# JOC Article
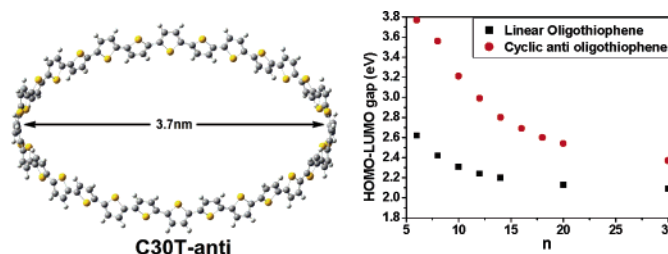
# Cyclic Oligothiophenes: Novel Organic Materials and Models for Polythiophene. A Theoretical Study

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C30T-anti

Cyclic oligothiophenes (C$n$T, $n = 6-30$, even only) in *syn-* and *anti-*conformations are studied theoretically at the B3LYP/6-31G(d) level of theory. Strain energies, ionization potentials, HOMO−LUMO gaps, bond length alternations, NICS values, and IR and Raman spectra have been studied. The properties of *anti-*conformers change systematically with increasing ring size and were studied in detail in neutral, radical cation, and dication forms. In *syn-*conformation, the oligomers lose their nearly planar ring shape and bend significantly for $n > 14$, and thus properties cannot be related to ring size. The HOMO−LUMO gap in C14T-syn is even lower than polythiopehene. IR and Raman spectra calculated at the B3LYP/6-31G(d) level are used to differentiate *syn-* from *anti-*conformations. The properties of cyclic oligomers are compared to those of the linear system, and cyclic oligothiophenes are revealed as good models for polythiophene. To assist the experimental study of known cyclic oligomers having dibutyl substituents on alternate thiophene rings, the corresponding dimethyl-substituted oligomers are also studied. The experimentally evaluated HOMO−LUMO gaps for alternately dibutyl-substituted cyclic oligomers match the calculated values; however, they are significantly higher than those of the unsubstituted analogues.

## Introduction

Oligo- and polythiophenes are among the most promising and frequently investigated conjugated systems as a result of their synthetic availability, stability in various redox states, widespread processability, and tunable electronic properties.[1] Consequently, these are promising candidates for molecular electronic devices such as field effect transistors (FET),[2] organic light-emitting diodes (OLED),[3] and solar cells.[4] Recently, a new family of oligothiophenes, namely, the cyclic oligothiophenes, has been obtained in a landmark synthesis by Bäuerle and co-

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workers.[5] Macrocyclic cyclo[*n*]thiophene (*n* = 12, 16, and 18) and fully conjugated oligothiophenediacetylenes, having dibutyl substituents on alternate thiophene units, have been synthesized.[5] Several papers describing these novel molecules and exploring their physical properties have been reported by the same group.[6] The STM studies combined with semiempirical calculations predicted a "spiderlike" cyclic structure for dibutyl-substituted C12T (cyclododecathiophene, **1**) on surfaces;[6c] however, X-ray structures of cyclic oligothiophenes have not been reported. It is further reported that the absorption maxima for the macrocyclic cyclo[*n*]thiophenes are found at approximately the energies at which linear compounds with half the number of repeating units absorb.[6a] This outcome is surprising if we consider a spiderlike, nearly planar structure for the cyclomer. The bonds connecting the thiophene units in oligothiophenes/polythiophene are not collinear; therefore, repeating thiophene units in planar *s*-cisoid conformation create the curvature in the oligothiophene chain.[7] A simple mathematical calculation indicates that 12 thiophene units arranged in such a fashion make a full circle, since the angle at the imaginary bisecting point of two interring bonds of the same thiophene ring is 150°.



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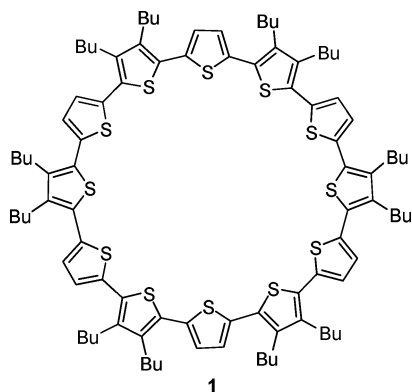
It is generally assumed that the HOMO−LUMO gap of oligomers changes linearly with $1/n$;[8,9] thus the HOMO−LUMO gap for $n = 10$ is already close to that of polythiophene. In this way, cyclic oligothiophenes with $n > 10$ can behave similarly to polythiophene from an electronic point of view. Cyclic oligothiophenes could afford tunable cavities of known dimension in the nanometer range for molecular recognition and host−guest chemistry.[6] Self-assembly of such macrocycles could lead to the formation of nanotubes, which would become a promising candidate for application in biological as well as material science.[6] An analogous pyrrole derivatives, cyclo[*n*]pyrrole (*n* = 6−8), can be seen as an expanded porphyrin without meso bridges and has been reported using a one-pot synthetic route

starting from dipyrrole units.[10] This macrocycle could emerge as a useful anion receptor.[10] The crystal structure of cyclo[8]-pyrrole (sulfate salt) was nearly planar (*syn*-conformer)[10b] and it was recently used in FET.[11]

Systematically studying a series of oligomers generates valuable information on the structure−property relationship.[12] Applications of cyclic oligothiophenes as a model of the polymers in which there are no confounding end effects has been proposed by Bäuerle and co-workers.[6] There are no data available on ring strain, the geometry of higher cyclic oligomers, and the factors influencing the band gap. It is also expected that cyclic oligothiophenes may find possible application in FET. Inspired by the work of Bäuerle et al., these observations led us to consider cyclic oligothiophenes as a subject for theoretical studies. Only neutral and dication *cyclo*-dodecathiophene in planar *syn*-conformation has been studied theoretically, and that was at a semiempirical level.[13] In neutral form, the strain energy is found to be only 0.4 kcal/mol using semiempirical calculations. The geometry of the larger and smaller ring size cyclic oligothiophenes remains an open question, as does the strain energy and HOMO−LUMO gap for such nano-objects. Studying them theoretically will also assist in the experimental determination of structure and, especially, of band gap. In this article, we present our investigations into cyclic oligothiophenes from 6- up to 30-mer in *s*-cisoid as well as *s*-transoid conformations, in neutral, radical cation, and dication states at the B3LYP/6-31G(d) level. These molecules have a diameter of 0.6−4 nm and can be considered nano-objects at the border between oligomers and polymers. The different properties of cyclic oligothiophenes, such as relative energies, ionization energies, bond lengths, HOMO−LUMO gap, charge distribution, and aromaticity (NICS values) are studied and compared with those of the linear system. In an attempt to differentiate the *s*-cisoid form from the *s*-transoid form, we have further studied IR and Raman spectra.

