeke, *Synth. Met.* **1985**, 10, 255–259. [http://dx.doi.org/10.1016/0379-6779\(85\)90031-1](http://dx.doi.org/10.1016/0379-6779(85)90031-1)
41. T. Koopmans, *Physica* **1934**, 1, 104–113. [http://dx.doi.org/10.1016/S0031-8914\(34\)90011-2](http://dx.doi.org/10.1016/S0031-8914(34)90011-2)
42. R. Notario, O. Castano, R. Comperts, L. M. Frutos, R. Palmeiro, *J. Org. Chem.* **2000**, 65, 4298–4302. <http://dx.doi.org/10.1021/jo000089r>

43. J. W. Ochterski, Gaussian white paper, Thermochemistry in Gaussian **2000**, [http://www.gaussian.com/g\\_whitepap/thermo.htm](http://www.gaussian.com/g_whitepap/thermo.htm).
44. M. A. V. Riberio da Silva, A. F. L. O. M. Santos, *J. Therm. Anal. Cal.* **2007**, *88*, 7–17. <http://dx.doi.org/10.1007/s10973-006-8326-3>
45. W. Koch, M. C. Holthausen, A Chemist's Guide to Density Functional Theory, Second Edition, Wiley-VCH Verlag GmbH, Germany, **2001**. <http://dx.doi.org/10.1002/3527600043>
46. P. Atkins, J. de Paula, Physical Chemistry for the Life Sciences, Oxford University Press, New York, **2006**.
47. Available from: <http://webbook.nist.gov/chemistry>.

## Povzetek

Z uporabo Hertree-Fockove (HF) teorije in teorije gostotnega funkcionala smo pri temperaturi 298.15 K izračunali vrednosti standardnih tvorbenih entalpij serije alkil tiofenov (ATs). Dobljene rezultate smo obravnavali z vidika vpliva substituenta na strukturne, elektronske in energijske lastnosti posamezne spojine. Ugotovili smo, da standardne tvorbenne entalpije spojin v plinski fazi,  $\Delta H_{f,298}^{\circ}(g)$ , ki smo jih dobili z uporabo B3LYP/6-31G(d,p) teorijskim nivojem, lahko uspešno koreliramo z dolžino alkilne verige substituenta, medtem ko eksperimentalnih lastnosti ni možno predvideti. Vendar tako DFT kot HF izračuni kažejo enak trend vrednosti za standardne tvorbenne entalpije tudi v kondenzirani fazi. Pričakujemo, da bi s temi metodami lahko uspešno napovedali tudi relativno termodinamsko stabilnost oligo- in polimerov zgrajenih iz teh gradnikov.