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## The Structure and C=C Vibrational Frequencies of the all- trans Polyenes $C_{2n}H_{2n+2}$ ( $n=2-15$ ), $C_{2n}H_{2n}(Me)_2$ ( $n=2-13$ ), and $C_{2n}H_{2n}(tert\text{-Butyl})_2$ ( $n=2-5$ ): Computational Results

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**The Structure and C=C Vibrational Frequencies of the all-*trans* Polyenes C<sub>2n</sub>H<sub>2n+2</sub>(n=2-15), C<sub>2n</sub>H<sub>2n</sub>(Me)<sub>2</sub>(n=2-13), and C<sub>2n</sub>H<sub>2n</sub>(*tert*-Butyl)<sub>2</sub>(n=2-5): Computational Results**

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## Abstract

Carbon-carbon bond lengths and C=C vibrational frequencies are reported for the linear, all-*trans* unsubstituted  $C_{2n}H_{2n+2}$  ( $n=2-15$ ), methyl capped  $C_{2n}H_{2n}Me_2$  ( $n=2-13$ ), and *tert*-butyl capped  $C_{2n}H_{2n}(tert\text{-butyl})_2$  ( $n=2-5$ ) polyenes ( $C_{2h}$ ) calculated at the B3LYP/6-311++G(*d,p*) level. The C=C/C–C bond length alternation remains evident at this level for the unsubstituted and methyl capped polyenes as the chain length increases; the center-most difference in the length of the C–C/C=C bonds is  $\sim 0.06$  Å for  $C_{30}H_{32}$  and  $C_{26}H_{26}Me_2$ . The  $A_g$ , in-phase, harmonic C=C Raman frequency for the unsubstituted polyenes decreases from  $1699.2$   $cm^{-1}$  ( $n=2$ ) to  $1528.9$   $cm^{-1}$  ( $n=15$ ); the anharmonic frequency decreases from  $1651.5$   $cm^{-1}$  ( $n=2$ ) to  $1547.7$   $cm^{-1}$  ( $n=8$ ). The harmonic C=C frequency for the methyl capped polyenes decreases from  $1717.9$   $cm^{-1}$  ( $n=2$ ) to  $1539.6$   $cm^{-1}$  ( $n=13$ ), and the anharmonic C=C frequency decreases from  $1675.0$   $cm^{-1}$  ( $n=2$ ) to  $1562.8$   $cm^{-1}$  ( $n=7$ ).

## Key Words

All-*trans* polyenes

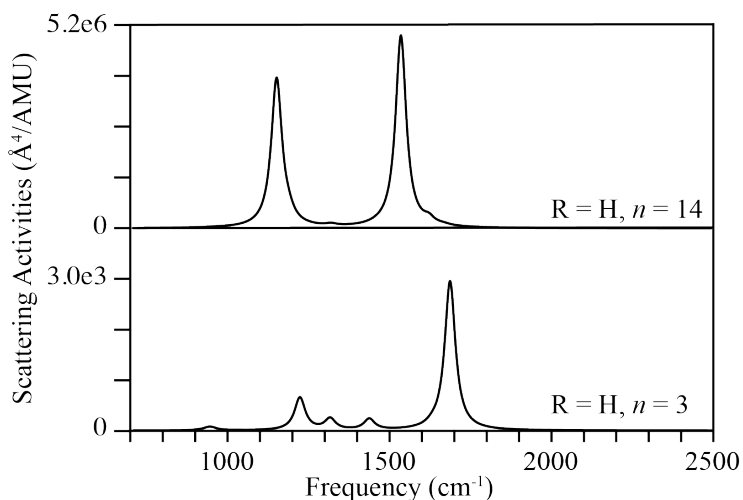
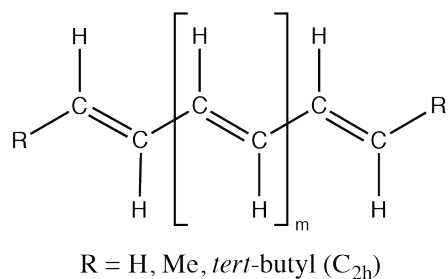
Carbon-carbon bond lengths

Anharmonic frequencies

Density functional theory (DFT)

B3LYP/6-311++G(*d,p*)

## Graphical Abstract



## Specification Table

<b>Subject area</b>	<b>Computational Chemistry</b>
<b>Compounds</b>	<b>All-<i>trans</i> polyenes</b>
<b>Data category</b>	<b>Quantum chemical calculations</b>
<b>Data acquisition format</b>	<b>DFT, DCPT2</b>
<b>Data type</b>	<b>Simulated</b>
<b>Procedure</b>	<b>Simulated</b>
<b>Data accessibility</b>	<b>Data provided in article</b>

## I. Rationale

Polyenes and their derivatives are ubiquitous in living organisms where they play important structural and regulatory functions in a variety of biological processes, including photosynthesis and vision [1-3]. Polyenes also play critical roles in pericyclic reactions, in homodesmotic reactions for the thermodynamic evaluations of aromaticity and strain energies, and in polymer science [4-10]. When doped, longer polyenes act as electrical conductors. These conducting conjugated polymers have found numerous applications in plastic electronic devices, including transistors and solar cells [11-13]. Refining our knowledge of how the structures and vibrational spectra of conjugated linear polyenes depend on the length of the chain will enhance our understanding of their function.