## Theoretical Methods

Calculations using density functional theory (DFT) were carried out with the Gaussian 03 series of programs.[14] We used Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP).[15] Linear oligothiophenes are denoted by *n*T, whereas *s*-cisoid and *s*-transoid cyclic oligothiophenes are denoted as C*n*T-syn and C*n*T-anti, respectively (*n* represents the number of heteroaromatic rings). The geometry of the *s*-transoid and *s*-cisoid C*n*T (*n* = 6, 8, 10, 12, 14, 16, 18, 20, and 30; note that a complete *anti*-conformation cannot be obtained in the case of an odd number of monomers, Figure 1) is fully optimized using B3LYP/6-31G(d) in the neutral, radical cation, and dication states. No symmetry constraints were applied to the molecules (except for the cases where vibrational frequencies were

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(a)



(b)
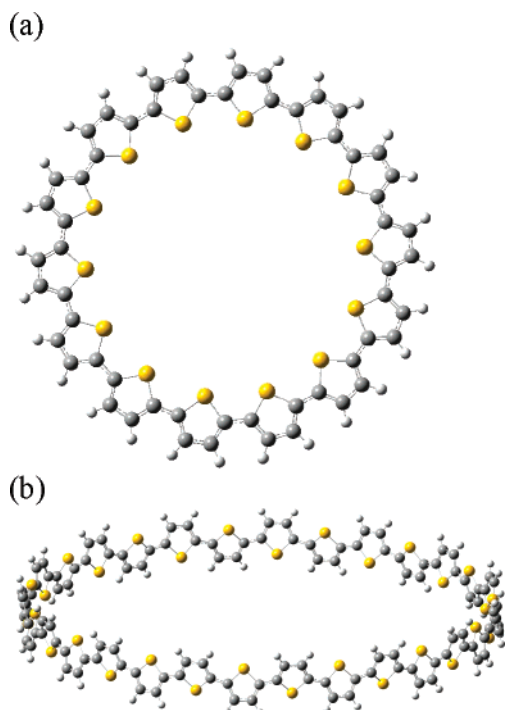


**FIGURE 1.** Views of the optimized structure of (a) C14T-syn and (b) C30T-anti.

calculated) in order to ensure locating of local minima. The IR and Raman frequencies were calculated only for C$n$T, $n$ = 6, 8, 10, and 12 at B3LYP/6-31G(d). For frequency calculations, *s*-cisoid conformers were calculated at the $C_{2v}$, $C_2$, $D_2$, and $C_{2v}$ symmetry point groups, respectively, and for the corresponding *s*-transoid conformers, the $D_{nd/2}$ point group was used. All structures showed zero imaginary frequencies. Frequency calculations on molecules larger than C12T are not feasible with our current computational power (use of 6-31G(d) basis set requires 996 basis functions for C12T). A scaling factor of 0.97[16] was used for IR and Raman frequencies. NICS values[17] were evaluated at B3LYP/6-311+G-

(d,p)//B3LYP/6-31G(d) level of theory for C$n$T ($n$ = 6, 8, 10, 12) *s*-cisoid and *s*-transoid conformers. The reorganization energies ($\lambda$) were calculated as the difference between vertical and adiabatic ionization energies at B3LYP/6-31G(d), as suggested by Malagoli and Brédas.[18] Reorganization energies are taken to be twice[19] the geometry relaxation energies for cation radical upon moving from the neutral-state geometry to the charged-state geometry. To compare with the experimental studies,[5,6] we have optimized C12T and C18T with dimethyl substitution on alternate rings at $\beta$-positions in different conformations. Orbital energies were calculated at B3LYP/6-31G(d). The calculations for polymers were performed using periodic boundary conditions (PBC) as implemented in Gaussian 03.[20] A detailed discussion of calculations for thiophene oligomers up to 30T will be the subject of a separate publication.[21]

## Results and Discussion

**Neutral Oligomer. (a) Structures, Strain Energies, and HOMO−LUMO Gaps.** Anti cyclic oligothiophenes are curved in order to make a full cycle. The smaller cyclic oligothiophenes require larger dihedral inter-ring angles to achieve curvature within the oligomer (the diameter of the rings varies from 0.6 to 4 nm for 6- to 30-mer). Consequently, they are also twisted. The average dihedral angle is 33.7° in C8T-anti and decreases gradually to 19.1° in C30T-anti. The optimized geometries in the *syn*-conformers (*s*-cisoid) exhibit a systematic decrease in the dihedral angle and increase in planarity. However, molecules larger than C14T-syn lose their nearly planar cyclic nature and circular shape significantly as oligomer size increases (see Figure 1 and Figure S1−S5 in Supporting Information for representative structures). The calculated shapes of C8T-syn and C10T-syn are similar to the experimentally reported, nearly planar structure of cyclo[8]pyrrole.[10a] C14T-syn possesses the completely planar ring shape.

Compared to linear oligothiophenes, cyclic oligothiophenes should have strain energies due to their curvature. A plot of total strain energy versus length for cyclic oligomers is presented in Figure 2a. The stain energy is calculated using the following:

$$E_n = E_{CnT} - nE_{Lpru} \qquad (1)$$

where $E_n$ is the strain energy of a cyclic oligomer having $n$ monomer units, $E_{CnT}$ is the absolute energy of a cyclic oligomer having $n$ monomer units, and $E_{Lpru}$ is the absolute energy per repeat unit for the linear oligothiophene or polythiophene that is strain-free.[22]

Total strain energy for C10T-anti is quite large (46.1 kcal/mol), whereas for C30T-anti it is only 11.2 kcal/mol (Figure 2a). For *anti*-isomers, the total strain energy is inversely

