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Bond Length Alternation and Energy Band Gap of Polyyne

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The bond length alternation (BLA) and energy band gap of polyyne are investigated by various first-principles theories, including Hartree−Fock, MP2, hybrid, and nonhybrid density functional theories. Both solid-state calculations utilizing periodic boundary conditions on polymers and molecular quantum mechanical calculations on extra-long oligomers were performed with consistent results. By validation on similar linear conjugated polymers, polyacetylene and polydiacetylene, the combination of hybrid-DFT schemes, B3LYP//BHandHLYP or B3LYP//KMLYP, is shown to give the best predictions for both geometry and band gap of polyyne based on available experimental data. We conclude that the best estimate of the BLA of polyyne is about 0.13 Å and that of the band gap is about 2.2 eV.

1. Introduction

Polyyne, the sp-hybridized allotrope of carbon, has been considered as a hypothetical polymer, although various claims about its observations can be found in the literature sometimes under the name of carbyne.[1] We distinguish polyyne, the infinite carbon chain, from its oligomers, which we term as oligoynes. Most recently, very long carbon chains (essentially polyyne) have been directly observed inside multiwalled carbon nanotubes by high-resolution transmission electron microscopy (HRTEM)[2,3] and with resonant Raman spectroscopy.[3,4] The assignment of the observed 1850 cm^{-1} Raman peaks to the carbon−carbon stretching mode of polyyne can also be justified by recent theoretical vibrational calculations.[5] Because of the high reactivity of the triple bonds in these systems, polyyne and oligoynes are difficult to synthesize and isolate experimentally.[1,6] Szafert and Gladysz did a complete review of the crystallographic structural data of a large number of end-capped oligoynes in 2003.[7] They proposed an extrapolated value for the bond length alternation (BLA, $\delta r = R_s - R_t$, the bond length difference between the single and triple bonds) at the infinite chain length (polyyne) limit to be 0.07−0.08 Å, based on various end-capped oligoynes. A complicating factor is that some capping units are involved in charge transfer. Furthermore, there is a lack of data on very long oligoynes, and the geometry is also influenced by various packing effects. Different asymptotic limits could be extrapolated from different end-capped oligoyne series or different packing motifs. The estimation of the band gap of polyyne from oligomer data is more straightforward. There are abundant optical spectra on long oligoynes,[6,8−11] although even longer oligoynes are still needed to accurately predict the gap at the polymer limit by minimizing the end group effects. The oligoyne calculations discussed here are all H-capped with the formula $H{-}(C{\equiv}C)_m{-}H$; $n = 2m$ is the number of carbon atoms in the oligomer.

For a quasi-1-D conjugated chain system, the band gap is strongly dependent on the BLA. This follows from the Peierls theorem,[12] which plays a central role in understanding the properties of polyacetylene[13,14] and polyyne.[15,16] Both of these systems have a “half-filled” energy band structure; in the case of polyyne this is due to the linear geometry and the degeneracy of the π orbitals perpendicular to the chain axis.[15] Being a very attractive target for theorists owing to its simplicity, various theoretical studies have addressed the problem of BLA and band gap of polyyne.[15−27] The difficulty of theoretically modeling carbon chains comes from the requirement of accurately describing electron correlation and electron phonon coupling, both of which depend on the level of theory used. Another difficulty is the notorious basis set linear dependency problem inherent with this system when larger atomic centered basis sets are used in the ab initio calculations.[18,28] Therefore, divergent theoretical predictions have been reported for polyyne, depending on theoretical levels and various calculation conditions. Conversely, this system is an excellent testing ground for various theoretical models.

For these reasons, the basic properties, including the BLA and energy band structure of polyyne, are still not yet converged in the literature. We report here theoretical investigations of the BLA and band gap from different theoretical levels based on both solid-state calculations of polyyne with periodic boundary conditions and extrapolated results from molecular quantum mechanical calculations on extra-long oligomers. We aim at the *polymer* properties or the properties of oligoynes at the *polymer* limit.