The primary data set reported in this paper includes calculated C=C vibrational frequencies of the all-*trans* unsubstituted linear polyenes,  $C_{2n}H_{2n+2}$  ( $n=2-15$ ) ( $C_{2h}$ ), as a function of chain length. Where possible, comparisons are made with experimental data, but such data are available only for the first few members of the series [14-24]. Computational studies have been extremely helpful in interpreting and augmenting the available experimental data [23-30]. Fortunately, Raman C=C vibrational in-phase stretching frequencies have been observed for the related *tert*-butyl capped polyenes,  $C_{2n}H_{2n}(tert\text{-Butyl})_2$  ( $n=3-12$ ) [31,32]; this totally symmetric mode has been implicated in vibronic coupling involving the  $1A_g$  and  $2A_g$  states of polyenes [33,34]. Since *tert*-butyl groups at the ends of the polyene chains proved computationally demanding, we only report C=C frequencies of  $C_{2n}H_{2n}(tert\text{-Butyl})_2$  ( $C_{2h}$ ) for  $n=2-5$ . However, calculated C=C frequencies for all-*trans* methyl-capped polyenes,  $C_{2n}H_{2n}(Me)_2$  ( $C_{2h}$ ) for  $n=2-13$  are included in the data collection

for comparison with the unsubstituted polyenes, see Figure 1 for a typical methyl-capped  $C_{2h}$  structure.

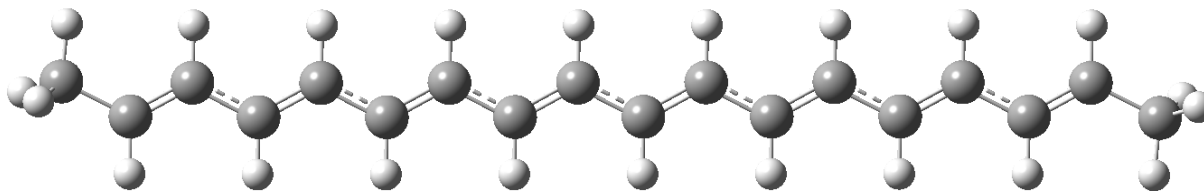


Figure 1. Structure of all-*trans*  $C_{16}H_{16}Me_2$  ( $C_{2h}$ ).

Since it was necessary to geometry optimize all the polyenes prior to calculating the frequencies, we also report carbon-carbon bond lengths and discuss the degree of C=C/C–C bond length alternation (BLA), a key geometrical parameter for conjugated molecules and polymers [35-39], closely correlated to electronic properties such as linear polarizability, first hyperpolarizability, and two-photon absorption phenomena [35-38,40].

## II. Procedure

The geometries of all the polyenes reported in this study were optimized using density functional theory (DFT) at the B3LYP/6-311++G(*d,p*) theoretical quantum-mechanical level [41-43]. The optimizations were performed using Gaussian 09 (Revision D.01 Win64) in conjunction with Gauss View 5.0 [44]; the “tight” option was used in all cases. Harmonic frequency analyses at this level confirm that the  $C_{2n}H_{2n+2}$  ( $n=2-14$ ) optimized structures are local minima on the potential energy surface (PES). (Raman intensities were also calculated in all cases.) Surprisingly, for  $n=15$  the  $C_{2h}$  structure proved to be a first-order transition state (the harmonic frequency of the lowest  $A_u$  mode was  $3.3i\text{ cm}^{-1}$ ); re-optimization of this  $C_{30}H_{32}$  structure with no symmetry constraints using Cartesian coordinates yielded a non-planar local minimum, although the torsional angles typically deviated from their corresponding planar values by less than  $\sim 0.5^\circ$ . It is not clear if this behavior is a consequence of using the B3LYP functional, the 6-311++G(*d,p*) basis set, grid sizes employed in the calculations, *etc.* Extensive unpublished calculations for all  $C_{2n}H_{2n+2}$  ( $n=2-15$ ) unsubstituted polyenes on various *Cis* (around C=C) conformers and *gauche* (around C–C) rotamers of  $C_{2n}H_{2n+2}$  ( $n=2-15$ ) consistently found the all-*trans* forms to be lowest in energy.

Significant experimental and computational progress has been made in assigning the vibrational spectra of the smaller linear polyenes. Computationally, two distinct approaches have been used: Pulay scaling procedures [25,29,45-50] and anharmonic calculations [23,51]. An extraordinary collection of articles involving new infrared and Raman gas-phase spectral data coupled with high-level anharmonic calculations by Craig *et al.* [24,52,53], Krasnoshchekov *et al.* [23,54], and Boopalachandran, *et al.* [55,56] have revealed new spectral details of 1,3-butadiene and 1,3,5-hexatriene. In this article, we concentrate on trends in the C=C vibrational frequencies as the length of the chain increases. When permitted by our computational resources, anharmonic calculations were carried out using vibrational second-order perturbation theory (VPT2) [51,57]. The structures were initially reoptimized at the B3LYP/6-311++G(*d,p*) computational level using the “integral=ultrafine” and “tight” options. (The use of the ultrafine grid has only a minor effect on the calculated harmonic frequencies (typically  $<1\text{ cm}^{-1}$ ) [58].) The degeneracy-corrected second-order perturbation theory (DCPT2) model was consistently employed for these anharmonic calculations (Martin test, DPT2Var=0.01  $\text{cm}^{-1}$ ; minimum value for Darling-Dennison term, DaDeMin=100.0  $\text{cm}^{-1}$ ) [44,59,60]. VPT2 methodology uses a Taylor expansion of the electronic energy in powers of the rectilinear normal coordinates at the equilibrium geometry. The expansion is truncated at the fourth order and quartic force constants with four different indices are omitted. As clearly pointed out in the work of Krasnoshchekov *et al.* [61] there can be problems with this approach, particularly the proper choice and treatment of vibrational resonances that manifest themselves both in the first order (Fermi resonances and associated *W*-constants) and in the second order (Darling-Dennison resonances, *K*-constants). Thus, the anharmonic results presented here must be considered a first step in the analysis of the C=C frequencies for the polyenes. The calculated DCPT2 anharmonic frequencies for  $n=2-6$  were all positive for the planar structures, but for  $n=7$  and 8, one small anharmonic imaginary frequency was found in each case associated with a torsional mode having a small positive harmonic frequency.