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(22) Absolute energy per thiophene repeat unit is −551.81525 au. This energy was obtained (i) from a PBC calculation of polythiophene at PBC/B3LYP/6-31G(d) (two thiophene units were used as the unit cell so the absolute energy of the unit cell was divided by 2) or (ii) from calculating the absolute energy of 30T minus 20T and then dividing by 10. Both methods give exactly the same absolute energy.
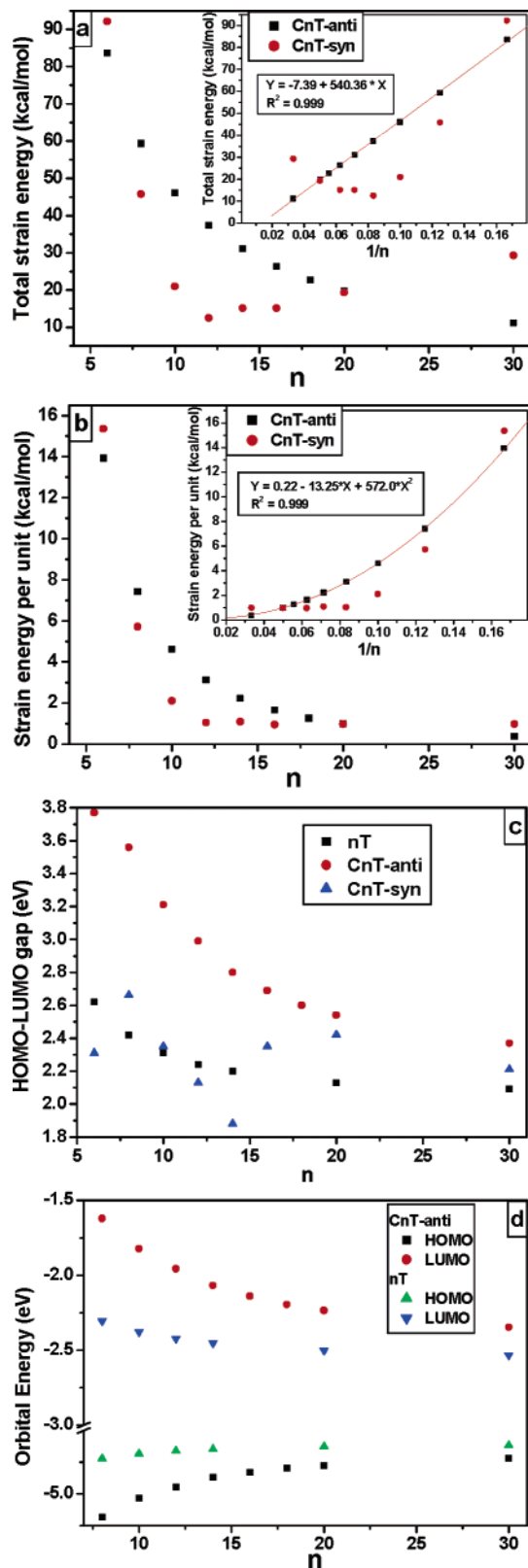
**FIGURE 2.** (a) Total strain energy versus chain length for cyclic oligothiophenes (inset graph, total strain energy versus the reciprocal of chain length for cyclic oligothiophenes). (b) Strain energy per unit versus chain length for cyclic oligothiophenes (inset graph, strain energy per unit versus reciprocal of chain length for cyclic oligothiophenes). (c) HOMO−LUMO gap versus chain length in linear oligothiophenes and in *syn* and *anti* cyclic oligothiophenes. (d) HOMO and LUMO energies versus chain length for linear and *anti* cyclic oligothiophenes.
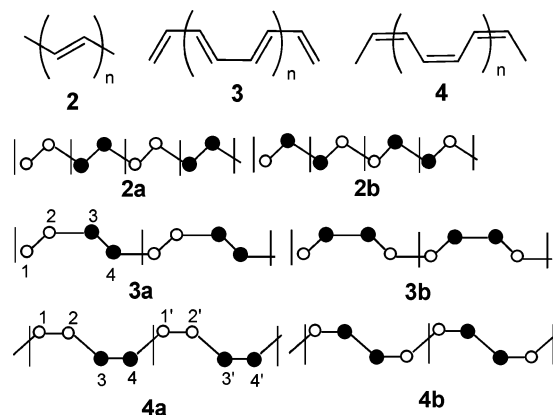


**FIGURE 3.** Schematic representation of HOCO (represented as **a**) and LUCO (represented as **b**) for the unit cells of **2**, **3**, and **4**.

proportional to chain length. For *syn*-isomers there is no correlation between total strain energy and chain length, with total strain energy ranging between 15 and 30 kcal/mol. Thus, for small cyclic oligothiophenes ($n < \sim20$), *syn*-isomers are more stable than *anti*-isomers. For C20T, both isomers have practically the same energy (energy difference is 0.4 kcal/mol), and for C30T, the *anti*-isomer is significantly (by 18.1 kcal/mol) more stable than the *syn*-isomer (Figure 2a). For *anti*-isomers, the strain energy per repeat unit decreases from $\sim4.6$ kcal/mol for C10T-anti to less than 0.4 kcal/mol for C30T-anti. Thus, C30T-anti may be considered a practically strain-free compound (Figure 2b). For *syn*-isomers, the strain energy per repeat unit is essentially constant ($\sim1.0$ kcal/mol) from C12T-syn to C30T-syn, whereas for C10T-syn, the strain energy per repeat unit is larger, $\sim2.1$ kcal/mol.

In the solid state, all linear oligothiophenes are planar with an *anti*-conformation of thiophene rings being the most stable.[12] In planar systems, there is maximal conjugation, which stabilizes the system. The deviation of dihedral inter-ring angles from planarity affects the electronic properties of cyclic oligomers and should increase the HOMO−LUMO gap. The HOMO−LUMO gaps versus the number of thiophene units, in linear[21] and cyclic oligothiophenes, are shown in Figure 2c, and the orbital energies of linear and cyclic oligothiophenes versus the number of thiophene units is shown in Figure 2d. In the short *syn*-conformers from C8T-syn up to C14T-syn, the HOMO−LUMO gaps decrease steeply with increasing chain length.

The HOMO−LUMO gap for C14T-syn is 1.88 eV, which is even smaller than the band gap of polythiophene calculated at the same level (2.05 eV).[23] We note that in *syn* cyclic oligothiophenes the arrangement of carbon backbone is *s-cis*, whereas in *anti* cyclic oligothiophenes as well as in polythiophene the arrangement of carbon backbone is alternation of *s-cis* and *trans*. Carbon backbone in *cis*-polythiophene can be schematically represented by structure **3**, and *cis*-polyacetylene is schematically represented by structure **4** (Figure 3). The band gap of *cis*-polyacetylene (1.8 eV)[24] is larger than the band gap of *trans*-polyacetylene (1.4 eV)[24] because of 1,4-attractive stabilizing interactions in HOCO (highest occupied crystal orbital) and 1,4-repulsive destabilizing interactions in LUCO (lowest unoccupied crystal orbital) of *cis*-polyacetylene (Figure

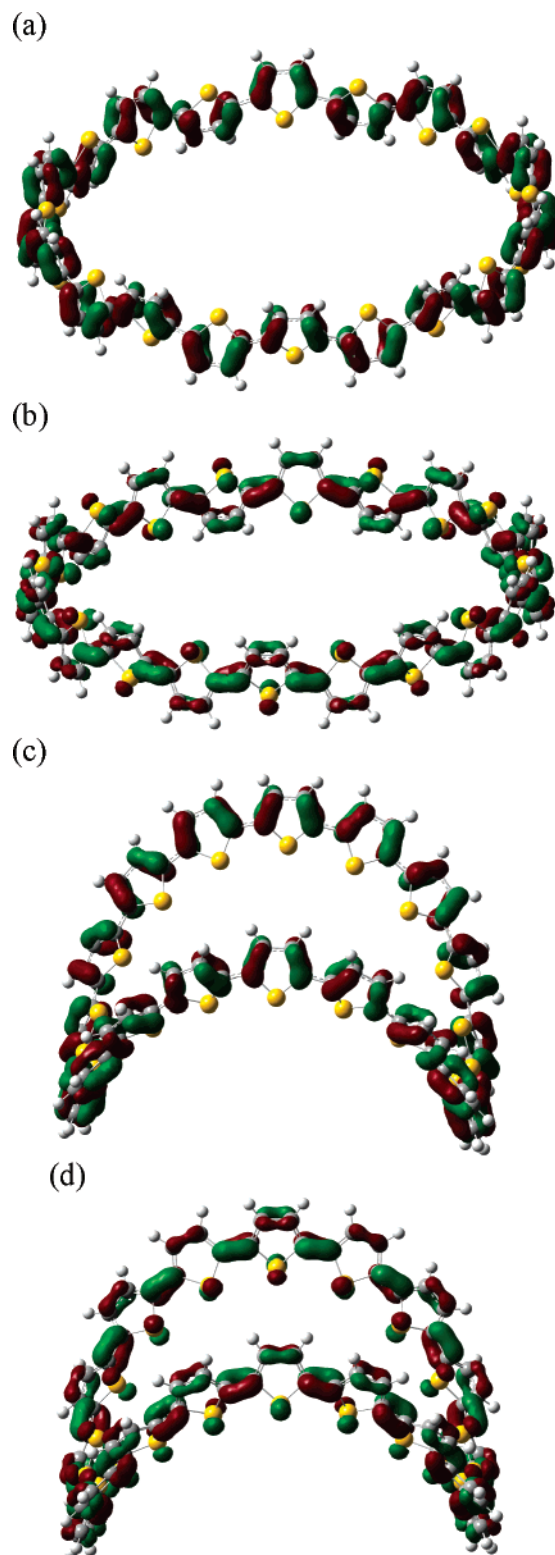(23) Cao, H.; Ma, J.; Zhang, G.; Jiang, Y. *Macromolecules* **2005**, *38*, 1123.

