Linear C_n Clusters: Are They Acetylenic or Cumulenic?

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Received: August 24, 2007; In Final Form: October 1, 2007

Uncapped linear C_n clusters have been studied with hybrid density functional theory focusing on the geometry, HOMO−LUMO gap, and the longitudinal optical (LO) vibrational mode. The latter two correlate well with the bond length alternation (BLA) of the optimized geometry. Due to end effects, the BLA is not constant along the chains. The degree of BLA changes continuously with increasing n: starting with essentially nonalternating structures (cumulenic), then turning into strongly alternating (acetylenic) structures. This transition has not yet been described or characterized and occurs at relatively large values of n. The implications for the widely observed characteristic LO vibrational bands of linear carbon clusters are discussed.

1. Introduction

Carbyne, the hypothetical linear allotrope of carbon, has attracted some interest both experimentally and among theorists.[1−3] It is an infinite chain formed exclusively by sp-hybridized carbon atoms, C_∞. Therefore, it is often called the fourth allotrope of carbon, after diamond, graphite, and fullerenes and nanotubes.

From the perspective of formal chemical valence, two forms of infinite carbon chains might exist based on the degenerate pair of π orbitals on each carbon atom oriented perpendicular to the chain axis: *polycumulene*, $(=C=)_\infty$, an equidistant carbon chain and *polyyne*, $(-C\equiv C-)_\infty$, which features a single−triple bond alternating pattern. All solid-state calculations[4−10] indicate that polyyne is more stable than polycumulene, because the latter has a degenerate pair of half-filled energy bands which are subject to Peierls distortion.[11] So do the oligomer methods by extrapolating properties from a series of finite carbon chain oligomers, to the infinite size limit.[12]

Linear C_n (n is finite) clusters are abundant in the interstellar clouds[13−17] and have been extensively studied in the laboratory.[18−32] It is generally understood that linear C_n (even or odd) carbon chains possess the cumulenic geometry with nearly equivalent bond lengths, as opposed to the possible acetylenic geometry with appreciable bond length alternation (BLA).[24] This is clearly in contrast to the acetylenic geometry found in the infinite linear carbon chain, C_∞[4−10] and in finite end-capped carbon chains.[12,33] In addition, discrepancies can also be found for other associated properties, such as the HOMO−LUMO gap (E_g), and the characteristic bond stretching frequency of carbon chains. We will show that in these cases, one cannot predict the properties of C_∞ based on the extrapolation from short- and medium-sized C_n chains found in the literature.

In this work, we report theoretical investigations on the geometric and vibrational properties of uncapped linear C_n clusters, with the aim at finding the transition from the cumulenic short chains to the strongly alternating polymer, C_∞. Implications for the important longitudinal optical Raman bands of linear carbon clusters are discussed. We show in this paper that the transition from a cumulenic (essentially nonalternating) structure to an alternating one occurs for relatively long chains. The transition from the essentially nonalternating (cumulenic) form to the alternating (acetylenic) form occurs because of the Peierls driving force that becomes more and more pronounced as the chain length is increased.

2. Computational Details

All molecular and periodic boundary condition (PBC) calculations are carried out using the Gaussian03 program,[34] *except* for the frequency calculations of the infinite carbon chains, which were done with the PWSCF program.[35]

Due to the notorious *basis set linear dependency* problem[36−40] for carbon chains,[6,9] PBC calculations on the infinite carbon chain with adequate *Gaussian-type basis sets* can only be done at nonhybrid density functional theory (DFT) levels. On the other hand, in programs using plane wave basis sets, PBC codes for Hartree−Fock (HF) and hybrid DFT methods are not available. Therefore, with the reliable basis sets such as 6-31G* or plane wave basis sets, both PBC calculations and oligomer extrapolation results are *only* available for pure DFT methods, including local density approximation (LDA) and generalized gradient-corrected approximation (GGA) levels. At these levels, we have shown that the oligomer extrapolation approach using hydrogen-capped polyyne oligomers (oligoynes, $H-(C\equiv C)_m-H$), agrees well with PBC results for BLA and gap for polyyne.[41] This validates the oligomer extrapolation approach based on end-capped oligoynes.

We used a few standard theoretical levels deemed reliable for carbon based systems, including HF, nonhybrid DFT, hybrid DFT, second-order Møller−Plesset perturbation theory (MP2), and CCSD(T) coupled cluster calculations. 6-31G* basis sets are used as the standard Gaussian-type basis set, except that Dunning's correlation consistent triple-ζ basis sets (cc-pVTZ)[42] are used with CCSD(T). STO-3G and 3-21G basis sets are also used in some calculations where qualitative results are needed on extremely long carbon chains. In the PWSCF calculations on C_∞, 327 eV cutoff energy for carbon and 73 irreducible k points are adopted.

