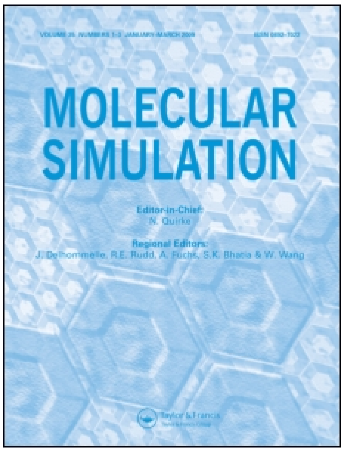

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Thieno[3,4-f]isothianaphthene and its *N*-substitutes: a theoretical insight

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Thieno[3,4-f]isothianaphthene and its *N*-substitutes: a theoretical insight

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Density functional theory is used to study the geometries, electronic structure, aromaticity, the singlet/triplet splitting energies and the vertical ionization energy of tricyclic nonclassical thiophene, Thieno[3,4-f]isothianaphthene, and its five *N*-substitutes at B3LYP/aug-cc-PVDZ level of theory. Geometry studies show that all of the compounds have a highly symmetric structure with a rigid planar. Calculated results confirm that there exists considerable conjugation and aromaticity over the rings and those tricyclic nonclassical thiophenes may be candidates for conductive polymers. The studies of electronic structure and splitting energies show that those nonclassical thiophenes have more or less a diradical structure.

Keywords: DFT; Thieno[3,4-f]isothianaphthene; *N*-substitutes; Nonclassical structure; Electronic structure

1. Introduction

Nonclassical condensed thiophenes, because of their unusual electronic structures, have attracted much attention from both theoretical and experimental studies [1–5]. In 1939, Schomaker and Pauling suggested that an expansion of the sulfur octet could be a special factor in stabilization of the thiophene molecule [6]. Cava and co-workers first reported the evidence for the formation of substituted thieno[3,4-c]thiophenes in 1967 [7,8]. The properties of thieno[3,4-c]thiophenes have been studied in detail by theories and experiment [9–11]. Potts and McKeough [2] first synthesized the perphenyl-subsituted thieno[3,4-f] thiophene (**A** in figure 1).

The formulas of nonclassical structures have been written with C═S═C for convenience and simplicity. For tetracovalent sulfur, people have several opinions [12–15]. First, the hypervalency with such structure was generally understood a model of valency including D-orbitals of sulfur. Second, the double bonds were replaced by a diradical. Third, the charge separation depicted by two resonance contributors (shown in following) and this structure indicates an ylidic.

$$-\overset{\oplus}{C}{=}S-\overset{\ominus}{C}- \leftrightarrow -\overset{\ominus}{C}-S{=}\overset{\oplus}{C}-$$

Nonclassical thiophene such as thieno[3,4-c]thiophene have been previously calculated by many theory methods [3–5,16]. And the band electronic structures of one-dimensional polymers composed of thiophene, pyrrole and tricyclic nonclassical thiophenes dithieno-[3,4-b:3′,4′-e]pyrazine (**2N − 1**), benzo[3,4-b:3′,4′-e]bis[1,2,5]thiadiazolo (**4N − 2**), [1,2,5]thiadiazolo[3,4-b]thieno[3,4-e]pyrazine (**4N − 1**) have been studied at the extended Hűckel level of theory by Tachibana and co-workers [17]. And those oligomers have been thought good candidate for an intrinsic conducting polymer without dopants.

The aim of our work is to study the geometric, electronic structure and properties of tricyclic nonclassical thiophene, thieno[3,4-f]isothianaphthene and its *N*-substitutes (figure 1), based on chemicals using a theoretical approach. In the illustrations, **A** means Thieno [3,4-f]isothianaphthene, **2N − 1** dithieno-[3,4-b:3′,4′- e]pyrazine, **2N − 2** thieno [5,6-c] benzo [c][1,2,5]thiadiazole,