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3).[25] Similar arguments applied to the HOMO and LUMO of *syn* cyclic oligothiophenes in which *cis*-conformation in *s-cis* form leads to smaller HOMO−LUMO gap in contrast to *cis*-polyacetylene. The 1,4-interactions within the unit cell of polyacetylene **3** (*s-cis*-conformation) destabilize HOCO and stabilize LUCO. There are no such interactions in polyacetylene **2** (*trans*). Thus, band gap in polyacetylene **3** is expected to be smaller than in **2**. Planar *syn*-cyclic oligothiophenes have polyacetylene **3**-type structure, and therefore lowering in the HOMO−LUMO gap is expected and indeed HOMO−LUMO gap of C14T-syn is lower than that of polythiophene. Poly-thiophene is the mix structure of polyacetylene **2** and **3**. Thus, we have shown that *syn* arrangement of thiophene rings lower considerably the band gap of oligo- and polythiophenes. Therefore, the band gap control in conjugated polyheterocylo-pentadiene can be achieved by *syn* and *anti* arrangement of the heterocycle rings. We also mention that C14T-syn can be a very attractive synthetic target due to its low HOMO−LUMO gap and expected planarity.

However, for longer *syn*-conformers there is no systematic relationship between changes in the HOMO−LUMO gaps and ring size. For shorter *anti* (*s*-transoid) cyclic oligothiophenes ($n = 8$), the difference in HOMO−LUMO gap between linear (2.42 eV) and cyclic (3.56 eV) oligomers is significant (1.14 eV) as a result of the high curvature of C8T-anti. As $n$ increases, the difference is greatly reduced (Figure 2c). It is generally assumed that the HOMO−LUMO gap of oligothiophenes correlates linearly with $1/n$.[8] A recent report has shown that this correlation does not hold for $n \geq 12$.[9] Here we used the second-order polynomial fit (because first-order polynomial fit did not result in good correlation)[21] to extrapolate the HOMO−LUMO gap for linear oligothiophenes and *anti*-conformers of cyclic oligothiophenes, and as expected both extrapolations led to roughly the same value (ca. 2.01−2.03 eV). This value is very close to the experimental band gap in polythiophene (2.0 eV)[26] and to the calculated value for linear polythiophene using PBC/B3LYP/6-31G(d) (2.05 eV).[23]

The energies of the HOMOs of C*n*T-anti oligomers are significantly lower than those of the corresponding linear oligomers (Figure 2d). The differences between the HOMO energies of C*n*T-anti oligomers and linear oligomers decrease with increasing chain length. A similar observation is obtained for the LUMO energies (Figure 2d). These observations can be explained on the basis of changes in the shapes of the frontier molecular orbitals with changing dihedral angle. As shown in Figure 4, the LUMO has bonding interactions located on the inter-ring bonds; therefore larger dihedral angles disturb the inter-ring bonding interactions and the LUMO is destabilized to a greater extent. The reverse situation applies to the HOMO, which has antibonding interactions located on inter-ring bonds. Thus, the HOMO is stabilized with increasing dihedral angle as the antibonding interactions are removed. The shapes of the HOMO and LUMO in cyclic (*syn* and *anti*) oligomers (Figure 4) are qualitatively similar to those of linear oligomers.

**(b) Bond Length Alternation (BLA) and Aromaticity Measurements (NICS Values).** Bond length alternation (BLA) is an important criterion for comparing the geometries, aroma-ticity and extents of conjugation in different oligothiophene
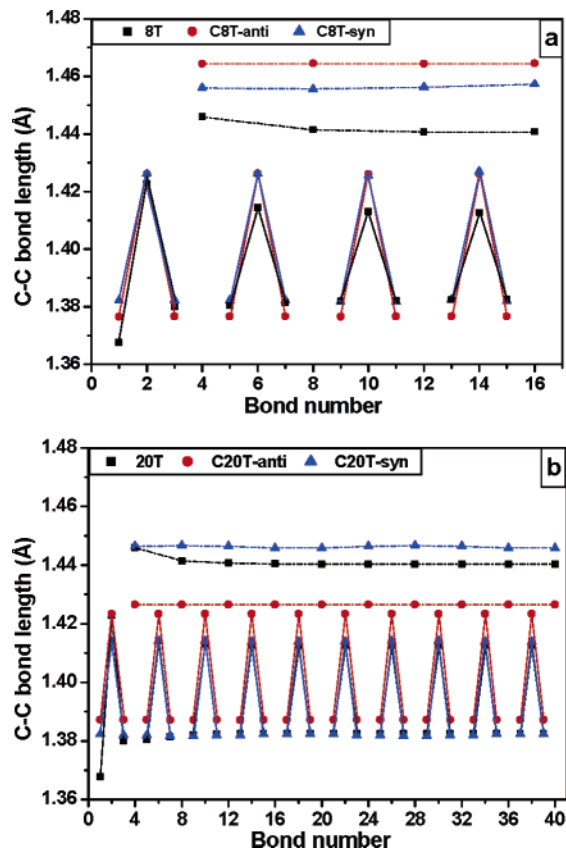
(25) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, Ser. A* **1979**, *366*, 23.

(26) (a) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702. (b) Kobayashi, M.; Chen, J.; Chung, T. C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77.

