

# Theoretical Studies of Symmetric Five-Membered Heterocycle Derivatives of Carbazole and Fluorene: Precursors of Conducting Polymers

Jacek Doskocz,<sup>†,‡</sup> Marek Doskocz,<sup>‡</sup> Szczepan Roszak,<sup>†,§</sup> Jadwiga Soloducho,<sup>‡</sup> and Jerzy Leszczynski<sup>\*,†</sup>

*Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217, and Department of Chemistry, Faculty of Medicinal Chemistry and Microbiology, and Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

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Structures, electron ionization and excitation energies, and electron density distribution are studied for carbazole and fluorene derivatives substituted symmetrically by thiophene, ethylenedioxythiophene, furane, or pyrrole. The calculated properties of the molecules directly or indirectly mimic molecular parameters that are important for the design of processes of polymerization or for modeling the final polymer. The studies have been focused on the variation in the properties as a function of the chemical composition of the central fragment and the external rings. The calculated properties of consecutive oligomers indicate their fast convergence to values characterizing polymers.

## 1. Introduction

Conducting polymers are a new class of modern materials of still growing technological importance. These synthetic metals are characterized by conductivity of a magnitude that is typical for pure metals as well as by typical properties of polymers such as processibility, corrosion resistance, and low density.<sup>1</sup> Anodic electropolymerization is an important procedure for synthesizing electroactive films. The properties of the resulting conjugated polymers are a function of the monomeric components of the polymerized moiety, the organic solvent and supporting electrolyte, and the material of the anode. The rapid development of electroactive materials constituted by conjugated poly(heterocycles) was initiated in 1979 with the synthesis of poly(pyrrole).<sup>2</sup> Electropolymerization was soon applied to other aromatic compounds, including carbazole<sup>3</sup> and fluorene.<sup>4</sup> Despite the large number of projects on conjugated poly(heterocycles), the mechanism of electropolymerization is still at the stage of discussions.<sup>5,6</sup> Researchers agree, however, that electropolymerization is a unique process composed from a number of steps with the adsorption of monomers on the electrode surface and the formation of radical cations being the first step.<sup>1,7</sup> Evidence for adsorption was obtained by in situ IR spectroscopy.<sup>6,8</sup> The electrooxidation is followed by chemical polymerization processes.<sup>7,9</sup> The diffusion of molecules to the vicinity of an electrode is probably also an important factor influencing the process. Studies of  $\beta$ -substituted poly(thiophene) films indicate a linear correlation between monomeric and polymeric oxidation potentials, giving an example of a property–structure correlation between the conducting polymer and its corresponding parent monomer.<sup>10</sup> The particular steps of polymerization are influenced by the different properties of the substrate

molecules. The mobility of a molecule in an inert solvent is governed by its shape, volume, and additionally the atomic charge distribution.<sup>11</sup> The adsorption on the anodic surface is controlled by chemical properties specifying the surface–molecule affinity.<sup>12</sup> The anodic oxidation process depends on the ionization properties of the molecule. The polymerization is governed by the properties of the cations, in particular their reactivity, stability, and aromaticity.<sup>1</sup> The conductivity depends on the band gap characteristics of the polymers.<sup>13</sup> The properties of the monomers have been determined to be key parameters in polymerization processes. Monomers to a large extent determine the characteristics of the resulting polymer. A reasonable first step in the prediction of the properties of prospective polymers are theoretical studies which provide useful information by utilizing the relations between the properties of interest (e.g., cationic reactivity) and the calculated molecular features (e.g., electron spin density).<sup>14–16</sup>

The properties of symmetrical five-membered heterocyclic derivatives of carbazole and fluorene constituting monomers for electropolymerization are predicted and discussed in this work. The selection of studied moieties was associated with the performed or planned synthetic work.<sup>17–19</sup> Thiophene-9-borofluorene was added to the studied set of compounds due to its potentially interesting properties. Additionally, the variation of the properties was studied as a function of the number of polymerized units at the initial stage of the processes. The studied oligomers of poly(thiophene) carbazole contain up to five units.

## 2. Theoretical Methods and Computational Details

The ground-state geometries of the studied monomers and short oligomers were optimized by applying the density functional theory (DFT).<sup>20</sup> The DFT approach applied here utilizes Becke's three-parameter functional<sup>21</sup> with the Vosko et al. local correlation part<sup>22</sup> and the Lee et al.<sup>23</sup> nonlocal part, abbreviated as B3LYP. Geometry searches were performed for a number of possible isomers to ensure the location of the global

\* Corresponding author.

