

tert-Butyl-End-Capped Polyynes: Crystallographic Evidence of Reduced Bond-Length Alternation**

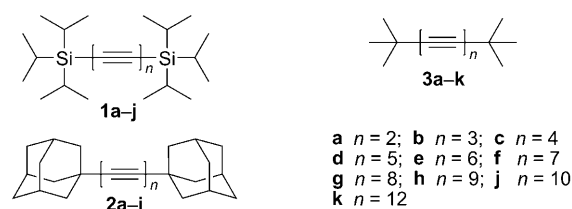
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For over five decades, conjugated polyynes have been challenging synthetic targets that have captured the interest of chemists working to develop innovative synthetic methods, new biologically active molecules, and improved molecular materials.^[1,2] Within the last decade, synthetic efforts toward polyynes have enjoyed a resurgence, driven in many cases by the possible applications of such molecules as molecular wires and new optical materials.^[3] Regardless of the projected application, the study of polyynes is also often motivated by an infatuation with the structural simplicity of these molecules, which are essentially devoid of both steric and conformational effects that might alter the electronic and optical properties. Experimentally, the electronic characteristics of polyynes are often probed by UV/Vis spectroscopy, and these analyses document a consistent lowering of the optical HOMO–LUMO gap as a function of increasing length.^[3d,g,4,5] These analyses also typically show that saturation of this trend has not yet been reached over the length of polyynes that are currently accessible by modern organic synthesis.

Given that polyynes are essentially 1D conjugated systems, the changes in the HOMO–LUMO gap versus length should be intricately dependent on the degree of bond length alternation (BLA = the difference in the bond length between the central single and triple bonds) in the polyyne structure.^[6,7] Recent theoretical studies have upheld the prediction that neither the HOMO–LUMO gap nor the BLA for polyynes will reach a value of zero,^[8] a phenomena commonly referred to as Peierls distortion.^[9] Experimentally, it should be possible to explore trends in BLA as a function of polyyne

length by X-ray crystallographic analysis. As polyynes become increasingly longer, however, the stability decreases significantly and obtaining single crystals of polyynes beyond the length of a hexayne for analysis has been a difficult task.^[10]

A particular objective in our study of polyynes has been to employ terminal groups that interact as little as possible with the sp-hybridized carbon chain so as to minimize the influence of “end-group effects” on the electronic properties. Ideally, the use of hydrogen atoms^[5a,11] or even methyl^[12] groups would achieve this goal, but the instability of such molecules often complicates their synthesis, purification, and analysis. To strike a balance between stabilization and electronic inertness, trialkylsilyl (**1**)^[3d] and 1-adamantyl (**2**)^[13] end groups have been employed (Scheme 1). In one



Scheme 1. Triisopropylsilyl (TIPS; **1**), 1-adamantyl (**2**), and *tert*-butyl (**3**) end-capped polyynes.

of these studies, 1-adamantyl polyynes were investigated experimentally by analysis of the electronic absorption spectra of radical ions generated by radiolysis.^[14] Unfortunately, the molecules proved difficult to study effectively by computational methods because of the size of the adamantyl groups. Thus, polyynes bearing the structurally similar, albeit smaller, *t*Bu end group were considered (**3a–k**).^[15] On the basis of earlier work, we were convinced that the *t*Bu-substituted polyynes would be sufficiently stable and chemically well-behaved for subsequent study. Thus, the Fritsch–Buttenberg–Wiechell (FBW) method^[16] for polyyne synthesis was applied to the construction of series **3**. In addition to characterization by NMR and UV/Vis spectroscopy, we report X-ray crystallographic analysis of polyynes **3a–c**, **3g**, and **3j**; compound **3j** is the only decane to be characterized by X-ray crystallography to date. An analysis of the solid-state structure of these five polyynes reveals a distinct trend in reduced BLA as a function of polyyne length, similar to that predicted by theory.

