

Does oligomerization in fused thiophene affect reactivity and aromaticity?

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Abstract. Reactivity and aromaticity of a few fused thiophene oligomers and their conformers are discussed in the light of density functional theory (DFT) and conceptual density functional theory. Reactivity parameters, such as hardness (η) and electrophilicity (ω), chemical potential (μ) and energy of the HOMO (highest occupied molecular orbital) have been studied. Oligomerization raises the E_{HOMO} of the species, which in turn increases the reactivity of the oligomers. The absorption spectra of the species are analysed using TDDFT (time dependent density functional theory). The absorption peaks show red shift with increasing size of the oligomers. Aromaticity of the species is gauged by nucleus independent chemical shift (NICS). The out-of-plane component, (NICS_{zz}) values advocate higher aromatic character at longer distance whereas, NICS supports the reverse.

Keywords. Optical materials; DFT; thiophene; absorption spectra; reactivity.

1. Introduction

Tremendous development in the field of organic conjugated materials and organic electronics has taken place after the discovery that conjugated oligomers and polymers can be productively used as an integral component in organic electronic devices, such as light-emitting diodes (LEDs), lasers, thin film transistors (TFT),^{1–5} solar cells^{6,7} etc. Heeger *et al.*, discovered high electrical conductivity in doped polyacetylene in the late 1970s.⁸ This discovery augmented a massive amount of interdisciplinary research activities on conjugated polymers to be used as a material in electronics and optoelectronics. Among different classes of conjugated polymers (polyaniline, polyacetylene, polythiophene, polypyrrole, polyphenylene and their derivatives), polythiophenes and thiophene oligomers display their efficacy in organic electronics and are among the best investigated conjugated polymers used in molecular electronics and organic electronic devices.^{9–13} These molecules are significantly advantageous over their silicon analogues.¹⁴ Extension of the π system increases the conjugation length of the molecule, decreases the band gap and increases charge carrier mobility. Fused thiophene subunits^{15,16} spur a greater conjugation in ground state¹⁷ and are used for fine-tuning of band gaps in organic semiconducting polymers.^{18–20} Contrary to thiophenes, fused thiophenes possess more rigid structures with extended π -conjugation. Because of its

wide applicability in electronic devices, a number of thiophene-based materials have been synthesized in recent years.^{4,9} In the present study, we have considered a few fused thiophene oligomers (figure 1) and studied their reactivity and aromaticity. The simplest fused thiophene named as thienothiophenes (TTs) consist of two annulated thiophene units which find application in organic semiconductors.^{15,18–20} TTs consist of four isomers, thieno[3,2-*b*]thiophene (**1a**), thieno[3,4-*b*]thiophene (**1b**), thieno[2,3-*b*]thiophene (**1c**), and thieno[3,4-*c*]thiophene (**1d**) (figure 1).^{15,16,18–20} Synthesis and polymerization of TTs, except **1d** (as it is unstable), have been studied extensively.

TTs, **1a–1c**, (figure 1) have a stable and electron-rich structure and are successfully used as building blocks in organic semiconductors.²¹ Fusion of another thiophene ring to TTs give rise to fused three thiophene units, called dithienothiophenes (DTTs), **2a–2f**, figure 1. This oligomer consist of six isomers with flat and rigid structures and find wide application in organic materials.²² Further addition of thiophene units yields thienoacenes.²³ Isomers of thienoacenes, **3a–3c**,²⁴ (figure 1), provide some control to the macromolecular structure and are used in preparation of films. Compound **3d** is a planar molecule with strong intermolecular orbital interactions in solid state.²⁵ Thiophene compound with five fused rings, **4**, figure 1 was reported by Zhang *et al.*,²⁶ Matzger *et al.*, prepared the 3,3'-isomer, β -DTT02, (**5a**) and β -linked thieno[3,2-*b*]thiophene trimer **5b** (both the oligomers contain six rings).²⁷ The eight-membered circulene **6b** is described

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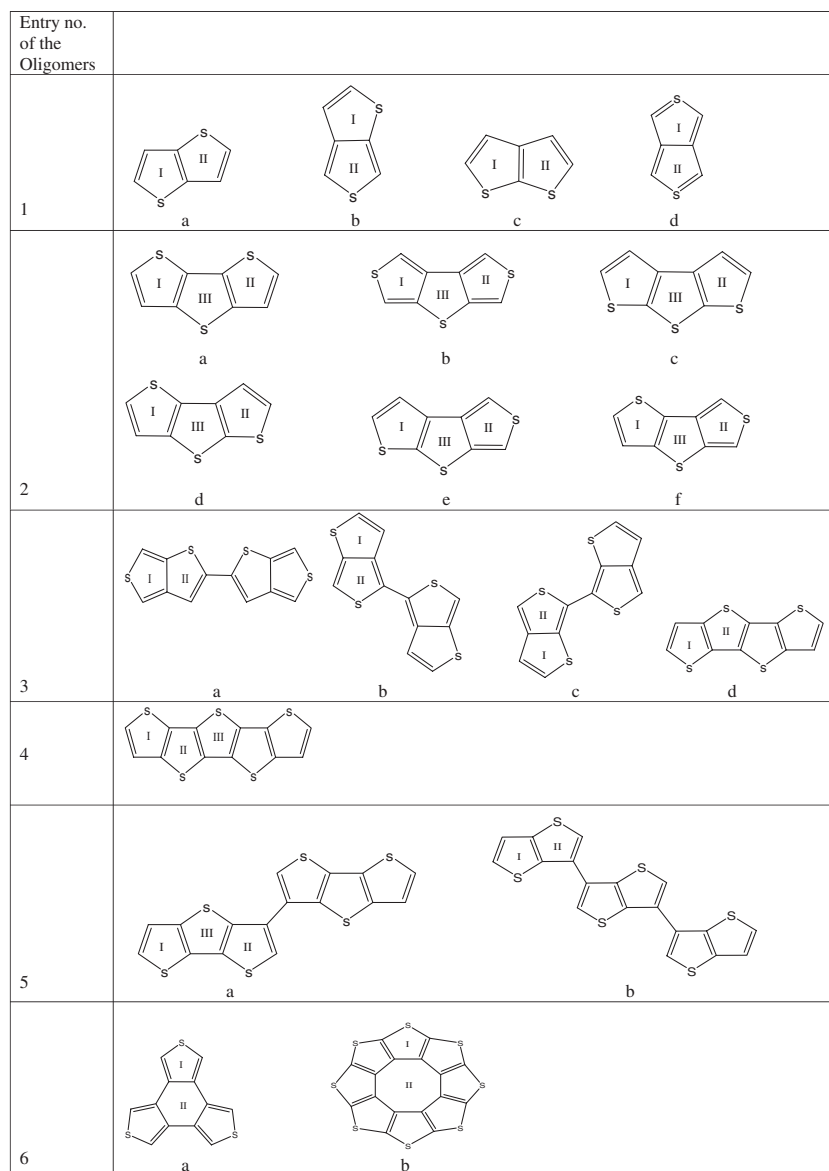


