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Torsion Potential in Polydiacetylene: Accurate Computations on Oligomers Extrapolated to the Polymer Limit

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Abstract: The optoelectronic properties of polydiacetylenes can be strongly modulated by torsions along the polymer chains. These as well as other distortions of the nominally coplanar polydiacetylene backbones result in the major color changes observed for these materials in response to a variety of external, low-energy stimuli; such color changes form the basis for the many applications of polydiacetylenes as sensor materials. There has been little theoretical work related to backbone distortions in polydiacetylenes; actually, previous estimates of the torsional barriers in these systems differ by an order of magnitude. Understanding the impact that polymer torsions have upon the properties of polydiacetylenes necessitates accurate estimates of the torsion potentials. Here, by using computationally efficient, wave-function-based electronic structure methods on increasingly larger oligomers, we present reliable estimates of the torsional barriers in model diacetylene oligomers and provide an accurate extrapolation of these values to the polymer limit.

1. Introduction

More than four decades have passed since the seminal work of Wegner on polydiacetylenes (PDAs)[1−4] that inspired a wealth of applications and investigations in a variety of scientific and engineering disciplines. This is in large part a consequence of the ability to solid-state polymerize diacetylene monomers via a thermal or radiation-initiated process and to produce highly ordered, single-crystalline conjugated polymers or isolated conjugated polymer chains in nanostructured matrices.[5] In both cases, the result is a material with a fascinating array of interesting physical properties[6] (see Figure 1 for the chemical structure of the PDA backbone). The dramatic color changes associated with the solid-state polymerization have led to commercial applications as "time−temperature" indicators[7] and radiation dosage monitors.[8] The various polymer forms have also been explored in a number of sensing applications due to the sensitivity of adsorption and fluorescent properties to applied stress,[9,10] light or heat exposure,[1,11−13] changes in the chemical environment,[14] or exposure to biochemicals.[15] Thus, the low cost, highly regular polymeric structure, and strong colorimetric response of PDAs have paved the way for numerous sensing/detector applications spanning analytical,[13] environmental,[16] and biomedical[8,14,15,17] fields. Interestingly, from a theoretical standpoint, there remains intense interest in understanding the relationship between torsional distributions and properties such as the excitation energy transport[18] and effective conjugation length[19] in linearly conjugated polymers.

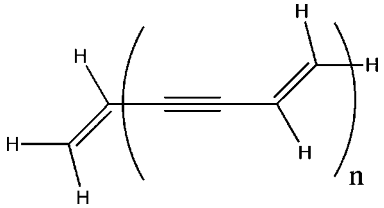

Figure 1. Schematic representation of the polydiacetylene oligomers examined in this study.

PDAs are often classified by the several colors they may exhibit, with the most prominent being the "red" and "blue"

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forms (corresponding to absorptions at 540 and 620 nm, respectively) and with "purple" and "yellow" forms having been reported in the literature as well.[5,20−25] The optoelectronic properties of PDAs have been extensively studied experimentally, although a comprehensive understanding of the underlying phenomena responsible for many of their unique properties remains elusive. It is clear, however, that many aspects of the optical properties of PDAs and their response to various environmental stimuli have their origins in distortions of the nominally coplanar conjugated polymer backbones.[26,27] The blue form of PDAs is generally associated with the coplanar structure, and the red form, with a distorted, likely nonplanar, chain structure.[26] An extreme example of backbone distortion is a PDA in solution, wherein good solubility can be achieved only via numerous rotations about the carbon−carbon bond; this can produce yellow solutions with an absorption peak at around 460 nm, corresponding to a "conjugation length" of about six coplanar repeat units.[24,25] Chromatic transitions can be induced thermally, optically, mechanically, and chemically; they are reversible in many cases, thus forming the basis for sensor applications.[5] All of these chromatic transitions are usually considered to involve perturbations of the PDA backbone structure.[26] The stimuli for these transitions are generally relatively low energy, and thus the phenomena critically depend on the softness of the potential energy surface for distortion of the PDA chains. In fact, the polymerization reaction itself relies upon the softness of the potential that is characteristic of PDAs, in that the solid-state transformation from monomer to polymer would be rendered highly unlikely if the PDA backbones were too rigid.[28]

A recent contribution[29] to this topic by Filhol et al. has provided considerable insight into PDA systems. Employing periodic density functional theory (DFT) calculations on a model PDA, the authors have investigated the relationship between chain torsion and such properties as electronic band structure, optical absorptions, vibrational frequencies, and ^{13}C NMR chemical shifts. While certainly not the foremost result of that work, the computation of the torsional energy barrier for rotation about the carbon−carbon bonds prefaces the remainder of ref 26. As noted by the authors, the computed barrier of 4.66 kcal mol^{-1} for poly(hexa-2,4-diyne) is nearly 1 full order of magnitude larger than the value previously reported in the literature (0.51 kcal mol^{-1}).[30] A barrier that high, however, would seem to be in contradiction to experimental estimates of the conjugation length in polydiacetylenes.[31,32] Since the discrepancy in these computed values corresponds to a difference roughly between slightly less than 1 and 8 kT at room temperature, gaining a reliable estimate of the magnitude of the torsion barrier in these systems will be key to a better understanding of the significance polymer twisting ultimately plays in modulating the properties of PDAs. The specific aim of the present work is accurate estimates of the torsion barriers in model PDA oligomers approaching the polymer limit.