<sup>†</sup> Jackson State University.

<sup>‡</sup> Department of Chemistry, Faculty of Medicinal Chemistry and Microbiology, Wrocław University of Technology.

<sup>§</sup> Institute of Physical and Theoretical Chemistry, Wrocław University of Technology.

**TABLE 1: Dihedral Angle between the Central Fragment and External Rings for Molecule ( $\phi_{\text{mol}}$ ) and Cation ( $\phi_{\text{cat.}}$ ), Projected Surface ( $S$ ), Total Volume ( $V$ ), Dipole Moments ( $D$ ), and Aromaticity Regarding One (arom-I) and Two (arom-II) External Rings (See Text for Definition)<sup>a</sup>**

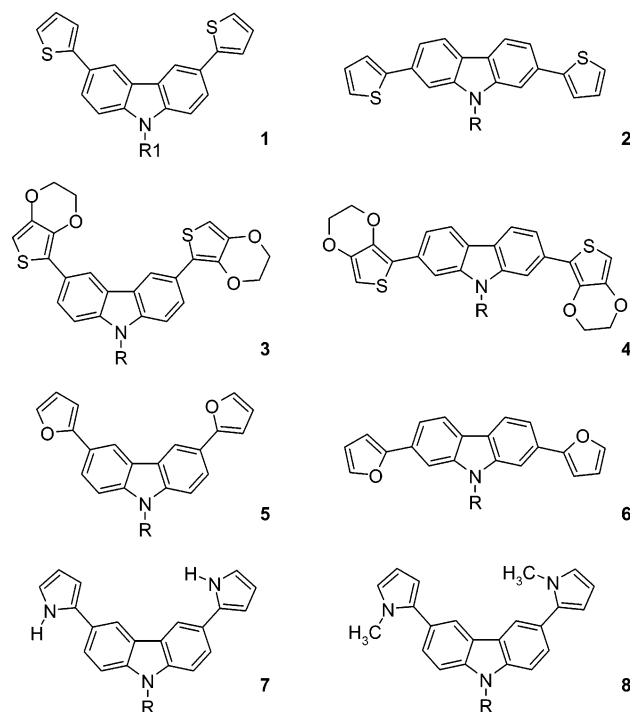
molecule no.	$\phi_{\text{mol}}$ , deg	$\phi_{\text{cat.}}$ , deg	$S$ , Å <sup>2</sup>	$V$ , Å <sup>3</sup>	$D$ , D	aromaticity	
						arom-I, kcal/mol	arom-II, kcal/mol
<b>1a</b>	34.4	8.6	105.1	425.6	2.59	2.12	4.36
<b>1b</b>	34.4	9.6	117.0	477.3	2.77	2.18	4.37
<b>1c</b>	34.4	10.1	119.4	501.9	2.86	2.24	4.39
<b>1d</b>	34.3	10.0	141.7	601.2	2.99	2.26	4.44
<b>1e</b>	34.3	9.5	143.4	626.0	2.98	2.30	4.48
<b>2</b>	32.6	2.7	126.3	510.7	1.96	2.49	5.11
<b>3</b>	24.9	7.5	151.7	624.9	3.26	2.60	5.49
<b>4</b>	23.2	5.6	147.9	636.2	2.36	3.64	6.49
<b>5</b>	0.8	0.1	119.2	479.1	2.34	4.92	9.75
<b>6</b>	0.6	−0.1	120.6	483.0	2.12	5.72	10.96
<b>7</b>	29.4	12.4	117.9	486.0	3.54	3.21	6.17
<b>8</b>	47.7	29.6	124.8	569.9	3.54	1.79	3.34
<b>9</b>	33.1	11.7	111.6	624.5	0.82	2.30	4.70
<b>10</b>	31.3	1.3	132.2	634.4	0.51	2.49	5.15
<b>10a<sup>b</sup></b>	30.7	0.1	128.1	484.0	0.67	2.51	5.11
<b>11</b>	23.7	8.9	136.2	750.8	3.21	3.25	6.14
<b>12</b>	20.4	4.1	136.4	759.4	1.04	3.29	6.77
<b>13</b>	0.1	0.0	116.9	602.6	0.69	5.18	10.45
<b>14</b>	0.1	0.0	110.5	604.6	0.52	5.68	11.28
<b>15</b>	31.2	0.7	125.5	509.7	0.65	2.70	5.26
<b>16</b>	30.3	0.1	127.2	513.6	0.28	2.63	5.22
<b>17</b>	33.1			983.4	1.06	2.22	4.42
<b>18</b>	36.4			1475.7	2.83		
<b>19<sup>c</sup></b>	38.6			501.4	2.31		
<b>20<sup>c</sup></b>	0.06			979.6	1.40		
<b>21<sup>c</sup></b>	0.13			1459.6	2.68		
<b>22<sup>c</sup></b>	0.24			1939.2	4.36		
<b>23<sup>c</sup></b>	18.5			2418.4	5.16		