Because of the lack of unambiguous experimental data for polyyne, we also studied two analogous 1-D conjugated carbon systems: polyacetylene (PA) and polydiacetylene (PDA). PA and PDA are similar to polyyne in the sense that they are also quasi-1-D highly conjugated linear chain systems with half-filled band structure and composed mostly of carbon skeletons, and there are no localized aromatic rings lying along the conjugation path.

2. Computational Details

All calculations on PA, PDA, and polyyne were carried out using the Gaussian03 program[29] with the 6-31G* Gaussian-type basis sets. Periodic boundary conditions (PBC) calculations were performed wherever it was feasible. Oligomer extrapolation method was used in the Hartree−Fock (HF) and hybrid density functional theory (DFT) calculations of polyyne due to basis

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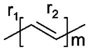
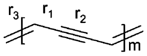
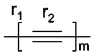
TABLE 1: Optimized BLA (*δr*) and Band Gap (*E_g*) Values for PA, PDA, and Polyyne (6-31G* Basis Sets Are Used)

system	theory	A_x[a]	Method[b]	δr (Å)	E_g (eV)
PA  $\delta r = r_1 - r_2$	HF	1	PBC(139)	0.122	7.202
	KMLYP	0.557	PBC(139)	0.087	3.613
	BHandHLYP	0.5	PBC(139)	0.088	3.306
	PBE1PBE	0.25	PBC(139)	0.059	1.476
	B3LYP	0.2	PBC(139)	0.055	1.203
	O3LYP	0.12	PBC(139)	0.040	0.695
	BLYP	0	PBC(139)	0.018	0.169
	LDA	0	PBC(139)	0.010	0.112
	MP2	-	Oligomer(30)	0.058	-
	experiment	**-**	**ref 38**	**0.07-0.09**	**1.5-1.8**
PDA  $\delta r = r_1 - (r_2+r_3)/2$	HF	1	PBC(69)	0.168	8.001
	KMLYP	0.557	PBC(69)	0.132	4.211
	BHandHLYP	0.5	PBC(69)	0.133	3.866
	PBE1PBE	0.25	PBC(69)	0.107	1.969
	B3LYP	0.2	PBC(69)	0.106	1.690
	O3LYP	0.12	PBC(69)	0.094	1.169
	BLYP	0	PBC(69)	0.076	0.517
	LDA	0	PBC(69)	0.068	0.447
	MP2	-	Oligomer(32)	0.108	-
	experiment	**-**	**ref 39**	**0.13-0.17**	**2.0**
Polyyne  $\delta r = r_1 - r_2$	HF	1	Oligomer(72)	0.183	8.500
	KMLYP	0.557	Oligomer(72)	0.135	4.438
	BHandHLYP	0.5	Oligomer(72)	0.134	3.946
	PBE1PBE	0.25	Oligomer(72)	0.093	1.801
	B3LYP	0.2	Oligomer(72)	0.088	1.487
	O3LYP	0.12	Oligomer(72)	0.067	0.895
	BLYP	0	PBC(133)	0.036	0.320
	LDA	0	PBC(133)	0.028	0.246
	MP2	-	Oligomer(40)	0.060	5.541
	experiment	**-**	-	n/a [c]	2.3-2.4 eV [d]

[a] A_x is the amount of exact exchange in the theory. [b] PBC calculations were performed whenever is possible, with the number of irreducible *k* points listed in parentheses. The number of carbon atoms (*n*) in the longest oligomer used in the oligomer extrapolations is given in parentheses. H-end groups were used throughout. [c] Estimated to be 0.13 Å based on Badger's rule, ref 5. [d] Extrapolated experimental results based on data from refs 9 and 11, see Figure 2.