This paper is structured as follows. Section 2 presents the rationale for our computational approach and the details of the methodologies. Our results are discussed in section 3. Section 3.1 addresses the performance of the dual basis set/resolution of the identity MP2 approach for the PDA torsions by comparison to high-accuracy approaches. Having established the reliability of the methodology, we turn in section 3.2 to an investigation of increasingly large oligomers and extrapolations to the polymer limit. In section 3.3, we address the energetic profile for two twisted structures that can be relevant for twisted PDAs reported in the literature. The main conclusions of this work are summarized in the final section.

2. Theoretical Methodology

While DFT approaches have certainly taken a major role in the computational chemistry community and especially in applications to organic systems, traditional DFT approaches exhibit systematic errors related to deficiencies of the functionals. Such errors are predominantly related to self-interaction errors,[33−35] the locality of the exchange functional,[36−38] or the lack of long-range dispersion interactions[39−41] inherent to traditional DFT approaches. These discrepancies manifest themselves in difficulties to describe the relative energies of linear and branched alkanes,[42] π-stacking interactions where dispersion interactions dominate,[43] and electronic response properties of conjugated polymers and oligomers.[44] Of importance to the present work, systematic failures for DFT functionals in describing the torsion potentials of conjugated systems have been demonstrated previously. Choi et al.[45,46] pointed out that traditional functionals overestimate the torsional barrier in butadiene, while Zhao and Truhlar[47] demonstrated the same effects in conjugated polyenes. While modern DFT approaches can alleviate

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many of these errors,[47−52] it will be important to keep benchmarking them further for π-conjugated materials.

Second-order Møller−Plesset perturbation theory (MP2) has been shown to provide reasonable descriptions of conjugated systems; for instance, it provides smaller mean unsigned errors than conventional DFT approaches for proton affinities and bond-length alternations in conjugated polyenes and Schiff bases[47] and an improved description of electronic hyperpolarizabilities in conjugated donor−acceptor complexes.[44] However, while MP2 can provide for an improved description of π-conjugated systems as compared to standard DFT functionals, the MP2 method scales with the fifth power of the size of the system and thus rapidly becomes intractable for larger systems. Importantly, the use of dual basis set approaches[53−55] combined with the resolution of the identity to approximate the molecular integrals[56] can help reduce the computational expense while maintaining the accuracy of the MP2 approach.[55] With the methods and basis sets employed here, the combination of the dual basis set approximation and the resolution of the identity approximation typically results in computational savings of more than 50%.

Specifically, dual-basis resolution of the identity MP2 (DB-RIMP2) computations were performed with the computational chemistry package Q-Chem 3.2.[57,58] Coupled cluster computations with singles, doubles, and perturbative triples [CCSD(T)], quadratic configuration interaction with singles and doubles (QCISD), and QCISD computations with a perturbative treatment of triples [QCISD(T)] were carried out with Molpro 2009.[59] The quadratic configuration interaction approaches are employed as they provide reliable approximations to the coupled-cluster approaches, and efficient analytic gradients are readily available.[60] In all cases, Dunning's correlation-consistent basis sets (aug-cc-pVXZ) were used and ranged in quality from double-ζ ($X = \mathrm{D}$) to sextuple-ζ ($X = 6$). For the DB-RIMP2 approaches, the restricted aug-cc-pVXZ (raug-cc-pVXZ) and auxiliary density fitting basis sets were considered as suggested by the Q-Chem authors. Potential energy surfaces (PESs) were constructed by constraining one or more torsions about the carbon−carbon bonds as described below and completely optimizing all remaining coordinates (maximum gradient 3×10^{-4}, maximum displacement 1.2×10^{-3}, energy change 1×10^{-6}) at either the DB-RIMP2, QCISD, or QCISD(T) level as described in the text. To obtain energies approaching the complete basis set (CBS) limit, the CCSD(T) correlation energies (not the total energies) were extrapolated from the CCSD(T)/aug-cc-pVXZ computations [$X = \mathrm{T}(3)$ and Q(4)] with the two-point extrapolation:[61]

$$\Delta E^{x}_{\mathrm{CCSD(T)}} = \Delta E^{x}_{\mathrm{CCSD(T)}} + a \cdot X^{-3} \tag{1}$$

along with the three-point extrapolation ($X = \mathrm{T}(3)$, Q(4), and 5) for the restricted Hartree−Fock (RHF) reference energies, as advocated by Feller:[62]