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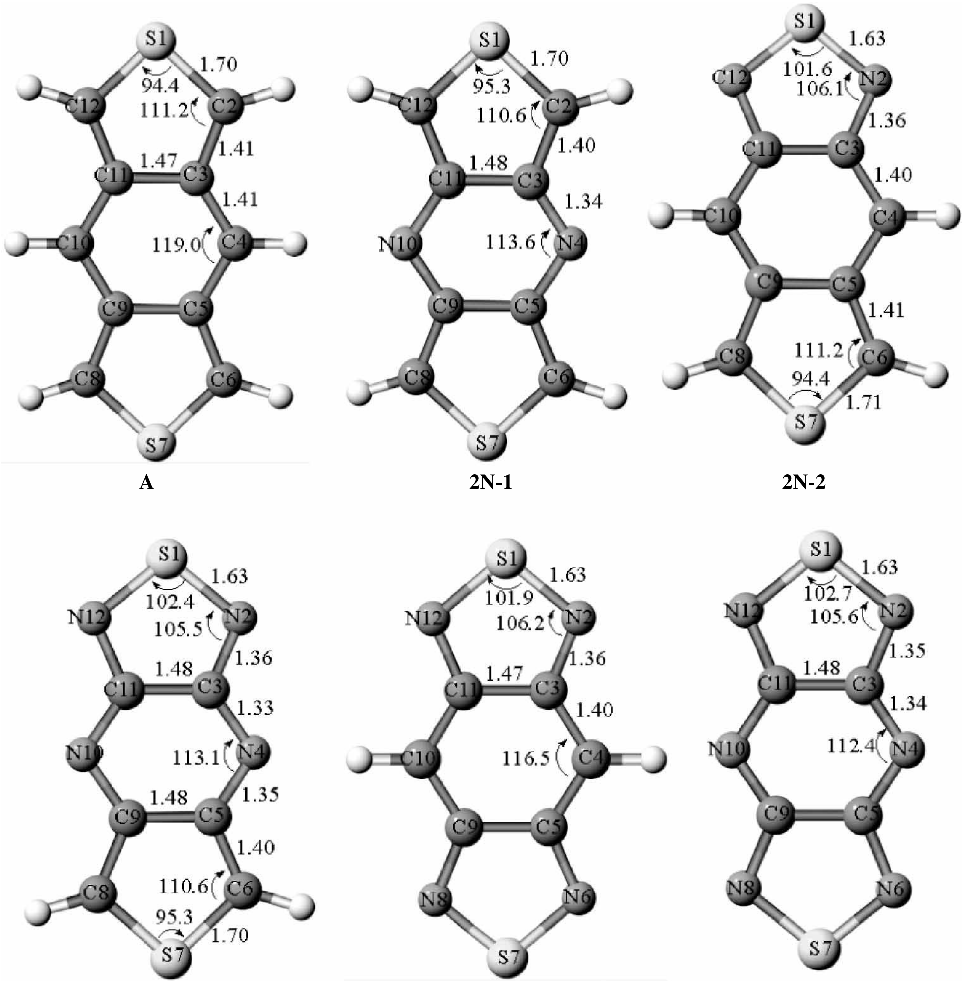

Figure 1. Optimized molecular structures for thieno[3,4-f]isothianaphthene, and its five *N*-substitutes, along with bond lengths (in Å) and angles (in deg).

4N − 1 [1,2,5]thiadiazolo[3,4-b]thieno[3,4-e]pyrazine, **4N − 2** benzo [3,4-b:3′,4′-e]bis[1,2,5] thiadiazolo, and **6N** Bis([1,2,5]thiadiazolo)[3,4-b:3′,4′- e]pyrazine.

2. Computational details

Density functional theory (DFT) [18] is applied to optimize all of the structures. Becke's three-parameter nonlocal exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [19,20] is employed. Dunning's aug-cc-pVDZ (5d) basis set [21] is used throughout. There are no imaginary frequencies for all of the structures at this theoretical level, which suggests that all of the obtained structures are the structures of local minima on the potential energy surface.

The natural bond orbital (NBO) [22–25] analysis and Nucleus-independent chemical shift (NICS) [26] calculation are carried out at the B3LYP/aug-cc-pVDZ level on the basis of the optimized geometries. NICS is defined as the negative of the magnetic shielding at a ring critical point (RCP), which attained from atom in molecule AIM analysis [27], and at 1 Å above the RCP. In this paper, the values have been denoted as NICS(0) and NICS(1), respectively. The vertical ionization energy ($\Delta E^{\mathrm{v}}_{\mathrm{S/D}}$) and the energy gap ($E_{\mathrm{g}}$) are calculated at same level. Vertical ionization energy is minimum energy that is required by ejecting an electron out of a neutral atom or molecule in its ground state. The energy gaps (E_{g}) were determined by taking differences in frontier orbital HOMO and LUMO energy levels. To examine the diradical nature of those nonclassical thiophenes, the adiabatic splitting energies $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$ and vertical splitting energies $\Delta E^{\mathrm{v}}_{\mathrm{S/T}}$ also are calculated at B3LYP/aug-cc-pVDZ level. All of these calculations are carried out using the Gaussian 03 program [28].

The topological properties of the electronic charge density have been characterized using the atoms in molecules (AIM) method of Bader with the AIM 2000 program package [29].

Table 1. WBIs of selected bond in nonclassical thiophenes.

