Theoretical Study on Structure and Electronic Properties of 2, 5-Bis [4-N, N-Diethylaminostyryl] Thiophene and Its Furan and Pyrrole Derivatives Using Density Functional Theory (Dft)

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ABSTRACT
Theoretical calculations using Density Functional Theory (DFT) were performed on 2,5-bis[4-N,N-diethylaminostyryl]thiophene and its furan and pyrrole derivatives The energy band gaps calculated at B3LYP/6-31G(d) level for thiophene derivatives are lower than that of furan and pyrrole analogues. The absorption λ_{max} calculated using DFT was shifted to longer wavelength by replacement of R = CH$_3$ by C$_2$H$_5$ for all studied molecules. The geometries and electronic properties of the compounds were also studied.

Keywords: Electronic Properties, 2, 5-bis (4'-*N*, *N*-diethylaminostyryl) thiophene, DFT

1. INTRODUCTION
The idea of using organic molecules in electronic devices has attracted tremendous attention in the past quarter century. Among various possible types and designs of such organic molecules, the π-conjugated molecules have been, perhaps, the most useful ones (Gill et al, 1994; Geig et al, 1993). Oligo- and poly-thiophenes offer remarkable potential as active elements in electronic devices that exploit their semiconducting properties, such as light-emitting diodes (LED) (Garnier et al, 1990) and field-effect transistors (FET) (Geig et al, 1993). Moreover, the oligothiophenes provide interesting models for understanding the structural and electronic peculiarities which control the charge transport and optical properties in polythiophenes (Bauerle, 1998; Cornil, et al, 1998; Bouzzine, et al, 2007). As a model approach toward electronic property modulation, chromophore sequences are arranged in such a way that electron-donor (D) and/or acceptor (A) units are linked through π-conjugation to a central electron relay at the ends (Kim, 1999).

The study of the electronic properties of such structures provides valuable information for understanding of relay role of the π-center and for developing functional tuning and enhancing the efficiency of electronic/photonic materials. The well recognized efficiency of oligothiophenes as property modulator is associated to the lower resonance energy as compared to benzene (and to the ability of sulfur d-orbitals to mix well with aromatic π-orbitals) (Moreira and Franco, 1992; Takahashi et al, 1992) such that electron-transfer through the π-center between the end moieties is facilitated, thereby anticipating a pronounced alteration in electronic/photonic properties.

In the past few years, various kinds of chromophores involving thiophenes were synthesized for two-photon excited fluorescence (TPEF) (Xia et al, 2003; Xia et al, 2005; Lu and Xia, 2005; Ortiz et al, 2004; Chung et al, 2002) which is caused by simultaneously absorbing two photons by each fluorophore molecule and the main attention was focused on the nonlinear optical (NLO) active molecules with vinyl or phenyl as conjugated electron relays.

In the study, the theoretical ground-state geometries and electronic structures of electronic and structural properties of 2,5-bis(4'-*N*,*N*-dimethylaminostyryl) thiophene (BMST) and 2,5-bis(4'-*N*,*N*-diethylaminostyryl)thiophene (BEST) synthesized by Lu and Xia, 2005 as relay in some D-π-D structures are studied. The two compounds are compared with their pyrrole (2,5-bis(4'-*N*,*N*-dimethylaminostyryl) pyrrole, BMSP and 2,5-bis(4'-*N*,*N*-diethylaminostyryl) pyrrole,BESP) and furan (2,5-bis(4'-*N*,*N*-dimethylaminostyryl) furan, BMSF and 2,5-bis(4'-*N*,*N*-dimethylaminostyryl) furan, BESF) analogues using DFT method at B3LYP level with 6-31G* basis set. The effects of the heterocyclic structure and the substituents on the geometries and electronic properties of these materials are discussed.

