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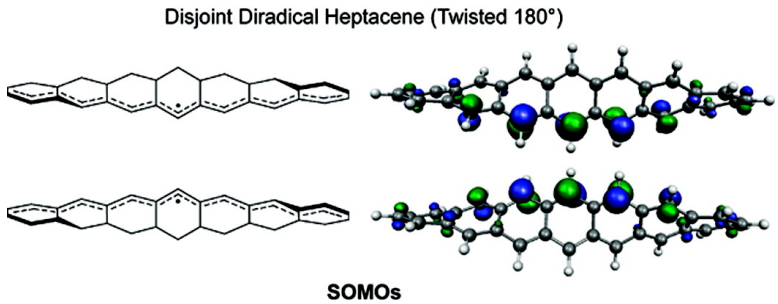

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Electronic Structures and Properties of Twisted Polyacenes

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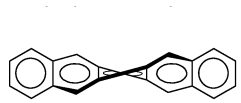
Polyacenes are linear polycyclic aromatic hydrocarbons with properties exploitable for organic electronics.[1] Highly twisted polyacenes with phenyl substituents strategically placed to induce end-to-end twisting of the acene backbone, as illustrated by **1**, have been synthesized.[2] Pascal et al.'s recent successful synthesis of a pentacene exhibiting a twist of 144°, **2**,[2j] has prompted us to investigate the effects of twisting on the electronic structures and properties of polyacenes. Such highly twisted molecules are expected to have unique chiroptical properties[3] and have already been incorporated into organic light-emitting diodes.[4] The use of substituents to overcome chemical instability[5] while maintaining the electronic properties necessary to serve as functional materials in semiconducting devices is currently being explored.[1,2] In recent years, our group and others have reported on the electronic structures of polyacenes.[6] Here, we provide a computational analysis of the electronic structures of twisted polyacenes and **2**[7] and have found a lack of sensitivity of their electronic features toward highly twisted geometrical distortions.



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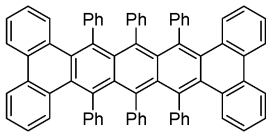

2

Heptacene has the first open-shell disjoint diradical ground state[8] of the series of polyacenes.[6b] Such diradicals have degenerate SOMOs confined to different sets of atoms and may have singlet ground states.[8] Anthracene through pentacene are known to be ground-state closed-shell singlets with the triplet state lying significantly above the singlet state.[6] The wave functions for polyacenes longer than hexacene become unstable and develop into open-shell singlets as a result of their disjoint diradical nature.[6] The closed- and open-shell solutions for hexacene are degenerate,[9] and the spin contamination in hexacene is small ($<S^2> = 0.26$) and decreases upon twisting ($<S^2> = 0.03$). However, spin contamination in heptacene becomes significant ($<S^2> = 0.80$) and increases slightly upon twisting ($<S^2> = 0.89$).

Figure 1 shows plots of distortion energy, ΔE, singlet−triplet gap, S_0-T_1, and B3LYP HOMO−LUMO gap as a function of twist angle for unsubstituted polyacenes. Since large twists in smaller polyacenes generate unrealistic geometrical distortions, only ΔE values in the range of 0−65 kcal/mol are shown. Figure 1a demonstrates that large twists occur in large polyacenes without causing considerable destabilization. The plot of distortion energy per benzene ring versus twist angle per benzene ring reveals that distortion energy is essentially a quadratic function of the twist of each benzene ring.[10] For comparison with Pascal's 144° twisted pentacene, **2**, planar pentacene is 60 kcal/mol lower in energy than pentacene with a 144° twist.