<sup>a</sup> The numbers of the molecules correspond to Figures 1–3; the letter in **1a–1e** depicts the aliphatic ring: (a) CH<sub>3</sub>; (b) C<sub>3</sub>H<sub>7</sub>; (c) C<sub>4</sub>H<sub>9</sub>; (d) C<sub>8</sub>H<sub>17</sub>; (e) C<sub>9</sub>H<sub>19</sub>. <sup>b</sup> Analogue of **10**: spiro(cyclopentane)-2,7-bis(2-thiophene)fluorine. <sup>c</sup> These structures were optimized at PM3 level of theory.

minimum on the potential energy surface. No symmetry constraints were imposed during the optimization process. The calculations were performed using the standard 6-311G(d,p) basis set.<sup>24</sup> The optimizations of oligomers were performed by applying the semiempirical PM3 approach.<sup>25,26</sup> The comparison with DFT (Table 1) indicates that MP3 does not properly reproduce the shallow potential energy surface characterized by dihedral angle between rings ( $\phi_{\text{mol}}$ ). The other molecular parameters are reasonably reproduced and are expected to lead to meaningful conclusions. The volume of the molecule was calculated according to the procedure applied in the C-PCM solvation model.<sup>27</sup> The electron distribution was studied using the natural bond orbital (NBO)<sup>28</sup> and the Mulliken (electron spin density) electron population analysis schemes. The computations were carried out using the Gaussian 03 suite of codes.<sup>29</sup> The projected surface of molecules was calculated by applying the Molekel program.<sup>30</sup>

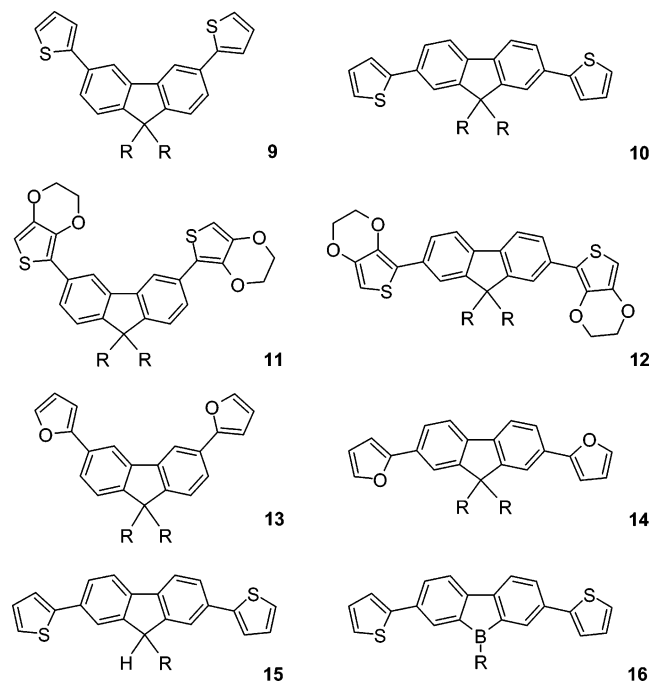
### 3. Molecular Structures

The studied molecules are composed from the central fragment (carbazole or fluorene) substituted symmetrically (in the 2,7 or 3,6 positions) by two external five-membered heterocyclic rings (external rings) (Figures 1–3). The corresponding coordinates are supplied as Supporting Information (Table 1S). The extent of the effective conjugation in the poly(thiophene) backbone was identified earlier as a crucial parameter to achieve high electrical conductivity.<sup>31,32</sup> The important structural property of the presented species is their planarity, which is directly related to the conjugation of  $\pi$  bond systems. The correlation between geometry and electric properties was demonstrated for bis(pyrrolyl)arylenes.<sup>16</sup> The planarity