The syntheses of diyne **3a**^[17] and tetrayne **3c**^[18] were accomplished, as previously reported, by oxidative homocoupling of *t*Bu-acetylene and *t*Bu-butadiyne, respectively. Triyne **3b** was easily assembled by a FBW rearrangement in a manner reported for other symmetrical triynes.^[16f] Pentayne

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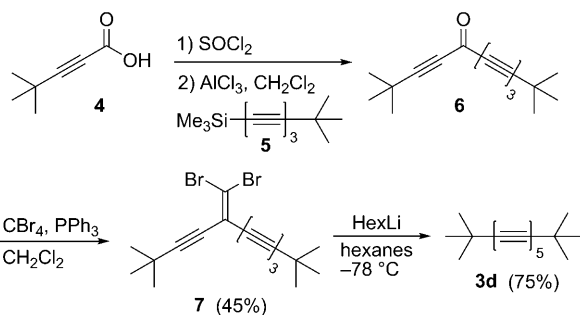
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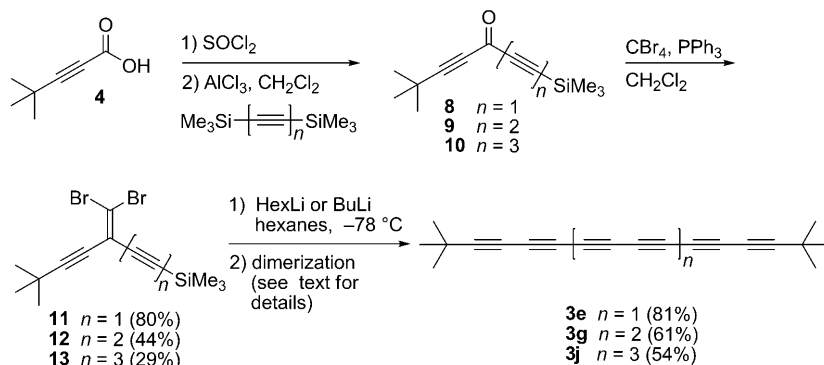
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3d was a bigger synthetic challenge, since oxidative dimerization reactions were not particularly applicable.^[19] In the present case, Friedel–Crafts acylation^[20] of triyne **5**^[21] using the acid chloride derived from **4** gave ketone **6**. Since **6** was not stable to isolation, it was carried on directly to the dibromoolefination protocol reported by Ramirez et al.,^[22] which gave **7** in 45 % yield over the two steps. In the final step, pentayne **3d** was produced in 75 % yield from **7** by a FBW rearrangement (Scheme 2).



Scheme 2. Synthesis of pentayne **3d**.

The construction of hexa-, octa-, and decaynes **3e**, **3g**, and **3j**, respectively, followed a comparable sequence of steps starting from the common precursor, acid **4**. Thus, reaction of **4** with thionyl chloride followed by the appropriate α,ω -bis(trimethylsilyl)polyyne gave the corresponding ketone intermediates **8–10** (Scheme 3). Given their instability, the



Scheme 3. Synthesis of hexayne **3e**, octayne **3g**, and decayne **3j**.

crude products (**8–10**) were used directly in the dibromoolefination step after purification through a short column of silica gel. This gave **11–13** in yields that ranged from 29 % (**13**) to 80 % (**11**) over the two steps. A FBW rearrangement effected on **11** or **12** gave the expected tri- or tetrayne product, respectively, which, following aqueous work-up, was subjected directly to Hay oxidative homocoupling (THF, MeOH, CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), O₂).^[23] Under these conditions, the trimethylsilyl protecting group was removed effectively, and homocoupling afforded **3e** or **3g** in acceptable yield. Attempts to use this same procedure with decayne precursor **13** led not only to the

desired product **3j**, but also to nonayne **3h**.^[24] Changing the catalyst system to that used by Eglinton and Glaser^[25] (Cu(OAc)₂·H₂O, THF, MeOH, pyridine) circumvented this problem and gave decayne **3j** in a respectable yield of 54 %.

Polyynes **3a–e**, **3g**, and **3j** were characterized by EI (**3a–e**, **3g**) and MALDI (**3j**) MS analysis to confirm their constitution. Their UV/Vis spectra are consistent with those previously published by Bohlmann^[5b] and Jones et al.,^[5c] showing considerable vibrational fine structure for the HOMO–LUMO transition, accompanied by a consistent lowering of the λ_{max} energy as a function of the polyyne length. This trend culminates in a λ_{max} value for **3j** at 362 nm (in hexanes), with a significant molar absorptivity ($\epsilon = 736\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$).^[26] Analysis of the ¹³C NMR spectra shows consistent trends in the observed chemical shifts as a function of length, as has been observed for other homologous series of polyynes.^[3d] The most deshielded acetylenic resonance moves consistently downfield from $\delta = 86.3$ ppm (**3a**) to $\delta = 89.6$ ppm (**3j**), while the most upfield resonance of each polyyne is found in a narrow range of $\delta = 61.7$ – 61.4 ppm (for **3a** it is observed at $\delta = 63.7$ ppm).^[27] The remaining resonances converge toward a value of about 63 ppm as the length is increased.