Figure 1. List of fused thiophene oligomers considered in this study.

as the ‘*sunflower*’ molecule. A molecule with three-member (**6a**) circulene has also been reported.²⁸

In the present work, we applied density functional theory (DFT) to make a proper understanding of the properties (reactivity and aromaticity) of the thiophene oligomers. DFT is a promising approach that provides accurate ground state electronic structure of different sized molecules.^{29–31} On the other hand, role of conceptual density functional theory (also called density functional reactivity theory (DFRT) in estimating reactivity parameters of molecular system has been particularly impressive.³² In DFRT, reactivity descriptors are used to quantify the reactivity of molecular systems. Among different reactivity descriptors (global and local), global hardness (η) (also called chemical hardness) and electrophilicity (ω)³³ have shown their usefulness in

rationalizing the reactivity patterns in numerous chemical systems.^{34–37} To make an in-depth understanding of reactivity of a molecule, it is thus important to quantify these descriptors. Time-Dependent Density Functional Theory (TDDFT) treats the electronically excited-states that usually results from light-matter interactions. Since its emergence, TDDFT has become increasingly popular to interpret the optical properties of molecular systems.^{38,39} A number of studies on absorption spectra of large molecules have outlined the utility of TDDFT.^{40,41} Many thiophene oligomers have been used in optical devices and an in-depth understanding and controlled manipulation of optical properties of molecular systems is therefore required.

Besides, a large number of experimental studies are devoted to the designing of new thiophene materials, a

number of pertinent theoretical studies have also been made on these materials.^{42–54} However, an understanding of the properties of these materials still forms a pre-requisite for further development. In view of this, herein, we have attempted to understand the reactivity, aromaticity, and absorption spectra of few fused thiophene oligomers.

2. Theoretical and computational details

In DFRT, global hardness (η) is defined as the second derivative of energy with respect to the number of electrons.^{55,56} Use of finite difference approximation and Koopmans' theorem⁵⁷ leads to the working formulae for η as: $\eta = (E_{LUMO} - E_{HOMO})/2$, where, E_{HOMO} is the energy of the highest occupied molecular orbital (HOMO) and E_{LUMO} is the energy of the lowest unoccupied molecular orbital (LUMO). Electrophilicity (ω)⁵⁸ is expressed as: $\omega = \mu^2/2\eta$, where, $\mu = (E_{LUMO} + E_{HOMO})/2$, (μ is called chemical potential). Theoretical calculation of hardness for chemical systems like atoms, ions, radicals, molecules and clusters using *ab initio* SCF,^{59,60} DFT,⁶¹ coupled cluster⁶² and other theories have been performed earlier, albeit mostly restricted to the ground state. Here the ground state geometrical minima of the species are obtained using 6-311++G(d,p) basis set with Becke three parameter exchange and Lee, Yang and Parr correlation functional (B3LYP)^{63,64} and are ascertained by the absence of any imaginary frequency. This functional has proven its applicability in predicting the band gaps in thiophene oligomers.^{45,46} TDDFT calculations were performed on the optimized structures to assign the observed electronic transitions in the absorption spectra using TD method (N = 30 states).⁶⁵ Present day TDDFT uses a variety of functionals to interpret absorption spectra of molecules.^{38,66} Earlier, it was shown that results obtained with CAM-B3LYP and PBE0 were closer to experimental results, when compared to other functionals like PBE, LC-PBE, LC- ω PBE, etc.⁶⁷ Tozer and collaborators concluded that CAM-B3LYP leads to much smaller deviations than B3LYP for a variety of transitions involving medium sized chromogens.⁶⁸ Herein, the B3LYP as well as CAM-B3LYP functionals are used to calculate the properties of the considered oligomers.

Aromatic character of ring structure is measured by nucleus independent chemical shift (NICS).^{69,70} Rings with large negative NICS values are considered as aromatic; the more negative the NICS values, the more aromatic the rings are. Non-aromatic species have NICS values closer to zero whereas a positive NICS

value indicates anti-aromaticity. NICS value is usually computed at ring centres, (NICS(0)), which is the non-weighted mean of heavy atom coordinates. It can also be calculated at a certain distance above or below the centre of the ring. Though both the in-plane and out-of-plane components of the NICS values contain σ (sigma) and π (pi) contributions, the out-of-plane component (NICS_{zz}) consists more of the π contribution.⁷¹ The NICS value is obtained at 1 Å above the molecular plane (NICS(1)) or its corresponding out-of-plane component (NICS(1)_{zz}) is considered to reflect the *p*-electron effects better than NICS(0).^{72–75} Moreover, it is suggested that for a better understanding of the aromatic character of a system, the NICS values should be scanned over a distance. It was also established that the shapes of the NICS-scan provide a better picture of the type of the ring current in aromatic and anti-aromatic systems.^{71,76} Reliability of the NICS-scan in assessing aromatic behavior of some planar six-membered heteroaromatic systems has also been explored earlier by Seal and Chakrabarti.⁷⁷ Therefore, in the present study, apart from the NICS(0) values, NICS(0.2), NICS(0.4), NICS(0.6), upto NICS(4.0) values were also obtained above the plane on a line passing through the point where NICS(0) value was evaluated, (figure 4a). These values were calculated using the Gauge-Independent Atomic Orbital method (GIAO)^{78,79} by placing a ghost atom (Bq) at the geometric mean of the ring atoms and the isotropic chemical shift (σ_{iso}) at this ghost atom is computed; the $-\sigma_{iso}$ values, (NICS = $-\sigma(Bq)_{iso}$) are reported throughout the manuscript.

Furthermore, the effect of solvent polarity on the chosen reactivity parameters and aromaticity of the oligomers were observed using PCM (Polarizable Continuum Model)⁸⁰ in different solvents (varying from non-polar to a polar solvents, carbon tetrachloride ($\epsilon = 2.23$), DMSO ($\epsilon = 46.83$), and water ($\epsilon = 78.35$)). Calculations were carried out using Gaussian09.⁸¹

3. Results and Discussion

Total energy of a species is an indicator of its stability, particularly for compounds having isomers; energetically favoured isomer often results in high yield. Among the chosen set of oligomers, oligomers **1**, **2**, and **3** (figure 1) possess isomers. The order of total energy, E_{el} (in Hartree) are: in thienothiophene isomers (**1a-1d**): **1a**>**1c**>**1b**>**1d**, where **1a** is the most stable. Among the poly(thieno[3,4-*b*]thiophene) isomers (**2a-2f**), **2a** isomer is observed to be energetically most stable and the order is **2a**>**2d**>**2f**>**2b**>**2c**>**2e**. In case of **3a-3c** isomers, the observed trend is: **3b**>**3a**>**3c**,

table 1. Thus, it is expected that the isomer **1a**, **2a** and **3d** are more stable among their respective sets of isomer.