set linear dependency problems, and in all the MP2 calculations due to the unavailability of PBC codes at this level. Hydrogen end-capped PA, PDA, and polyyne segments are used as respective model oligomers in the oligomer extrapolation method. The properties of a polymer were obtained by extrapolating the corresponding properties of a series of finite oligomers to the infinite size limit using linear regression in terms of inverse size. Because of the need for including very long oligomers in the extrapolation, we focused on various forms of nonhybrid *and* hybrid DFT (B3LYP of the B3 hybrid scheme;[30] BHandHLYP[29] of the half and half hybrid scheme,[31] PBE1PBE,[32] KMLYP,[33] and the recent O3LYP[34] scheme), in addition to Moller−Plesset perturbation theory (MP2) and HF theory. In the oligomer calculations, the center-most triple and single bonds were chosen to best represent the respective bonds in the polymer.

A typical extrapolation for BLA is shown in Figure S1, which is given in the Supporting Information. Convergency is quite slow, and the linear trend in the small *n* range changes around the size of $n = 20$ C atoms. This slow convergency necessitates the calculations on large oligomers. The present paper is based on hundreds of full geometry optimization calculations and a large number of single-point (nonoptimized) calculations for band gaps. We report only a fraction of the results that pertain to the trends and the most relevant data for geometry and band gaps.

3. Results and Discussion

The highest occupied crystal orbital to lowest unoccupied crystal orbital gap, E_g, of polyyne and by analogy of polyacetylene, is approximately in linear relationship with the BLA δr at HF or various DFT levels[35]

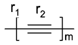
$$E_g = k\delta r + b \tag{1}$$

where *k* and *b* are positive parameters. At Hückel level, $b = 0$.

To predict the band gap of polyyne accurately, we first need to find out the best theory for the prediction of the geometry. The PBC code of Gaussian03 is limited to HF and various DFT levels. Because of the strong basis set linear dependency problem with PBC calculations of polyyne using HF related theories,[18,28] solid-state calculations can only be done at nonhybrid "pure" DFT levels, including LDA and GGA functionals. At other theoretical levels, we have to choose the oligomer extrapolation approach, where the properties of polyyne are extrapolated from those of a series of oligoynes based on the size dependency of the corresponding properties. To ensure that the calculations on oligomers are sufficiently converged for the purpose of extrapolation, molecular calculations on large oligomers are necessary. Highly conjugated systems such as oligoynes are extremely sensitive to the size of oligomers. This essentially limits the selection of the theoretical levels to various forms of pure and hybrid DFT and HF theory.

3.1. Prediction for the Geometry of Polyyne. Table 1 shows the performance of different theories for the geometry prediction of polyyne, together with the results for PA and PDA. The band gaps predicted at each level are also listed for reference. Comparison with the experimental data is also provided. It is no surprise that different levels of theory give significantly different predictions[36] for all three quasi-1-D conjugated

TABLE 2: Comparison of PBC and Oligomer Extrapolation Methods for the Optimized BLA (*δr*) of Polyyne (Notations Are the Same as in Table 1)

System	Theory	Method	r_1	r_2	δr (Å)
Polyyne  $\delta r = r_1 - r_2$	BLYP	PBC(133)	1.273	1.309	0.036
		Oligomer(72)	1.276	1.306	0.030
	LDA	PBC(133)	1.269	1.297	0.028
		Oligomer(72)	1.271	1.294	0.022

systems. Pure DFT theory underestimates the BLA of PA and PDA, while HF overestimates it. MP2 theory predictions are close to those of B3LYP and PBE1PBE. Among all the DFT theories, the amount of exact exchange plays a dominant role for the prediction of BLA.[37] We designate by A_x the percentage of exact exchange in the hybrid density functional. For example, $A_x = 0$ for all nonhybrid DFT functionals, $A_x = 1$ in HF, $A_x = 0.20$ for B3LYP, and $A_x = 0.50$ for BHandHLYP. As can be seen from the data presented in Table 1, with about 50% of exact exchange mixed in the hybrid DFT scheme, BHandHLYP and KMLYP functionals provide the best fit for the experimental geometries of PA[38] and PDA.[39] Likewise, it can be inferred that polyyne is likely to exhibit a BLA of about 0.134 Å based on BHandHLYP/6-31G* calculations. This is in good agreement with our scaled vibrational calculations on polyyne.[5] These calculations provided accurate frequencies for long oligoynes, and therefore we trust the force constants we obtained by our recently established linear/exponential scaling scheme.[5] By relating these high-quality stretching force constants and the carbon−carbon bond lengths through Badger's rule, the BLA of polyyne was estimated to be about 0.13 Å.