### III. Data, value and validation

#### A. C=C and C-C Bond Lengths

Progress has been made over the past few years in refining the structural parameters of the early members of the linear polyene series. Specifically, “semi-experimental” equilibrium ( $r_e^{SE}$ ) structures of *s-trans*-1,3-butadiene [62] and *tTt*-1,3,5-hexatriene [63] have been reported, see Table 1. (The notations “*trans(t)*” and “*Trans(T)*” are used for substituents relative to classical single C–C and double C=C bonds, respectively.) In this approach, high-level geometry optimizations are initially performed and corrected for possible deficiencies in the methodology employed. Next, the observed ground state rotational constants are adjusted to the required equilibrium rotational constants using quantum chemical calculations [64]. In addition to these semi-experimental structures, high-level geometry optimizations have also been reported at a consistent level for *tTt*-1,3,5-hexatriene and *tTtTt*-1,3,5,7-octatetraene [63,64], see Table 2. These highly accurate results are essential for assessing the reliability of lower level calculations.

In Table 3 we list calculated B3LYP/6-311++G(*d,p*) C=C and C–C bond lengths for the all-*trans* polyenes  $C_{2n}H_{2n+2}$  ( $n=2-15$ ), the methyl capped all-*trans* polyenes  $C_{2n}H_{2n}Me_2$  ( $n=2-13$ ), and the *tert*-butyl capped polyenes  $C_{2n}H_{2n}(tert\text{-Butyl})_2$  ( $n=2-5$ ). Similar results for some of the unsubstituted all-*trans* polyenes for have been reported by Schettino *et al.* [65], Choi *et al.* [36], Fogarasi *et al.* [66], and Hirata *et al.* [67]. Comparing the data given in Tables 1-3 for  $C_{2n}H_{2n+2}$  ( $n=2-4$ ), it is evident that there is reasonable agreement with the calculated B3LYP/6-311++G(*d,p*) carbon-carbon bond lengths and the corresponding semi-experimental and/or higher-level estimates.

The decrease of the BLA toward the middle of the chain is evident in Table 3. Furthermore, as has been noted previously [35-38,40,57-60], this BLA approaches an asymptotic value as the chain lengthens, *e.g.* the values of  $|\Delta(r(C=C) - r(C-C))|$  for the center-most bonds are 0.1179, 0.0991, 0.0867, 0.0799, 0.0747, 0.0712, 0.0684, 0.0664, 0.0646, 0.0634, 0.0622, 0.0614, 0.0607, 0.0601 Å for  $C_{2n}H_{2n+2}$  ( $n=2-15$ ), and 0.1133, 0.0971, 0.0858, 0.0783, 0.0742, 0.0710, 0.0690, 0.0662, 0.0645, 0.0633, 0.0621, 0.0613 Å for  $C_{2n}H_{2n}Me_2$  ( $n=2-13$ ).

## B. C=C Frequencies

The available experimental  $A_g$  and  $B_u$  C=C frequencies for the unsubstituted linear polyenes are given in Table 4; clearly the spectral data for these polyenes are quite limited,  $n=2-5$ , and incomplete. In Table 5 we list the calculated harmonic (no scaling) and, where possible, the corresponding DCPT2 anharmonic B3LYP/6-311++G( $d,p$ )  $A_g$  and  $B_u$  C=C stretching frequencies for the all-*trans* polyenes ( $C_{2h}$ ):  $C_{2n}H_{2n+2}$  ( $n=2-15$ ),  $C_{2n}H_{2n}Me_2$  ( $n=2-13$ ), and  $C_{2n}H_{2n}(tert\text{-Butyl})_2$  ( $n=2-5$ ); the Raman scattering activities for the  $A_g$  modes, IR intensities for the  $B_u$  modes, and C=C stretching phases for all modes ((+) for stretch and (-) for contraction) are also included in Table 5. Our calculated anharmonic C=C frequencies for butadiene and hexatriene are consistent with those reported by other authors [23,24,52,53] and are in reasonable agreement with experiment, considering limitations in the basis set, approximations inherent with in the DCPT2 methodology, grid sizes employed in the calculations, *etc.*

Additional Raman C=C vibrational frequencies have been reported for the related *tert*-butyl-capped polyenes,  $C_{2n}H_{2n}(tert\text{-Butyl})_2$  ( $n=3-12$ ). These have been assigned to the in-phase C=C stretching mode [31], see Table 6. Also included in Table 6 are the calculated anharmonic frequencies for  $C_{2n}H_{2n+2}$  ( $n=2-8$ ),  $C_{2n}H_{2n}Me_2$  ( $n=2-7$ )( $C_{2h}$ ), and  $C_{2n}H_{2n}(tert\text{-Butyl})_2$  ( $n=2-4$ )( $C_{2h}$ ). The  $A_g$  totally symmetric C=C peak in the resonant Raman spectra of the structurally related carotenoids is sensitive to the length of the conjugated chain [32,68-71]. Merlin [68] quantified this relationship as

$$\nu_{C=C} = 1459 + 720/(n+1),$$

where  $n$  is the number of C=C bonds in the chain [72]. The C=C frequencies from Merlin's relationship are also given in Table 6.