3.1 Reactivity of the conformers

Reactivity of the oligomers is measured using the reactivity parameters, energy of the HOMO (E_{HOMO}), global hardness (η) and electrophilicity (ω). The global descriptor of hardness has been known to quantify the overall stability of the system.^{82,83} Various applications of global reactivity descriptors particularly global hardness and electrophilicity in the context of chemical reactivity have been reviewed earlier.^{36,84,85}

3.1a Variation of energy of HOMO (E_{HOMO}): Measurement of E_{HOMO} of a species is important for two reasons; firstly, it measures the electron donating ability, and secondly, it governs the absorption spectra of the molecule (along with E_{LUMO}). E_{HOMO} of the oligomers are presented in table 1. Usually a lower (more negative) E_{HOMO} implies a more stable HOMO. The order of the gas phase E_{HOMO} are as follows. In thienothiophene isomers (**1a-1d**, figure 1), **1c**>**1a**>**1b**>**1d**; **1c** possesses the most stable HOMO. Among the poly(thieno[3,4-*b*]thiophene) isomers (**2a-2f**, figure 1), isomer **2c** is observed to possess most stable HOMO and the order is **2c**>**2d**>**2a**>**2b**>**2f**>**2e**. In case of oligomer **3**, figure 1, the observed order is: **3a**>**3d**>**3b**>**3c**. The E_{HOMO} of oligomer **4** is calculated to be -128.61 kcal/mol. The E_{HOMO} of **5a** and **5b**

oligomers are very close, -134.63 kcal/mol and -134.52 kcal/mol, respectively. E_{HOMO} for three and eight-membered circulene, **6a** and **6b**, are -139.68 kcal/mol and -136.68 kcal/mol, respectively. The range of the E_{HOMO} for all the considered isomers lies in the range -146.18 kcal/mol to -118.19 kcal/mol, with the lowest value shown by **1c** (-146.18 kcal/mol) and the highest by **1d** (-118.19 kcal/mol). Lowest E_{HOMO} of **1c** may be attributed to the fact that the S atoms are closer (3.19 Å) to each other which facilitates interaction between the *d* orbitals of the S atoms. Interestingly, the HOMO of the system becomes less stable on increasing the number of fused rings; for example, comparison of similar type of stable oligomers gives the order as: **1c**>**2c**>**3d**>**4**. Whereas, at the same level of theory, E_{HOMO} of thiophene is calculated to be -154.24 kcal/mol. Thus, oligomerization of thiophene imparts chemical instability (lower E_{HOMO} leads to stability) to the oligomer. Variation of the E_{HOMO} of the oligomers leads to different reactivity to the isomers that are important from synthetic chemistry view point. Moreover, it is interesting to see in figure 2 that the number of lobes in the HOMO increases with the increasing number of rings, which reduces the symmetry of the HOMO and in turn makes the HOMO unstable.

In recent years, functionalization of the oligothiophenes has been extensively studied because of their numerous applications in OLEDs,⁸⁶⁻⁸⁸ OFETs,⁸⁹⁻⁹¹ chemo-sensors,⁹² biosensors⁹³ and electro-chromic devices.⁹⁴ The functionalization of oligothiophenes has allowed the synthesis of materials with specific electronic properties. Results here advocate that oligomerization

Table 1. Total electronic energy (E_{el}) and E_{HOMO} of the oligomers at B3LYP/6-311++G(d,p) level of theory. Values are in kcal/mol.

Oligomer	E_{el} in gas phase	E_{HOMO} in gas phase	E_{HOMO} in CCl_4	E_{HOMO} in DMSO	E_{HOMO} in Water
1a	-644775.54	-142.17	-142.25	-143.25	-143.29
1b	-644771.07	-134.95	-135.12	-136.16	-136.19
1c	-644773.32	-146.18	-146.29	-147.40	-147.43
1d	-644752.30	-118.19	-118.32	-119.33	-119.37
2a	-942492.15	-136.27	-136.23	-137.14	-137.18
2b	-942488.69	-135.93	-136.09	-137.25	-137.29
2c	-942488.17	-140.95	-140.88	-141.79	-141.82
2d	-942490.43	-138.11	-138.05	-139.02	-139.06
2e	-942487.93	-133.11	-133.06	-133.95	-133.99
2f	-942489.64	-133.77	-133.80	-134.81	-134.85
3a	-1288791.52	-131.81	-131.67	-132.51	-132.54
3b	-1288791.73	-123.45	-123.39	-124.41	-124.45
3c	-1288791.26	-121.80	-122.45	-124.38	-124.44
3d	-1240208.68	-131.69	-131.44	-132.32	-132.36
4	-1537925.23	-128.61	-128.33	-129.09	-129.13
5a	-1884232.22	-134.63	-134.37	-135.32	-135.35
5b	-1932822.66	-134.52	-134.50	-135.79	-135.84
6a	-1038924.14	-139.68	-139.64	-140.89	-140.95
6b	-2381713.19	-136.68	-135.42	-135.04	-135.05

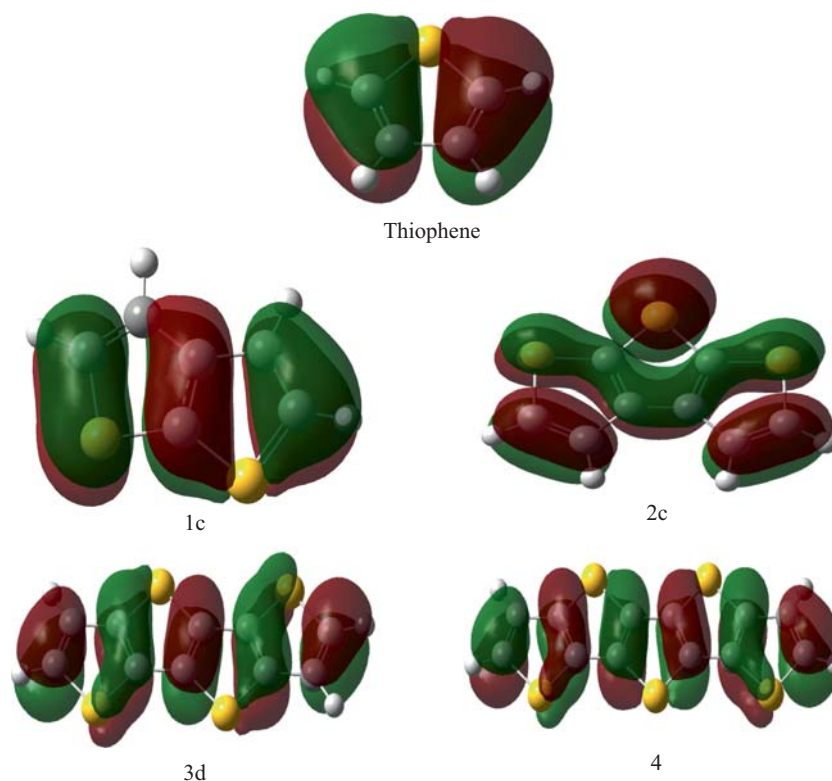


Figure 2. Shape of the HOMO of thiophene and a few oligomers which are shown in figure 1.

raises the E_{HOMO} which might facilitate the functionalization. Solvent phase results are observed to be similar to gas phase results. Thus solvent polarity is observed to exert no significant changes on the E_{HOMO} values (table 1). Results obtained at CAM-B3LYP/6-311++G(d,p) level of theory also corroborate with the results obtained at B3LYP/6-311++G(d,p) level of theory. See table S1 in Supplementary Information (SI).