3. Results and Discussion

3.1. Geometry of the Infinite Carbon Chain C_∞. Consistent with literature results,[4−12] our PBC calculations at LDA and

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10.1021/jp076805b CCC: $40.75

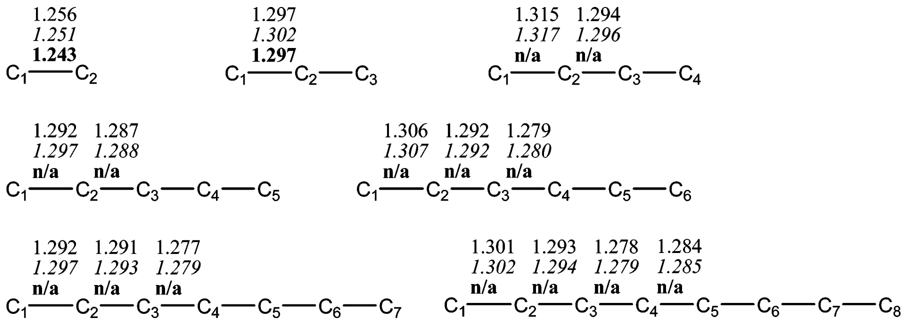

Figure 1. Bond lengths of linear C_n ($n = 2-8$) molecules in their ground states (singlet: C_2, C_3, C_5, C_7; triplet: C_4, C_6, C_8), in angstroms. B3LYP/6-31G*, CCSD(T)/cc-pVTZ, and available experimental results (ref 45 for C_2 and ref 46 for C_3) are listed from top to bottom, in plain, italic, and bold styles, respectively.

TABLE 1: Relative Stability of Polyyne and Polycumulene Per C_2 Unit at Various Theoretical Levels with Periodic Boundary Condition Calculations

theory	LDA/6-31G*	PBE/6-31G*	B3LYP/STO-3G
polycumulene (a.u.)	−75.7083554	−76.0717107	−75.2027478
polyyne (acetylenic form) (a.u.)	−75.7083909	−76.0717723	−75.2060947
ΔE (polyyne−polycumulene) (kcal/mol)	−0.02	−0.04	−2.10

GGA-PBE level with the 6-31G* basis sets show that polyyne with alternating triple−single bond geometry is slightly more stable than the equidistant polycumulene geometry. The energy differences are listed in Table 1. Theoretical prediction for the energy difference values varies significantly with the levels of theory. With the more accurate Becke's three-parameter hybrid density functional scheme (B3)[43] in the form of B3LYP, but with minimum Gaussian-type basis sets, the energy difference is qualitatively larger at 2.10 kcal/mol per C_2, which is also listed in Table 1. With the ab initio G3 theory and the oligomer extrapolation approach on linear chains including up to 10 carbon atoms, Rodriguez et al. predicted that polyyne is 3.8 kcal/mol per C_2 more stable than polycumulene.[12]

The vibrational calculations for the equidistant polycumulene at the GGA-PBE level with the PWSCF program gave an imaginary frequency at 2237i cm^{-1} at Γ point corresponding to the longitudinal optical stretching mode. The same mode has a real frequency at 1155 cm^{-1} for polyyne at the same theoretical level. This implies that the hypothetical polycumulene structure is actually a saddle point on the potential energy surface of linear C_∞. As expected by the Peierls theorem, there is only one minimum for the infinite carbon chain, which is the bond alternating polyyne that has a significant band gap.

3.2. Geometry and Gap of Linear C_n Chains. As opposed to the single−triple bond alternating (acetylenic) geometry of the infinite carbon chain, $-(C{\equiv}C)_\infty-$, shorter linear C_n chains have been predicted to have the cumulenic geometry, $(:C{=}C{=}\cdots{=}C{=}C:)$.[24] This is the case for both even- and odd-numbered linear carbon clusters, despite the fact that C_n chains possess a singlet ground state $^1\Sigma_g^+$ when n is odd, or a triplet ground stated $^3\Sigma_g^-$ when n is even, with the only exception in C_2 which is a singlet in the ground state.[18,24]

The B3LYP/6-31G* theoretical level is used in this work for the prediction of the geometry of C_n chains. The only problem with the B3LYP theory is that it incorrectly predicts the ground state of C_2 to be the triplet, but this error also occurs with other hybrid and nonhybrid DFT theories, in addition to HF and MP2. Multiconfiguration reference methods or coupled cluster methods are needed for the correct prediction of the ground state of C_2.[18,24] Since we are aiming at the evolution of the properties of linear C_n with size n, and the connection between C_n and C_∞, this deficiency does not affect our study. Figure 1 shows that for the ground state geometry of C_n ($n = 2-8$), B3LYP/6-31G* predictions agree well with our presented and with earlier[44] CCSD(T)/cc-pVTZ calculations and available experimental data.[45,46] This justifies our selection.

We did a series of geometry optimization calculations at the B3LYP/6-31G* level on C_n, with n ranging from 2 to 64. Aside from the end effects, we also found equidistant cumulenic geometries for various small- and medium-sized even-numbered C_n chains with n ranging up to 40 and for all odd-numbered C_n in this study with n up to 63. This is consistent with literature results.[24] The geometry of C_{40} is shown in Figure 2 as a representative example for an even-numbered linear carbon cluster, and that of C_{63} is shown in Figure 3 as a representative for an odd-numbered linear carbon cluster. There are clearly two series of bonds alternating along a C_n chain: the longer bonds and the shorter bonds. The only exceptions occur at the two ends of the chain where the first two bonds belong to the longer series. This is due to the strong valence deficiency at the two ends of the chain, which significantly elongates the first two C−C bonds. For the majority of the C−C bonds along the chains, the BLA (bond length differences between adjacent