(a)



(b)

(c)

(d)

**FIGURE 4.** Frontier molecular orbitals for C20T in *syn*- and *anti*-conformations: (a) HOMO of C20T-anti, (b) LUMO of C20T-anti, (c) HOMO of C20T-syn, (d) LUMO of C20T-syn.

conformations.[27] All thiophene rings in both C*n*T-syn and C*n*T-anti, as well as in linear oligothiophene, show an aromatic nature (Figure 5), while inter-ring bonds and the middle bonds in the rings have more of a single-bond nature. For the shorter oligomers comprising 8-thiophene units (Figure 5a), the inter-ring C−C bond length is at its shortest for the linear oligomer,

**FIGURE 5.** Bond length alternation in (a) octamer and (b) 20-mer for linear and cyclic oligotheophene systems (*syn* and *anti*). The *x*-axis is the C−C bond number starting from one end of the conjugated chain, the repeating sets of three linked points represent intra-ring bonds, while every fourth point on the *x*-axis corresponds to an inter-ring C−C bond. The points are linked solely as a visual aid.

followed by the *syn*-isomer and *anti*-isomer. In both cyclic isomers, inter-ring C−C bond length is significantly elongated (1.457 Å for the *syn*-isomer and 1.464 Å for the *anti*-isomer vs 1.441 Å for polythiophene). For the longer oligomer comprising a 20-thiophene ring, the picture is somewhat different (Figure 5b). BLA in the *syn*-conformer of C20T is similar to in the linear system (interring C−C bond length for linear oligothiophene is 1.441 Å and for the *syn*-conformer of cyclic oligothiophene it is 1.446 Å). For C20T-anti, the inter-ring C−C bond length (1.427 Å) is significantly shorter than even that of the linear isomer (Figure 5b). Also, in C20T-anti, the C−C bond distances for inter-ring bonds (1.427 Å) and for the middle bond in the rings (1.423 Å) are very close to each other (Figure 5b).

The nucleus independent chemical shift (NICS) is a useful measure of the magnetic shielding effect of aromatic ring current, which in turn provides a measurement for aromaticity.[17,28] Cyclic oligothiophenes in the *syn*-conformation have $4n$-electrons in the perimeter of the ring, thus being formally antiaromatic. The NICS values for C$n$T ($n$ = 6, 8, 10, and 12; *syn*- and *anti*-conformers) are given in Table 1. The NICS values

(27) (a) Brédas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808. (b) Dkhissi, A.; Louwet, F.; Groenendaal, L.; Beljonne, D.; Lazzaroni, R.; Brédas, J.-L. *Chem. Phys. Lett.* **2002**, 359, 466. (c) Geskin, V. M.; Dkhissi, A.; Brédas, J. L. *Int. J. Quantum Chem.* **2003**, *91*, 350. (d) Geskin, V. M.; Brédas J. L. *ChemPhysChem* **2003**, *4*, 498.

(28) However, we note that NICS values cannot be used as a single criterion for aromaticity; see: Stanger, A. *J. Org. Chem.* **2006**, *71*, 883 and references therein.

**TABLE 1. NICS (0) Values for C6T−C12T (*syn* and *anti*, even only), thiophene and benzene at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)**

| | | compound | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | thiophene | benzene | C6T-anti | C6T-syn | C8T-anti | C8T-syn | C10-anti | C10T-syn | C12T-anti | C12T-syn |
| NICS(0) | −18.6 | −8.1 | −1.3 | 3.0 | −1.1 | 1.3 | −0.8 | 1.2 | −0.7 | 0.8 |

for all cyclic oligothiophenes are very small, and therefore all cyclic oligothiophenes can be considered as nonaromatic.

**(c) Calculated IR and Raman Spectra.** The calculated vibrational spectra of $\pi$-conjugated cyclic oligomers constitute a very rich source of information on their structure and properties and can be used to differentiate between *syn*- and *anti*-conformers. In infrared spectra of cyclic oligothiophenes, two intense bands are observed, one for symmetric C−C stretching and the other for antisymmetric C−C stretching. For the *syn*-conformation, these bands (scaled, as mentioned earlier, by 0.97) appear at 1435−1455 cm$^{-1}$ (symmetric) and at 1500−1525 cm$^{-1}$ (asymmetric), whereas the corresponding bands for the *anti*-conformation are slightly shifted to lower energies, 1420−1445 and 1460−1480 cm$^{-1}$, respectively (Figure 6). There are two more characteristic regions in the IR spectra of the *syn*- and *anti*-conformations, the out-of-plane and in-plane C−H bending vibrations (at 765−785 and 1105−1165 cm$^{-1}$ for *syn* and at 775−795 and 1165−1195 cm$^{-1}$ for *anti*, respectively). Two intense bands at 505−575 cm$^{-1}$, which are associated with the symmetric and antisymmetric ring deformations, are not present in the more planar structures (C10T-syn and C12T-syn) but are present in all C$n$T-anti (nonplanar), C6T-syn and C8T-syn (nonplanar) structures. Thus, we believe that the calculated spectra presented in Figure 6 will assist in experimental determination of cyclic oligothiophene structures.
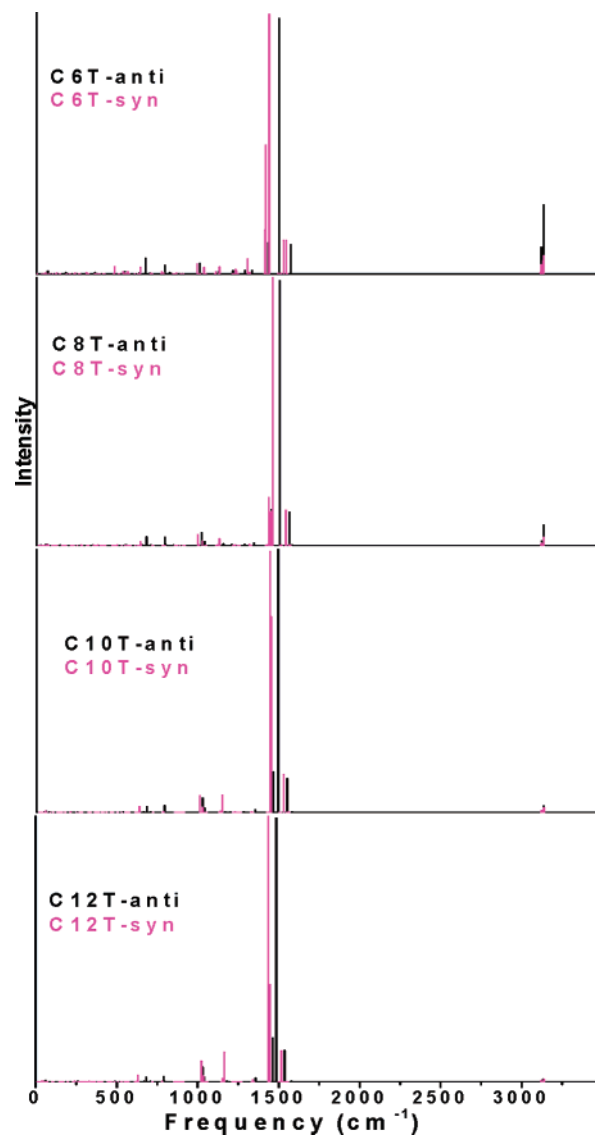
Raman spectra of cyclic oligothiophenes should be even more useful in differentiating between *syn*- and *anti*-conformers, since they appear very simple with few intense bands (Figure 7). Distinguishable frequencies are the in-plane symmetric ring deformation (sulfur pointing inside the ring and all other atoms pointing outside the ring), symmetric C−H in-plane bending, symmetric ring C−C stretching coupled with C−H in-plane symmetric bending, and C−H symmetric stretching. The ring size dependence of the Raman spectral pattern has not been observed. There are two frequencies which can be used to differentiate between the two conformations. The first stems from C−H in-plane deformation (bending), which forms two circular arrays in the *anti*-conformation, whereas in the *syn*-conformation, it forms a single array around the periphery of the ring (636−642 and 674−681 cm$^{-1}$ for *syn*- and *anti*-conformations, respectively). However, it is of low intensity and difficult to observe experimentally. The second stems from the more intense symmetric C−C ring stretching, usually coupled with symmetric C−H deformation (1420−1460 and 1485−1505 cm$^{-1}$, respectively, for *syn*- and *anti*-conformations). Thus, the frequency of symmetric C−C ring stretching differs between the *syn*- and *anti*-conformers by at least 45 cm$^{-1}$ and can be reliably distinguished on the basis of our calculations. We note, however, that our calculations are performed on unsubstituted systems and cannot be directly applied to experimental[6] systems.