2. COMPUTATIONAL METHODS
The equilibrium geometries and the frequencies for all the studied molecules were fully optimized at the DFT level of theory with the standard 6-31G* basis set. The DFT calculations were carried out with the three-parameter B3LYP density functional, which includes Becke's gradient exchange correction (Becke, 1993) and the Lee, Yang, Parr correlation functional (Lee et al, 1988). The absorption transitions were calculated from the optimized geometry in the ground S$_0$ state by DFT/6-31G*/CIS theory. We also examined HOMO and LUMO levels; the energy gap was evaluated as the difference between the HOMO and LUMO energies. All calculations were performed by Spartan 06 program implemented on an Intel Pentium M 2.0 GHz Computer.
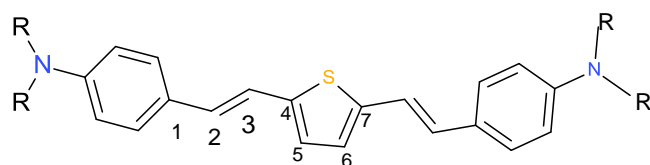
BMST; R=methyl and BEST; R=ethyl
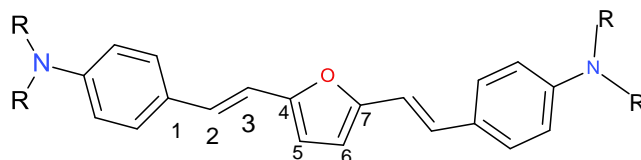
BMSF; R=methyl and BESF; R=ethyl
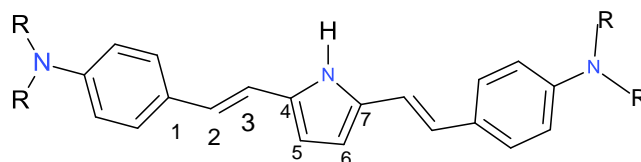
BMSP; R=methyl and BESP; R=ethyl

Fig-1: Schematic structure of the studied molecules.

3. RESULTS AND DISCUSSION

3.1 *Geometries*

The schematic structures were depicted in figure 1 and the optimized geometries obtained by B3LYP 6-31G* of the studied molecules were displayed in figure 2. To investigate the effect of the substituent (R=CH$_3$ and C$_2$H$_5$) and heteroatom (X=O, S and N) on the geometries and electronic properties, the optimized structures and electronic properties of BMSF, BESF, BMSP and BESP were compared with that of thiophene derivatives (BMST and BEST) as shown in Table-1. The results revealed that the heteroatom X has profound effect on the geometries of heterocycle, i.e. C$_3$-C$_4$, C$_4$-X, C$_4$-C$_5$ and C$_5$-C$_6$ bonds were affected whereas C$_1$-C$_2$ and C$_2$-C$_3$ were not affected by changing X for BMSF, BMSP and BMST or BESF, BESP and BEST (Table-1). The same trend was observed for bond angles and dihedral angles.

**Table-1:** Selected geometry parameters obtained by B3LYP/6-31G* for the studied molecules

	BMSF	BESF	BMSP	BESP	BMST	BEST
C$_1$ – C$_2$	1.457	1.457	1.458	1.457	1.458	1.458
C$_2$ – C$_3$	1.354	1.355	1.354	1.355	1.355	1.355
C$_3$ – C$_4$	1.437	1.437	1.441	1.441	1.445	1.444
C$_4$ – X	1.373	1.373	1.381	1.381	1.754	1.754
C$_4$ – C$_5$	1.381	1.381	1.399	1.399	1.386	1.386
C$_5$ – C$_6$	1.415	1.416	1.405	1.406	1.411	1.412
C$_1$,C$_2$,C$_3$	127.42	127.04	127.80	127.52	127.27	126.89
C$_2$,C$_3$,C$_4$	125.25	125.64	125.50	125.76	125.65	125.91
C$_3$,C$_4$,X	115.96	115.76	121.26	121.09	119.44	119.61
C$_3$,C$_4$,C$_5$	135.28	135.51	132.75	132.92	131.14	131.37
X,C$_4$,C$_5$	108.76	108.73	106.00	105.98	109.14	109.12
C$_3$,C$_4$,X,C$_7$	-179.33	-175.37	-179.12	178.28	-179.96	-176.84
C$_2$,C$_3$,C$_4$,X	-178.32	177.26	-179.29	179.01	-178.75	-177.69
C$_2$,C$_3$,C$_4$,C$_5$	0.95	3.09	0.86	-0.62	0.52	2.56
C$_1$,C$_2$,C$_3$,C$_4$	-179.30	-178.84	-179.30	-179.58	179.41	178.45

However, changing R from CH$_3$ to C$_2$H$_5$ had little effect on the dihedral angles which in turn affect the planarity of the molecules in each series. For instance, C$_2$,C$_3$,C$_4$,C$_5$ (C$_1$,C$_2$,C$_3$,C$_4$) were 0.95 (-179.30) and 3.09 (-178.84) for BMSF

and BESF; 0.86 (-179.30) and -0.62 (-179.58) for BMSP and BESP; 0.52 (-179.41) and 2.56 (-178.45) for BMST and BEST respectively. This could be attributed to the steric effect caused by the bulkiness of C_2H_5 (Table-1).