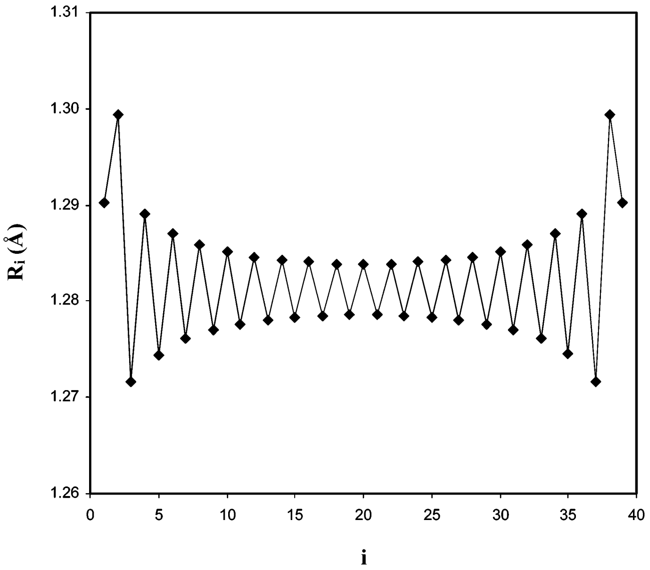

Figure 2. Bond length of all the C−C bonds along the linear C_{40} chain at the B3LYP/6-31G* level. "i" is numbered starting from one end to the other.

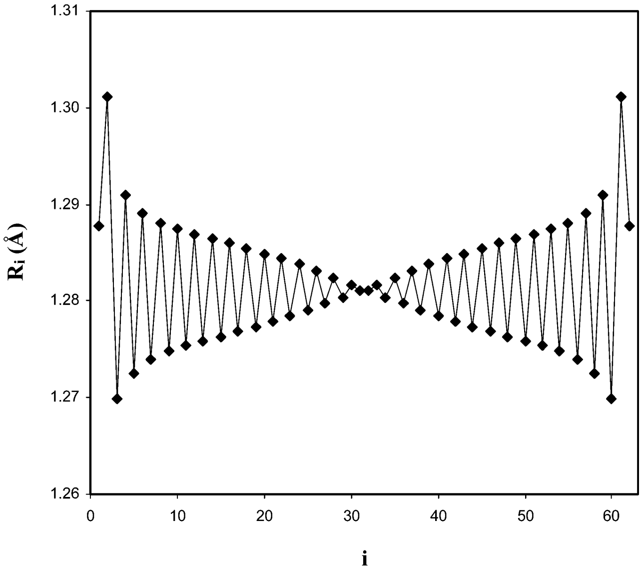

Figure 3. Bond length of all the C−C bonds along the linear C_{63} chain at the B3LYP/6-31G* level. "i" is numbered starting from one end to the other.

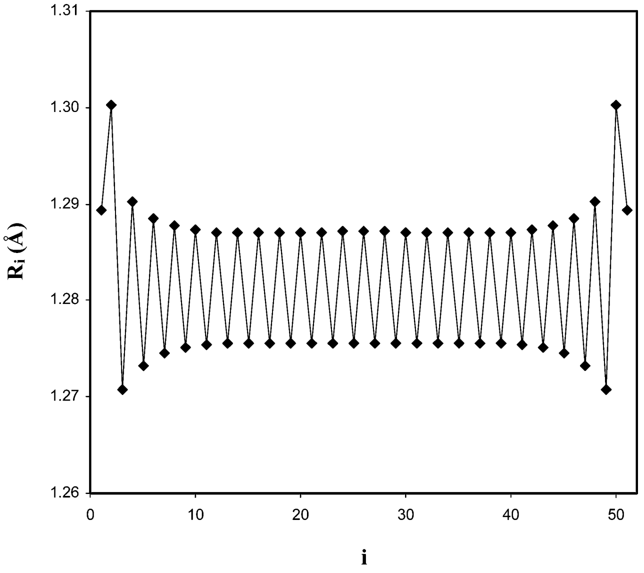

Figure 4. Bond length of all the C−C bonds along the linear C_{52} chain at the B3LYP/6-31G* level. "i" is numbered starting from one end to the other.

bonds) is less than 0.02 Å. For odd-numbered C_n, the BLA in the middle is zero by symmetry. Both C_{40} and C_{63} are essentially cumulenic, rather than acetylenic.

For the even-numbered carbon chain series starting with C_{48}, the BLA first decreases from one end toward the middle of the chain; then it slightly increases near the middle. This transition to an alternating middle section is slightly more visible in C_{52} as shown in Figure 4. As *n* further increases, the alternating character becomes dominant. C_{52} is near the changeover from the cumulenic character preferred by the end effect in linear C_n chains and the acetylenic character stabilized by the Peierls distortion in very long or infinite carbon chains. The geometry of a typical longer alternating C_n chain is shown in Figure 5 with C_{64} as an example. Beyond the crucial chain length, the oligomer extrapolation approach can be applied to predict the properties of C_∞. This radical change of the geometry with increasing *n* establishes the link between the geometry of long linear C_n chains and C_∞ which was mentioned in the Introduction and also explains why extrapolations from shorter chains to the infinite chain should not be pursued for these systems.