Conjugation in polyacenes is not greatly influenced by twisting. Vogel's bridged annulenes were among the first to clearly

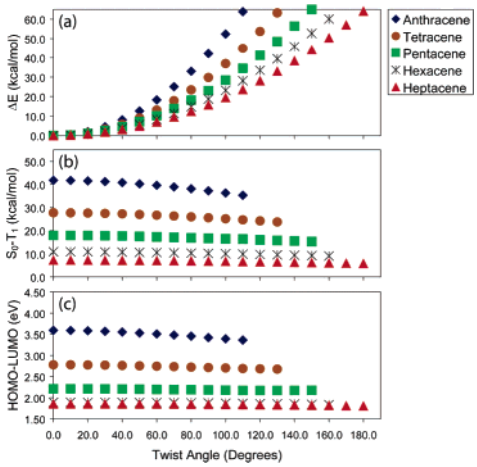

Figure 1. (a) ΔE, (b) S_0-T_1, and (c) HOMO−LUMO energies plotted as a function of twist angle ((U)B3LYP/6-31G(d)).

demonstrate that delocalization in conjugated systems is permitted as long as the angle between adjacent p-orbitals does not become exceedingly large.[11] This is observed for polyacenes and is due to even distribution of distortion throughout the molecule, allowing deformation in individual benzene units to be minimized. For heptacene at 180°, the benzene units have an end-to-end twist ranging from 24 to 27°. Notably, the dihedral angles of individual partial double bonds along the acene backbone distort only 13−15° from planarity, thereby maintaining 97% overlap between adjacent p-orbitals. Consequently, twisting results in minimal electronic changes. S_0-T_1 decreases from 42 to 30, 28 to 24, 18 to 15, and 11 to 9 kcal/mol for anthracene through hexacene, in that order. S_0-T_1 for heptacene changes very little; decreasing from 7 to 6 kcal/mol. Similarly, slight decreases in HOMO−LUMO gaps are observed with that for anthracene decreasing from 3.6 to 3.3 eV and those for tetracene through heptacene remaining nearly constant at 2.8, 2.2, 1.9, and 1.9 eV. A negligible decrease in the HOMO energy is also observed, which, according to Koopmans' theorem, predicts a small effect on ionization potentials. Heptacene maintains its disjoint diradical nature; the disjoint SOMOs of heptacene with a 180° twist are shown in Figure 2a.

Vertical S_0-S_1 transition energies were calculated using TDDFT (B3LYP/6-31G(d)). Experimentally, S_0-S_1 is 3.35, 2.61, 2.14, and 1.79 eV for anthracene through hexacene.[12] TDDFT slightly underestimates these values and predicts only a minor decrease through twisting of 90°. S_0-S_1 decreases from 3.3 to 3.0 eV for anthracene and 2.5 to 2.4 eV for tetracene, but remains nearly constant at 1.9, 1.5, and 1.2 eV for pentacene through heptacene. Wudl et al. proposed that a bathochromic shift observed in their twistacene was, in part, due to twisting of the π-system,[2i] which is predicted here for unsubstituted polyacenes.

We have found previously that polyacenes can be represented as two parallel nonalternating polyacetylene ribbons arising from a lack of Peierls' distortion in each ribbon.[6a] This idea also applies

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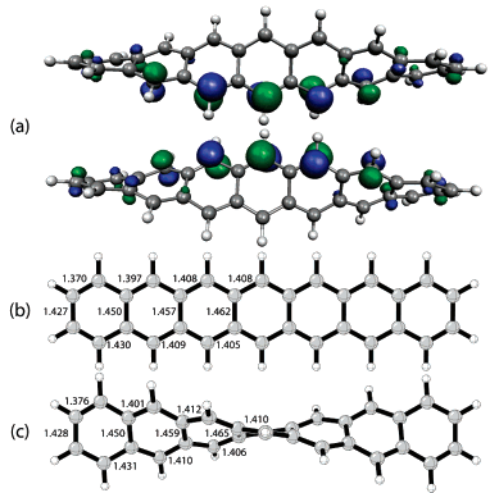

Figure 2. (a) SOMOs of disjoint diradical heptacene twisted at 180° and geometries of open-shell singlet heptacene at (b) 0° and (c) 180° (UB3LYP/6-31G(d).