**(d) Comparison with Experimental Systems.** Recently, Bäuerle and co-workers have synthesized macrocyclic oligothiophenes ($n$ = 12 (**1**), 16, and 18) with dibutyl substituents
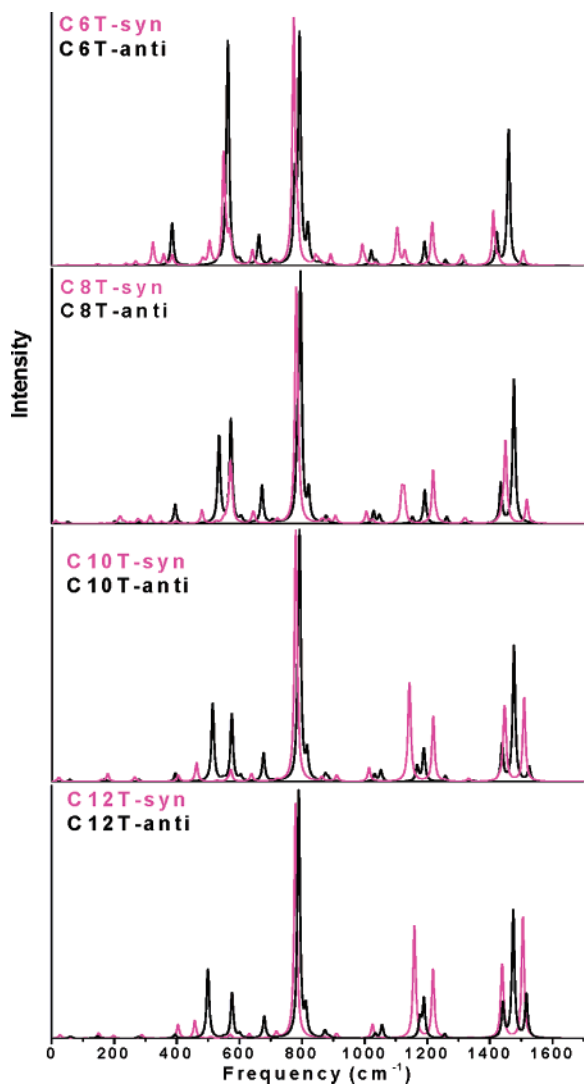
**FIGURE 6.** Calculated IR spectra for *anti*- and *syn*-conformers of cyclic oligothiophenes.



**FIGURE 7.** Calculated Raman spectra for *anti*- and *syn*-conformers of cyclic oligothiophenes.

on alternate thiophene units and have explored their properties.[5,6] However, their attempts to grow single crystals of these oligomers failed. Thus, structural data for cyclic oligothiophenes are not available. To acquire a deeper understanding of the structural features and other properties of these oligomers, we have optimized the corresponding 12- and 18-mer by replacing the butyl groups with methyl groups (denoted as C12T-Me and C18T-Me). We have studied in detail the two conformations of C12T-Me that we anticipate should be the least strained (C12T-Me-a and C12T-Me-b, Figure S6, Supporting Information). We started optimization from a planar *syn* geometry. The final optimized structure (C12T-Me-a) has two of the unsubstituted rings pointing up while the remaining four unsubstituted rings point down (Figure S6a). In C12T-Me-b, all unsubstituted rings point in the same direction, while all substituted rings point in the other direction, which leads to a spider-like structure (Figure S6b) similar to that suggested by Bäuerle et al.[6d] based on STM images combined with semiempirical calculations. Both structures have practically the same energies (C12T-Me-b is more stable than C12T-Me-a by as little as 0.3 kcal/mol). The HOMO−LUMO gap is also similar for both structures (2.84 and 2.89 eV for C12T-Me-a and C12T-Me-b, respectively); however, it is slightly smaller than the experimental gap

calculated from the $\lambda_{max}$ of the butyl-substituted analogue (3.17 eV).[29] The HOMO−LUMO gap for unsubstituted analogue of C12T-syn is significantly smaller (2.13 eV). For comparison, the HOMO−LUMO gap for C12T-anti is 2.99 eV. The 18-mer structure with dimethyl substituents on alternate thiophene rings is optimized in different conformations to achieve a minimal energy conformer. We first consider initial geometries having completely *syn* (C18T-Me-syn, relative energy is 0 kcal/mol) or *anti* (C18T-Me-anti, 5.2 kcal/mol) thiophene units (Figure S7). We then altered the geometry of 4 or 6 *syn*-thiophene rings

(29) The disagreement between our calculations and the experimental value is 0.3 eV. Our PBC calculations performed on polymer **2** have shown that replacing a methyl group with an ethyl group increases the band gap by 0.1 eV. The remaining 0.2 eV is in the order of common errors for B3LYP/6-31G(d) estimated HOMO−LUMO gaps.
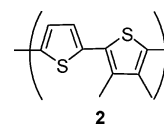
to an *anti*-conformation to obtain C18T-Me-a (0.3 kcal/mol) or C18T-Me-b (3.2 kcal/mol), respectively (Figure S8 and S9). The optimized geometry of the *syn*-conformer is obtained with one *anti*-thiophene ring. The HOMO−LUMO gap for C18T-Me-anti (3.04 eV) is smaller than that for C18T-Me-syn (3.13 eV). C18T-Me-a showed the minimum HOMO−LUMO gap (2.82 eV, whereas for C18T-Me-b it is 3.02 eV). The HOMO−LUMO gaps for all four calculated conformers are close to the experimental value for butyl-substituted analogue (2.96 eV). For comparison, the HOMO−LUMO gap for C18T-anti is 2.60 eV and for C18T-syn is 2.41 eV. The considerable dihedral twisting imposed by the substituents disturbs planarity in both the *syn* and *anti* forms, which is in turn reflected in the large HOMO−LUMO gap compared to the unsubstituted oligomers.