BMSF

BESF

BMSP

BESP

BMST

BEST
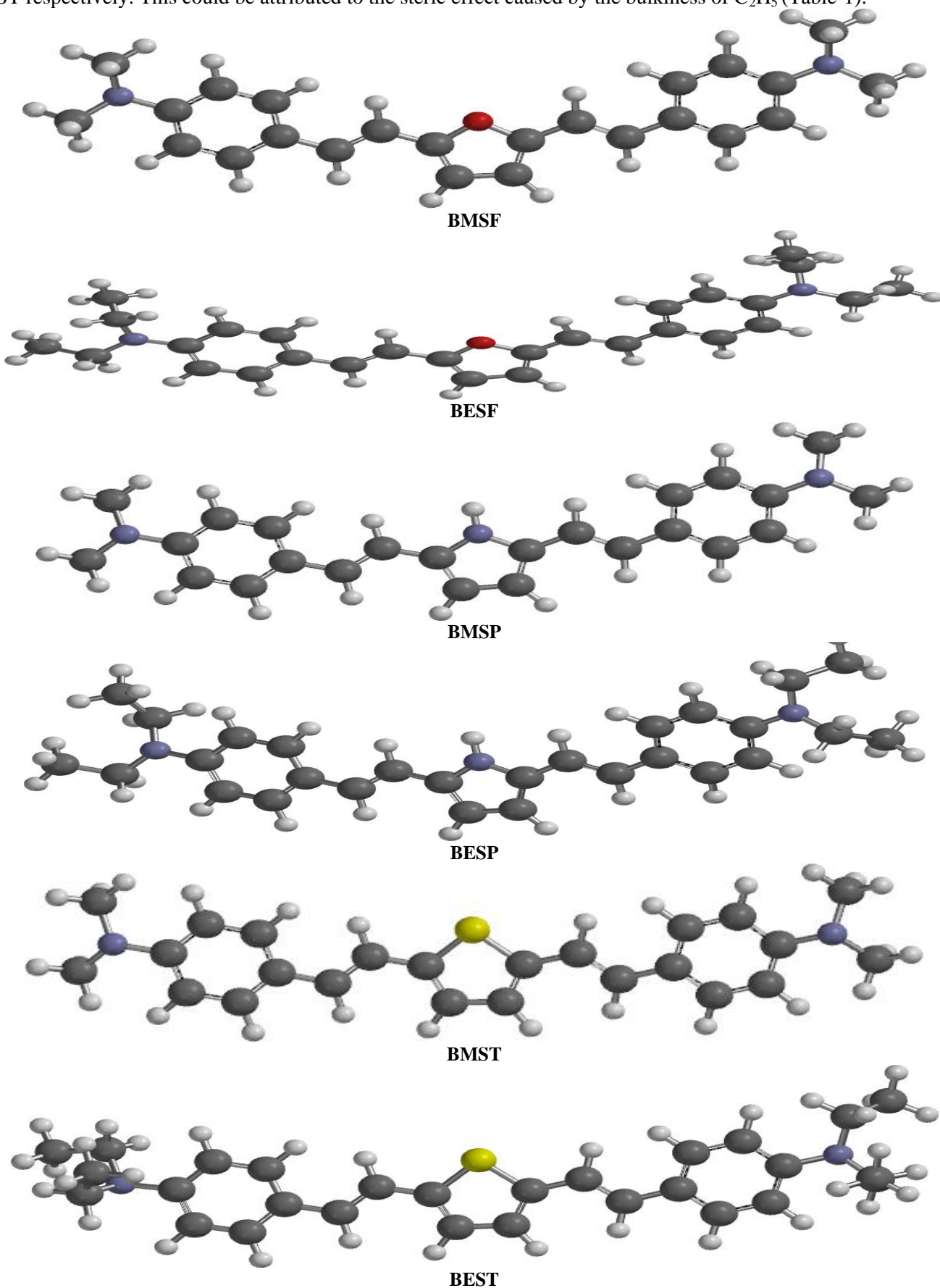
Fig-2: Optimized geometry obtained by B3LYP 6-31G* of the studied molecules.
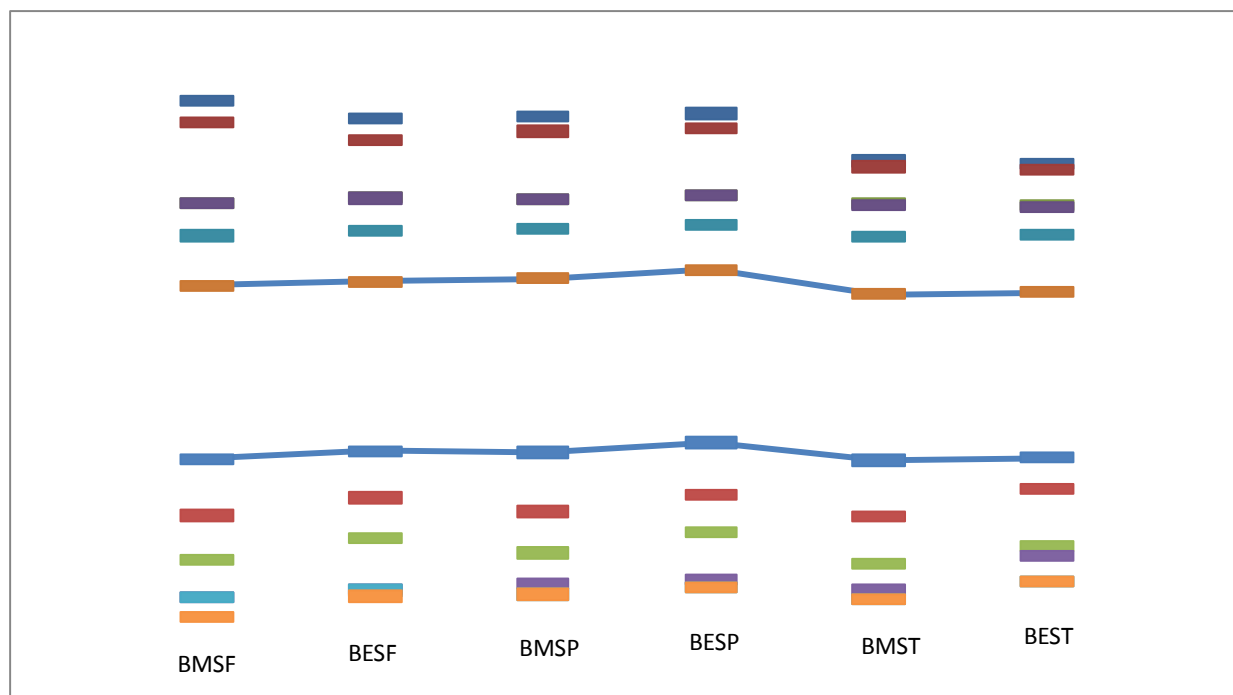
Fig-3: Absolute energy of the frontier orbitals: HOMOs and LUMOs.