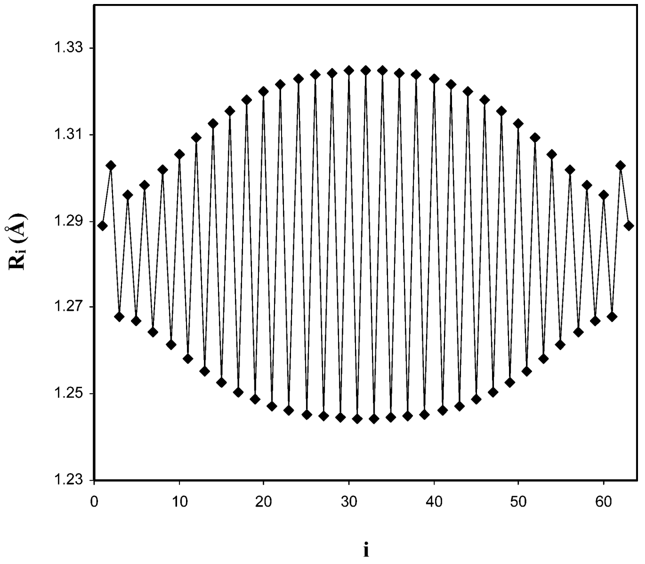

Figure 5. Bond length of all the C−C bonds along the linear C_{64} chain at the B3LYP/6-31G* level. "i" is numbered starting from one end to the other.

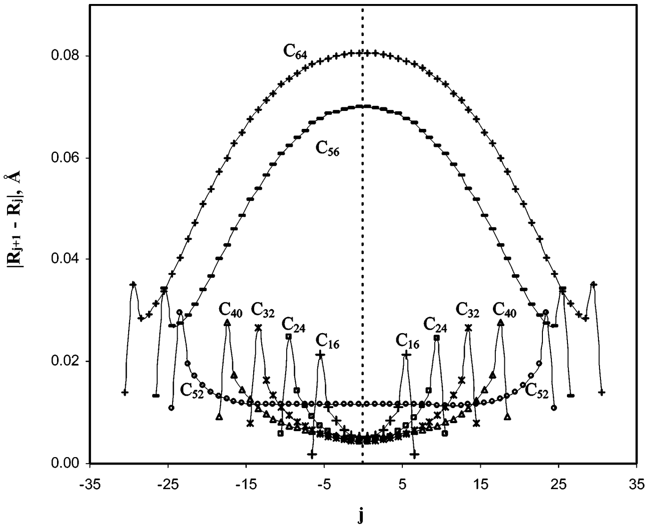

Figure 6. Bond length alternation pattern along various linear C_{2m} clusters at the B3LYP/6-31G* level, with $2m = 16, 24, 32, 40, 52, 56,$ and 64, are selectively shown. All chains are centered on the vertical dotted line. "j" is the bond numbered from the center.

The bond length alternation pattern changes along an even-numbered C_n ($n = 2m$) chain and between different C_{2m} clusters are illustrated in Figure 6. The cumulenic to acetylenic transition is predicted to occur at about $n = 48-52$. Accompanying the geometric transition from the cumulenic structure of short C_{2m} to the acetylenic character for long C_{2m}, the electronic and vibrational properties of C_{2m} also undergo fundamental changes. B3LYP/6-31G* calculations on the properties of long C_{2m} chains are limited by the strong linear dependency problems known for this system[6,9] and by the computational resources. To reveal properties at longer C_{2m} region qualitatively with smaller basis sets, we did a basis set convergence study. Figure 7 shows how, with three different basis sets, the bond length alternation at the center of C_{2m} varies with the size $2m$. The predicted geometric differences between 6-31G* and 3-21G are very small, implying that 3-21G basis sets might be sufficient for the systems under study. B3LYP with the STO-3G minimum

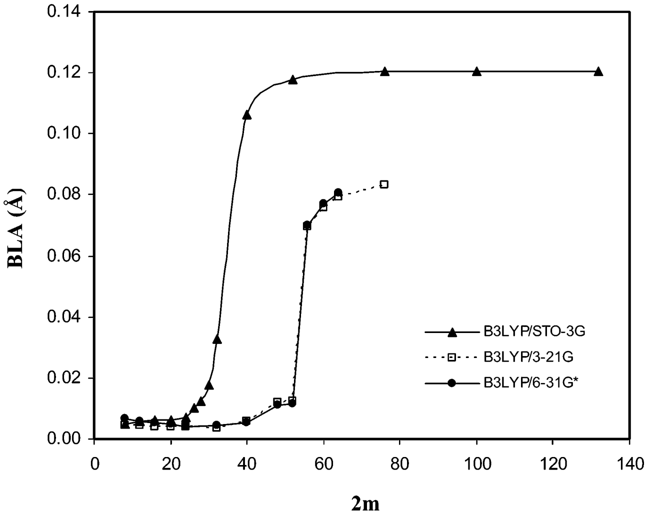

Figure 7. Dependence of the bond length alternation at the center of even-numbered linear C_n clusters with the cluster size $n = 2m$.

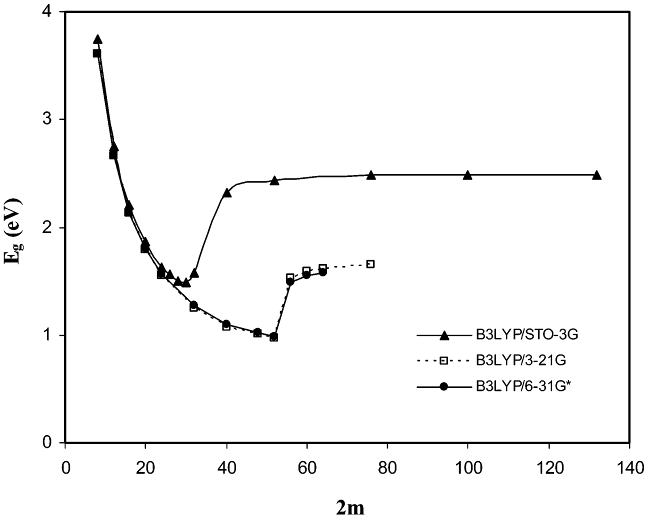

Figure 8. HOMO−LUMO gap of linear C_n clusters changes with size $n = 2m$.

basis set predicts this geometric transition only qualitatively. The transition in Figure 7 is around $2m = 30$ at B3LYP/STO-3G level, compared with $2m = 52$ predicted with 3-21G and 6-31G* basis sets.