3.1b Variation of η and ω : The HOMO-LUMO gap, i.e., the global hardness (global hardness is the half of this gap) measures the stability of a molecular system. HOMO-LUMO gap is important for materials that are used in optical devices. This gap is governed by a number of factors such as, rigidity of the structure, aromaticity of the molecule, position of the heteroatom, chain length, etc. Earlier, it was shown that the HOMO-LUMO band gap of an oligomer shows a relationship with the number of monomers.^{45,46} Figure 3 represents the gas phase η and ω of the oligomers of thiophene.

It can be noticed from figure 3a that the oligomers differ in their hardness values. Among the oligomers, **1c** possesses maximum hardness (also most stable HOMO) and **1d** shows minimum hardness. On the other hand, electrophilicity exhibits the opposite trend. In numerous cases, maximum hardness principle (MHP) and minimum electrophilicity principle (MEP) showed

their applicability.^{95–99} According to MHP, maximum hardness leads to maximum stability and MEP states that minimum electrophilicity leads to maximum stability. Here, both the MHP and MEP are obeyed (figure 3). Earlier studies also confirmed that these two principles worked well in conformational studies.¹⁰⁰ Interestingly, global hardness trend tallies with the order of E_{HOMO} ; oligomers having maximum hardness (**1c**) possess lowest E_{HOMO} (−146.18 kcal/mol). This implies that in this case, E_{HOMO} governs the chemical stability of the oligomers. Earlier, it was also noted that the stability measured from total energy values does not tally with the trend observed from the HOMO-LUMO perspective.¹⁰¹ This is because the total energy of a system is contributed by not only the FMO, but also from other core orbitals. From chemical view point, the HOMO-LUMO trends or hardness is more important compared to the total energy of the system. Total energy contributes to the thermodynamic stability whereas FMO energies contribute to the chemical reactivity/stability.

To assess the impact of solvent phase we recomputed the parameters in three different solvents. Plots of η and ω in solvent phase are shown in figures 3c–3e. Results advocate that neither polar nor non-polar solvents impart any change in the reactivity trends. Moreover, the values obtained in different solvents do not vary to a significant level. However, earlier study showed that these parameters vary quite significantly

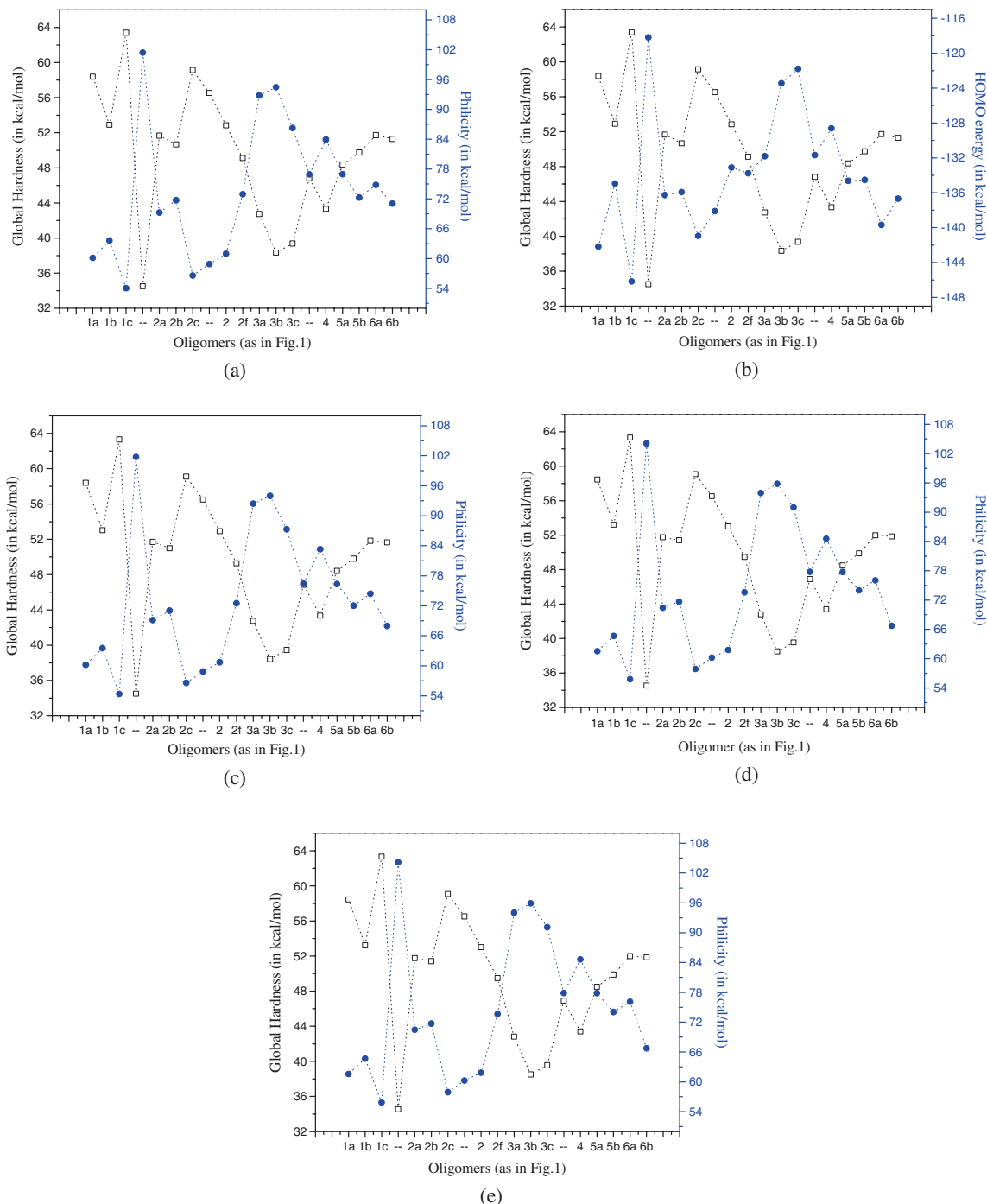


Figure 3. Plot η and ω of oligomers of thiophene. (a) Plot of gas phase η and ω . (b) Plot of gas phase η and E_{HOMO} . Plot of η and ω (c) in carbon tetrachloride, (d) in DMSO, (e) in water. Calculations were carried out at B3LYP/6-311++G(d, p) level of theory.