The calculated B3LYP/6-311++G( $d,p$ ) level harmonic and anharmonic totally symmetric  $A_g$  frequency decreases dramatically as the length of the chain increases (harmonic,  $1692.6\text{ cm}^{-1}$  ( $n=2$ ) to  $1528.9\text{ cm}^{-1}$  ( $n=15$ ), see Table 5; anharmonic,  $1651.5\text{ cm}^{-1}$  ( $n=2$ ) to  $1547.7\text{ cm}^{-1}$  ( $n=8$ ), see Table 6), in agreement with the available experimental data. The calculated Raman scattering activity is largest for the fully symmetric  $A_g$  mode in all cases and increases markedly as the length of the chain increases,  $399.6\text{ \AA}^4/\text{AMU}$  ( $n=2$ ) to  $7,119,931.9\text{ \AA}^4/\text{AMU}$  ( $n=15$ ), see Table 5. It may



be noted that for *tTt*-hexatriene the calculated anharmonic C=C totally symmetric frequencies of the unsubstituted, methyl capped, and *tert*-butyl capped polyenes are nearly the same, see Table 6; this is also the case for *tTtTt*-octatetraene.

The highest calculated C=C harmonic frequencies for  $C_{2n}H_{2n+2}$  ( $n=2-15$ ) with  $B_u$  symmetry have the highest IR intensities, and consistently involve all C=C bonds stretching on one side of the chain while compressing on the other side, see Table 5. The lowest calculated C=C harmonic frequency with  $B_u$  symmetry for these polyenes has a very low IR intensity, and the phase typically alternates on each side.

#### IV. Conclusions

Carbon-carbon bond lengths, C=C harmonic and, where possible, DCPT2 anharmonic vibrational frequencies are reported at the B3LYP/6-311++G(*d,p*) computational level for the linear, conjugated, all-*trans* unsubstituted polyenes  $C_{2n}H_{2n+2}$  ( $n=2-15$ ) ( $C_{2h}$ ), the methyl capped polyenes  $C_{2n}H_{2n}Me_2$  ( $n=2-13$ ) ( $C_{2h}$ ), and the *tert*-butyl capped polyenes  $C_{2n}H_{2n}(tert\text{-Butyl})_2$  ( $n=2-5$ )( $C_{2h}$ ). The C=C/C-C BLA is manifest at this computational level,  $\sim 0.06$  Å for both the longer unsubstituted and methyl capped polyenes. The calculated B3LYP/6-311++G(*d,p*) DCPT2 anharmonic C=C frequencies for the  $A_g$  in-phase modes agree reasonably well with the available experimental values. They are the lowest C=C frequencies for  $n > 8$ , with the highest Raman scattering activity. The latter increases dramatically with lengthening of the polyene chain.

## Tables

**Table 1.** Semi-experimental  $r_e^{\text{SE}}$  C=C and C–C Bond Lengths (Å) for Ethylene, *s-trans*-1,3-Butadiene, and *tTt*-1,3,5-Hexatriene.

Ethylene <sup>a</sup>	1.3305(10)		
<i>s-trans</i> -1,3-Butadiene <sup>a</sup>	1.3376(10)	1.4539(10)	
<i>tTt</i> -1,3,5-Hexatriene <sup>b</sup>	1.3390(8)	1.4494(7)	1.3461(14)

<sup>a</sup> Ref [62].

<sup>b</sup> Ref [63]. The bond lengths in Table 1 used the MP2/VTZ level of theory to calculate the cubic force field; if the B3LYP/VTZ level of theory is used, the corresponding values are 1.3389(9), 1.4495(9), and 1.3462(16) Å.

**Table 2.** Theoretical CCSD(T)(FC)/cc-pVTZ (upper) and  $r_e(\text{I})^{\text{a,b}}$  (lower) C=C and C–C Bond Lengths (Å) for *tTt*-1,3,5-Hexatriene and *tTtTt*-1,3,5,7-Octatetraene.<sup>c</sup>

<i>tTt</i> -1,3,5-Hexatriene <sup>b</sup>	1.3455	1.4557	1.3517	
	1.3401	1.4503	1.3465	
<i>tTtTt</i> -1,3,5,7-Octatetraene <sup>b</sup>	1.3460	1.4544	1.3537	1.4495
	1.3406	1.4488	1.3485	1.4441

<sup>a</sup>  $r_e(\text{I}) = \text{CCSD(T)}(\text{FC})/\text{cc-pVTZ} + [\text{MP2}(\text{FC})/\text{cc-pVQZ} - \text{MP2}(\text{FC})/\text{cc-pVTZ}] + [\text{MP2}(\text{FULL})/\text{cc-pwCVQZ} - \text{MP2}(\text{FC})/\text{cc-pwCVQZ}]$

<sup>b</sup> Ref [63].

<sup>c</sup> The corresponding CCSD(FC)/cc-pVDZ optimized bond lengths for *s-trans*-1,3-butadiene and *tTt*-1,3,5-hexatriene are 1.3366 Å, 1.4621 Å and 1.3378 Å, 1.4575 Å 1.3429 Å respectively (this work).