	Bond	*WBIs*		*Bond*	*WBIs*
A	S1–C2	1.30	**4N − 1**	S1–N2	1.26
	C2–C3	1.37		N2–C3	1.33
	C3–C4	1.38		C3–N4	1.37
2N − 1	S1–C2	1.30		N4–C5	1.34
	C2–C3	1.36		C5–C6	1.38
	C3–N4	1.35		C6–S7	1.30
2N − 2	S1–N2	1.26	**4N − 2**	S1–N2	1.26
	N2–C3	1.33		N2–C3	1.35
	C3–C4	1.36		C3–C4	1.34
	C4–C5	1.33	**6N**	S1–N2	1.26
	C5–C6	1.37		N2–C3	1.35
	C6–S7	1.30		C3–N4	1.35

3. Results and discussion

3.1 Molecular geometry

The geometries of captioned molecules are optimized at B3LYP/aug-cc-pVDZ level. The molecular structures, along with their geometrical parameters, are illustrated in figure 1. The Wiberg bond indexes (WBIs) [23] are collected in table 1.

As shown in figure 1, all of the molecules have a plane geometry and high-symmetry structure. The S1–C2 bonds in **A** and **2N − 1** have uniform bond length (1.70 Å), and they are shorter than the normal S–C single bond length (1.79 Å) and longer than the normal S═C double bond length (1.65 Å). S1–N2 bond lengths in **2N − 2**, **4N − 1**, **4N − 2** and **6N** are 1.63 Å, and they are shorter than the normal S–N single bond length (1.77 Å) and longer than the normal S═N double bond length (1.56 Å). Analyzed by the NBO analysis, the WBIs of S–C in **A**, **2N − 1**, **2N − 2** and **4N − 1** are uniform (1.30) and those of S–N in **2N − 2**, **4N − 1**, **4N − 2**, **6N** are also uniform (1.26). The fact that all of the WBIs are between the standard values of the single bond (1.0) and the double bond (2.0) suggests that there may exist considerable conjugation over the ring. The C–S–C bond angle are 94.4° for **A**, 95.3° for **2N − 1**, 94.4° for **2N − 2** and 95.3° for **4N − 1**, and they are a little bigger than the C–S–C bond angle in thiophene (92.3°). Affected by lone pair (LP) electrons of N atom and S atom, the N–S–N bond angles are increased, and they are 101.6°, 102.4°, 101.9° and 102.7° in **2N − 2**, **4N − 1**, **4N − 2** and **6N**, respectively.

3.2 Electronic structures

For those nonclassical thiophenes, the S-atom's electronic configurations are calculated and analyzed by NBO and MO. In **A**, **2N − 1**, **4N − 2** and **6N**, which are D2H symmetry, there exist completely same environments and hybrid for the two sulfur atoms. The electronic configurations are $3s^{1.60}3p^{3.79}3d^{0.02}$ for S1 in **A**, $3s^{1.61}3p^{3.76}3d^{0.02}$ for S1 in **2N**, $3s^{1.64}3p^{3.32}$ for S1 and $3s^{1.60}3p^{3.78}3d^{0.02}$ for S7 in **2N − 2**, $3s^{1.65}3p^{3.28}$ for S1 and $3s^{1.61}3p^{3.74}3d^{0.02}$ for S7 in **4N − 1**, $3s^{1.65}3p^{3.31}$for S1 in **4N − 2** and $3s^{1.65}3p^{3.26}$ for S1 in **6N**, respectively. It can be easily see that few D-orbital of sulfur take part in bonding, and all of the S-atoms are sp^x hybrid. Accordingly, the model of sulfur octet expansion is not justified.

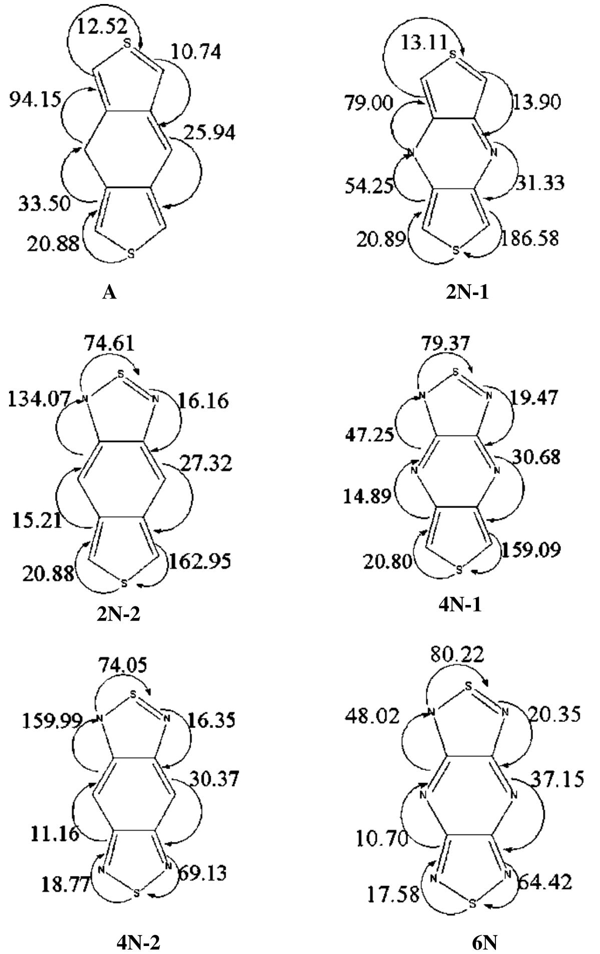

Figure 2. Kekulé structure formula and selected stabilization interaction energies $E(2)$ for nonclacssical thiophenes.