in solvent phases.¹⁰² The effect of solvent phase on the molecule can be argued as follows. For a system in solution, the Hamiltonian can be written as:

$$\hat{H}_{tot}(q_M, q_S) = \hat{H}_M(q_M) + \hat{H}_S(q_S) + \hat{H}_{SS}(q_S) + \hat{H}_{MS}(q_M, q_S)$$

For an infinitely dilute solution, \hat{H}_M refers to the Hamiltonian for single molecule (M), \hat{H}_S is the Hamiltonian for

a large number (say n) of solvent molecules (S) (though the number of solvent molecules is infinite even at infinite dilution). The third term in the total Hamiltonian, \hat{H}_{SS} represents the interaction between solvent molecules and the last term, \hat{H}_{MS} includes the interactions between M and n , the number of solvent molecules. The coordinates, q_M and q_S apply to both electrons and nuclei of M and S , respectively. The interaction of a system with

solvent molecule depends on its dipole moment. Usually molecules with lower dipole moments are reluctant to interact with solvent molecules. In case the solute molecule possesses sufficient dipole moment, the fourth term in the total Hamiltonian dominates. However, in this case low dipole moment of the oligomers restricts them to interact with the solvent molecules. As a result of this, we do not observe any significant change in the E_{HOMO} or E_{LUMO} values and hence observe almost same value for global hardness and electrophilicity. Moreover, similar trends are also observed at CAM-B3LYP/6-311++G(d,p) level of theory (figure S1 in SI).

3.2 Aromaticity of the oligomers

Estimating aromaticity in terms of NICS values is of increasing interest among the researchers and in recent years, a number of studies have been devoted to estimate the aromatic character of biomolecules.^{103,104} Herein, the aromatic character of the five membered rings of the oligomers has been analyzed in terms of variation of NICS values with the distance from the plane of the rings and results are presented in figure 4. It is evident that the gas phase NICS values vary with the variation of the distance from the plane of the rings. In all the cases, the NICS values remain almost constant below 0.6 Å, (aromatic character is maximum), and thereafter it becomes less negative, indicating lesser aromatic character at larger distances.

In case of **1a-1d** isomers, it is interesting to note that one of the rings (I) in isomer **1b** loses its aromatic character due to lack of conjugation. All the other rings exhibit a comparable aromatic character. In case of **2a-2f** isomers, most of the central rings are less aromatic as compared to the other isomers. Aromatic character of **2b(III)** ring is observed to be least among the rings and **2e(I)** ring exhibits maximum aromatic character. In **3a-3d** oligomers, rings II possess more aromatic character compared to the rings I; aromaticity of **3a(I)** ring is observed to be maximum with a comparable value to that of thiophene. In contrast, **3a(II)** is observed to be least aromatic. Oligomer **4** consists of five rings (with three different types) and it is seen that the ring at the centre of the oligomer is less aromatic as compared to other rings; aromaticity is in the order: **4(I)** > **4(II)** \approx **4(III)**. Similar to other oligomers, central ring in oligomer **5a** possesses less aromatic character as compared to other rings.

Both the rings in **5b** oligomer are of comparable aromatic character. *Sunflower*-like oligomers **6a** and **6b** are less aromatic compared to other oligomers or thiophene. Inner portion (ring II) in **6a** and **6b** is

observed to be anti-aromatic (possess positive NICS values). It is important to note that neither of the rings in **4**, **5** and **6** oligomers possesses more or comparable aromatic character to that of thiophene. Interestingly, the rings at the centre of the oligomer are observed to be less aromatic compared to other rings. Results thus suggest that oligomerization leads to drop in aromatic character that might lead to high reactivity, which in turn facilitates functionalization. Further, NICS values of the oligomers are calculated in different solvents. As a representative case, solvent phase NICS values of the oligomer **1** are shown in figure 5 and rest are shown in figure S2 in SI. It is to be noted that the solvent polarity imparts no effect on the aromatic character of the oligomers.

Earlier studies mentioned that the out-of-plane component NICS_{zz} provides more information regarding the π electrons than the NICS values.⁷¹ Therefore, we obtained the NICS_{zz} values of the oligomers at the same level of theory and the plots are presented in figures 6a–6f. Figure 6h presents a comparison of the NICS and NICS_{zz} of oligomer **1** (rest are shown in figure S3 in SI). It is important to note that in contrast to the NICS, the out-of-plane component follows different trends. The out-of-plane component of the chemical shift in many cases is paratropic at shorter distances. It gradually becomes more diatropic with the distance from the plane of the molecule, and attains maximum at ~ 1.0 Å; and at longer distances it becomes less diatropic. Few rings are showing anti-aromatic character (positive NICS_{zz} values). In all the cases, the rings are observed to be less aromatic (less negative) compared to thiophene. Comparison of the NICS_{zz} (at 1.0 Å) of the most aromatic ring of the oligomers exhibit the following order: **1d(II)** (−30.42) > thiophene (−27.66) > **3a(I)** (−26.45) > **2e(I)** (−25.73) > **6a(I)** (−22.74) > **5b(I)** (−20.93) > **4(I)** (−17.54). NICS_{zz} values in ppm are given within brackets and plotted in figure 6g.

These values clearly indicate that even the most aromatic ring of each of the oligomers differ by a large magnitude. It is observed from figure 6h that the variation of NICS is shallower in comparison to its corresponding out-of-plane component. Variations of NICS and NICS_{zz} also project a contrasting conclusion; NICS values indicate that the rings are more aromatic at shorter distances (below 0.5 Å) whereas NICS_{zz} values advocate that the rings are highly aromatic at a longer distance (~ 1.0 Å from the ring centre) (figures 4 and 6). Earlier, Sranger also reported the same trends on the variation of NICS and NICS_{zz} values.⁷¹ This indicates that both the NICS and NICS_{zz} values measure rather different effects; NICS_{zz} values accounts mainly for the π aromatic character, while NICS results reflect the σ and