**Table 3.** The C=C and C–C Bond Lengths (Å) of the All-*trans* Unsubstituted Polyenes  $C_{2n}H_{2n+2}$  ( $C_{2h}$ ) ( $n=2-15$ ), (Methyl-Capped Polyenes,  $C_{2n}H_{2n}(Me)_2$  ( $C_{2h}$ ) ( $n=2-13$ )), and [*tert*-Butyl-Capped Polyenes,  $C_{2n}H_{2n}(Tert-Butyl)_2$  ( $C_{2h}$ ) ( $n=2-5$ )] Calculated at the B3LYP/6-311++G(*d,p*) Computational Level (Integral=Fine).<sup>a,b,c,d</sup>

n	C=C	C–C	C=C	C–C	C=C	C–C	C=C	C–C	C=C	C–C	C=C	C–C	C=C	C–C	C=C
1 <sup>e</sup>	1.3289														
2 <sup>f</sup>	1.3383 (1.3410) [1.3409]	1.4562 (1.4543) [1.4570]													
3 <sup>g</sup>	1.3410 (1.3433) [1.3433]	1.4488 (1.4477) [1.4491]	1.3497 (1.3506) [1.3504]												
4 <sup>h</sup>	1.3420 (1.3444) [1.3443]	1.4465 (1.4454) [1.4468]	1.3531 (1.3538) [1.3537]	1.4398 (1.4396) [1.4400]											
5	1.3425 (1.3479) [1.3447]	1.4455 (1.4449) [1.4458]	1.3546 (1.3561) [1.3550]	1.4369 (1.4361) [1.4370]	1.3570 (1.3578) [1.3573]										
6	1.3428 (1.3451)	1.4450 (1.4438)	1.3554 (1.3559)	1.4355 (1.4353)	1.3588 (1.3592)	1.4335 (1.4334)									
7	1.3429 (1.3452)	1.4447 (1.4435)	1.3557 (1.3563)	1.4248 (1.4346)	1.3597 (1.3600)	1.4319 (1.4319)	1.3607 (1.3609)								
8	1.3430 (1.3453)	1.4445 (1.4433)	1.3560 (1.3566)	1.4343 (1.4341)	1.3602 (1.3605)	1.4310 (1.4310)	1.3617 (1.3620)	1.4301 (1.4310)							
9	1.3431 (1.3453)	1.4444 (1.4432)	1.3561 (1.3567)	1.4341 (1.4339)	1.3605 (1.3608)	1.4305 (1.4305)	1.3623 (1.3625)	1.4292 (1.4292)	1.3628 (1.3630)						
10	1.3431 (1.3454)	1.4444 (1.4431)	1.3563 (1.3568)	1.4339 (1.4337)	1.3608 (1.3610)	1.4302 (1.4301)	1.3627 (1.3629)	1.4286 (1.4285)	1.3635 (1.3636)	1.4281 (1.4281)					
11	1.3431 (1.3454)	1.4443 (1.4431)	1.3563 (1.3568)	1.4338 (1.4336)	1.3608 (1.3611)	1.4300 (1.4299)	1.3629 (1.3631)	1.4282 (1.4282)	1.3638 (1.3640)	1.4275 (1.4275)	1.3641 (1.3642)				
12	1.3432 (1.3455)	1.4443 (1.4430)	1.3564 (1.3569)	1.4337 (1.4335)	1.3610 (1.3612)	1.4298 (1.4297)	1.3631 (1.3633)	1.4280 (1.4279)	1.3641 (1.3643)	1.4271 (1.4271)	1.3646 (1.3647)	1.4268 (1.4268)			
13	1.3431 (1.3455)	1.4443 (1.4430)	1.3564 (1.3570)	1.4337 (1.4334)	1.3610 (1.3613)	1.4298 (1.4296)	1.3631 (1.3634)	1.4278 (1.4278)	1.3643 (1.3644)	1.4268 (1.4268)	1.3648 (1.3650)	1.4264 (1.4264)	1.3650 (1.3651)		
14	1.3432	1.4443	1.3564	1.4337	1.3611	1.4297	1.3633	1.4277	1.3644	1.4266	1.3650	1.4261	1.3653	1.4260	
15 <sup>d</sup>	1.3432	1.4442	1.3564	1.4336	1.3611	1.4296	1.3633	1.4276	1.3645	1.4265	1.3652	1.4259	1.3655	1.4257	1.3656

<sup>a</sup> The default (fine) grid size was employed for all these optimizations, along with opt=(calcall, tight).

<sup>b</sup> The calculated C=C bond length of ethylene ( $n=1$ ) is included for comparison.

<sup>c</sup> The B3LYP/6-311++G(*d,p*) carbon-carbon bond lengths for benzene are 1.3947 Å.

<sup>d</sup> The optimized structure is slightly non-planar for  $C_{30}H_{32}$  at this computational level; the planar  $C_{2h}$  form is first-order transition state.

<sup>e</sup> A semi-experimental  $r_e$  C=C bond length is 1.3305(10) Å [62].

<sup>f</sup> Semi-experimental carbon-carbon  $r_e$  bond lengths are: 1.3376(10) Å; 1.4539(10) Å [62].

<sup>g</sup> Semi-experimental carbon-carbon  $r_e$  bond lengths are: 1.3390(8) Å; 1.4494(7) Å; 1.3461 Å [63].

<sup>h</sup> Semi-experimental carbon-carbon  $r_e$  bond lengths are: 1.3406 Å; 1.4488 Å; 1.3485 Å; 1.4441 Å [63].

**Table 4.** Experimental C=C frequencies ( $\text{cm}^{-1}$ ) for All-*Trans*  $\text{C}_{2n}\text{H}_{2n+2}$  ( $n=2-5$ ).