Whereas trends from NMR and UV/Vis spectroscopic analysis for polyynes have become almost routine in recent years,^[3d,g,4,13,16e,28] there is one particular question that remains unanswered to date: Do extended polyynes show experimental evidence of reduced bond length alternation (BLA) as a function of increasing length? X-ray crystallographic data for extended polyynes that might offer an answer to this query are, however, essentially nonexistent.^[10]

For polyyne series **3**, useful diffraction patterns have been obtained for diene **3a**, triyne **3b**, tetrayne **3c**, octayne **3g**, and decayne **3j** (Figure 1).^[29,30] Before examining structural effects for this series, the structure of decayne **3j** deserves comment, given that it is the only successful crystallographic analysis of a polyyne with more than 16 contiguous sp-hybridized carbon atoms.^[31] Crystals of **3j** were grown by slow evaporation of a CH₂Cl₂ solution at 4 °C. The structure contains two crystallographically independent molecules in the unit cell (labeled as molecules **3jA** and **3jB** in Figures 1 and 2). The unsymmetrical molecule **3jA** adopts a sort of helical conformation with C–C $\equiv$ C bond angles that range from 174.4(6)° to 179.3(5)°. The centrosymmetric molecule **3jB** adopts a gentle S shape, with a slightly smaller deviation from linearity and C–C $\equiv$ C bond angles that range from 176.1(6)° to 179.5(8)°. Perhaps the most impressive aspect of decayne **3j** is its length: the molecule spans an amazing 2.7 nm from end to end (namely, from C2A to C23A or C2B to C2B').

A recent review by Szafert and Gladysz estimated a BLA of about 0.07–0.08 Å for an infinite polyyne system, a prediction made from the comprehensive analysis of X-ray crystallographic data for polyyne structures with at least eight contiguous sp-hybridized carbon atoms.^[31] This estimate is

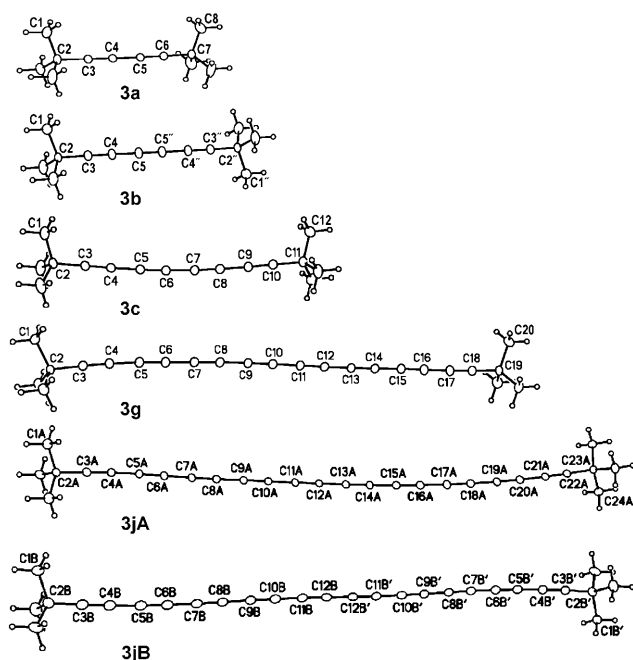


Figure 1. ORTEP drawings (20% probability level) for **3a–c**, **3g**, **3jA**, and **3jB**.

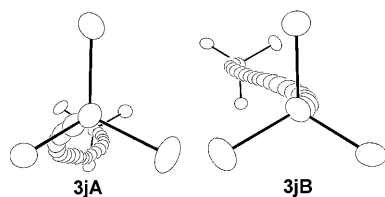


Figure 2. End-on view of **3jA** and **3jB** highlighting the nonlinearity of each molecule (hydrogen atoms are removed for clarity).

potentially complicated by “end-group effects”, however, since many of the polyynes in this analysis are terminated with groups that are strongly conjugated with the polyyne core. Computational chemists have frequently addressed BLA in polyynes, partly, at least, because of the relative structural simplicity of these molecules.^[8] From these theoretical studies, it is clear that the choice of basis set and electron correlation can have a dramatic effect on the results.^[8,32] Nevertheless, a consistent trend has emerged from recent investigations that predict that BLA values, as defined by the difference in the length between the central single and triple bonds, converge to a value of about 0.13 Å (Table 1, entries 13–17).^[8a,b,d]