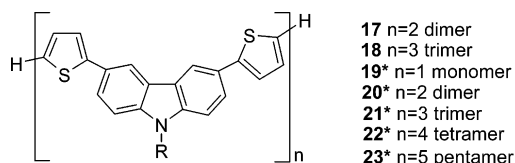


**Figure 1.** Carbazole derivatives substituted by R = C<sub>4</sub>H<sub>9</sub> and R1 = CH<sub>3</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>, C<sub>8</sub>H<sub>17</sub>, C<sub>9</sub>H<sub>19</sub> aliphatic chains.

of the studied structures is controlled by the dihedral (torsion) angle  $\phi$  between the plane of the central fragment and external planar five-membered heterocycles. Such an angle between fluorene and the thiophene rings in the crystal of 1,9-spiro(cyclopentane)-2,7-bis(2-thiophene)fluorene amounts to 22–



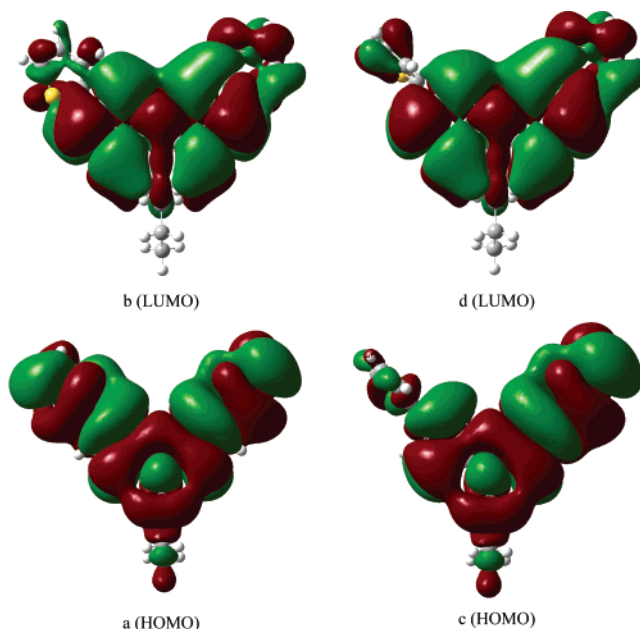
**Figure 2.** Fluorene derivatives. R represents the aliphatic  $C_4H_9$  chain.



**Figure 3.** Schematic representation of short polymers of thiophene carbazole including numbers denoting oligomers discussed in the text. Structures **17** and **18** were optimized by applying the DFT method. Other molecules indicated by the asterisk (\*) were optimized within the PM3 level of theory. R represents the aliphatic  $C_4H_9$  chain.

$27^\circ$ .<sup>33</sup> The calculated angle (for the gas phase) amounts to  $31^\circ$ . This agreement indicates that the predicted torsion angles presented in Table 1 are reasonable. The replacement of the heteroatom in the central fragment insignificantly influences the total nonplanarity of the molecule. The dihedral angle  $\varphi$  decreases for the heteroatom sequence N, C, B in the **2**, **10**, and **16** thiophene derivatives. Similarly, a small but consistent change of  $\varphi$  is observed compared to the substitution in positions 2,7 and 3,6 of the central fragment. Positions 2,7 are characterized by the smaller torsion angle, indicating a higher  $\pi$  coupling. The variation in the chemical composition of the external rings is the most important factor controlling the  $\pi$ -bond coupling. The furane ring forces the planarity of the entire molecule regardless of the other chemical parameters of the molecule (compounds **5**, **6**, **13**, and **14**). The derivatives containing ethylenedioxythiophene rings constitute the group characterized by an angle of about  $20^\circ$ , while the torsion angle in thiophene derivatives is higher by  $10^\circ$ . The ionization of the monomers forces the complete planarity of parent molecules.