**Cation Radical.** The first step in the oxidative doping of the conjugated oligomer is the formation of a cation radical (polaron). These cationic species are responsible for a hole transfer phenomenon by a hopping-type mechanism between adjacent spatially separated molecules or chains accompanied by geometric relaxation.[30] Studies of the reorganization energy of the isolated oligomer/polymer are an important step in understanding such a charge-transfer phenomenon.[31] Generally, reorganization energies decrease with increasing oligomer chain length as a result of greater positive charge delocalization in a longer oligomer.[31] Yet, interestingly, we have found that the cyclic oligothiophenes require significantly larger reorganization energies (see Theoretical Methods Section for details of calculation of reorganization energies) than do linear oligomers. For example, 10T and 30T[21] require reorganization energies of 0.18 and 0.04 eV, whereas the related values for C10T-anti and C30T-anti are about twice as large, at 0.4 and 0.08 eV, respectively (Figure 8a). A large reorganization energy might hamper the applications of cyclic oligothiophene in FET. It is known that reorganization energy is linearly related to the square root of the chain length of the linear oligomer.[31] However, cyclic oligothiophenes do not fit in this criterion (Figure 8a).

The cation radicals of the *anti*-conformers of cyclic oligomers exhibit similar average inter-ring angles (16−17°) for $n = 10-30$, in contrast to the corresponding neutral oligomers for which the dihedral angle decreases from 29.5° for C10T-anti to 19.1° for C30T-anti. This fact accounts for the deviation from linearity in the relationship of reorganization energy with the square root of chain length. As expected, the longer oligomers generally have smaller ionization potentials (Figure 8b). The *anti*-conformers of cyclic oligomers possess a higher IP$_1$ (5.73 and 5.09 eV for C10T-anti and C30T-anti, respectively) than the corresponding linear oligomers (5.39 and 4.98 eV for 10T and 30T, respectively); however, this difference reduces for longer chains.

With respect to the BLA pattern, the behavior of the *syn*- and *anti*-conformers of the cyclic oligomers in the cation radical state is closer to that of the radical cations of the linear oligothiophenes than to that of neutral molecules (Figure 5b and 9c). Thus, cation radicals of cyclic oligomers can be considered as a model for doped polythiophene. Charge distribution in the radical cation of C*n*T-anti oligomers shows the complete delocalization of charge (probably due to symmetry reasons; however, DFT is known to strongly delocalize the
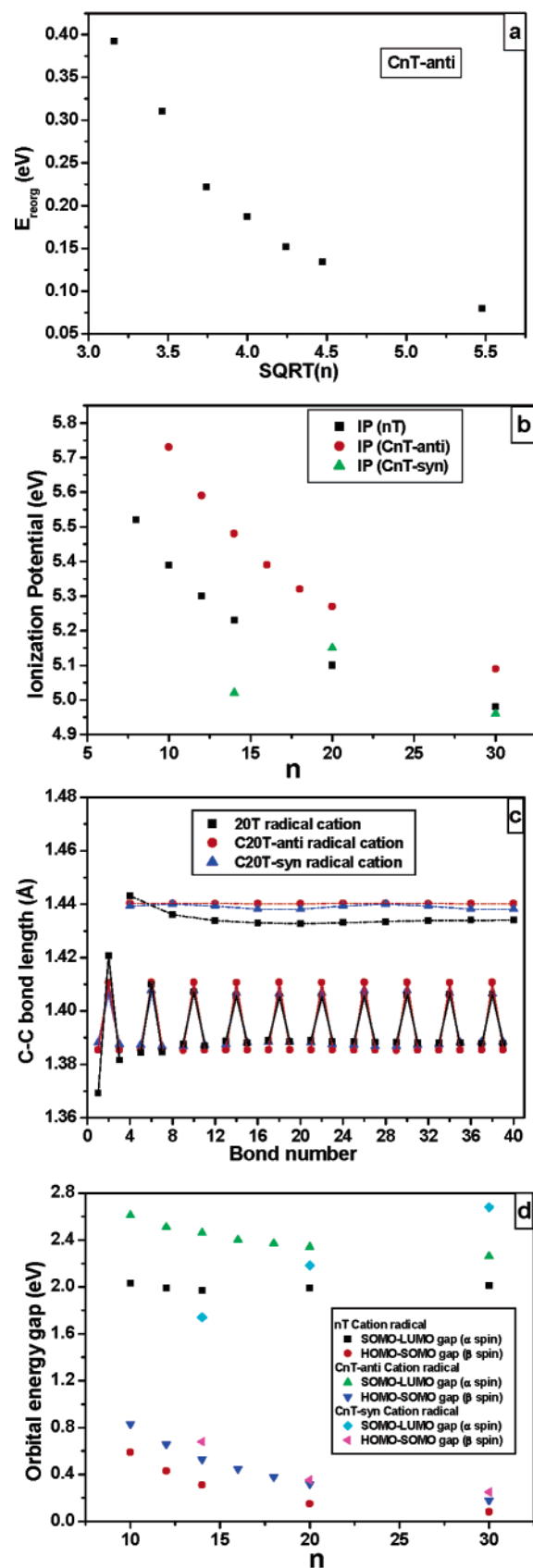


**FIGURE 8.** (a) Calculated reorganization energy for C*n*T-anti versus the square root of the number of thiophene units. (b) Ionization potential for *n*T and C*n*T-anti. (c) BLA for the 20-mer cation radical for linear and cyclic oligothiophenes (*syn*- and *anti*-conformations); see caption of Figure 5. (d) Orbital energy gap for linear and cyclic oligothiophenes (*syn*- and *anti*-conformations).

(30) (a) Brédas, J. L.; Calbert, J. P.; da Silva, D. A.; Cornil, J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5804. (b) Cornil, J.; Beljonne, D.; Calbert, J. P.; Brédas, J. L. *Adv. Mater.* **2001**, *13*, 1053.

(31) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 2339.

charge in cation radicals[27d]), with each ring carrying exactly $1/n$ unit charge.

The frontier orbitals of the cation radical in both cyclic conformations have similar shapes and resemble those of the linear oligothiophenes (Figure S10, Supporting Information). Figure 8d shows two possible transitions in the radical cation, i.e., SOMO → LUMO ($\alpha$) and HOMO → SOMO ($\beta$). The SOMO → LUMO ($\alpha$) transition in the linear oligomers shows saturation for $n > 12$ (1.99 and 2.01 eV for 12T and 30T), whereas the energy of this transition decreases with increasing chain length in C$n$T-anti oligomers (from 2.51 eV for C12T-anti to 2.26 eV for C30T-anti). However, the SOMO → LUMO ($\alpha$) transition occurs at higher energy for C$n$T-anti oligothiophenes than for the linear oligomer even up to 30-mer. In contrast to the SOMO → LUMO ($\alpha$) transition, the HOMO−SOMO($\beta$) gap decreases with increasing chain length for both linear and cyclic oligomers (0.43, 0.66, 0.08, and 0.18 eV for 12T, C12T-anti, 30T, and C30T-anti, respectively). *syn*-Conformers do not show any sequential regularity in any of the above-mentioned properties as the higher members ($n \geq 16$) deviate strongly from the regular cyclic structure.