Polyene	$A_g$	$B_u$
<i>s-trans</i> -1,3-Butadiene	1644.3 <sup>a</sup> vvs	1596.45 <sup>a</sup> s
<i>tTt</i> -1,3,5-Hexatriene	v5 1625 <sup>b</sup> vs, p v6 1576 <sup>b</sup> m,p  v5 1623 <sup>b,c</sup> vs, p v6 1574 <sup>b,c</sup> m, p  v5 1626 <sup>g</sup> vs v6 1576 <sup>g</sup> m	v29 1630 <sup>b</sup> s,A  v29 1629 <sup>c</sup> [s],A  v29 1624 s
<i>tTtTt</i> -1,3,5,7-octatetraene	v6 1613 <sup>d</sup> vs v7 (1613) <sup>d,e</sup>	v38 1632 <sup>d</sup> s v39 (1558,1569) <sup>d</sup> m
<i>tTtTtTt</i> -1,3,5,7,9-decapentaene	v7 1621 <sup>f</sup> w v8 1593 <sup>f</sup> vs	v47 1626 <sup>f</sup> m v48 1595 <sup>f</sup> m

<sup>a</sup> Ref [23].

<sup>b</sup> Ref [24].

<sup>c</sup> Ref [17].

<sup>d</sup> Ref [21].

<sup>e</sup> Probably hidden by the strong band at  $1613 \text{ cm}^{-1}$ .

<sup>f</sup> Ref [22].

<sup>g</sup> Ref [73].

**Table 5.** The C=C Unscaled Harmonic (Anharmonic) Frequencies ( $\text{cm}^{-1}$ ), Raman Scattering Activities ( $\text{\AA}^4/\text{AMU}$ ), IR Intensities (KM/Mol), and C=C Phases of the Unsubstituted All-*Trans*  $\text{C}_{2n}\text{H}_{2n+2}$  ( $\text{C}_{2n}$ ) Polyenes ( $n=2-15$ ), the {Corresponding Methyl Capped  $\text{C}_{2n}\text{H}_{2n}(\text{Me})_2$  Polyenes ( $\text{C}_{2n}$ ) ( $n=2-13$ )}, and the [*tert*-Butyl Capped  $\text{C}_{2n}\text{H}_{2n}(\text{tert-Butyl})_2$  Polyenes ( $n=2-5$ ) ( $\text{C}_{2n}$ )] Calculated at the B3LYP/6-311++G(*d,p*) Computational Level.

n	$A_g$			$B_u$		
	Frequency ( $\text{cm}^{-1}$ )	Raman Scattering Activity ( $\text{\AA}^4/\text{AMU}$ )	C=C Phase	Frequency ( $\text{cm}^{-1}$ )	IR Intensity (KM/Mol)	C=C Phase
	Grid=Ultrafine	Grid-Fine		Grid=Ultrafine	Grid-Fine	
1	1683.6(1653.4)	30.4	+			
2	1699.2(1651.5) {1717.9(1675.0)} [1706.8(1668.3)]	399.6 {1682.9} [1450.0]	++ {++} [++]	1645.5(1610.6) {1683.1(1643.7)} [1672.3(1632.0)]	24.5 {5.8} [3.3]	+− {+−} [+−]
3	1684.3(1645.7) 1628.4(1592.3) {1690.9(1647.9)} {1649.3(1608.8)} [1684.1(1646.0)] [1643.9(1607.5)]	2994.4 37.9 {4632.8} {102.6} [7832.6] [4.9]	+++ +−+ {+++} {+−+} +++ +−+	1678.8(1642.5) {1705.1(1659.9)} [1694.6(1653.9)]	37.3 {10.7} [9.4]	+0− {+0−} [+0−]
4	1663.0(1629.1) 1660.0(1619.0) {1687.8(1646.4)} {1660.2(1617.0)} [1678.1(1635.0)] [1659.6(1616.8)]	4357.5 6782.7 {2404.8} {14910.9} [2014.5] [24326.7]	+−+ ++++ {+−+} {++++} [+−+] [++++]	1686.4(1646.3) 1614.9(1587.4) {1701.6(1660.2)} {1627.6(1592.0)} [1693.4(1661.3)] [1623.9(1661.3)]	38.0 15.4 {18.9} {1.1} [19.6] [1.2]	+−+− +−+− {+−+−} {+−+−} [+−+−] [+−+−]
5	1677.4(1640.7) 1639.6(1599.8) 1604.5(1571.0) {1686.9(1641.9)} {1635.0(1592.9)} {1605.3(1569.6)} [1687.7] [1637.5] [1609.7]	610.8 32909.2 25.9 {1782.8} {41821.8} {384.1} [2991.3] [65747.5] [1.5]	+−+−+ ++++ +−+−+ {+−+−+} {++++} {+−+−+}	1681.2(1640.0) 1647.6(1611.2) {1684.0(1641.3)} {1654.2(1613.2)} [1683.9] [1660.1]	34.7 31.8 {11.4} {11.6} [35.6] [1.3]	+−+−+ +−+−+ {+−+−+} {+−+−+} [+−+−+] [+−+−+]
6	1681.5(1641.1) 1636.2(1602.6) 1619.8(1579.2) {1695.5(1650.2)} {1649.0(1609.7)} {1618.4(1577.6)}	2148.2 77.7 80545.5 {5403.7} {67.6} {106841.3}	+−+−+ +−+−+ ++++ {+−+−+} {+−+−+} {++++}	1670.4(1629.5) 1666.3(1630.4) 1595.9(1565.3) {1689.6(1646.2)} {1668.5(1624.3)} {1600.7(1563.7)}	37.0 35.7 8.1 {38.6} {12.1} {1.1}	+−+−+ +−+−+ +−+−+ {+−+−+} {+−+−+} {+−+−+}