3.2 *Electronic properties*

The HOMO and the LUMO are important parameters to provide reasonable qualitative information about the excitation properties of molecules (Bouachrine et al, 2009; Yang et al, 2005). To further understand the electronic properties of these molecules, some frontier molecular orbitals levels obtained from B3LYP/6-31G(d) were shown in Fig-3. All the molecules had degenerate HOMOs orbitals, BMSP, BESP, BMST and BEST were HOMO-4 degenerate while BMSF and BESF (furan derivatives) were HOMO-3 degenerate. In general, the HOMOs of C=C units are π-bonding and have alternating phase with respect to their neighboring C=C units which indicates that in these sites an electrophilic attack can occur. The LUMOs of C=C units are π-antibonding and concentrated over the C-C single bonds; therefore, these are most likely sites for a nucleophilic attack (Figure-4). From the calculations, it becomes evident that the HOMO and LUMO topologies and sizes are almost identical for all the symmetrical D-π-D molecules.

The calculated electronic parameters band gap of the studied molecules BMSF, BESF, BMSP, BESP, BMST and BEST are 3.01eV, 2.95eV, 3.02eV, 3.00eV, 2.92eV and 2.84eV respectively as shown in Table 2.Therefore, band gap could be ordered as BEST < BMST < BESF < BESP < BMSF < BMSP, this indicates that replacement of CH_3 with C_2H_5 lowers the band gap and higher value of dipole moment. The replacement of CH_3 with C_2H_5 leads to stabilization of the HOMO and LUMO levels due to stronger electron-donating character of C_2H_5. The stabilization energies of the HOMO and LUMO by replacing CH_3 with C_2H_5 are 0.14eV and 0.07eV for BESF, 0.17eV and 0.15eV for BESP and 0.09eV and 0.04eV for BEST respectively.