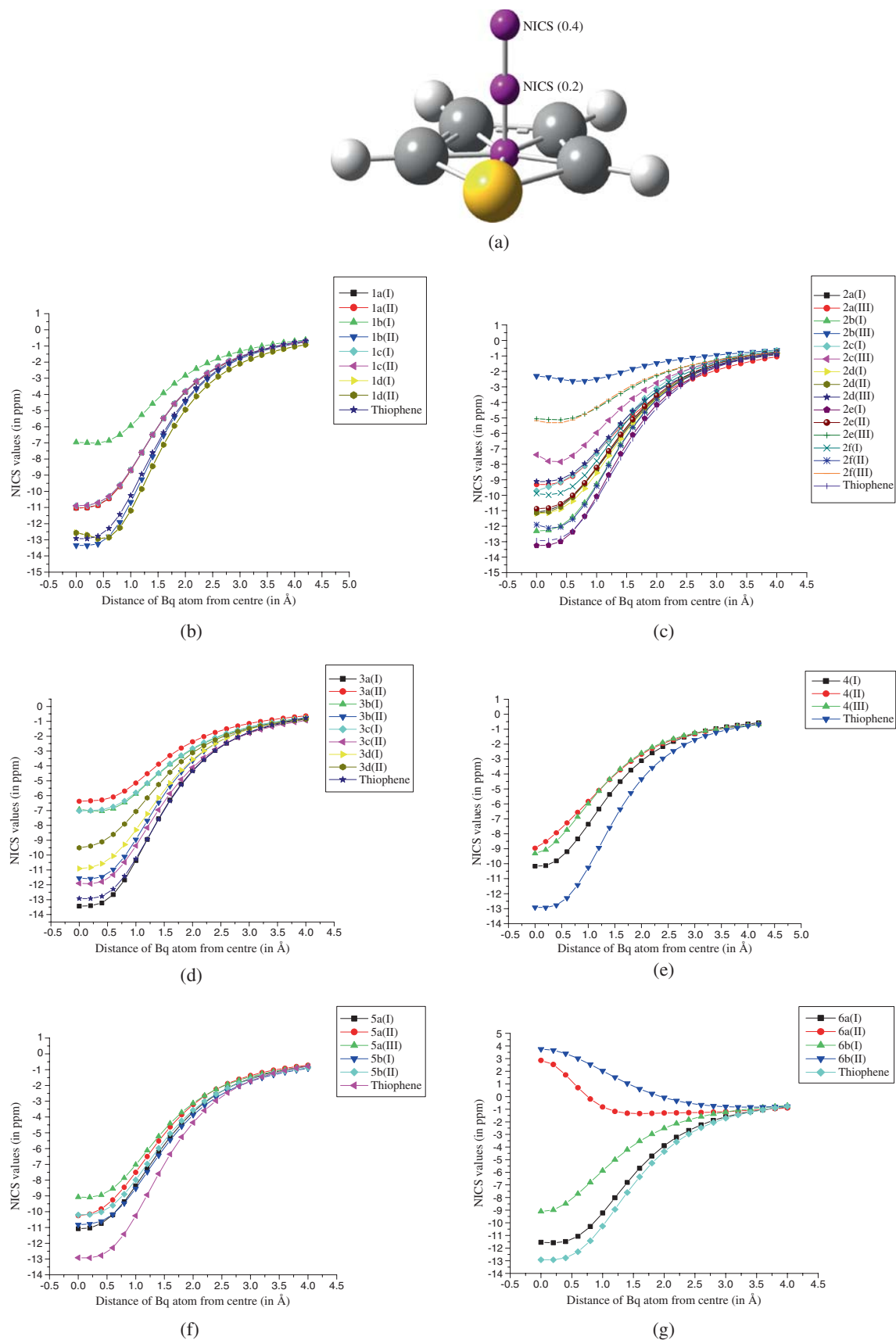


Figure 4. Variation of gas phase NICS values with the distance of the ghost atom (Bq) from the centre of the ring obtained at B3LYP/6-311++G(d, p) level of theory. (Numbering of the rings I, II and III are shown in figure 1).

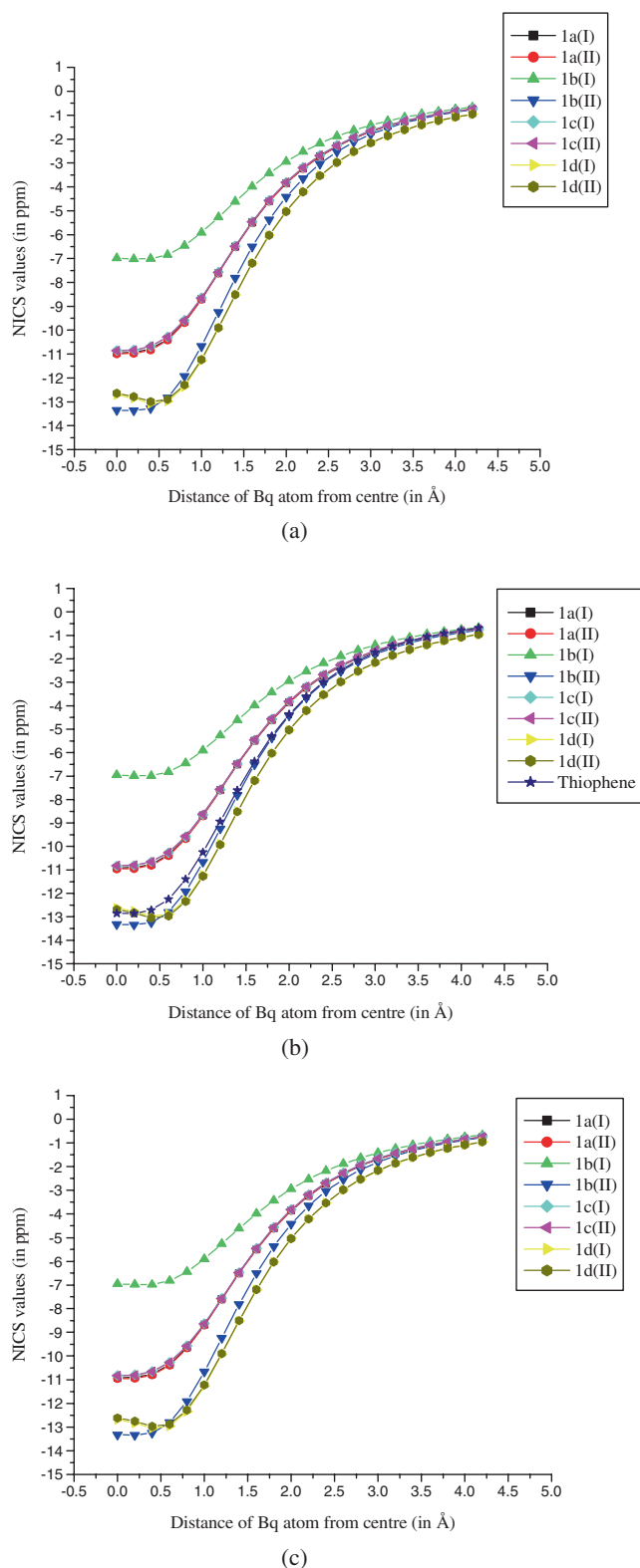


Figure 5. Variation of NICS values of oligomer **1** in solvents. (a) carbon tetrachloride, (b) DMSO and (c) water at B3LYP/6-311++G(d, p) level of theory.