7	1679.0(1634.6)	5222.3	+-+--+	1675.8(1631.6)	48.9	+-+0+-
	1656.2(1617.6)	76.8	+--+--	1657.9(1617.8)	23.0	+++0---
	1603.0(1563.4)	172922.4	++++++	1626.4(1591.1)	22.0	+--+0+-
	1589.0(1554.6)	1.5	+--+--+			
	{1691.8(1650.3)}	{10033.7}	{+--+--+}	{1692.6(1656.9)}	{38.2}	{+-+0+-}
{1666.8(1624.6)}	{480.5}	{+--+--+}	{1657.4(1610.6)}	{33.8}	{+++0---	
{1601.7(1562.8)}	{219327.3}	{++++++}	{1636.0(1598.0)}	{1.12}	{+--+0+-}	
{1592.0(1551.3)}	{1337.7}	{+--+--+}				
8	1673.4(1633.2)	11129.9	+++--+	1678.6(1638.5)	50.7	+-+--+
	1667.8(1620.3)	77.4	+--+--	1647.5(1610.4)	8.7	+--++-
	1618.1(1583.8)	3.6	+--+--+	1644.5(1602.2)	44.0	++++---
	1588.4(1547.7)	334658.3	++++++	1583.4(1550.5)	4.3	+--++-
	{1690.3}	{12604.9}	{++++--+}	{1692.4}	{46.3}	{+-+--+}
{1669.6}	{6681.8}	{+--+--+}	{1657.1}	{3.4}	{+--++-}	
{1625.2}	{21.6}	{+--+--+}	{1644.0}	{46.9}	{++++---	
{1586.7}	{414592.3}	{++++++}	{1585.1}	{0.6}	{+--++-}	
9 <sup>a</sup>	1675.4	4667.9	+-+--+	1677.9	53.9	+-+0+-
	1664.9	16177.2	+++--+	1660.8	30.9	+--++-
	1639.1	137.0	+--+--+	1633.2	21.4	++++0---
	1579.1	943.2	+--+--+	1611.4	13.9	+--+0+-
	1576.3	598100.0	++++++			
{1692.0}	{13655.6}	{++++--+}	{1691.8}	{59.3}	{+-+0+-}	
{1664.4}	{19472.1}	{+++--+}	{1667.9}	{0.1}	{+--++-}	
{1647.8}	{140.4}	{+--+--+}	{1632.4}	{64.9}	{++++0---	
{1580.3}	{2767.0}	{+--+--+}	{1616.8}	{0.7}	{+-+0+-}	
{1575.1}	{720199.5}	{++++++}				
10 <sup>a</sup>	1677.1	6285.3	+-+--+	1674.5	75.7	+-+--+
	1656.1	26210.6	+++--+	1668.0	13.0	+--++-
	1652.8	3867.8	+0--+0+	1631.3	20.2	+++--+
	1604.7	11.2	+--+--+	1621.2	21.9	++++---
	1564.9	1006481.6	++++++	1574.5	2.4	+--++-
{1691.3}	{16737.5}	{+-+--+}	{1690.5}	{67.6}	{+-+--+}	
{1660.9}	{451.0}	{++++--+}	{1669.5}	{4.9}	{+--++-}	
{1655.2}	{36908.3}	{+0--+0+}	{1638.6}	{2.7}	{+--++-}	
{1608.7}	{2.4}	{+--+--+}	{1620.1}	{79.0}	{++++0---	
{1563.7}	{1190154.6}	{++++++}	{1574.4}	{0.4}	{+--++-}	
11 <sup>a</sup>	1677.0	9723.8	+-+--+	1675.2	79.8	+-+0+-
	1663.1	3.3	+--+--	1667.4	8.6	+++0---
	1647.5	48880.4	++++--	1646.5	30.1	+0+-0+-
	1625.1	162.1	+0--+0+	1611.2	17.4	++++0---
	1571.9	48.4	+--+--+	1599.8	8.7	+--+0+-
1556.2	1604758.6	++++++				
{1691.6}	{21256.9}	{+-+--+}	{1691.5}	{71.9}	{+-+0+-}	
{1668.1}	{963.4}	{+--+--+}	{1666.9}	{17.2}	{+++0---	
{1647.1}	{61404.7}	{++++--}	{1653.9}	{1.1}	{+0+-0+-}	
{1631.1}	{196.5}	{+0--+0+}	{1610.2}	{96.9}	{++++0---	
{1572.3}	{115.0}	{+--+--+}	{1602.7}	{0.2}	{+--+0+-}	
{1555.2}	{1863035.1}	{++++++}				
12 <sup>a</sup>	1674.8	14769.6	+-+0+-	1676.0	73.2	+-+--+
	1667.8	475.0	+--+--	1661.1	12.2	+++--+
	1639.9	7999.8	+--+--+	1656.5	37.6	+--++-
	1637.8	67094.1	++++--	1618.6	15.9	+--++-
	1594.4	10.8	+--+--+	1600.7	16.3	++++---
1547.4	2452121.3	++++++	1568.5	1.4	+--++-	