The planar structure of the entire molecule indicates the highest possible  $\pi$ -electron coupling. The total uncoupling between the central fragment and the external rings occurs for  $\varphi = 90^\circ$  (Figure 4). The shape of molecular orbitals influences the conducting properties of polymers. Two energetic characteristics are defined as a measure of aromaticity. The first one refers to the energy of the variation in the structure from  $\varphi = 90^\circ$  to its actual optimized value in the molecule ( $\varphi_{\text{mol}}$ ) calculated for the single external ring (arom-I) or for both external heterocycles (arom-II). The obtained results indicate



**Figure 4.** HOMO and LUMO molecular orbitals of thiophene carbazole (**1c**) for the optimized structure (a, b) and the structure with a decoupled single thiophene ring ( $\varphi = 90^\circ$ ) (c, d).

the close correlation between  $\varphi_{\text{mol}}$  and the aromaticity. The largest stabilization energy, amounting to 5 kcal/mol, characterizes furane derivatives. Both the arom-I and arom-II indexes are almost equivalent. The small difference between  $2 \times \text{arom-I}$  and arom-II results from long-distance interactions between the external rings which utilize the  $\pi$ -system of the central fragment for communication.

Table 1 lists the projected surfaces and volumes of molecules. The molecular surfaces correlate with the aggregation properties of the Langmuir–Blodgett films.<sup>17</sup> The measured surface pressure versus surface area ( $\pi$ – $A$ ) isotherms are associated with the total molecular surfaces as well as with the surface change due to the nonrigidity of the molecular alkyl chains. The molecular volume is an important property influencing molecular mobility in the solution. As expected, the surface and volume of the molecule are functions of the size of the alkyl chain. Interestingly, although changes are small, the aromaticity systematically increases with a lengthening of the alkyl chains.

#### 4. Electronic Properties of Molecules and Corresponding Cations

The oxidation reaction leads to the ionization of molecules and to the formation of a radical cation. The oxidation is a necessary first step for the electropolymerization. The polymerization is believed to proceed through the  $\alpha$  positions of the external heterocyclic rings.<sup>10</sup> Repeated potential scanning polymerization experiments are the source of monomer oxidation potentials. High oxidation potentials lead to high reactivity of the corresponding radicals, which can undergo rapid reactions with solvent or anions rather than electropolymerization.<sup>34</sup> It was observed in the case of thiophene that its derivatives possessing oxidation potentials higher by 0.5–0.7 eV do not electropolymerize.<sup>9,31</sup> The ionization energy of the monomer correlates with the measured electropolymerization potential.<sup>16</sup> The differences in the vertical ionization energy between **3** and **4** and **4** and **9** of 0.1 and 0.76 eV compare well with the measured values of the difference of the oxidation potential ( $E_{\text{p,m}}$ ), which are 0.1 and 0.65 eV, respectively.<sup>35</sup> This excellent agreement is probably fortuitous; however, ionization potential

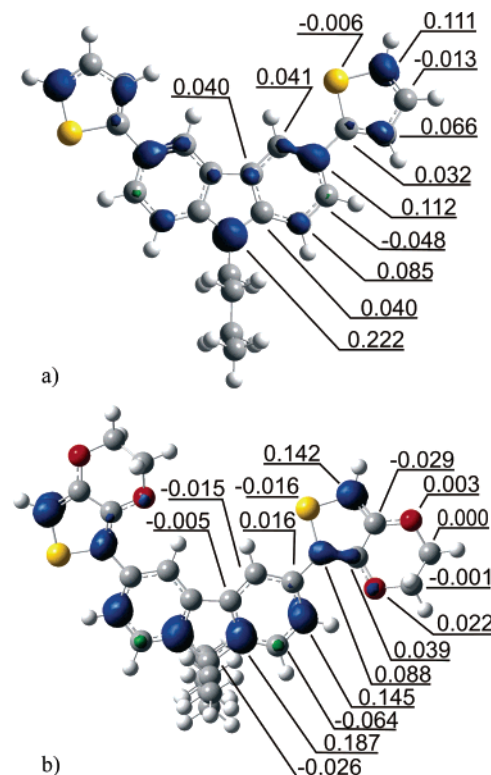
**TABLE 2: Vertical ( $IP_{\text{ver}}$ ) and Adiabatic ( $IP_{\text{ad}}$ ) Ionization Energy, Total Atomic Charge on the External Ring, Atomic Charges on the  $\alpha$ -Carbon of the External Rings, and Selected Heteroatoms in Molecules and Cations, Adiabatic Electron Spin Densities on  $\alpha$ - and  $\gamma$ -Carbon Atoms in External Rings and the Heteroatom of the Central Fragment, the Energy of the HOMO–LUMO Gap ( $\Delta E_{\text{H-L}}$ ), the  $IP_{\text{ver}} + EA_{\text{ver}}$  Sum, and the Singlet–Triplet Separation Energy ( $\Delta E_{\text{S/T}}$ ) in the Molecule<sup>a</sup>**