π aromaticity or anti-aromaticity effects much better. More negative values of NICS_{zz} imply high aromatic character at ~ 1.0 Å which might facilitate cation-

π or π - π interactions in thiophene oligomers. It was previously demonstrated that π - π interactions in these oligomers are possible.^{105,106} Moreover, variation of the functional from B3LYP to CAM-B3LYP does not yield any significant variation in the results, see figure S4 in SI. Solvent phase NICS_{zz} values of the oligomers are very close to the gas phase values, denying any significant impact of solvents, see figure S5 in SI.

3.3 Absorption spectra of the oligomers

Earlier, the absorption spectra of the thiophene oligomers were studied in a number of occasions.^{107–111} Zhang *et al.* reported the HOMO-LUMO gap in oligomer **1** to be 5.13 eV.^{107,108} TTs with four thiophene units have also been studied using TDDFT method at B3LYP/6-311++G(d,p) level of theory and the absorption peaks were observed to be in the range of 340 nm to 370 nm, which agreed well with the experimental data.¹⁰⁹ Some oligomers like 2,5-bis(5-phenylthien-2-yl)thieno-[3,2-b]thiophene, 2,5-bis(5-(4-dodecylphenyl)thien-2-yl)thieno-[3,2-b]thiophene and 2,5-bis(5-(4-(trifluoromethyl)phenyl)thien-2-yl)thieno-[3,2-b]thiophene show absorption maxima above 400 nm.¹¹⁰ In many occasions, steric hindrance governs the optical spectra of TTs^{111,112} and hence they show absorption spectra over a wide range. The gas phase absorption spectra of the considered oligomers are shown in figure 7.

Absorption spectra of both **1a** and **1b** oligomers are of similar pattern, exhibiting two intense peaks; for **1a**, the peaks appear at 260 nm and 175 nm, which is close to the experimental peak at 280 nm in chloroform.¹⁰⁸ For **1b**, peaks appear at 295 nm and 195 nm. **1c** also exhibits two peaks at 219 nm (s) and 184 nm (b), whereas **1d** shows three peaks at 211 nm (s), 264 nm (s) and 439 nm (b). **2a** exhibits two peaks at 295 nm (s) and 203 nm (b). Spectra of **2b**, **2c**, and **2d** show peaks at ~ 200 nm and ~ 250 nm. In contrast, **2f** isomer exhibits peaks at higher wavelengths, 281 nm and 294 nm. Spectra of **3a** comprises of two peaks at 363 nm and 311 nm; **3d** shows peaks at 325 nm and 204 nm and the former is close to the experimental peak at 333 nm.¹¹³ However, for both **3b** and **3c**, two equally intense peaks at ~ 250 nm and ~ 400 nm are observed. Loss of planarity of a molecule usually leads to a shift in the absorption maxima and hence in comparison to **3d**, the absorption maxima of **3a-3c** decrease. Oligomer **4** shows an intense peak at 354 nm and one less intense peak at 220 nm (experimental peak is observed at 357 nm).¹¹³ Oligomers **5a** and **5b** show intense peaks at 296 nm and 252 nm which are also closer to the experimental

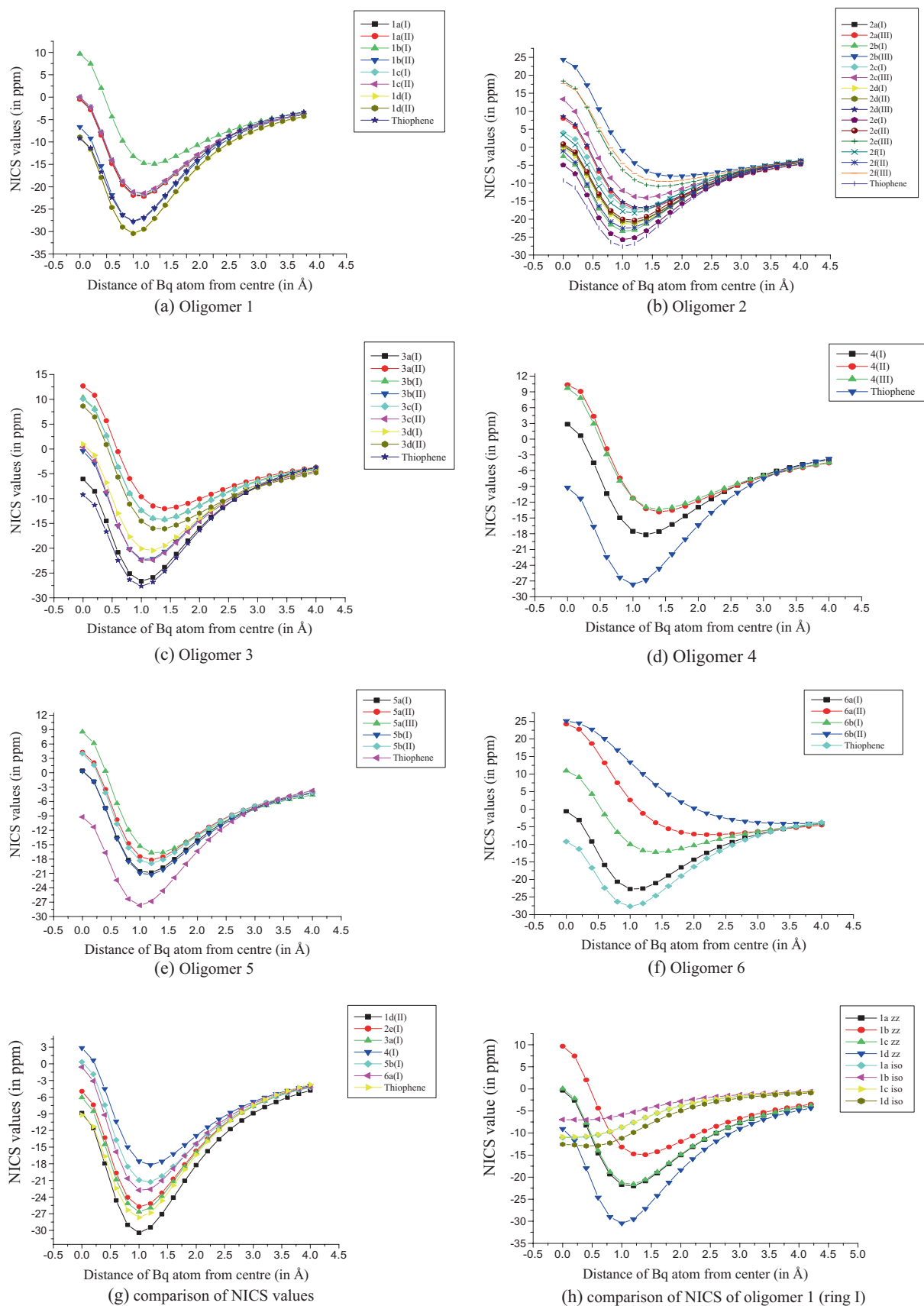


Figure 6. Variation of gas phase NICS_{zz} values with the distance of the ghost atom (Bq) from the centre of the ring obtained at B3LYP/6-311++G(d, p) level of theory. (Numbering of the rings I, II and III are shown in figure 1).