The error associated with the oligomer extrapolation approach by using finite oligomers with up to $2m = 72$ carbon atoms in $\mathrm{H{-}(C{\equiv}C)_{\mathit{m}}{-}H}$ oligoynes are estimated in Table 2 for two different levels of theory (LDA and BLYP) for which both PBC and oligomer extrapolation methods are available. There is qualitative agreement between the oligomer extrapolation and the PBC results for these two methods. The deviation between the PBC and the oligomer extrapolation at the BHandHLYP level is expected to be smaller than for the two nonhybrid DFT cases represented in Table 2. This is due to the fact that the convergence of bond lengths with respect to the oligomer size is faster at this level than at the notoriously slowly converging nonhybrid DFT levels.[22]

3.2. Prediction of the Band Gap of Polyyne. The experimental band gap corresponds to the vertical excitation energy from the ground state to the first dipole-allowed excited state. This energy, in principle, is different from the energy gap between the highest-occupied crystal orbital (HOCO) and the lowest-unoccupied crystal orbital (LUCO). Excited-state theories, such as CIS,[40] Green's function approach,[41] ZINDO,[42] and time-dependent DFT (TDDFT),[43] are justified methods to reproduce experimental band gaps. Among them, TDDFT has enjoyed great success in predicting excited states with increasing popularity in molecular quantum chemistry.[44,45] But, TDDFT is expected to have minimal effect in predicting excitations for extended systems.[45] It has been shown that the excitation energies for polymers predicted by TDDFT converges to about the same value as the HOCO−LUCO band gap at the same theoretical level within the errors and uncertainties of theoretical calculations.[46,47] Therefore, in this work we adopted the theoretical HOCO−LUCO gap to compare with the optical excitation gaps of polymers.

On the basis of the BHandHLYP geometry determined above, B3LYP electronic calculations are performed to predict the HOCO−LUCO band gaps of PA, PDA, along with polyyne. The gaps of PA and PDA at B3LYP//BHandHLYP level (geometry optimization at BHandHLYP level followed by electronic structure calculation at B3LYP level) were obtained by PBC band calculations. In the case of polyyne, the band gap at B3LYP//BHandHLYP level was obtained through the oligomer extrapolation method from the long oligoyne region, which is shown in Figure 1. The results on all three systems discussed in this paper are listed in Table 3. As for the case of predicting BLA, the good agreement between theoretical and experimental gaps for PA and PDA justifies B3LYP//BHandHLYP for the prediction of the band gap for polyyne. The gap value is predicted to be around 2.158 eV.

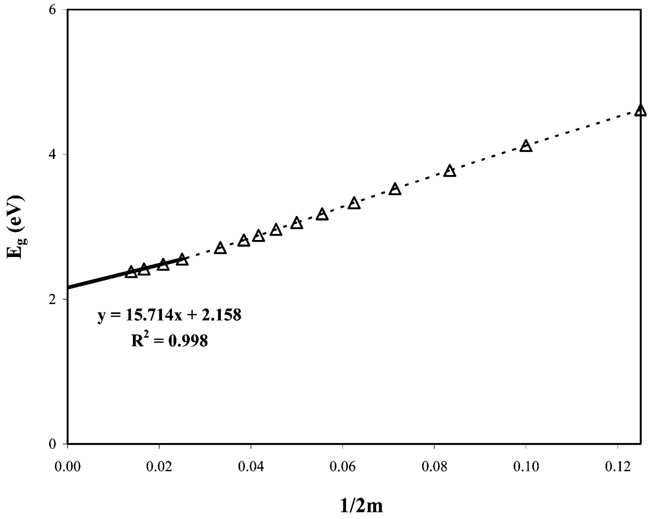


Figure 1. Extrapolation of the B3LYP/6-31G*//BHandHLYP/6-31G* band gap of polyyne from those of $\mathrm{H{-}(C{\equiv}C)_{\mathit{m}}{-}H}$ oligoynes with $2m$ up to 72.