Table-2: Theoretical electronic properties parameters (HOMO, LUMO, Gap, Dipole moment and UV/vis max) obtained by B3LYP/6-31G(d) of the studied molecules

	BMSF	BESF	BMSP	BESP	BMST	BEST
E_{HOMO} (eV)	-4.30	-4.16	-4.18	-4.01	-4.32	-4.23
E_{LUMO} (eV)	-1.28	-1.21	-1.16	-1.01	-1.43	-1.39
Band gap (eV)	3.01	2.95	3.02	3.00	2.92	2.84
D.M	1.17	1.46	2.57	2.83	0.15	0.32
λmax	412.76 nm	421.17 nm	402.15 nm	413.72 nm	413.51 nm	432.02 nm

To investigate the substitution effect of heteroatom and R on the adsorption of the molecules, DFT/6-31G*/CIS method was used to calculate the λ_{max} as presented in Table 2. All the molecules with R= C_2H_5 exhibit a blue shift relative to that of CH_3 as case may be. The experimental and theoretical adsorption λ_{max} for BMST are 436nm and 438nm while that of BEST are 413.51nm and 432.02nm respectively (Lu and Xia, 2005). Therefore, the calculated λ_{max} are lower by 23nm and 6nm for BMST and BEST respectively. Mulliken charges for selected atoms of the studied molecules are listed in Table 3. It was observed that all the atoms selected have negative values of varying degree except that of C_1, C_4 and C_7 which have positive values (Table-3 and Figure-1).

Table-3: Mulliken charges on selected carbon atoms of the studied molecules

	BMSF	BESF	BMSP	BESP	BMST	BEST
C_1	0.176	0.180	0.178	0.183	0.179	0.185
C_2	-0.181	-0.181	-0.189	-0.190	-0.177	-0.179
C_3	-0.215	-0.217	-0.194	-0.196	-0.164	-0.166
C_4	0.377	0.378	0.376	0.377	0.375	0.376
C_5	-0.215	-0.216	-0.222	-0.222	-0.128	-0.128
C_6	-0.215	-0.216	-0.222	-0.223	-0.128	-0.129
C_7	0.377	0.378	0.376	0.377	-0.127	-0.128
X	-0.515	-0.515	-0.730	-0.729	-0.218	-0.217

The IR frequencies calculated at B3LYP/6-31G* methods are shown in figure 6. The prominent C=C stretching bands for C_4=C_5 and C_6=C_7 bonds in the six molecules are 1529 cm^{-1} for BMSF, 1530 cm^{-1} for BESF, 1449 cm^{-1} for BMSP and BESP, 1584 cm^{-1} and 1402 cm^{-1} for BMST and 1608 cm^{-1} and 1554 cm^{-1} for BEST respectively which are heteroaromatic-like pattern of the π-conjugated backbone (Casado et at, 2004). Single stretching band for C_4=C_5 and C_6=C_7 was observed for furan (BMSF and BESF) and pyrrole (BMSP and BESP) derivatives, this was up-shifted and split into two components in thiophene derivatives at 1584 cm^{-1} and 1402 cm^{-1} for BMST and 1598 cm^{-1} and 1535 cm^{-1} for BEST (Figure 5). This has been ascribed to a typical indicator of the attainment of a heteroquinonoid-like pattern for the π-conjugated path (Casado et al, 1998; Casado et at, 2004).