$$E^{x}_{\mathrm{HF}} = E^{x}_{\mathrm{HF}} + a \cdot \exp(-b \cdot X) \tag{2}$$

For the sake of brevity, the notation XZ will be used in a number of instances (in the discussion and in figures and tables) to denote the aug-cc-pVXZ basis set. For composite methods where the energy is computed at a level of theory different from that employed for the geometry, the first method listed corresponds to that employed for the energy, and the second level to that for the geometry (for instance, CCSD(T)/TZ//DB-RIMP2/DZ corresponds to CCSD(T) energies computed with an aug-cc-pVTZ basis using geometries optimized at the DB-RIMP2 level with the aug-cc-pVDZ basis). Although the largest oligomers examined here present torsional barriers very close to the polymer limit, estimates of the barrier at the limit of an infinite polymer were obtained via the extrapolations described below.

3. Results and Discussion

3.1. Benchmark Computations on Hexa-1,5-diene-3-yne. To assess the performance of the DB-RIMP2/aug-cc-pVDZ approach for describing the torsion potentials in PDA oligomers, we first focused on the smallest ($n = 1$) member of the series, hexa-1,5-diene-3-yne (see Figure 1). Potential energy surfaces were initially constructed by constraining the torsion (Θ) defined by the dihedral angle between the two C−C double bonds to values between 0° and 180° in 30° intervals and completely optimizing all other coordinates at the DB-RIMP2/aug-cc-pVDZ level. The PES at the DB-RIMP2/aug-cc-pVDZ level is displayed in Figure 2 (black dashes), and the relative energies for the cis ($\Theta = 0°$), perpendicular ($\Theta = 90°$), and trans ($\Theta = 180°$) conformations are included in Table 1. The computed barrier of 0.63 kcal mol^{-1} is slightly larger than that calculated by Brédas and Heeger at the MP2/6-31G*//RHF/3-21G level[30] but is still many times smaller than the barrier predicted by Filhol et al.[29] At the DB-RIMP2/aug-cc-pVDZ level, the minimum-energy structure is predicted to be one where the C−C double bonds are in a cis ($\Theta = 0°$) conformation. The trans structure is predicted to be a local minimum 0.01 kcal mol^{-1} higher in energy. Additional DB-RIMP2 optimizations with the larger TZ and QZ basis sets demonstrate that increasing the basis set at the DB-RIMP2 level has very little overall impact on the computed torsional barriers; these evolve as 0.63, 0.62, and 0.71 kcal mol^{-1} with the double-ζ, triple-ζ, and quadruple-ζ basis sets, respectively. The inclusion of larger basis sets also increasingly destabilizes the trans conformer with respect to the cis conformer: from 0.01 to 0.05 and 0.07 kcal mol^{-1}.

In order to assess the role of finite basis sets and electron correlation in obtaining reliable energies for hexa-1,5-diene-3-yne, we performed CCSD(T) computations with large correlation-consistent basis sets at the DB-RIMP2/DZ optimized geometries. The PES at the DB-RIMP2/DZ level is compared in Figure 2 (values in Table 1) to those computed at the CCSD(T)/TZ, CCSD(T)/QZ, and estimated CBS-CCSD(T) levels using the DB-RIMP2/DZ optimized geometries (blue curves). The barrier at the CCSD(T)/TZ level is reduced to 0.46 kcal mol^{-1}, and the trans conformer is further destabilized, being now 0.05 kcal mol^{-1} above that of the cis conformer. Including larger basis sets, at either the CCSD(T)/QZ or the estimated CBS-CCSD(T) level, further increases the torsion barrier (to 0.57 and 0.63 kcal mol^{-1}, respectively) as well as further destabilizes the trans conformer (to 0.08 and 0.10 kcal mol^{-1}, respectively).

The extrapolated CBS-CCSD(T) energies at QCISD(T)/DZ optimized structures provide overall the most reliable treatment