**Dication.** We note that the restricted wave function (at B3LYP/6-31G(d)) for the oligothiophene dication starting from sexithiophene[32] and for the *syn*- and *anti*-conformers of cyclic oligothiophenes (from C10T-anti and C12T-syn) studied in this paper shows RHF to UHF instability. Unfortunately, optimization of cyclic oligothiophene dications at UB3LYP/6-31G(d) is well beyond our computational facilities, even for the medium-length member of the family, C14T-anti (due to the quadratic convergence algorithm required for SCF convergence in this case). Thus, all calculations on the dication were performed at RB3LYP/6-31G(d) and will be discussed here briefly. Our single point calculations have shown that UB3LYP/6-31G(d) energies are only a few kcal/mol below RB3LYP/6-31G(d) energies.

The energy cost for the formation of a dication from the corresponding neutral oligomer (double ionization potential, IP$_2$) decreases with increasing chain length (Figure 9a). Our calculations show that cyclic oligomers require more energy to form a dication than do linear oligomers (13.59 eV for C10T-anti compared to 12.79 eV for 10T); however, the energy difference decreases slowly with increasing chain length (to 11.21 eV for C30T-anti compared to 10.87 eV for 30T). A similar trend is observed for the HOMO−LUMO gap in dications (0.57, 0.07, 0.95, and 0.19 eV for 10T, 30T, C10T-anti, and C30T-anti, respectively, Figure 9b). The BLA data indicate that *anti*-conformers of cyclic dications are very similar to the corresponding linear dication, except for the end-effect (Figure 9c).

## Conclusions

Cyclic oligothiophenes are interesting organic electronic materials. Cyclic oligothiophenes having a *syn*-conformation are more stable than in the *anti*-conformation for smaller oligothiophenes; however, the reverse is true for larger cyclic oligothiophenes. In the *syn*-conformation, cyclic oligomers longer than C14T-syn lose their regular ring shape and bend significantly. The HOMO−LUMO gaps in small cyclic oligothiophenes are relatively large. HOMO−LUMO gaps differ for C$n$T-anti and linear systems (HOMO−LUMO gaps in C$n$T-anti systems are always larger); however, both converge to the value for polythiophene. Consequently, *anti* cyclic oligothiophenes are good models for polythiophene due to absence
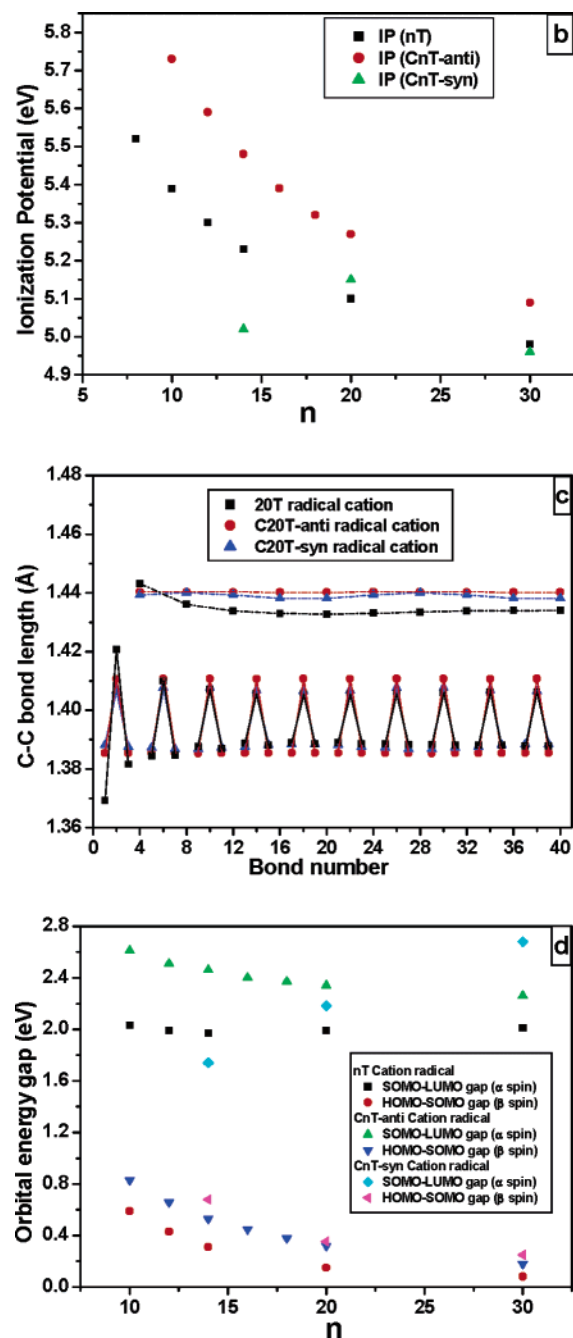


**FIGURE 9.** (a) Calculated double ionization potential for linear and cyclic oligothiophenes. (b) HOMO−LUMO gap for oligothiophene dications. (c) BLA for linear and *anti* cyclic oligothiophene dications; see caption of Figure 5.

of the chain ends effect. Interestingly, the HOMO−LUMO gap in C14T-syn is even lower than that of polythiophene as a result of its *syn* arrangement of thiophene rings and high planarity. Thus, we have identified this molecule is an attractive synthetic target. The fact that *syn* arrangement of polythiophene rings results in lower HOMO−LUMO gap should be important for control of HOMO−LUMO gap in conjugated system. *syn*-Conformers and *anti*-conformers should be distinguishable using IR and Raman spectroscopy. The reorganization energy for cyclic oligothiophenes is larger than for the corresponding linear

(32) Gao, Y.; Liu, C.-G.; Jiang Y. S. *J. Chem. Phys. A* **2002**, *106*, 5380.

oligomer, which may hamper the application of cyclic oligo-thiophenes in FET. Cation radical of these oligomers can be considered as a doped polythiophene model without chain ends effect. The experimentally evaluated HOMO−LUMO gaps for alternately dibutyl-substituted cyclic oligomers closely match the calculated values; however, they are significantly higher than those for the unsubstituted analogues.

**Supporting Information Available:** Absolute energies and Cartesian coordinates of all optimized geometries; figures showing the optimized geometries of C12T-Me-a, C12T-Me-b, C16T-syn, C18T-Me-syn, C18T-Me-anti, C18T-Me-a, C18T-Me-b, C20T-syn, and C30T-syn; graphs of reorganization energy versus $n$ and of dihedral angle vs $1/n$; frontier molecular orbitals for the C20T radical cation (*syn* and *anti*). This material is available free of charge via the Internet at http://pubs.acs.org.

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