TABLE 3: B3LYP/6-31G*//BHandHLYP/6-31G* Band Gaps, in eV (Notations Are the Same as In Table 1)

system	method	E_g theor	E_g expt
PA	PBC (133)	1.672	1.5−1.8
PDA	PBC (133)	2.063	2.0
polyyne	oligomer (72)	2.158[a]	2.3−2.4[b]

[a] The B3LYP/6-31G*//KMLYP/6-31G* value is 2.211 eV. [b] Extrapolated experimental results based on data from refs 9 and 11, see Figure 2. Ref 11 reported the extrapolated value of 2.175 eV.

Currently there are no accurate direct experimental band gap values available for polyyne. On the basis of recent optical absorption experiments on longest available oligoynes,[9,11] the band gap of polyyne can be estimated from Figure 2 to be at 2.3−2.4 eV. This extrapolation has a relatively large uncertainty due to the lack of data on very long oligomers. Recent resonant Raman experiments on carbon chains inside carbon nanotubes offer another opportunity to determine the band gap of polyyne through the resonant excitation energy. The resonance data indicate a gap of about 2.4−2.5 eV, although no excitation profile was published,[3,4] and therefore it is difficult to assess the accuracy of this information. Nevertheless, the predicted band gap value of approximately 2.2 eV at the B3LYP//BHandHLYP level is very close to the extrapolated experimental value of 2.3−2.4 eV shown in Figure 2.

4. Conclusions

Through the validation on similar quasi-1-D conjugated systems, PA and PDA, we determined that the combination of the B3LYP//BHandHLYP or B3LYP//KMLYP method to be

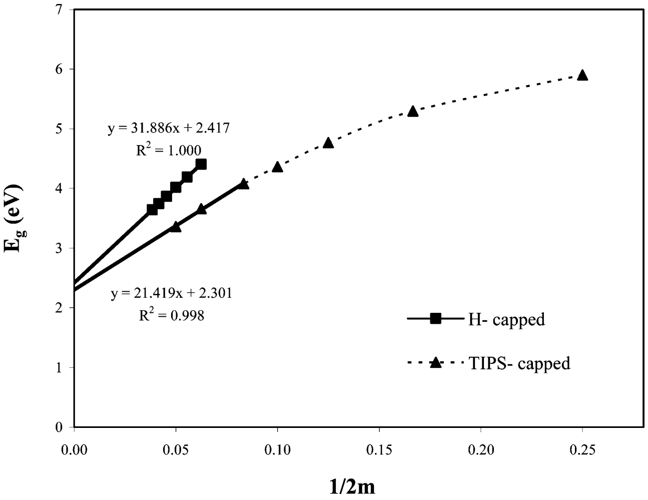


Figure 2. Experimental band gaps of selected oligomer series. Data are taken from ref 9 (hydrogen end-capped) and ref 11 (triisopropylsilyl or TIPS capped). Lines are drawn to guide the eye.

an adequately accurate theoretical level for the prediction of the geometry and electronic band gap of polyyne. The BLA of polyyne is predicted to be approximately 0.13 Å and the band gap at about 2.2 eV, which are very close to estimates from available experimental data on oligoynes and on polyyne encapsulated in carbon nanotubes.

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Supporting Information Available: Figure showing BLA as a function of 1/*n* and the complete ref 29. This material is available free of charge via the Internet at http://pubs.acs.org.

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