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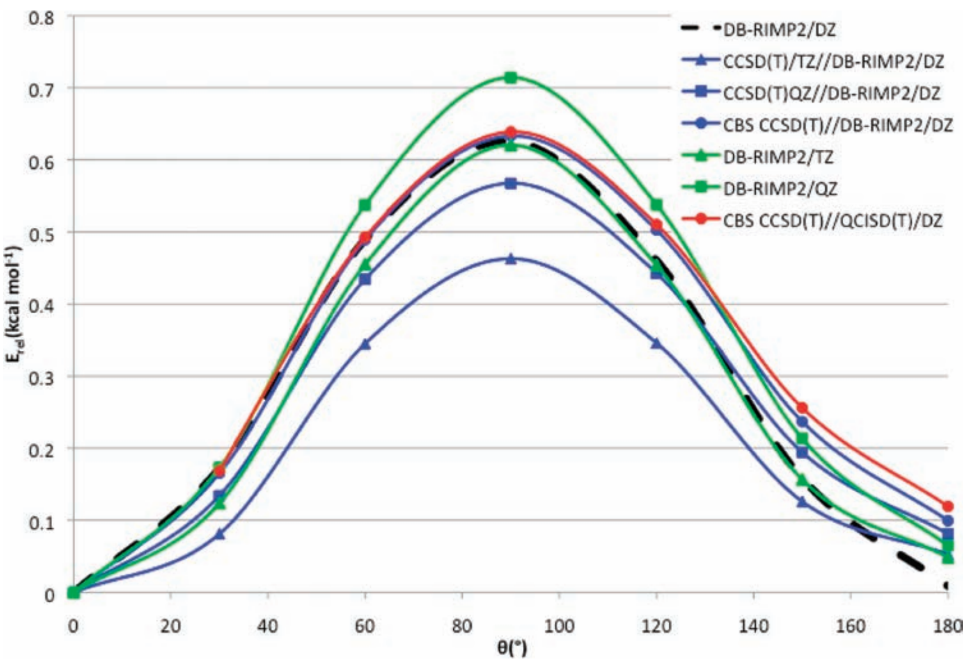

Figure 2. Potential energy surfaces for torsion in hexa-1,5-dien-3-yne at various levels of theory (see text for details).

Table 1. Relative Energies for the Cis ($\Theta = 0°$), Perpendicular ($\Theta = 90°$), and Trans ($\Theta = 180°$) Conformations of Hexa-1,5-dien-3-yne from Various Levels of Theory

Method	$E_{\Theta=0°}$ (kcal mol^{-1})	$E_{\Theta=90°}$ (kcal mol^{-1})	$E_{\Theta=180°}$ (kcal mol^{-1})
DB-RIMP2/DZ	0.00	0.63	0.01
DB-RIMP2/TZ	0.00	0.62	0.05
DB-RIMP2/QZ	0.00	0.71	0.07
CCSD(T)/TZ//DB-RIMP2/DZ	0.00	0.46	0.05
CCSD(T)/QZ//DB-RIMP2/DZ	0.00	0.57	0.08
CBS-CCSD(T)//DB-RIMP2/DZ	0.00	0.63	0.10
CBS-CCSD(T)//QCISD(T)/DZ	0.00	0.64	0.12

of the torsional potential and conformational stability of hexa-1,5-diene-3-yne. At the CBS-CCSD(T)//QCISD(T)/DZ level the torsional barrier is found to be 0.64 kcal mol^{-1} for conversion from the minimum-energy cis conformer to the locally stable trans conformer (at 0.12 kcal mol^{-1}).

The geometric parameters for the three most relevant geometries ($\Theta = 0°$, 90°, and 180°) of hexa-1,5-diene-3-yne are presented in Table 2 for all methods. The bond lengths depend only very slightly (on the order of 0.1 pm) upon the torsional conformation and vary even less between the cis and trans conformers. At the DB-RIMP2/DZ level, the bond lengths are approximately 1.43, 1.36, and 1.24 Å for the C−C single, double, and triple bonds, respectively, with little impact from the conformation. The angle formed by the single and triple bond is found to be bent by nearly 5° in the cis conformation, becoming increasingly more linear in the transition from cis through perpendicular to the trans conformer. Increasing the basis set at the DB-RIMP2 level results in a systematic shortening of the computed bond lengths. Going from the DB-RIMP2 level to the QCISD level, the C−C triple bond is shortened by 0.013 Å and the double bond by approximately 0.004 Å, while the single bond elongates by approximately 0.013 Å. We note that the QCISD(T) geometries compensate for the overcorrection that the QCISD method brings relative to the DB-RIMP2 geometries and produce bond lengths and bond angles close to the DB-RIMP2 values.

Table 2. Computed Bond Lengths (Å) and Bond Angles (deg) for the Cis ($\Theta = 0°$), Perpendicular ($\Theta = 90°$), and Trans ($\Theta = 180°$) Conformations of Hexa-1,5-dien-3-yne[a]

	Θ	r_{12}	r_{23}	r_{34}	a(1,2,3)	a(2,3,4)
DB-RIMP2/DZ	0.00	1.359	1.432	1.244	123.69	175.92
	90.00	1.357	1.435	1.243	123.69	176.26
	180.00	1.359	1.432	1.243	123.69	179.04
DB-RIMP2/TZ	0.00	1.343	1.419	1.225	123.74	177.91
	90.00	1.342	1.422	1.225	123.76	178.31
	180.00	1.344	1.419	1.225	123.69	179.33
DB-RIMP2/QZ	0.00	1.341	1.417	1.222	123.60	179.31
	90.00	1.340	1.421	1.222	123.65	178.40
	180.00	1.341	1.418	1.222	123.61	178.31
QCISD/DZ	0.00	1.354	1.446	1.230	123.73	176.14
	90.00	1.354	1.448	1.230	123.67	176.95
	180.00	1.354	1.446	1.230	123.70	178.99
QCISD(T)/DZ	0.00	1.362	1.444	1.239	123.62	175.42
	90.00	1.361	1.446	1.238	123.64	177.78
	180.00	1.362	1.444	1.238	123.63	178.90

[a] The carbon atoms are numbered (1−6) successively from one end of the molecule.