The HOMO−LUMO gap (E_g) of conjugated systems is strongly correlated with the degree of BLA.[4,11] The consequence of this relationship leads to a changeover of the gap as a function of increasing chain size: first a decreasing gap of the nonalternating chains and, then, a sudden rise of the gap as the alternation develops in longer chains. The gap value of longer linear C_{2m} clusters approaches that of the infinite alternating chain[41] as $2m$ increases. This crossover is shown in Figure 8 for various C_{2m} chains. The three different basis sets behave similarly as in the BLA versus $2m$ curve. Again, B3LYP/STO-3G predicts that the cumulenic−acetylenic transition occurs at $2m = 30$, earlier than that happens with 3-21G and 6-31G* basis sets ($2m = 52$). The predicted gap with B3LYP/STO-3G is larger than B3LYP/3-21G and B3LYP/6-31G*, mostly due to the larger BLA predicted by the minimum basis set.

3.3. Differences between Even and Odd Linear C_n Clusters.

For the odd-numbered C_n series, the geometry remains cumulenic for all the chains studied at the B3LYP/6-31G* level with n up to 63 and at B3LYP/3-21G level with n up to 75. B3LYP calculations with STO-3G basis sets are performed to qualitatively investigate the possible cumulenic−acetylenic transition in longer odd linear carbon chains. Although cumulenic geometry is still dominant for odd-numbered C_n with n up to 59 at the B3LYP/STO-3G level, acetylenic character is found to emerge as n increases to 63. This transition n value is about doubled compared with the transition point at around C_{30} for even-numbered carbon clusters at the same theoretical level. This is because for odd C_n the two ends of the chain possess the cumulenic geometry due to the end effect, and the center of the chain is also equidistant by symmetry. As a result, an odd-numbered C_n is essentially divided into two halves of even-numbered clusters. The cumulenic to acetylenic transition occurs at the center of *both* halves when n is large enough to overcome the end effect of C_n. In other words, acetylenic character starts to grow near the one-quarter and three-quarter points of the original C_n chain. Therefore, it is reasonable to estimate that at the B3LYP/6-31G* level, the cumulenic−acetylenic transition in odd-numbered carbon clusters will be reached at twice of the transition size for the even-numbered clusters: in the $n =$ 96−104 region.

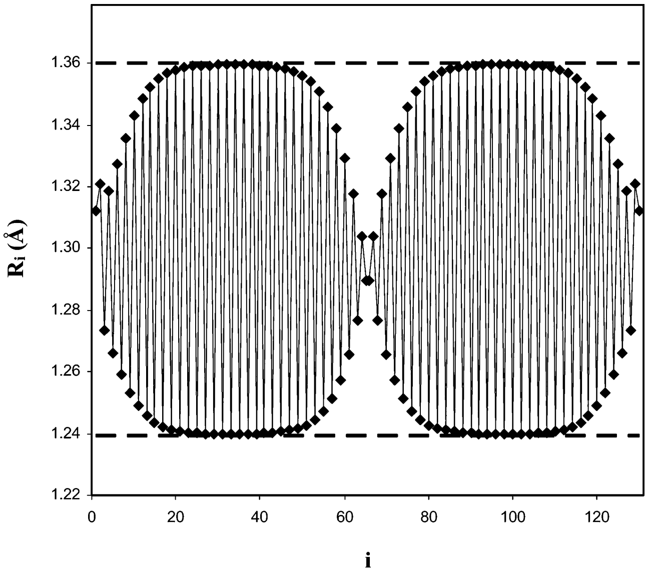

Figure 9. Bond length of all the C−C bonds along the linear C_{131} chain at the B3LYP/STO-3G level. “i” is numbered starting from one end to the other. The two dashed lines represent the bond length values of polyyne from periodic boundary condition calculations at the same level.

Figure 10. Longitudinal optical (LO) mode of alternating carbon chains.

With PBC calculations at the B3LYP/STO-3G level, the short and long bonds of polyyne are predicted to be 1.240 and 1.360 Å, respectively, and the BLA is 0.120 Å. Figure 9 shows that the convergency of odd-numbered C_n to the polymer limit is already achieved in C_{131} at the B3LYP/STO-3G level. As can be expected, the convergency is reached about 2 times faster at the same theoretical level for even-numbered C_n as previously shown in Figure 7.

3.4. Vibrational Properties of Linear Carbon Clusters.

There is a well-known connection between bond length alternation and the longitudinal carbon−carbon bond stretching modes in linear carbon chains.[8,47] For the bond length alternating polyyne, there is only one Raman-active bond stretching mode which is called the longitudinal optical (LO) mode, as shown in Figure 10. This is an all in-phase stretching mode for all short bonds and for all long bonds. This mode is enhanced as

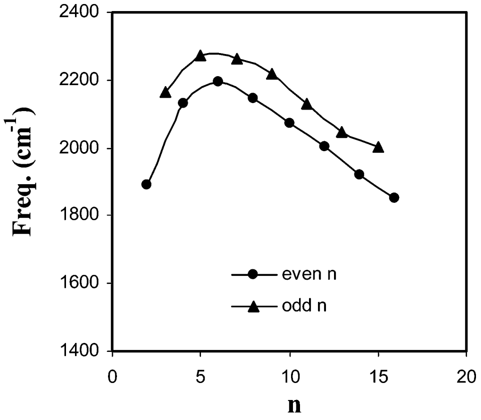

Figure 11. Longitudinal optical (LO) mode frequencies of short linear C_n clusters at the B3LYP/6-31G* level.