3.2.1 The resonance structure. Analyzed by NBO, the Kekulé expression of weightiest resonance structures for those molecules are illustrated in figure 2. In fact, those Kekulé formula just is one expression for many resonance structures. The figure clearly shows all of molecules have two atoms without double bond, and one is sulfur atom and another is carbon or nitrogen. Moreover, for those atoms without double bond, there exist two 3-center 4-electrion hyperbonds analyzed by 3CHB (3-center, 4-electron hyperbond). For example, in **2N − 2**, four 3-center 4-electrion hyperbonds (C5–C6–S7, S7–C8–C9, C10–C11–N12 and N12–S1–N2) be found, and those hyperbonds include the two atoms (S7 and N12), which are without double bond. There are similar hyperbonds in other nonclassical thiophene

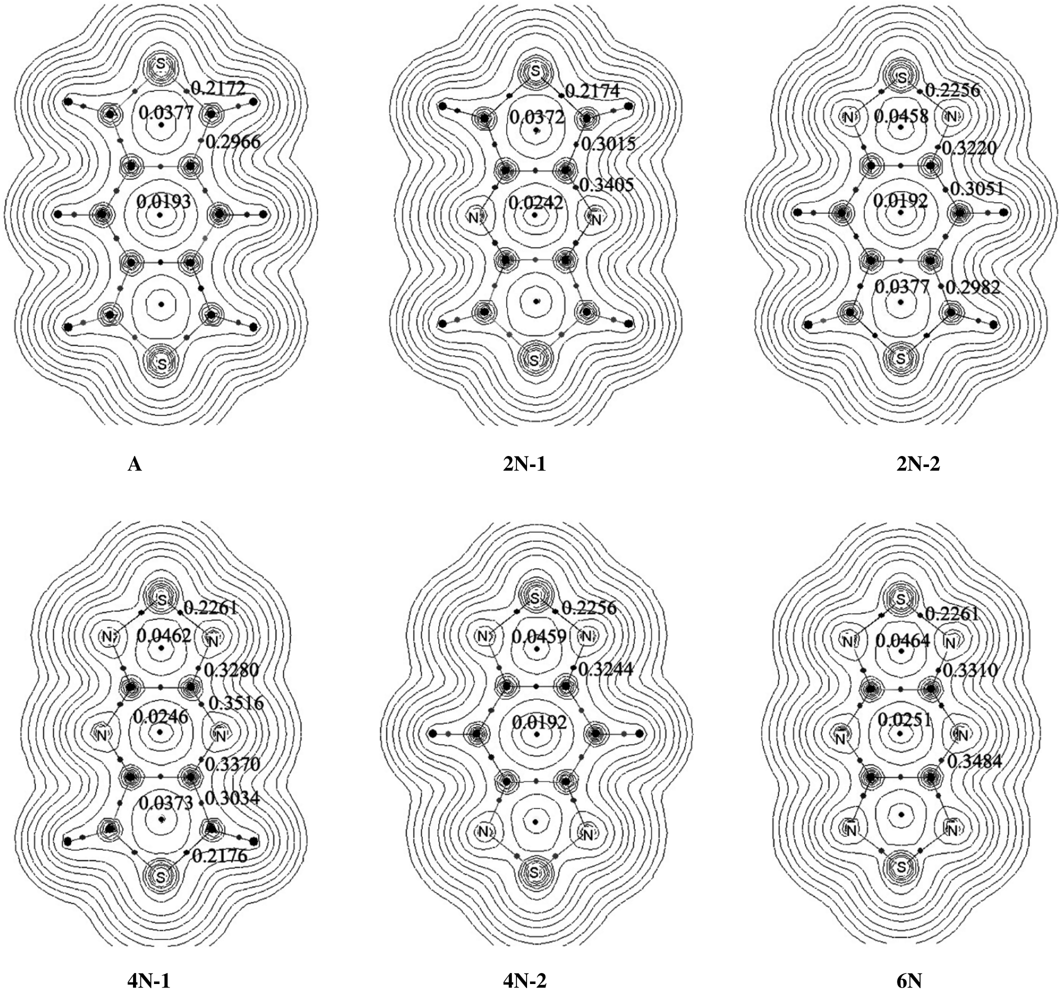

Figure 3. Contour map of $\rho_{(r)}$ in the molecular plane for nonclassical thiophenes and $\rho_{(r)}$ at selected BCP and RCP.

molecules. Those 3-center 4-electrion hyperbonds show that the LP electrons in S7 and N12 are strongly delocalization.