Overall, the DB-RIMP2/aug-cc-pVDZ approach is found to provide a very good description of the geometries and torsional energies of the model hexa-1,5-diene-3-yne compound while balancing the computational expense. The computed geometries (from Table 2) differ typically by not more than 0.01 Å in bond lengths and a maximum of 2° in bond angles from methods that include the effects for larger basis sets and increased descriptions of electron correlation. The computed torsional barriers at the DB-RIMP2/DZ level are underestimated by merely about 2% when compared to the CBS-CCSD(T) values (differing by at most 0.01 kcal mol^{-1}). For comparison, DFT computations with the PBE functional and the same aug-cc-pVDZ basis set provide geometries very similar to those from the DB-RIMP2/DZ approach but very substantially overestimate the barrier at 1.06 kcal mol^{-1}.

3.2. Torsion Potential in PDAs at the Polymer Limit. In order to assess the polymer limit for the torsion potential in PDA chains, we start by investigating at the DB-RIMP2/DZ level the potential energy surfaces for torsion about one of the central-most single bonds for a series of PDA oligomers having the general formula $C_{4n+2}H_{2n+4}$ (see Figure 1). For odd n values,

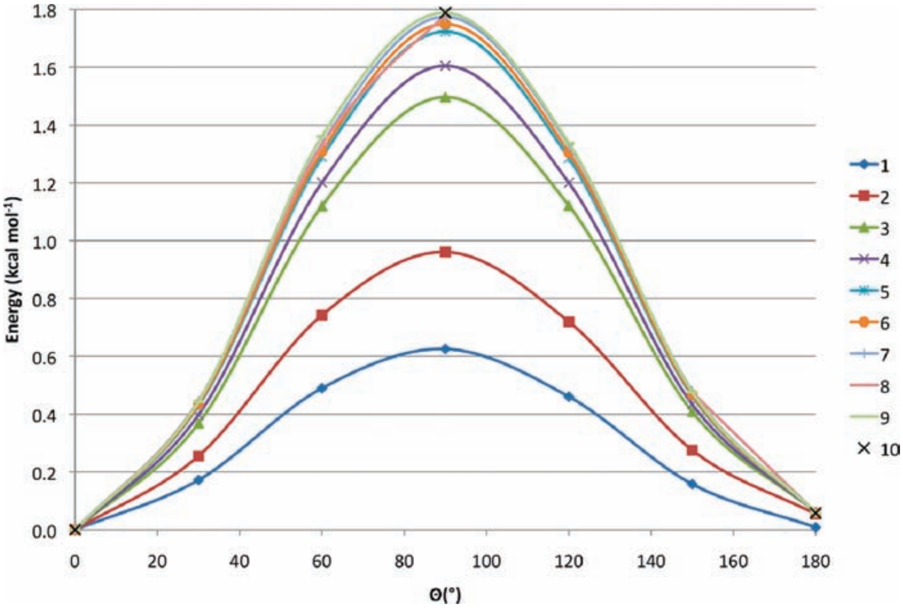

Figure 3. DB-RIMP2/aug-cc-pVDZ potential energy profiles for the torsion potential in diacetylene oligomers, $n = 1-10$.

Table 3. Relative Energies for Torsion about the Central Triple Bond in Oligomers of PDA ($n = 1-10$) Computed at the DB-RIMP2/aug-cc-pVDZ Level

n	$E_{\Theta=90°}$ (kcal mol^{-1})	$E_{\Theta=180°}$ (kcal mol^{-1})
1	0.63	0.01
2	0.96	0.05
3	1.50	0.06
4	1.61	0.06
5	1.72	0.06
6	1.75	0.06
7	1.77	0.06
8	1.78	0.06
9	1.79	0.06
10	1.79	0.06

the central torsion is well understood, corresponding to the dihedral angle between the innermost C−C double bonds located on opposite sides of the central C−C triple bond. For even n values, there exist two equivalent "central-most" triple bonds; however, by symmetry, the torsion profile is the same for either of the two possible definitions. In Figure 3, the PESs are displayed for PDAs ranging from hexa-1,5-diene-3-yne ($n = 1$) to the analogous decayne [tetracontakaido-1,5,9,13,17,21,25,29,33,37,41-hendecaene-3,7,11,15,19,23,27,31,35,39-decayne] ($n = 10$). The relative energies for all systems at both minima ($\Theta = 0°$ and $\Theta = 180°$) as well as the transition state ($\Theta = 90°$) at the DB-RIMP2/DZ level are presented in Table 3 (where all remaining torsions are in the trans conformation).