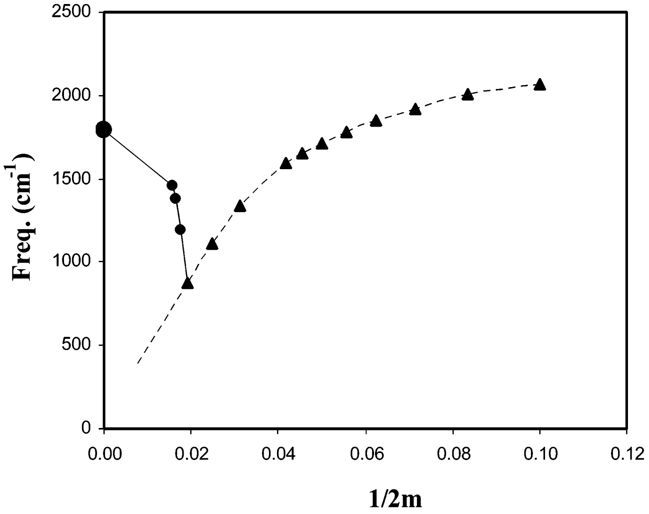

Figure 12. Longitudinal optical (LO) mode frequencies of C_{2m} carbon clusters as a function of the inverse of the size $1/2m$, at the B3LYP/6-31G* level. The lines are drawn to guide the eye and are discussed in the text. The filled circle on the vertical axis represents the LO mode frequency of polyyne from ref 48.

the size of the chain increases. For the hypothetical equidistant polycumulene, adjacent carbon−carbon stretches cancel each other and the mode would be inactive.[47]

In finite linear carbon clusters C_n, there are several optically active longitudinal modes, one of which corresponds best to the one shown in Figure 10 determined by the phases of the stretching motions in the different carbon−carbon bonds along the chain. For the rest of this paper we refer to this mode when talking about the LO mode of the finite linear carbon chains. By symmetry, the LO mode is Raman active when n is even or IR active when n is odd. The LO mode frequencies of the short C_n clusters at the B3LYP/6-31G* level are shown in Figure 11. Despite the frequency differences between nearby even- and odd-numbered carbon clusters, they show the same trend as the oligomer size increases. Considering the slow convergency of odd-numbered C_n, in the following we only study the vibrational properties of even-numbered C_n clusters.

Vibrational calculations on medium to long even-numbered C_{2m} clusters are performed at the B3LYP/6-31G* level, with $2m$ up to 64. The dependence of the LO mode frequency with the inverse of the cluster size ($1/2m$) is shown in Figure 12. It is apparent that as the cluster size increases ($1/2m$ decreases), the LO mode frequency decreases until a sharp upturn is observed at $2m = 52$. This critical size is the same as discussed in the transition of the geometry and band gap above. On the basis of the cumulenic C_{2m} ($2m \leq 52$) region, the LO mode frequency is expected to be extrapolated to a very small number at the polymer limit ($1/2m \rightarrow 0$), shown as the dotted line in the figure. This is because all the cumulenic C_{2m} chains have a very small bond length alternation. If the BLA is zero, then the LO mode frequency extrapolation will go exactly to zero. The harmonic LO mode frequency of polyyne at the same theoretical level was recently predicted to be 1795 cm^{-1},[48] labeled as a dark circle on the vertical axis in Figure 12. It is obtained by extrapolating the frequencies of $H-(C{\equiv}C)_m-H$ ($48 \leq 2m \leq 72$) oligoynes to the $1/2m \rightarrow 0$ limit. A series of vibrational calculations on acetylenic C_{2m} linear clusters with $2m > 56$ should be included in the extrapolation to correctly predict the vibrational properties of polyyne. The longer the clusters calculated, the more accurate the extrapolation will be.[49] Currently this cannot be done due to the limitations arising from the aforementioned linear dependence problem and the limitations of computer resources. However, it is clear that the properties of the uncapped long chains and the infinite extrapolated properties of H-capped alternating chains match as accurately as expected. The extrapolation based on shorter C_n oligomers have nothing to do with the properties of very long chains. With properly terminated oligomers, such as the $H-(C{\equiv}C)_m-H$ oligoynes, the convergency of properties is continuous: there is no transition from a qualitatively low alternation to a large alternation as for the C_n chains.