Moreover, for those resonance structures, the stabilization interaction energies are studied. The stabilization interaction energies, $E(2)$, are calculated by means of the second-order perturbation theory. In the NBO analysis, $E(2)$ is used to describe the delocalization trend of electrons from the donor bond to the acceptor bond. The selected stabilization interaction energies $E(2)$ for calculated molecules at the B3LYP/aug-cc-pVDZ level are summarized in figure 2. As shown in the figure 2, there exist strong donor-acceptor interactions among those systems. Interaction energies $E(2)$ between π bonding orbitals and vicinal π^* antibonding orbitals are from 10.70 to 37.15 kcal/mol, respectively. Comparatively, the $E(2)$ values between donor LP orbitals and acceptor π^* antibonding orbitals, and between donor π bonding orbitals and acceptor LP* orbitals are bigger. They are from 20.80 to 186.58 kcal/mol. It also indicate there are strongly delocalization in those molecules.

3.2.2 Topological properties. These geometry variations are consistent with the topological properties of electron density at the bond critical points (BCP), which analyzed by AIM. In Bader's theory of topology, the electronic structure is described in uniform and unbiased way. The critical points are points of minimum electron density along the bond. Laplacian of the charge desity, $\nabla^2_\rho(r)$, which determines the regions of space wherein electronic charge of a molecule is locally concentrated and depleted, provided electronic structures. It is observed that for open-shell interation (covalent and polar bonds), and the $\nabla^2_\rho(r)$ are negative. The ellipticity (ε) of the BCP is a measure of the ratio of the rate of intensity decrease in the two directions perpendicular to the bond path. The ellipticity provides a measure for the π character of a bond and structural stability.

The contours of the charge density of molecules are drawn in figure 3. Density $\rho_{(r)}$, density Laplacian ($\nabla^2_\rho(r)$) and ellipticity (ε) at selected BCPs at the B3LYP/aug-cc-pVDZ level are listed in table 2. The charges, which collected from Nature population analysis and Mulliken

Table 2. Density $\rho_{(r)}$, density laplacian $\nabla^2_{\rho}(r)$ and ellipticity ε at selected BCPs by means of B3LYP/aug-cc-PVDz level of theory.

	Bond	$\rho_{(r)}$	$\nabla^2_{\rho}(\mathrm{r})$	ε
A	S1–C2	0.2172	− 0.4609	0.2962
	C3–C4	0.2993	− 0.7182	0.1965
2N-1	S1–C2	0.2174	− 0.4605	0.2912
	C3–N4	0.3405	− 1.1609	0.1143
2N-2	S1–N2	0.2256	− 0.4412	0.4180
	C3–C4	0.3051	− 0.7119	0.1875
	C6–S7	0.2172	− 0.4616	0.2929
4N-1	S1–N2	0.2261	− 0.4447	0.4178
	C3–N4	0.3516	− 1.1445	0.1054
	C6–S7	0.2176	− 0.4619	0.2877
4N-2	S1–N2	0.2256	− 0.4422	0.4156
	C3–C4	0.3032	− 0.7396	0.2129
6N	S1–N2	0.2261	− 0.4457	0.4151
	C3–N4	0.3484	− 1.2221	0.1351

population, are summarized in table 3. It is indicated clearly in the figure 3 that $\rho_{(r)}$ in investigated molecules are similar, and the electron cloud around N-atom shows a greater concentration of charge. From table 3, it can be seen that all of the S-atoms have positive charge, which indicate that sulfur is a better electron donor in nonclassical thiophene. Furthermore, the NBO charges of S-atom at S–N bond are more positive than that at S–C bond. It can be concluded that there is much greater polarization at the S–N bonds than that at the S–C bonds.

As summarized in table 2, the value of $\nabla^2_{\rho}(r)$ are $-0.4605- -0.4619$ for S–C bonds, $-0.7119- -0.7396$ for C–C bonds and $-0.4412- -0.4457$ for S–N bonds, respectively. All of the values are negative, which shows that those bonds have typical open-shell interaction and have covalent and polar bonds characters. According to table 2, the positive values for Ellipticitys (ε) lying in the range of 0.1143–0.4180. By reason of the positive Ellipticitys (ε), the S–C and S–N bonds are of a π-bond character. It also proves that there exist conjugate systems in those molecules.