The results for the longer PDA oligomers (Table 3) demonstrate a strong dependence upon oligomer length, varying from 0.63 kcal mol^{-1} in the smallest oligomer to 1.79 kcal mol^{-1} in the largest. The DB-RIMP2/DZ torsion potential for the ($n = 2$) deca-1,5,9-trien-3,7-diyne oligomer of 0.96 kcal mol^{-1} is slightly larger than the RHF/3-21G value of 0.71 kcal mol^{-1} computed by Brédas and Heeger.[30] Importantly, the barrier computed for this oligomer remains far from the barrier at the polymer limit, as it is only slightly more than half (54%) that computed for the longest oligomers examined here. For the longest oligomers, the differences in computed barriers from one compound to the next have fallen below the accuracy of the calculations. Thus, the computed barrier of 1.79 kcal mol^{-1} for the longest oligomer ($n = 10$) should be only slightly below that of an infinite polymer. For comparison, the barrier computed with PBE and the same basis set for an oligomer of only six repeat units is 3.78 kcal mol^{-1} (a value already twice that of the DB-RIMP2 predicted polymer limit (see below) and rather close to the 4.66 kcal mol^{-1} calculated by Filhol et al.).

While the DB-RIMP2 computed values for the longest oligomers appear to be very close to the polymer limit, we have investigated the anticipated impact of the finite length of the oligomers examined here using various extrapolation procedures. Gierschner et al.[63] have previously discussed the difficulties encountered when attempting to extrapolate the optical properties of polymers from experimental and/or theoretical values for a series of oligomers. It is quite common with regard to optical properties to extrapolate the oligomer values using a model depending only linearly upon the inverse number of repeat units (or inverse number of double bonds) in the system. While this captures the overall trend for the small to medium size oligomers, the linear relationship does not hold for oligomers approaching the polymer limit (and thus the conjugation length) of the particular material. This effect can be observed from the linear fit in Figure 4, where the polymer limit (predicted from the extrapolated intercept) for the torsional barrier predicted by a linear fit is 1.95 kcal mol^{-1}. This is well above what could be reasonably anticipated based upon results for the largest oligomers. Meier et al.[64] have proposed an empirical model for optical absorptions in conjugated polymers based upon the concept of an *effective conjugation length* (ECL). Given that the rotational barrier (much like the transition energy) in π-conjugated oligomers depends upon both the oligomer length and the extent of π-electron delocalization, the ECL model seems to be particularly relevant for the case of the torsional potentials as well. To that end, we have examined in Figure 4 an ECL fit of the form:

$$E(n) = E_\infty + (E_1 - E_\infty)e^{-A(n-1)} \tag{3}$$

where we have taken the energy of the infinite polymer (E_∞), the energy barrier for the monomer (E_1), and the exponent (A) as free

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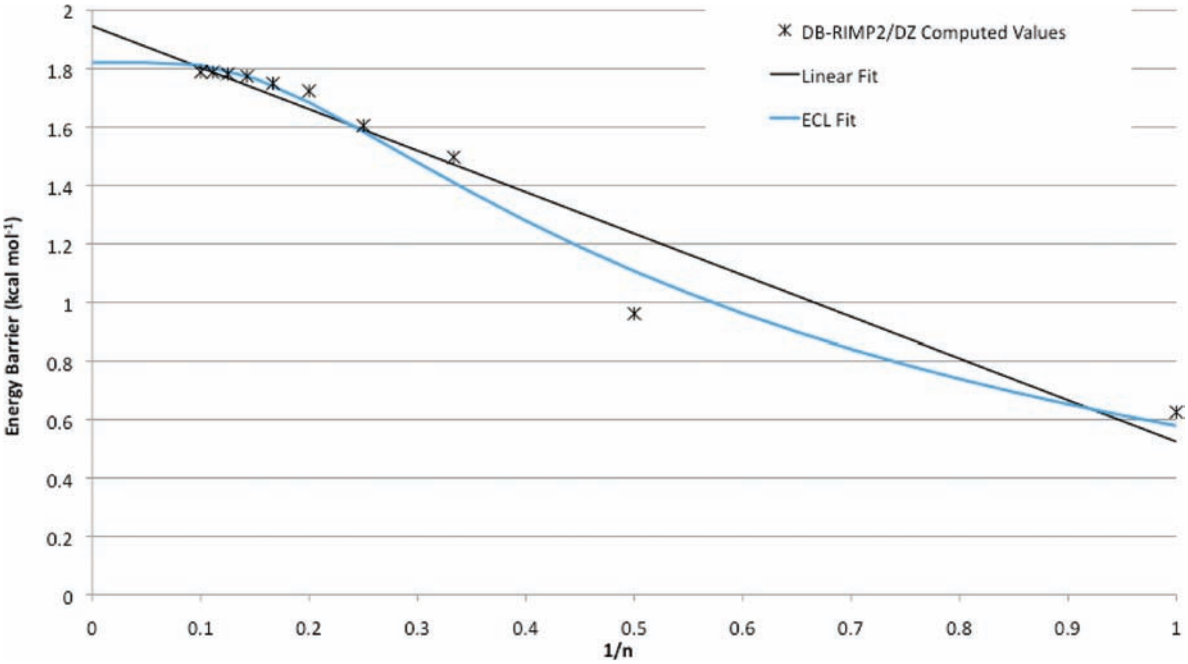