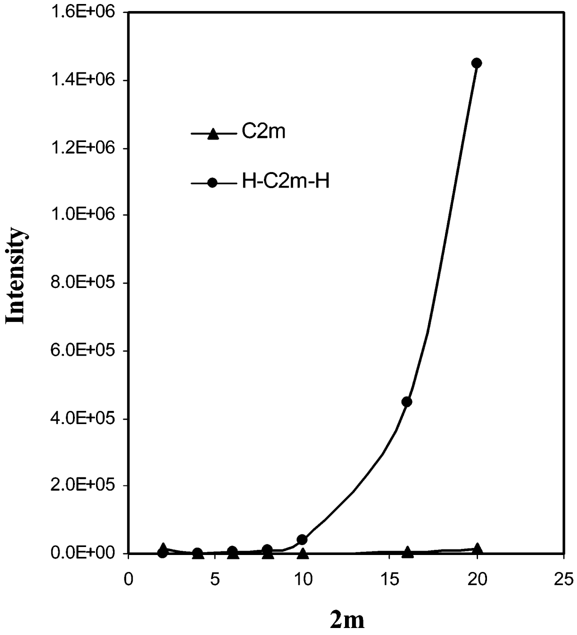

Figure 13. Calculated Raman scattering intensity for the longitudinal optical (LO) mode of linear C_{2m} and $H-C_{2m}-H$ chains as a function of the oligomer size of the chains, at the B3LYP/6-31G* theoretical level.

The LO mode intensity of the carbon chain oligomers is dependent on both the size of the oligomer and the BLA of the chain. Figure 13 shows that at the same size, the LO mode intensity of the hydrogen end-capped oligoynes are much larger than that of the C_n carbon clusters. This is due to the differences in the BLA which is much larger for H-capped chains than for the cumulenic short C_n chains. Analysis shows that the intensity for both oligomer series varies roughly as a power function of the size $2m$, as shown in Figure 14. It is interesting to note that the intensity for the end-capped oligoyne series is proportional to the 5.3 power of the size, roughly doubled compared with the 2.8 power on the size for oligoenes which was analytically derived with Hückel theory.[50]

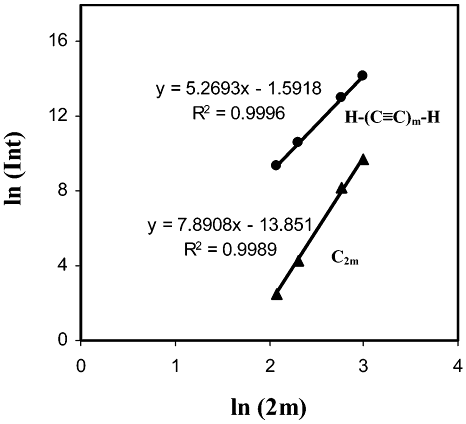

Figure 14. Relationship between the longitudinal optical (LO) mode Raman scattering intensity (Int) and the oligomer size for linear C_{2m} clusters, predicted by B3LYP/6-31G* calculations.

4. Conclusions

With state of the art theoretical calculations, we investigated the properties of long linear carbon clusters. For the first time we observed a transition for long linear C_n chains, from essentially nonalternating cumulenic structures to bond length alternating acetylenic structures. This dramatic structural change is reflected in the very unusual dependences of the HOMO−LUMO gap and the LO mode frequency on the size of the linear carbon clusters. The interpretation of this vibrational band critically depends on the bond length alternation. This mode plays an important role in the IR Raman spectroscopy of linear carbons, including the recently discovered very long carbon chains encapsulated in carbon nanotubes.[51−54] One cannot predict the properties of C_∞ based on the extrapolation from short- and medium-sized C_n chains found in the literature. But with the cumulenic−acetylenic transition found in this work, extrapolations to the properties of infinite C_∞ polyyne can be obtained once sufficiently long C_n chains or chains capped with Hs are studied.

Acknowledgment. Support from the U.S. National Science Foundation (Grant No. DMR-0331710) and the Graduate School Dissertation Fellowship of Georgetown University are gratefully acknowledged.

References and Notes

(1) Kavan, L. *Chem. Rev.* **1997**, *97*, 3061.

(2) *Carbyne and Carbynoid Structures*; Heimann, R. B., Evsyukov, S. E., Kavan L., Eds.; Kluwer: Dordrecht, The Netherlands, 1999.

(3) Baughman, R. H. *Science* **2006**, *312*, 1009.

(4) Shustorovich, E. M. *Zh. Strukt. Khim.* **1965**, *6*, 123.

(5) Kertesz, M.; Koller, J.; Azman, A. *J. Chem. Phys.* **1978**, *68*, 2779.

(6) Karpfen, A. *J. Phys. C: Solid State Phys.* **1979**, *12*, 3227.

(7) Springborg, M. *J. Phys. C: Solid State Phys.* **1986**, *19*, 4473.

(8) Kastner, J.; Kuzmany, H.; Kavan, L.; Dousek, F. P.; Kürti, J. *Macromolecules* **1995**, *28*, 344.

(9) Jacquemin, D.; Champagne, B. *Int. J. Quantum Chem.* **2000**, *80*, 863.

(10) Poulsen, T. D.; Mikkelsen, K. V.; Fripiat, J. G.; Jacquemin, D.; Champagne, B. *J. Chem. Phys.* **2001**, *114*, 5917.

(11) Peierls, R. *Quantum Theory of Solids*; Oxford: Oxford, 1955; p 108.

(12) Rodriguez, K. R.; Williams, S. M.; Young, M. A.; Teeters-Kennedy, S.; Heer, J. M.; Coe, J. V. *J. Chem. Phys.* **2006**, *125*, 194716.

(13) Douglas, A. E. *Nature* **1977**, *269*, 130.

(14) Fulara, J.; Lessen, D.; Freivogel, P.; Maier, J. P. *Nature* **1993**, *366*, 439.

(15) Freivogel, P.; Fulara, J.; Maier, J. P. *Astrophys. J.* **1994**, *431*, L151.

(16) Maier, J. P. *J. Phys. Chem. A* **1998**, *102*, 3462.