The analysis of the BLA from the X-ray data of **3a–c**, **3g**, and **3jA/3jB** was conducted in two ways. First, as reported for computed structures in entries 13–17, the BLA was calculated as the difference in the bond lengths of the central single and triple bonds in each structure.^[34] This leads to a consistent reduction in BLA values from a maximum of 0.184 Å for dimer **3a** to a minimum of 0.139 Å (average of **3jA** and **3jB**). This analysis also suggests that the reduction in BLA is approaching saturation by the stage of the decayne, similar to that predicted by theory;^[8] a plot of BLA versus $1/n$ predicts a

Table 1: Summary of experimental and theoretical BLA data.

Entry	Polyne	BLA ^[a] [Å]	C–C _{avg} [Å]	C≡C _{avg} [Å]	BLA _{avg} ^[b] [Å]	Ref
1	3a	0.184	1.382	1.199	0.183	[29]
2	3b	0.164	1.368	1.202	0.166	[29]
3	3c	0.151	1.365	1.204	0.161	[29,30]
4	3g	0.140	1.356	1.209	0.147	[29]
5	3jA	0.144	1.350	1.207	0.143	[29]
6	3jB	0.134	1.354	1.206	0.148	[29]
7	3jA/B_{avg}	0.139	1.352	1.206	0.146	[29]
8	1a	0.169	1.373	1.204	0.169	[33]
9	1c	0.157	1.366	1.209	0.157	[3d]
10	1d	0.148	1.362	1.209	0.153	[3d]
11	1e	0.149	1.361	1.208	0.153	[3d]
12	1g	0.153	1.361	1.200	0.161	[3d]
13	H–(C≡C) ₉ –H	0.1291 ^[c]	1.36175	1.2254	0.13675	[8a]
14	H–(C≡C) _∞ –H	0.1276 ^[c]	–	–	–	[8a]
15	H–(C≡C) _∞ –H	0.133 ^[d]	–	–	–	[8d]
16	H–(C≡C) _∞ –H	0.131 ^[e]	–	–	–	[8d]
17	H–(C≡C) _∞ –H	0.134 ^[f]	–	–	–	[8b]

[a] See text and Ref. [34]. [b] $[C-C_{avg}] - [C\equiv C_{avg}]$; note: the calculation does not include terminal C–C bonds (e.g., C2–C3). [c] Calculated at the CCSD(T)/cc-PVTZ level of theory. [d] Results obtained with the BHHLYP functional. [e] Results obtained with the CAM-B3LYP functional. [f] Results obtained with the B3LYP//BH&HLYP functional.

limiting value of BLA = 0.135 Å at the asymptotic limit.^[35] One potential issue with this BLA analysis is however that it relies on the difference of two specific bonds, where small errors in either of these bond lengths might be over emphasized in comparison with other bond lengths. In an attempt to minimize such an error, the difference between the average of all single and triple bonds (BLA_{avg}) has also been examined. Similar to the pure BLA values, the BLA_{avg} values also decrease consistently as a function of length for **3a–c**, **3g**, and **3j**, and the onset of saturation is also suggested by the stage of the decayne.^[35] A comparison of the BLA and BLA_{avg} values for **3g** and **3j** versus those predicted theoretically for H–(C≡C)₉–H (entry 13) shows that the experimental values are greater by only about 0.01 Å.

The TIPS-end-capped polyynes **1** allow the only substantive comparison of similar experimental BLA and BLA_{avg} analyses, as shown in entries 8–12. While there is an overall reduction in both the BLA and BLA_{avg} values as one moves from diyne **1a** to octayne **1g**, neither the individual values nor the overall trend compare well with the data for molecules in the *t*Bu series. It is particularly interesting that the BLA_{avg} data for molecules **1** show no real trend. It seems plausible that this could result from an end-group effect in which the silane moiety reduces the BLA toward the termini of the polyyne, which effectively negates any apparent overall BLA that might be present toward the center of the molecule.

In summary, a series of *t*Bu-end-capped polyynes has been synthesized to explore the properties of conjugated oligomers composed of sp-hybridized carbon atoms. The resulting polyynes exhibit reasonable stability under ambient conditions, which has allowed for X-ray analysis of several derivatives, including the first crystallographic analysis of a decayne. Analysis of the bond lengths provides the first

experimental evidence for reduced BLA as a function of polyyne length.