HOMO   LUMO
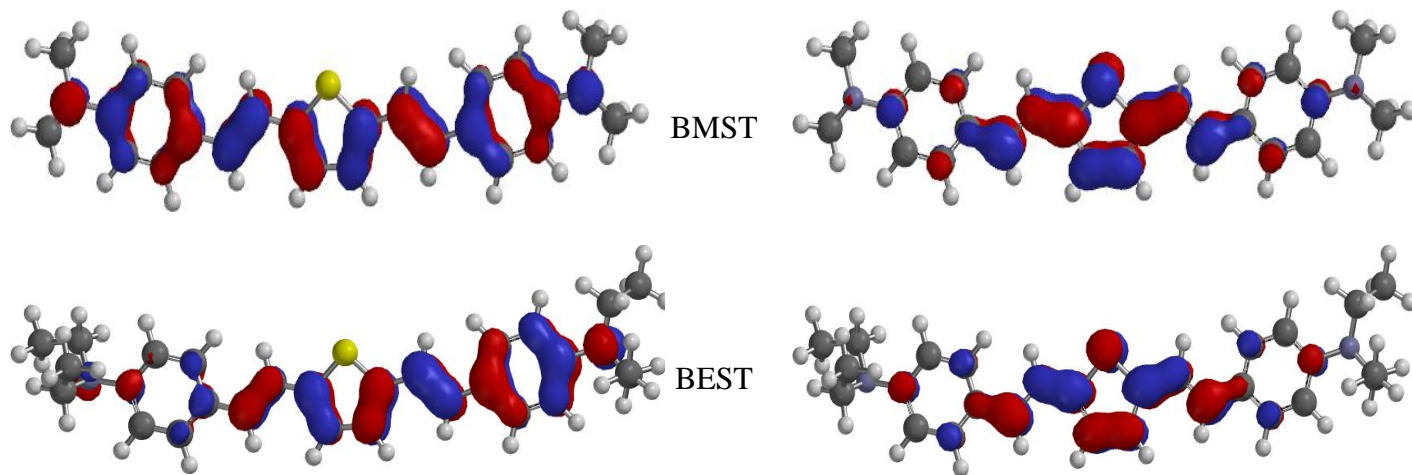

BMSF

BESF

BMSP

BESP
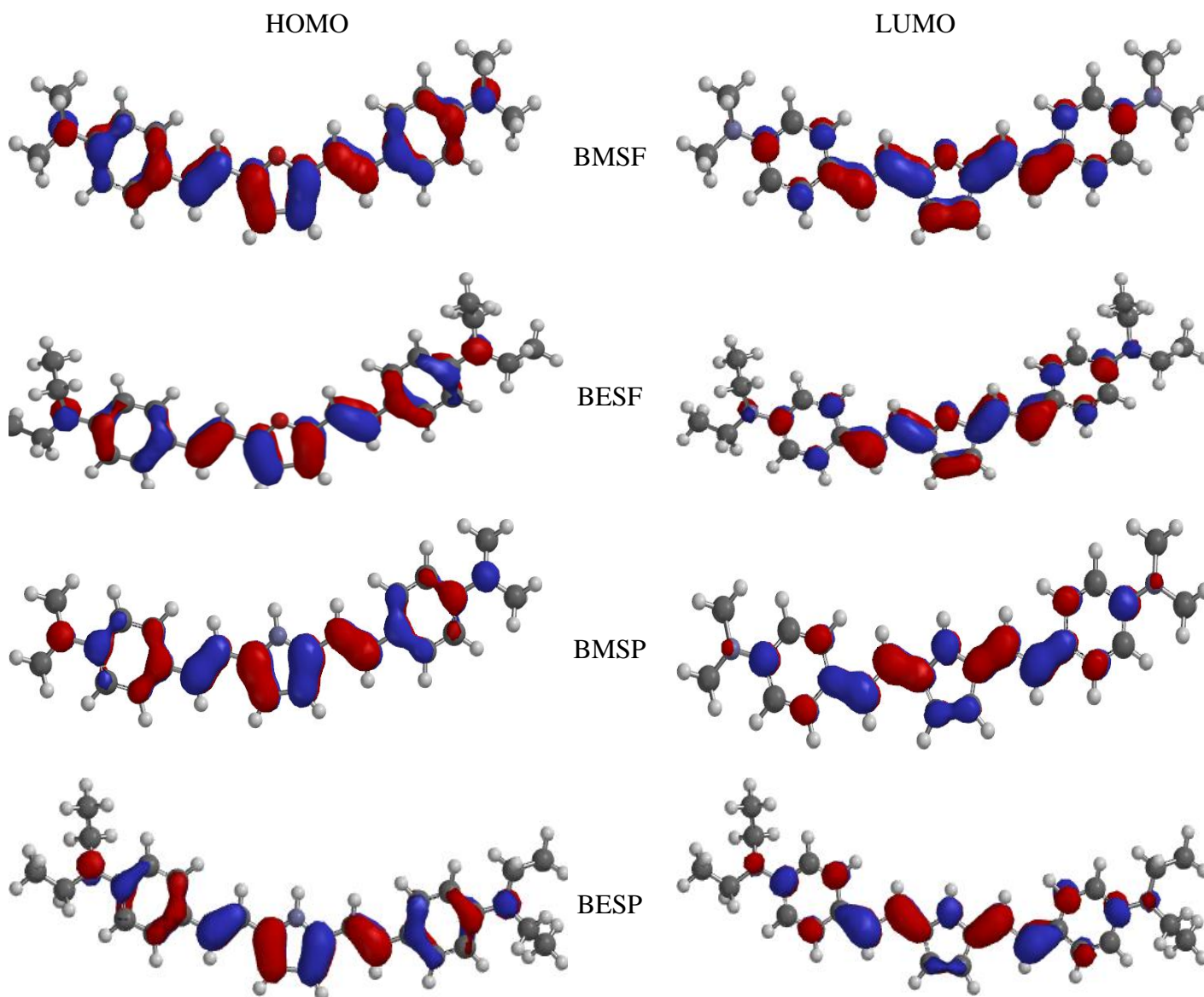
Fig-4: The contour plots of HOMO and LUMO orbitals of the studied compounds