(17) Thaddeus, P.; McCarthy, M. C. *Spectrochim. Acta, Part A* **2001**, *57A*, 757.

(18) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713.

(19) Von Helden, G.; Hsu, M.-T.; Kemper, P. R.; Bowers, M. T. *J. Chem. Phys.* **1991**, *95*, 3835.

(20) Von helden, G.; Kemper, P. R.; Gotts, N. G.; Bowers, M. T. *Science* **1993**, *259*, 1300.

(21) Giesen, T. F.; Vanorden, A.; Hwang, H. J.; Fellers, R. S.; Provencal, R. A.; Saykally, R. J. *Science* **1994**, *265*, 756.

(22) Szczepanski, J.; Ekern, S.; Vala, M. *J. Phys. Chem. A* **1997**, *101*, 1841.

(23) Ott, A. K.; Rechtsteiner, G. A.; Felix, C.; Hampe, O.; Jarrold, M. F.; Van Duyne, R. P.; Raghavachari, K. *J. Chem. Phys.* **1998**, *109*, 9652.

(24) Orden, A. V.; Saykally, R. J. *Chem. Rev.* **1998**, *98*, 2313.

(25) Ding, X. D.; Wang, S. L.; Rittby, C. M. L.; Graham, W. R. M. *J. Chem. Phys.* **2000**, *112*, 5113.

(26) Szczepanski, J.; Fuller, J.; Ekern, S.; Vala, M. *Spectrochim. Acta, Part A* **2001**, *57*, 775.

(27) Rechtsteiner, G. A.; Felix, C.; Ott, A. K.; Hampe, O.; Van Duyne, R. P.; Jarrold, M. F.; Raghavachari, K. *J. Phys. Chem. A* **2001**, *105*, 3029.

(28) Neubauer-Guenther, P.; Giesen, T. F.; Berndt, U.; Fuchs, G.; Winnewisser, G. *Spectrochim. Acta, Part A* **2002**, *59*, 431.

(29) Gakwaya, S.; Abusara, Z.; Moazzen-Ahmadi, N. *Chem. Phys. Lett.* **2004**, *398*, 564.

(30) Fulara, J.; Shnitko, I.; Batalov, A.; Maier, J. P. *J. Chem. Phys.* **2005**, *123*, 044305.

(31) Nicolas, C.; Shu, J.; Peterka, D. S.; Hochlaf, M.; Poisson, L.; Leone, S. R.; Ahmed, M. *J. Am. Chem. Soc.* **2006**, *128*, 220.

(32) Neubauer-Guenther, P.; Giesen, T. F.; Schlemmer, S.; Yamada, K. M. T. *J. Chem. Phys.* **2007**, *127*, 014313.

(33) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian Inc.; Wallingford, CT, 2004.

(35) Baroni, S.; Dal Corso, A.; de Gironcoli, S.; Giannozzi, P.; Cavazzoni, C.; Ballabio, G.; Scandolo, S.; Chiarotti, G.; Focher, P.; Pasquarello, A.; Laasonen, K.; Trave, A.; Car, R.; Marzari, N.; Kokalj, A. PWsci Home Page. http://www.pwscf.org/.

(36) Löwdin, P.-O. *Adv. Phys.* **1965**, *5*, 1.

(37) Cox, S. B.; Fry, J. L. *J. Comput. Phys.* **1977**, *23*, 42.

(38) Karpfen, A. *Chem. Phys. Lett.* **1979**, *61*, 363.

(39) Suhai, S.; Bagus, P. S.; Ladik, J. *Chem. Phys.* **1982**, *68*, 467.

(40) Kudin, K. N.; Scuseria, G. E. *Phys. Rev. B* **2000**, *61*, 16440.

(41) Yang, S.; Kertesz, M. *J. Phys. Chem. A* **2006**, *110*, 9771.

(42) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(43) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(44) (a) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem.* **1996**, *100*, 6047. (b) Botschwina, P. *Chem. Phys. Lett.* **2006**, *421*, 488. (c) Botschwina, P. *J. Phys. Chem. A* **2007**, *111*, 7431.

(45) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(46) Hinkle, K. W.; Keady, J. J.; Bernath, P. F. *Science* **1988**, *241*, 1319.

(47) See, e.g.: (a) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Saunders College: Philadelphia, PA, 1976. (b) Burns, G. *Solid State Physics*; Academic: Boston, MA, 1990.

(48) Yang, S.; Kertesz, M.; Zolyomi, V.; Kurti, J. *J. Phys. Chem. A* **2007**, *111*, 2434.

(49) Zade, S. S.; Bendikov, M. *Org. Lett.* **2006**, *8*, 5243.

(50) Hameka, H. F. *J. Chem. Phys.* **1977**, *67*, 2935.

(51) Wang, Z.; Ke, X.; Zhu, Z.; Zhang, F.; Ruan, M.; Yang, J. *Phys. Rev. B* **2000**, *61*, R2472.

(52) Zhao, X.; Ando, Y.; Liu, Y.; Jinno, M.; Suzuki, T. *Phys. Rev. Lett.* **2003**, *90*, 187401.

(53) Jinno, M.; Ando, Y.; Bandow, S.; Fan, J.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2006**, *418*, 109.

(54) Cazzanelli, E.; Castriota, M.; Caputi, L. S.; Cupolillo, A.; Giallombardo, C.; Papagno, L. *Phys. Rev. B* **2007**, *75*, 121405.