molecule no.	$IP_{\text{ver}}$	$IP_{\text{ad}}$	atomic charges in the molecule			atomic charges in the cation			electron spin density			$\Delta E_{\text{H-L}}$	$IP_{\text{ver}} + EA_{\text{ver}}$	$\Delta E_{\text{S/T}}$
			ring	$\alpha$	H <sup>b</sup>	ring	$\alpha$	h <sup>c</sup>	$\alpha$	$\gamma$	H <sup>c</sup>			
<b>1a</b>	6.61	6.46	0.009	−0.379	0.396	0.235	−0.309	0.440	0.135	0.083	−0.006	4.14	6.50	3.14
<b>1b</b>	6.56	6.42	−0.003	−0.379	0.395	0.228	−0.311	0.439	0.133	0.083	−0.006	4.13	6.46	3.12
<b>1c</b>	6.55	6.41	−0.002	−0.379	0.395	0.227	−0.312	0.439	0.132	0.083	−0.007	4.13	6.45	3.12
<b>1d</b>	6.53	6.40	−0.003	−0.379	0.395	0.226	−0.312	0.439	0.131	0.083	−0.006	4.12	6.43	3.12
<b>1e</b>	6.54	6.39	−0.003	−0.379	0.395	0.225	−0.312	0.439	0.131	0.083	−0.006	4.12	6.43	3.12
<b>2</b>	6.69	6.48	0.008	−0.377	0.399	0.262	−0.303	0.449	0.153	0.099	−0.021	3.84	7.10	2.81
<b>3</b>	6.13	5.98	−0.005	−0.425	0.394	0.256	−0.354	0.423	0.148	0.059	−0.019	3.99	5.94	2.98
<b>4</b>	6.23	6.03	0.012	−0.315	0.393	0.294	−0.344	0.336	0.166	0.070	0.193	3.62	6.51	2.65
<b>5</b>	6.34	6.27	0.006	0.125	−0.465	0.235	0.202	−0.454	0.145	0.102	0.193	4.02	6.04	3.05
<b>6</b>	6.46	6.35	0.019	0.130	−0.464	0.268	0.215	−0.450	0.166	0.119	−0.020	3.67	6.73	2.63
<b>7</b>	6.18	6.05	0.025	−0.040	−0.524	0.294	0.281	−0.517	0.158	0.075	0.166	3.85	5.92	2.95
<b>8</b>	6.23	6.06	0.019	−0.039	−0.374	0.299	0.053	−0.369	0.160	0.072	0.159	3.96	5.93	3.07
<b>9</b>	6.99	6.86	0.012	−0.376	0.311	0.253	−0.306	0.445	0.123	0.052	−0.029	4.46	7.14	3.24
<b>10</b>	6.70	6.50	0.011	−0.375	0.400	0.264	−0.303	0.450	0.150	0.096	−0.011	3.78	7.22	2.74
<b>11</b>	6.54	6.41	0.014	−0.421	0.399	0.296	−0.345	0.428	0.145	0.030	−0.010	4.25	6.57	3.16
<b>12</b>	6.24	6.05	0.016	−0.420	0.398	0.298	−0.344	0.433	0.163	0.068	−0.028	3.55	6.67	2.55
<b>13</b>	6.80	6.72	0.024	0.131	−0.463	0.271	0.127	−0.254	0.164	0.072	−0.028	4.35	6.79	3.07
<b>14</b>	6.50	6.39	0.020	0.132	−0.466	0.271	0.216	−0.449	0.162	0.116	−0.011	3.62	6.92	2.57
<b>15</b>	6.73	6.52	0.012	−0.375	0.400	0.270	−0.301	0.451	0.153	0.096	−0.009	3.80	7.21	2.76
<b>16</b>	6.76	6.56	0.014	−0.375	0.400	0.275	−0.300	0.452	0.151	0.094	−0.006	3.10	7.90	2.14
<b>1c</b>	6.55		−0.002	−0.379	0.395	0.210 <sup>e</sup>	−0.310 <sup>e</sup>	0.432 <sup>e</sup>	0.105 <sup>e</sup>	0.057 <sup>e</sup>	−0.005 <sup>e</sup>	4.13		3.12
<b>17</b>	6.55		−0.001	−0.379	0.396	0.072 <sup>e</sup>	−0.355 <sup>e</sup>	0.410 <sup>e</sup>	0.032 <sup>e</sup>	0.019 <sup>e</sup>	−0.001 <sup>e</sup>	3.35		2.28
<b>18</b>	5.90		−0.002	−0.379	0.396	0.041 <sup>e</sup>	−0.388 <sup>e</sup>	0.445 <sup>e</sup>	0.019 <sup>e</sup>	0.012 <sup>e</sup>	−0.001 <sup>e</sup>	3.26		2.64
<b>19<sup>d</sup></b>	6.63		0.002	−0.392	0.410	0.215 <sup>e</sup>	−0.327 <sup>e</sup>	0.447 <sup>e</sup>	0.107 <sup>e</sup>	0.058 <sup>e</sup>	−0.008 <sup>e</sup>	4.19		3.21
<b>20<sup>d</sup></b>	5.88		0.005	−0.388	0.406	0.091 <sup>e</sup>	−0.359 <sup>e</sup>	0.421 <sup>e</sup>	0.041 <sup>e</sup>	0.026 <sup>e</sup>	−0.003 <sup>e</sup>	3.28		2.28
<b>21<sup>d</sup></b>	5.63		0.005	−0.388	0.406	0.057 <sup>e</sup>	−0.370 <sup>e</sup>	0.415 <sup>e</sup>	0.023 <sup>e</sup>	0.016 <sup>e</sup>	−0.001 <sup>e</sup>	3.19		2.27
<b>22<sup>d</sup></b>	5.53		0.005	−0.388	0.405	0.044 <sup>e</sup>	−0.374 <sup>e</sup>	0.416 <sup>e</sup>	0.017 <sup>e</sup>	0.011 <sup>e</sup>	−0.001 <sup>e</sup>	3.19		2.28
<b>23<sup>d</sup></b>	5.43		0.005	−0.388	0.488	0.032 <sup>e</sup>	−0.378 <sup>e</sup>	0.413 <sup>e</sup>	0.011 <sup>e</sup>	0.008 <sup>e</sup>	−0.001 <sup>e</sup>	3.17		2.28