3.2.3 Frontier orbitals. The shape and location of the frontier orbital, HOMO and LUMO, for all molecules are illustrated in figure 4. The calculated result for the HOMO and LUMO energies and the energy gap for all molecules are listed in table 4. It is observed that all of the molecular frontier orbitals are similar. The shape of HOMO for every molecule include few the orbitals of sulfur, and there are anti-bonding character from a ring to another ring in those tricyclic molecules. For LUMO shape, there exist anti-bonding character between the S-atom and the neighbouring atom. Both HOMO and LUMO include fewer orbitals of nitrogen than those of carbon. Listed in table 4, the HOMO–LUMO energy gaps of those nonclassical thiophenes are obvious low. Comparatively, calculated at same level, the energy gap of thiophene is bigger and it is 5.93 eV. Known from table 4, the Eg of **A** is lowest, only is 2.12 eV. From **A** to **6N**, along with increasing in the number of nitrogen, the HOMO energies and LUMO energies are lowered and the HOMO–LUMO gaps (Eg) are increased. It can be predict the energies gaps of oligomers and polymers will are lower than that of monomer. The fact that this system has a low HOMO–LUMO gap (Eg) suggests those molecules may be potential candidates for conductive polymers.

3.3 The splitting energies and ionization energies

By means of B3LYP/aug-cc-pVDZ, the diradical nature of the studied systems has been estimated from calculations of the S/T splitting energies, which are calculated by the energy difference between the singlet and triplet states. Both adiabatic splitting energies $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$ and vertical splitting energies $\Delta E^{\mathrm{v}}_{\mathrm{S/T}}$ are listed in table 4. Contrastively, we have calculated the $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$ and $\Delta E^{\mathrm{v}}_{\mathrm{S/T}}$ of thiophene, and the values also are listed in table 4. The S/T energies gap for these nonclassical structures are in fact low, and the adiabatic splitting energies $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$ are smaller than the vertical splitting energies $\Delta E^{\mathrm{v}}_{\mathrm{S/T}}$. Along with the numbers of N-atom increased, the $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$ are increased. The $E_{\mathrm{S/T}}$ energy gap increase in following sequence: $\mathbf{A} < \mathbf{2N-1} < \mathbf{2N-2} < \mathbf{4N-1} < \mathbf{4N-2} < \mathbf{6N}$. The $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$ value of **A** is smallest, only 10.82 kcal/mol. Comparatively, the $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$ and $\Delta E^{\mathrm{v}}_{\mathrm{S/T}}$ of thiophene, which is classical structure, calculated at same level, are very large and they are 69.20 and 81.90 kcal/mol, respectively. It can be concluded that the nonclassical thiophenes are more or less diradical structure.

The vertical ionization energies, $\Delta E^{\mathrm{v}}_{\mathrm{S/D}}$, calculated by B3LYP/aug-cc-pVDZ, are also summarized in table 4.

Table 3. Natural charge and Mulliken charge of selected atoms for nonclassical thiophenes.

	Natural charge						*Mulliken charge*					
	A	***2N − 1***	***2N − 2***	***4N − 1***	***4N − 2***	***6N***	***A***	***2N − 1***	***2N − 2***	***4N − 1***	***4N − 2***	***6N***
S1	0.554	0.585	0.975	1.013	0.987	1.032	0.152	0.409	0.708	0.736	0.752	0.745
C2	− 0.504	− 0.466					0.012	0.444		− 0.743		
N2			− 0.658	− 0.650	− 0.649	− 0.640			− 0.840		− 0.825	− 0.716
C3	− 0.006	0.123	0.119	0.326	0.088	0.333	0.979	0.212	− 0.662	0.461	− 0.049	0.432
C4	− 0.277		− 0.240		− 0.258		0.520		1.049		1.717	
N4		− 0.428		− 0.424		− 0.419		− 0.357		− 0.307		− 0.179
C5	− 0.006	0.123	0.033	0.128	0.253	0.333	0.979	0.212	1.730	0.254	− 0.044	0.434
C6	− 0.504	− 0.466	− 0.494	− 0.457			0.012	0.444	− 0.088	0.379		
N6					− 0.680	− 0.640					− 0.828	− 0.715
S7	0.554	0.585	0.569	0.600	0.987	1.032	0.152	0.409	0.278	0.515	0.752	0.745