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0.71073 Å; $T = -80^\circ\text{C}$; 2θ max = 51.34° ; total data collected = 4517; $R_1 = 0.0787$ (560 observed reflections with $[F_o^2 \geq 2\sigma(F_o^2)]$); $wR_2 = 0.2573$ for 40 variables and 672 unique reflections with $[F_o^2 \geq -3\sigma(F_o^2)]$; residual electron density = 0.413 and $-0.169 \text{ e \AA}^{-3}$ (CCDC 729157). Data for **3c**: $\text{C}_{16}\text{H}_{18}$, $M_r = 210.30$; orthorhombic; space group *Pbcn* (no. 60), $a = 11.0520$ (12), $b = 11.6678$ (13), $c = 22.507$ (3) Å; $V = 2902.4$ (6) Å³; $Z = 8$; $\rho_{\text{calcd}} = 0.963 \text{ g cm}^{-3}$; $\mu = 0.054 \text{ mm}^{-1}$; $\lambda = 0.71073$ Å; $T = -80^\circ\text{C}$; 2θ max = 52.80° ; total data collected = 21568; $R_1 = 0.0516$ (2275 observed reflections with $[F_o^2 \geq -2\sigma(F_o^2)]$); $wR_2 = 0.1549$ for 145 variables and 2975 unique reflections with $[F_o^2 \geq -3\sigma(F_o^2)]$; residual electron density = 0.189 and $-0.152 \text{ e \AA}^{-3}$ (CCDC 729158). Data for **3g**: $\text{C}_{24}\text{H}_{18}$, $M_r = 306.38$; orthorhombic; space group *Pnma* (no. 62), $a = 16.4819$ (10), $b = 6.8028$ (4), $c = 17.4876$ (10) Å; $V = 1960.8$ (2) Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.038 \text{ g cm}^{-3}$; $\mu = 0.059 \text{ mm}^{-1}$; $\lambda = 0.71073$ Å; $T = -100^\circ\text{C}$; 2θ max = 51.44° ; total data collected = 14185; $R_1 = 0.0412$ (1407 observed reflections with $[F_o^2 \geq 2\sigma(F_o^2)]$); $wR_2 = 0.1330$ for 139 variables and 2043 unique reflections with $[F_o^2 \geq -3\sigma(F_o^2)]$; residual electron density = 0.353 and $-0.111 \text{ e \AA}^{-3}$ (CCDC 729159). Data for **3j**: $\text{C}_{28}\text{H}_{18}$, $M_r = 354.42$; monoclinic; space group *P2₁/n* (an alternate setting of *P2₁/c* [no. 14]), $a = 5.3923$ (17), $b = 18.777$ (6), $c = 31.598$ (10) Å; $\beta = 94.474$ (4)°; $V = 3189.6$ (17) Å³; $Z = 6$; $\rho_{\text{calcd}} = 1.107 \text{ g cm}^{-3}$; $\mu = 0.063 \text{ mm}^{-1}$; $\lambda = 0.71073$ Å; $T = -100^\circ\text{C}$; 2θ max = 50.70° ; total data collected = 22855; $R_1 = 0.0896$ (4076 observed reflections with $[F_o^2 \geq 2\sigma(F_o^2)]$); $wR_2 = 0.2304$ for 389 variables and 5938 unique reflections with $[F_o^2 \geq -3\sigma(F_o^2)]$; residual electron density = 0.964 and $-0.235 \text{ e \AA}^{-3}$ (CCDC 729160). Crystallographic data (excluding structure factors) for the structures reported in this paper have been

deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.comcam.ac.uk).

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- [34] For non-centrosymmetric structures, the BLA was calculated using the average of positionally equivalent bonds [namely, BLA (**3a**) = (C4–C5) – [(C3≡C4) + (C5≡C6)]/2]. See the Supporting Information for further discussion of calculated BLA and BLA_{avg} values. Given the estimated standard deviation (ESD) associated with individual bond lengths, it is the overall trend of BLA values that should be appreciated, rather than the exact BLA value for each molecule.
- [35] See the Supporting Information for a table of bond lengths for **3a–c**, **3g**, and **3j** (including ESD values), plots of BLA and BLA_{avg} as a function of n and $1/n$ (where n is the number of triple bonds), as well as a graphical depiction of the decrease in BLA as a function of length in comparison to BLA_{avg}.