<sup>a</sup> See Table 1 for the definitions of the molecules. Energies, in eV; charges, in electron. <sup>b</sup> H, heteroatom of central fragment. <sup>c</sup> h, heteroatom of external ring. <sup>d</sup> Structures optimized at the PM3 level. <sup>e</sup> Calculated for the optimized structure of molecule.

(IP) values may be treated as a meaningful measure of the oxidation potential of the polymerizing material. The lowest ionization energy characterizes ethylenedioxythiophene and pyrrole complexes (Table 2). The highest ionization energy is found in derivatives containing thiophene rings. Derivatives substituted by ethylenedioxythiophene are also the most stabilized due to the geometry relaxation ( $IP_{\text{ad}}$ ). According to the NBO analysis the electron is detached from the central fragment. The loss of an electron, however, is partially compensated by the donation of electronic density by external rings. The amount of electronic density donated by heterocycle rings is similar; however, derivatives with ethylenedioxythiophene groups are characterized by a transfer that is slightly greater. Contrary to the direct ionization of thiophene, in the studied compounds the central ring controls the density distribution of the external rings. The most charged atoms of the external rings are heteroatoms and carbon atoms in the  $\alpha$  position ( $\alpha$ -carbon) and are characterized by a positive charge. The delocalization of the charge on the extended structures influences their chemical reactivity because of the significant stabilization of the formed species. The stability of the radical cations is measured as their lifetimes, which are determined on the basis of the assumed dimerization mechanism.<sup>36–38</sup>

The electronic density distribution in the cations governs the electron spin density (ESD), which is believed to be the main factor controlling the polymerization.<sup>14,15,34,39</sup> Experimental spin densities are obtained from EPR spectra using the McDonnell equation.<sup>14</sup> Due to its privileged position with few steric obstacles, the  $\alpha$ -carbon of external rings constitutes a site for polymerization (Figure 5). The highest atomic electron spin density is observed in derivatives possessing furane and ethylene dioxythiophene external rings (Table 2). Despite the relatively