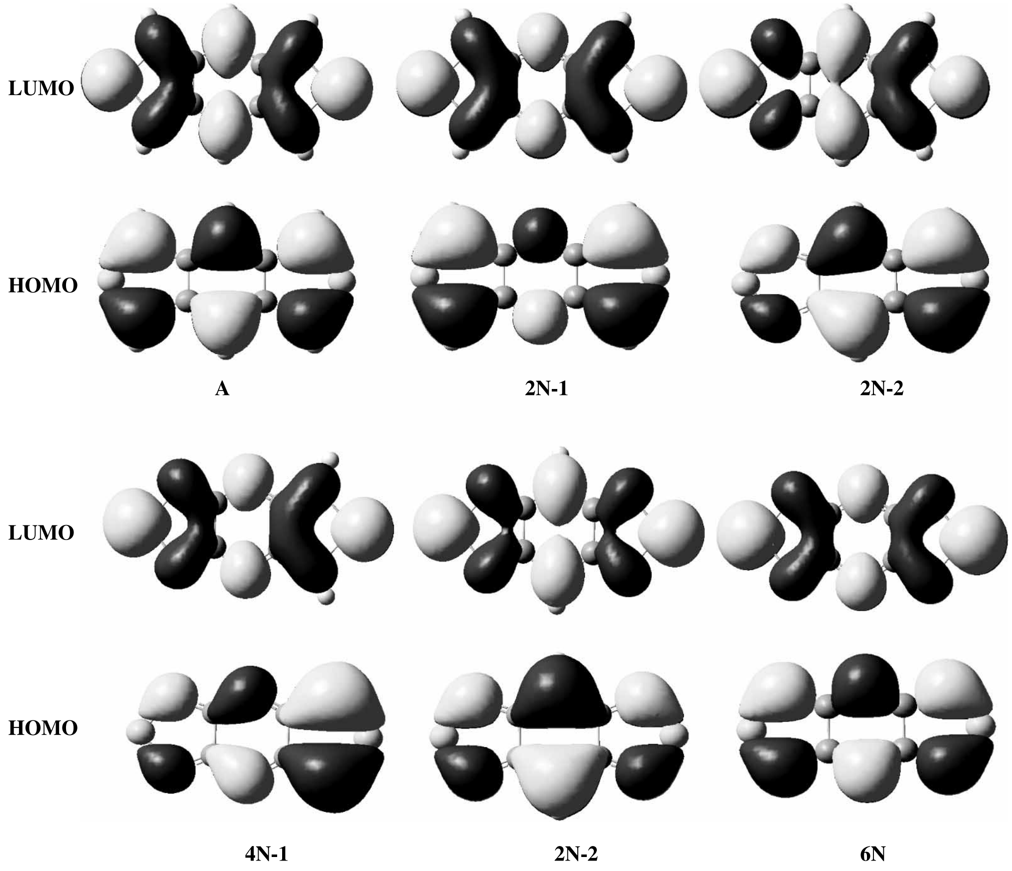

Figure 4. Shape of HOMO and LUMO molecular orbitals for thieno[3,4-f]isothianaphthene and its *N*-substitutes.

The vertical ionization energy is the difference between the energy of +1 valence ion and its ground state. The vertical ionization can predict the reaction activity. Resembling the splitting energies, the $\Delta E^{\mathrm{v}}_{\mathrm{S/D}}$ are increased from **A** to **6N**. And they are 6.34 eV for **A**, 7.19 eV for **2N − 1**, 7.14 eV for **2N − 2**, 8.11 eV for **4N − 1**, 8.16 eV for **4N − 2** and 10.13 eV for **6N**, respectively. $\Delta E^{\mathrm{v}}_{\mathrm{S/D}}$ of thiophene is 9.37 eV, and it has no evident different for nonclassical thiophene.

3.4 Aromaticity

Aromaticity has been recognized as one of the most fascination attributes of cyclic of polycylic hydrocarbons and heterocycles with π-electrons. Cyclic electron delocalization results in enhanced stability, bond length equalization, and special magnetic as well as chemical and physical properties [30–32]. In this paper, all of the nonclassical thiophene molecules have a 14 π-electrons system, and which obeyed $4n + 2$ rule. Magnetic properties, such as proton chemical shift and diamagnetic susceptibility exaltation, are often used for determining the degree of aromaticity in various mono- and polycyclic systems. In 1996, Schleyer *et al.* proposed a novel magnetic probe for local aromaticity: a NICS, which is defined as the negative of the magnetic shielding at some selected point in space. In general, negative and positive NICS values at ring centers are associated with local aromaticity and antiaromaticity, respectively. The CH single bond will influence the magnetic environments, we

Table 4. Symmetry, total energy Et (in a.u.), adiabatic splitting energies $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$, vertical splitting energies $\Delta E^{\mathrm{v}}_{\mathrm{S/T}}$ (in kcal/mol), vertical ionization energy $\Delta E^{\mathrm{v}}_{\mathrm{S/D}}$, HOMO–LUMO energy, and the energy gap Eg (in eV).