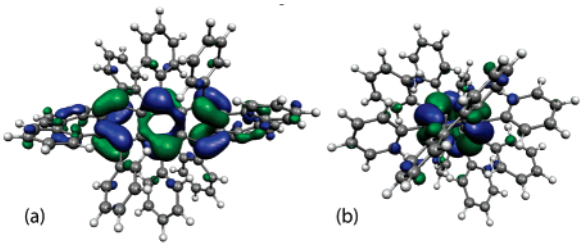

Figure 3. HOMO of **2** shown looking (a) from the side and (b) down the pentacene backbone (RB3LYP/6-31G(d)).

to highly twisted polyacenes. The geometries and bond lengths of open-shell singlet heptacene at 0° and 180° are shown in Figure 2. The peripheral bond lengths, neglecting the terminal benzene rings, range from 1.40 to 1.41 Å, and the bonds spanning each six-membered ring are between 1.45 and 1.47 Å. In an isolated polyacetylene ribbon, Peierls' stabilization occurs when bond lengths alternate between 1.37 and 1.43 Å.[13] In contrast, planar and twisted polyacenes undergo stabilizing geometrical changes without causing bond alternation.

For Pascal's highly distorted **2**, B3LYP/6-31G(d) predicts a ground-state closed-shell singlet with the triplet state lying 30 kcal/mol above the singlet state. The S_0-S_1 transition energy is calculated to be 2.1 eV, and the HOMO−LUMO gap 2.6 eV. The HOMO of **2** (Figure 3) is localized on the central anthracene unit. A calculated twist of 149° with the anthracene unit twisted 94° is in excellent agreement with the X-ray crystal structure (144° and 86°).[2j] The geometry of **2** shows the acene backbone shifting toward a nonalternating bond structure. The peripheral bond lengths of the anthracene unit range from 1.39 to 1.45 Å, and the peripheral bond lengths of the central benzene unit all equal 1.42 Å. The bonds spanning each ring range from 1.44 to 1.46 Å.

To investigate the effects of phenyl substituents on **2**, a model system without phenyls, tetrabenzo[*a,c,l,n*]pentacene, was studied. Constraining the twist angle to 149° results in the anthracene unit being twisted 77° (17° less than with phenyls) and a HOMO−LUMO of 2.9 eV, S_0-T_1 of 33 kcal/mol, and S_0-S_1 of 2.5 eV. Unconstrained, the system optimizes to a planar geometry that is 41 kcal/mol lower in energy. The planar conformation has a HOMO−LUMO gap of 2.7 eV, S_0-T_1 of 29 kcal/mol, and S_0-S_1 of 2.4 eV. Both the planar and twisted conformations are electronically similar to **2**.

The lack of sensitivity of the electronic features of polyacenes toward twisting of the backbone are shown to have significant implications for the likely success of synthesis of new substituted polyacenes that will be less susceptible to photooxidation, insolubility, and polymerization, while maintaining the electronic properties of the polyacene.

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Supporting Information Available: Details of computational procedure, Cartesian coordinates, and absolute energies for all calculated compounds at B3LYP/6-31G(d). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) All calculations were carried out using the *Gaussian 03* program (Frisch, M. J. et al. *Gaussian 03*, revision C.02, Gaussian, Inc.: Wallingford, CT, 2004). Geometries were fully optimized under specified twist angle restraints. The hybrid density functional B3LYP with the 6-31G(d) basis set was used. S_0-S_1 transition energies were computed with TDDFT (B3LYP/6-31G(d)) methods. See Supporting Information.

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(9) BLYP, PW91, and BPW91 functionals predict hexacene to be a closed-shell singlet.[6b]

(10) The plot of distortion energy per benzene ring versus twist angle per benzene ring yields a quadratic relationship, $\Delta E = 0.0157\, d^2/n - 0.0283\, d$ with $R^2 = 0.9975$, where ΔE is total distortion energy (kcal/mol), d is twist angle (degrees), and n is the number of benzene rings in the acene.

(11) It is especially noteworthy that 1,6-methano[10]- and *syn*-1,6:8,13-bismethano[14]annulene are aromatic and have twists up to 34°, while *anti*-bismethano[14]annulene is twisted by 70° and is nonaromatic. (a) Vogel, E.; Roth, H. D. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 228−229. (b) Vogel, E.; Haberland, U.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 513−514. (c) Vogel, E.; Sombroek, J.; Wagemann, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 564−565. (d) Vogel, E.; Deger, H. M.; Hebel, P.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 919−921.

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