**Figure 5.** Isovalent surfaces (0.004 electron/bohr<sup>3</sup>) of spin electron density (in blue) in thiophene carbazole (**1c**) and ethylenedioxythiophene fluorene (**11**). Atomic electron spin densities are given in electron.

large atomic charge located on the heteroatoms of the external rings, their ESD is negligible. Due to the ionization of an



electron on the N atom in carbazole, nitrogen possesses significant spin electron density; however, because of unfavored steric effects, electropolymerization does not involve this site. A comparison of spin density calculated for the vertical cation (geometry of molecule) and the optimized planar cation indicates an enhancement of the spin density values by the higher  $\pi$  conjugation.

The conducting properties of the  $\pi$ -conjugated polymers are controlled by the energy band gap ( $E_g$ ). The reduction of band gap enhances the thermal population of the conduction band and increases the number of charge carriers. The decrease of  $E_g$  may lead to the creation of a true "organic metal". The values of the band gap can be deduced from the optical (e.g., electronic adsorption spectra) or electrochemical characteristics of the material.<sup>13</sup> The polymer band gap is closely related to the structure of the electronic states of the precursor molecules. The energies of HOMO and LUMO are related to the oxidation and reduction potentials corrected for the solvation energies.<sup>39–41</sup> On the other hand, the oxidation and reduction potentials correspond respectively to the ionization energy and electron affinity of the molecule. The transition energy from the electronic ground state to the lowest excited state ( $\Delta E_{ST}$ ) may also be considered as a possible measure of  $E_g$  for conducting polymers.<sup>9</sup> As indicated in Table 2, the HOMO–LUMO gaps, although higher in value, closely reproduce the singlet ground state to triplet lowest electronic state transitions. The electrochemically measured value of  $E_g$  for molecule **7** of 2.5 eV<sup>9</sup> agrees with our singlet/triplet energy difference of 2.97 eV. The results of the  $\Delta E_{ST}$  calculations indicate its sensitivity to the chemical composition of both the central and the external fragments. The substitution in positions 2,7 of the central fragment leads to a smaller energy gap compared to its analogue with the substitution in the 3,6 positions. The smallest HOMO–LUMO gap is found in derivatives of ethylenedioxythiophene.

## 5. Property Variation with Increasing Size of Small Oligomers

The studies of short-chain oligomers (dimer, trimer, tetramer, and pentamer) reveal the evolution of properties from a single molecule to extended structures such as polymers.<sup>42,43</sup> The differences between a monomer and consecutive oligomers provide useful data for speculations on the reaction mechanism. The extrapolated properties of oligomers serve as an approximate measure of the properties characterizing polymers. The experimental oxidation potentials and bondgaps decrease as the length of the oligomers increases. Molecular parameters such as vertical ionization energy, HOMO–LUMO energy difference, and singlet–triplet excitation energy for the studied consecutive oligomers of thiophene carbazole (**1c**) follow experimental trends. The red shift of adsorption and emission spectra resulting from decreasing  $E_g$  due to consecutive polymerization leads some conjugated systems to become transparent in the visible spectral range.<sup>44</sup> As oligomers grow, the total atomic charge located on the external rings of the cations decreases. The spin electron density on the  $\alpha$ -carbon also shrinks significantly, resulting in lower reactivity of the longer cation, which is in agreement with experimental findings.<sup>1</sup>

## 6. Conclusions

Molecular structures and electronic properties of monomers influence every step of polymerization and are probably the most important factors shaping the final polymer.<sup>1</sup> Each step of the polymerization is influenced by distinct molecular parameters. Molecular and cationic properties, which are difficult to measure,

are often directly or indirectly related to the gas-phase molecular characteristics and may be considered as a useful approximation. An attempt to unveil such relations is reported in this work. Examples of relations are experimental oxidation potential and ionization energy or energy band gap of the polymer and the singlet/triplet separation energy. The presented calculations were performed for a selected group of compounds based on carbazole and fluorene substituted symmetrically by thiophene, ethylenedioxythiophene, furane, and pyrrole. Studies of the variation in the properties as a function of the chemical composition of the central fragment and the external rings include structure, electron ionization and excitation energies, and electron density distribution. The calculated properties of consecutive oligomers indicate their fast convergence to values characterizing polymers.

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**Supporting Information Available:** Optimized coordinated of molecules and cations (Table 1s). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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