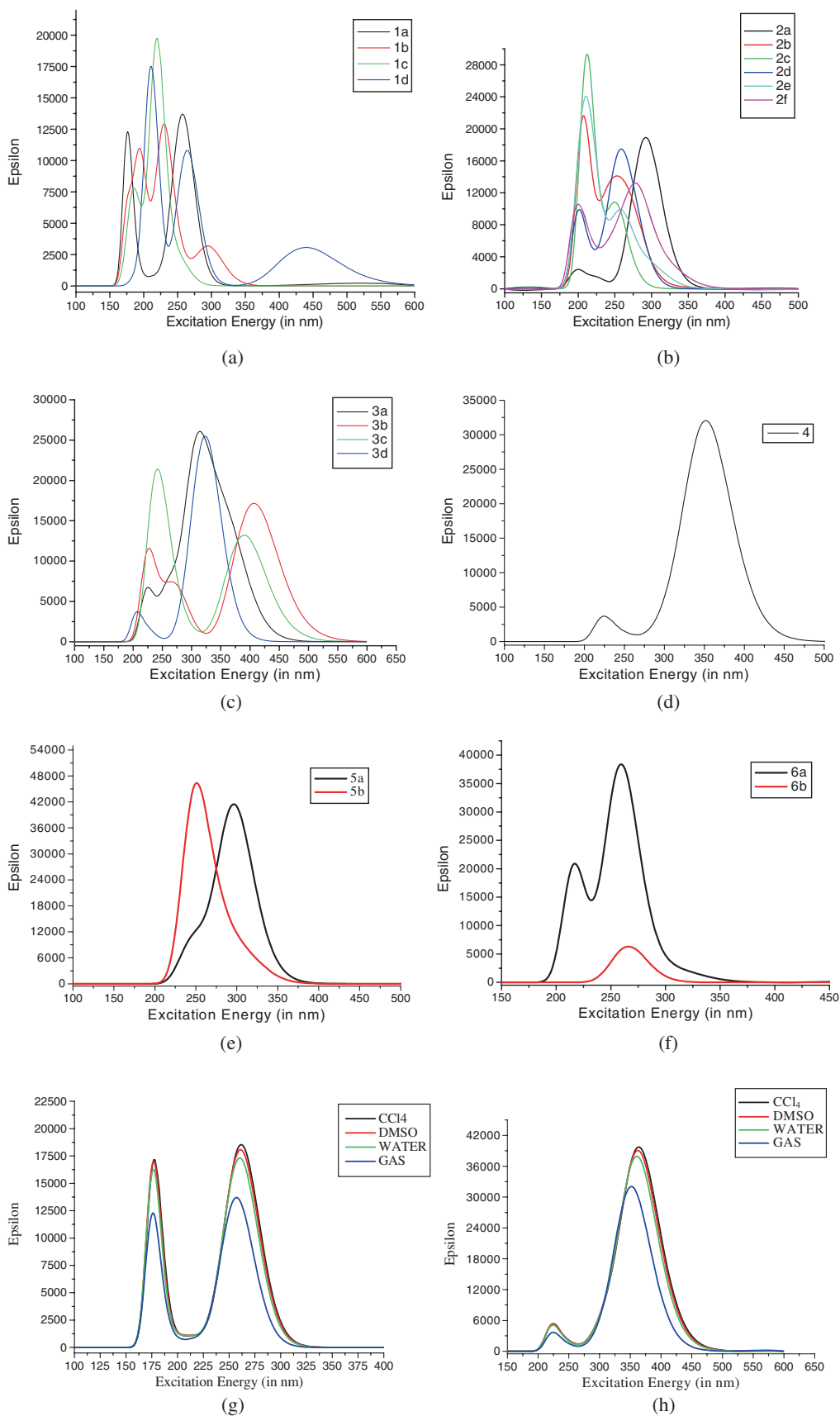


Figure 7. (a)-(f) gas phase absorption spectra of the oligomers. Comparison of absorption spectra in gas phase and solvents obtained at B3LYP/6-311++G(d,p) level of theory. Comparison of excitation energies in solvent phases (g) oligomer **1** and (h) oligomer **4**.

observations.¹¹² The isomer **5b** is less planar compared to **5a** and hence a decrease in the absorption maxima of **5b** is observed. Oligomer **6a** shows two peaks (at 258 nm and 217 nm) whereas **6b** shows only one less intense peak at 266 nm. Usually increase in conjugation leads to the increase in the maxima of the absorption peaks; our results also advocate the same. Interestingly, many of the transitions involve HOMO→LUMO transition.

Usually reduction in the symmetry of the HOMO of a molecule raises E_{HOMO} which has a direct impact on the absorption spectrum of the molecule. Here, as seen in figure 2, the number of lobes in the HOMO increases with the increase in the size of oligomers, which in turn results in a narrower HOMO-LUMO gap and hence a red shift in the absorption spectrum is observed in case of higher oligomers. Transition from deeper orbitals like HOMO-3 and HOMO-4 are also involved (table 2 in SI). Interestingly, solvent phase does not impart any significant impact on the position of the peaks of the spectra, as seen in figures 7g-7h.

4. Conclusions

Thiophene oligomers are of great interest and the present study gives an insight into the reactivity and aromatic character of a few fused oligomers. The oligomers differ in their reactivity and aromatic character. Moreover, the reactivity pattern follows both MHP and MEP. Variation pattern of NICS and NICS_{zz} values are different and lead to opposite conclusions. The results thus indicate the importance of NICS_{zz} over NICS and suggest further insightful studies. Highly aromatic character of thiophene is affected during oligomerization, however, the large aromatic character leaves scope for π - π or cation- π interactions.

Supplementary Information (SI)

Total electronic energy (E_{el}) and E_{HOMO} of the oligomers obtained at CAM-B3LYP/6-311++G(d,p) level of theory are provided in table S1. Table S2 contains the molecular orbitals, wavelength, and oscillator strength involved in transitions. Figure S1 contains plots of η and ω at CAM-B3LYP/6-311++G(d,p) level of theory in different solvents. Figure S2 shows variation of NICS values in solvent phases at B3LYP/6-311G++(d,p) level of theory.

Figure S3 provides a comparison of the gas phase NICS and NICS_{zz} values. Figure S4 shows the variation of gas and solvent phase NICS values at CAM-B3LYP/6-311++G(d,p) level of theory. Variation of

solvent phase NICS_{zz} values at B3LYP/6-311++G(d,p) level of theory is shown in figure S5. Supplementary Information is available at www.ias.ac.in/chemsci.

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