4. CONCLUSION

The geometrical and electronic structure, UV-visible absorption band and IR spectra of 2,5-bis[4-N,N-diethylaminostyryl]thiophene and its furan and pyrrole derivatives were investigated through quantum chemical method using B3LYP/6-31G*(D). In the study, we found out that:

The substitution of methyl by a more electron-donating group like C_2H_5 stabilizes the HOMO and the LUMO levels with decrease in the band gap, which brought about a blue shift in the absorption spectrum.
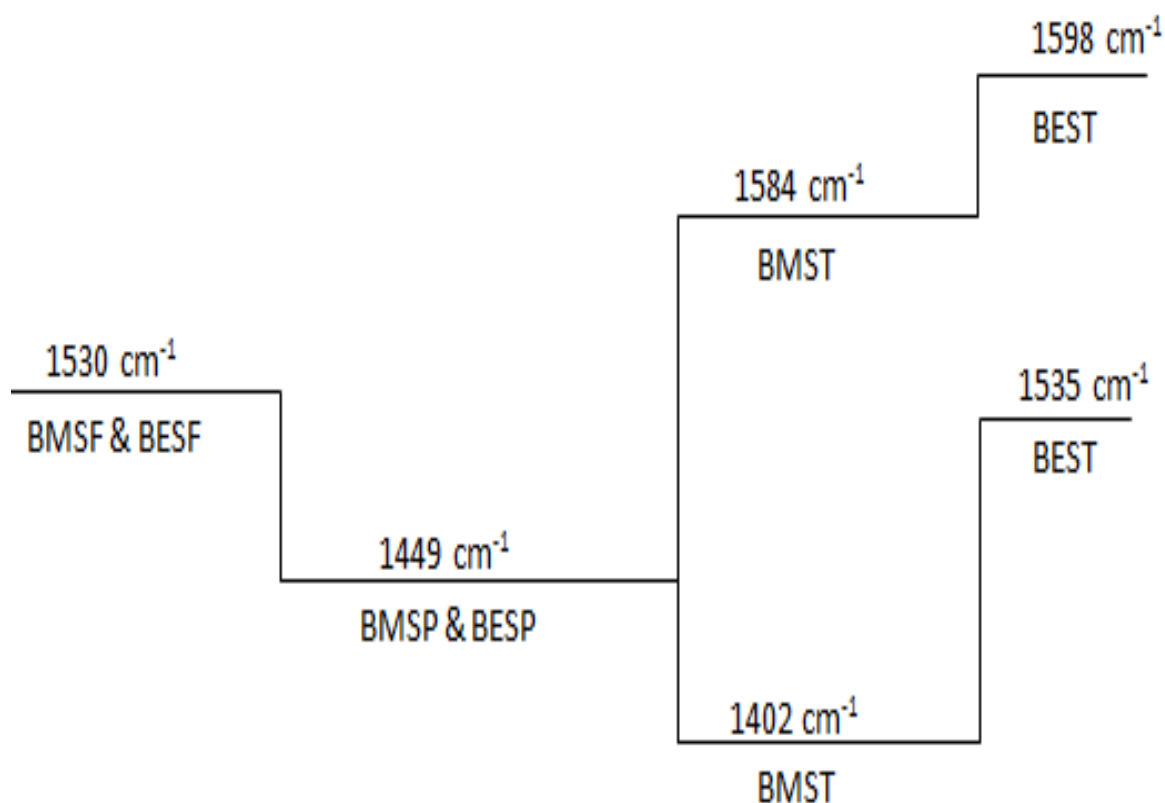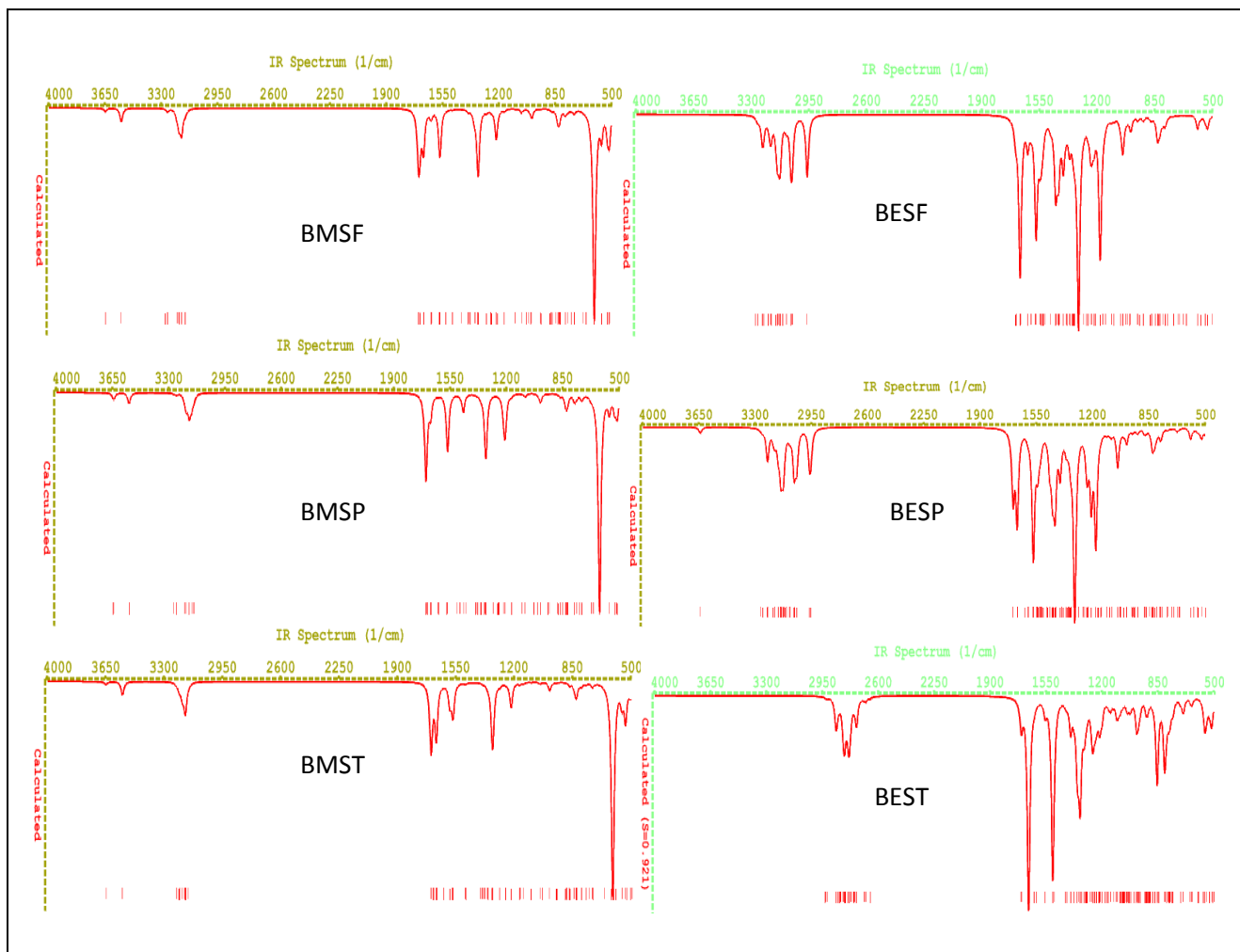

Fig-5: Splitting of five numbered ring C=C stretching vibration

Fig-6: Infra-red spectra of the molecules BMSF, BESF, BMSP, BESP, BMST and BEST calculated at B3LYP/6-31G* level..

Thiophene derivatives have superior quality as reflected in their electronic properties calculated i.e. lower band gaps, longer absorption wavelengths and attainment of heteroquinonoid-like π-conjugated structures. The absorption wavelengths calculated are in good agreement with experimental values reported in the literature (Lu and Xia, 2005).

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