	Symm	$\Delta E_t{}^*$	$\Delta E^a_{S/T}$	$\Delta E^v_{S/T}$	$\Delta E^v_{S/D}$	*HOMO*	*LUMO*	*Eg*
A	D2H	− 1180.9652	10.82	14.79	6.34	− 4.73	− 2.60	2.12
2N − 1	D2H	− 1213.0710	12.33	16.28	7.19	− 5.57	− 3.38	2.19
2N − 2	C2V	− 1213.0784	12.88	17.88	7.14	− 5.48	− 3.28	2.20
4N − 1	C2V	− 1245.1803	16.38	21.66	8.11	− 6.43	− 4.06	2.37
4N − 2	D2H	− 1245.1891	18.14	24.42	8.16	− 6.47	− 3.90	2.57
6N	D2H	− 1277.2861	27.24	32.76	10.13	− 7.78	− 4.72	3.06
Thiophene	C2V	− 552.9775	69.20	81.90	9.37	− 6.66	− 0.73	5.93

[*] E_t, $\Delta E^{\mathrm{a}}_{\mathrm{S/T}}$, $\Delta E^{\mathrm{v}}_{\mathrm{S/T}}$ and $\Delta E^{\mathrm{v}}_{\mathrm{S/D}}$ are corrected by zero-point energy (ZPE).

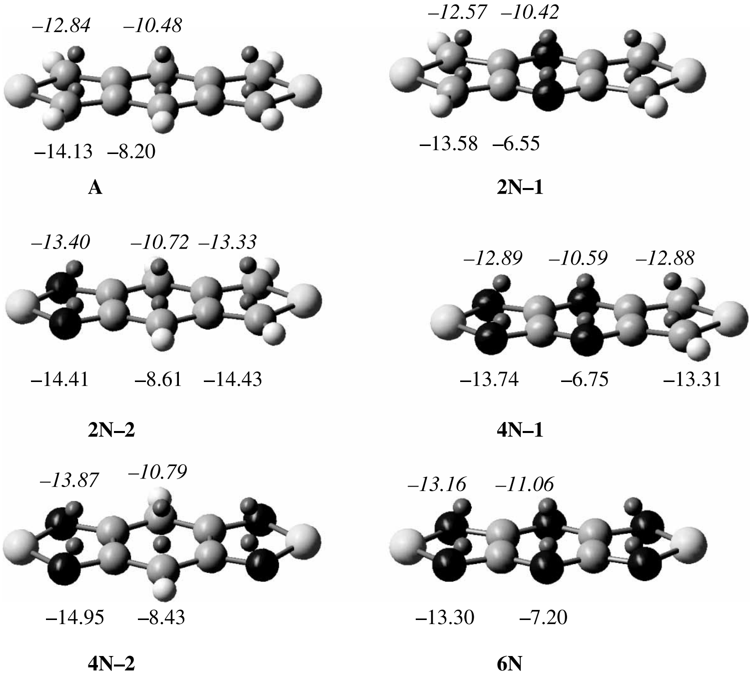

Figure 5. Figure of NICS(0) and NICS(1), italics denote the values of NICS(1).

have calculated the NICS(1) values at 1 Å above the RCP, where the local contributions are diminished relative to the ring current effects.

The values of NICS(0) and NICS(1) are shown in figure 5. From the figure, it can be noticed that all of the molecules have negative NICS, which predicated that there are electronic current in the rings and all of the molecules have aromaticity characters. The NICS values of central ring are smaller than that of side rings. Deshielded by C–C or C–N single bond, the NICS(0) are less than NICS(1) for central ring. Influenced by C–H and C–C single bond, the NICS(0) of side rings are bigger than the corresponding NICS(1). Comparatively, the NICS(0) and NICS(1) of benzene are calculated at B3LYP/aug-cc-pVDZ level, and the value are 7.47 and 9.91 ppm, respectively. In those nonclassical thiophenes, all of the values of NICS are bigger than that in benzene. It indicates that those molecules contain considerable conjugation system, which means there are electronic cyclic current in those molecules.

4. Summary

In this study, we investigated the geometries, electronic structures and aromaticity of nonclassical thiophene, thieno[3,4-f]isothianaphthene and its five *N*-substitutes. The bond lengths and Wierg bond indexes of S–C bond and S–N bond are in the range between single bond and double bond. The NBO charge of sulfur is always positive, and it indicated that the sulfur atom is a better electron donor in nonclassical thiophenes. Analyzed by NBO, there exist several 3-center 4-electron bonds in those resonance structures. Both the result of NBO and topological properties calculation shows there are strongly delocalization in those molecules. Furthermore, Compared with the classical thiophene, the adiabatic splitting energies of studied molecules are considerable low, and it indicates the structure of those molecules including diradical structure. The facts that all of the NICS values at the RCP are negative suggest that all of those molecules have aromatic character, and there exist electron current. According to small vertical ionization energies and low HOMO–LUMO energy gaps, those tricyclic nonclassical thiophenes may be potential candidates for conductive polymers.

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