Figure 4. DB-RIMP2/aug-cc-pVDZ computed torsional energy barriers as a function of the inverse number of repeat units, *n*.

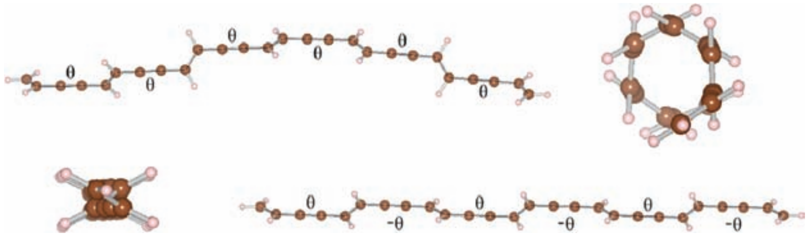

Figure 5. Schematic of the helical (upper) and alternating (lower) structures of icosikaihexa-1,5,9,13,17,21,25-heptaene-3,7,11,15,19,23-hexayne.

parameters. Overall the ECL model provides a very reasonable description of the length dependence of the torsion potential (especially for the case of the longest oligomers). For both the ECL and linear models the largest discrepancies are observed for the shortest ($n = 2, 3$) oligomers, where end effects are expected to be the most pronounced. It is anticipated that such effects are enhanced by the relatively small size of the repeat unit examined here. The extrapolated potential barrier for an infinite polymer based on the ECL model is predicted to be 1.82 kcal mol^{-1} and appears to be in very good agreement with what would be anticipated from the values for large oligomers.

The height of the torsional barrier has direct implications on the conformational disorder and effective conjugation lengths expected in PDAs.[65] A barrier of almost 8 kT (at 298 K) as predicted by Filhol et al.[29] is difficult to reconcile with available experimental data. From a statistical mechanical model describing the dependence of the conformational conjugation lengths in π-conjugated polymers upon the torsional barrier,[65] a barrier of 4.66 kcal mol^{-1} would imply a conjugation length of more than 15 repeat units at room temperature. This contrasts sharply with experimental estimates based on either thermodynamic arguments (3−4 repeat units) or spectroscopic data on the "optical conjugation length" giving estimates of 6−7 repeat units.[24,25] Using the barrier of 1.82 kcal mol^{-1} predicted here leads to an anticipated conjugation length (using this same model) of approximately 6 repeat units, in good agreement with the available experimental results.[24,25]

We note that a conjugation length of 6 repeat units might seem to contradict the observation of conformational disorder for PDA oligomers with as little as 3 repeat units as observed by Wudl and Bitler.[32] However, given the strong length dependence of the computed barrier (see Figure 4), this observation can actually be readily understood; the small barrier ($\sim kT$) for the smallest oligomers would indicate a conjugation length of only 2−3 repeat units that gradually increases to the predicted 6−7 repeat units in the case of long oligomers.

3.3. Twisted Polydiacetylene Oligomers. For the model PDA oligomers examined here, we observe the anticipated energy minima corresponding to the planar cis and trans conformations. In actual PDAs, where the side groups are generally bulky, steric effects can induce nonplanar distortions and twisted conformers can correspond to the global and/or local minima. The amount of twisting will be a function of (i) the inherent barrier to nonplanarity that we have computed above for the model PDA oligomers and (ii) the degree and strength of the interactions between side groups. The fact that chiral PDA structures have been observed experimentally from achiral chains[66−70] implies