	{1690.6} {1669.1} {1646.4} {1637.5} {1596.7} {1546.5}	{25018.9} {5336.8} {486.8} {93639.9} {2.0} {2805094.5}	{+-0++0-+-+} {+---+---+---+} {+---+---+---+} {+++++-----+ {+---+---+---+} {+++++-----+}	{1690.8} {1662.9} {1660.5} {1623.6} {1599.8} {1568.8}	{77.3} {4.6} {24.7} {1.8} {111.9} {0.2}	{+---+---+---+} {+++-----+ {+---+---+---+} {+---+---+---+} {+++++-----+ {+---+---+---+}
<b>13<sup>a</sup></b>	1675.3 1668.2 1651.4 1630.3 1613.9 1566.8 1541.2  {1690.6} {1667.3} {1657.0} {1629.1} {1617.3} {1566.3} {1539.6}	13733.3 8962.3 56.8 110333.0 160.7 13.5 3603864.9  {28027.3} {13211.0} {81.9} {136506.6} {388.9} {12.6} {4074371.9}	+---+---+---+ +++++-----+ +---+---+---+ +++++0-----+ +---+---+---+ +---+---+---+ +++++-----+  {+---+---+---+} {+++-----+ {+---+---+---+} {+++++0-----+ {+---+---+---+} {+---+---+---+} {+---+---+---+}	1676.4 1664.3 1655.1 1634.3 1592.6 1590.8  {1690.6} {1667.5} {1654.2} {1639.6} {1592.1} {1590.8}	77.2 21.8 23.8 24.5 14.4 5.4  {85.0} {0.1} {40.3} {1.1} {14.8} {114.6}	+---+0---+ +---+0---+ +++0---0++ +---+0---+ +++++0----- +---+0---+  {+---+0---+} {+---+0---+} {+++0---0++ {+---+0---+} {+++++0-----+ {+---+0---+}
<b>14<sup>a</sup></b>	1675.5 1663.9 1659.0 1628.4 1621.5 1586.5 1534.3	13306.2 19088.8 647.8 237.8 155702.8 5.1 5139330.7	+---+---+---+ +++++-----+ +---+---+---+ +---+---+---+ +++++-----+ +---+---+---+ +++++-----+	1675.0 1667.6 1648.0 1645.2 1608.5 1583.7 1564.2	94.1 7.9 10.6 39.4 11.4 13.3 0.8	+---+---+---+ +---+---+---+ +++++-----+ +---+---+---+ +---+0---0+ +++++-----+ +---+---+---+
<b>15<sup>a</sup></b>	1675.6 1664.5 1658.9 1640.2 1613.9 1604.1 1562.5 1528.9	15993.3 150.9 29989.4 107.7 213696.7 129.6 3.5 7119931.9	+---+---+---+ +---+---+---+ +++++-----+ +---+---+---+ +++++-----+ +---+---+---+ +---+---+---+ +++++-----+	1674.8 1667.8 1654.2 1641.0 1623.4 1583.2 1576.3	102.5 0.76 27.1 23.2 18.5 3.6 12.1	+---+0---+ +---+0---+ +---+0---+ +++++0-----+ +---+0---+ +---+0---+ +++++0-----+

<sup>a</sup> Harmonic frequencies were calculated using Grid=Fine.

**Table 6.** Experimental Raman C=C ( $A_g$ , totally symmetric) Frequencies ( $\text{cm}^{-1}$ ) of ***tert*-Butyl Capped Polyenes**  $\text{C}_{2n}\text{H}_{2n}(\textit{tert}\text{-Butyl})_2$  ( $n=3-12$ ), **Unsubstituted Polyenes**  $\text{C}_{2n}\text{H}_{2n+2}$  ( $n=2-5$ ), Calculated Anharmonic B3LYP/6-311++G(d,p) Frequencies of ***tert*-Butyl Capped Polyenes**  $\text{C}_{2n}\text{H}_{2n}(\textit{tert}\text{-Butyl})_2$  ( $n=2-4$ ), **Methyl Capped Polyenes**  $\text{C}_{2n}\text{H}_{2n}(\text{Me})_2$  ( $n=2-7$ ), and **Unsubstituted Polyenes**  $\text{C}_{2n}\text{H}_{2n+2}$  ( $n=2-8$ ).

n	Experimental Raman Frequency <i>tert</i> -Butyl Capped ( $\text{cm}^{-1}$ ) <sup>a</sup> $A_g$	Calculated Anharmonic Frequency <i>tert</i> -Butyl Capped ( $\text{cm}^{-1}$ ) $A_g$	Calculated Anharmonic Frequency Methyl Capped ( $\text{cm}^{-1}$ ) $A_g$	Experimental Raman Frequency Unsubstituted ( $\text{cm}^{-1}$ ) $A_g$	Calculated Anharmonic Frequency Unsubstituted ( $\text{cm}^{-1}$ ) $A_g$	$\nu_1 = 1459 + 720/(n + 1)^e$ <b>Polyacetylenic Molecule Frequencies</b> ( $\text{cm}^{-1}$ ) $A_g$
2		1668.3	1675.0	1644.3 <sup>b</sup>	1651.5 1642.5 <sup>b</sup>	
3	1638.5	1646.0	1647.9	1625 <sup>c</sup>	1645.7 1647 <sup>c</sup>	1639
4	1613.8	1616.8	1617.0	1613 <sup>d</sup>	1619.0	1603
5	1587.3		1592.9 <sup>f</sup>	1593 <sup>d</sup>	1599.8	1579
6	1570.6		1577.6		1579.2	1562
7	1555.6		1562.8		1563.4	1549
8	1542.2				1547.7	1539
9	1530.9					1531
10	1520.9					1524
11	1514.0					1519
12	1505.9					1514

<sup>a</sup> Ref [31].

<sup>b</sup> Ref [23].

<sup>c</sup> Ref [24].

<sup>d</sup> Ref [22].

<sup>e</sup> Ref [68,74]; n is the number of double bonds.

<sup>f</sup> Ref [75].



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