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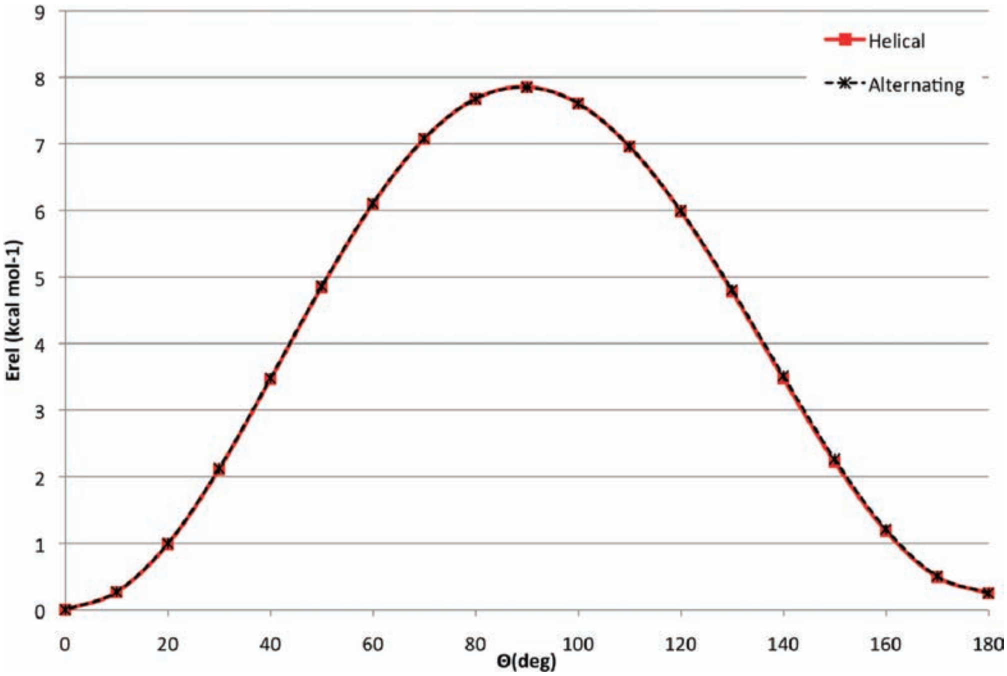

Figure 6. Potential energy profiles for the helical and alternating structures of icosikaihexa-1,5,9,13,17,21,25-heptaene-3,7,11,15,19,23-hexayne as a function of the torsion angle (see Figure 5 and the text for a description of these structures).

that such nonplanar structures can be produced. Employing an oligomer consisting of six repeat units [icosikaihexa-1,5,9,13,17,21,25-heptaene-3,7,11,15,19,23-hexayne], we have investigated two such twisted structures (see Figure 5). We have considered a helical model that produces a chiral structure in which consecutive torsions are constrained to the same value as well as an alternating model that is an achiral structure where the torsions on consecutive repeat units differ by a sign. It should be noted that, unlike in the case of the periodic DFT computations of Filhol et al. where the torsion angles Θ are restricted by the system size,[29] the oligomer approach employed here allows us to examine the entire range of torsions.

The relative energies for both the helical and alternating structures are plotted in Figure 6 as a function of the degree of torsion. For all practical purposes, the helical and alternating structures are found to be isoenergetic for any value of Θ (they differ by less than 0.01 kcal mol^{-1}). The helical structure with a Θ of 120° is 5.99 kcal mol^{-1} above the ground state (i.e., 1.00 kcal mol^{-1} per repeat unit); this is roughly 2/3 the energy per monomer repeat unit of 1.55 kcal mol^{-1} calculated by Filhol et al.[29] The most interesting point is that both helical and alternating twisted structures can be formed with little energetic penalty. For instance, a twist of 10° per polymer repeat unit can be observed to be roughly kT at 298 K (of course, these model calculations do not take into account specific interactions that might exist between the side groups).

4. Summary and Conclusions

In this work, we have employed high-level wave-function-based electronic structure approaches to address the torsional potential in polydiacetylenes. Given the overall very good agreement with the CBS-CCSD(T) results for hexa-1,5-diene-3-yne, the DB-RIMP2/aug-cc-pVDZ approach was found to provide a reliable description of the torsional potential for rotation about central carbon−carbon bonds in PDA oligomers; thus, it was used to examine the torsional barrier in oligomers very near the polymer limit.

From extrapolation of the barrier energy computed for large PDA oligomers (up to 10 repeat units), the barrier to rotation in polydiacetylene is predicted to lie at approximately 1.8 kcal mol^{-1}. Such a computed barrier, while substantially larger than that predicted by Brédas and Heeger approximately 20 years ago,[30] is less than half the value recently reported by Filhol et al. based upon periodic DFT computations.[29] Based on our calculated barrier, the effective conjugation length in polydiacetylene is estimated to be approximately 6 repeat units. This predicted conjugation length and the observed strong dependence upon the length of the oligomer are found to be in very good agreement with available experimental observations.[32,65]

Finally, it should be kept in mind that DFT results with the PBE functional are found to significantly overestimate the computed barrier (a result that is actually not limited to the PBE functional). The overestimation (by nearly 3 kcal mol^{-1}) proves to be significant when considering the role of polymer torsions in modulating the properties of PDAs. Benchmarking the use of both traditional and modern DFT approaches and oligomer extrapolation procedures in predicting the properties of π-conjugated polymers is the emphasis of ongoing work.

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Supporting Information Available: Complete refs 57 and 59, *XYZ* coordinates of the DB-RIMP2/aug-cc-pVDZ optimized structures, and total energies for all oligomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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