

Synthesis, Structure, and Nonlinear Optical Properties of Diarylpolyynes

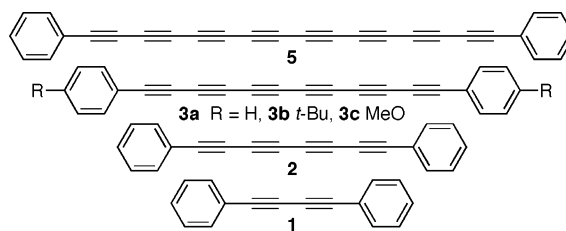
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ABSTRACT



A series of α,ω -diarylpolyynes has been synthesized. In addition to the synthesis of three hexaynes (**3a–c**), a notably improved synthesis of 1,16-diphenylhexadecaoctayne (**5**) is described. The third-order nonlinear optical characteristics for these molecules have been studied and show a substantial increase in molecular hyperpolarizability (γ) as a function of increasing length. The unusual solid-state structures of compounds **3a** and **3b** are reported.

It is easy to appreciate the allure of conjugated polyynes, from their structural simplicity to their potential to function as linear molecular wires. A number of classical syntheses have been developed for polyynes during the middle of the past century,¹ many of which have recently been applied to the synthesis of more structurally diverse derivatives.² A common characteristic of these syntheses is the use of an oxidative homocoupling reaction as the final step, reactions that require terminal alkynes as starting materials.³ Such homocoupling reactions under Hay,⁴ Glaser,⁵ or Eglinton–

Galbraith⁶ conditions can be quite efficient for the formation of shorter polyyne molecules. Instability of the terminal alkyne starting materials can, however, pose a problem in the formation of longer derivatives. This often results in low yields and difficult purification, which has historically limited the ability to study the unique properties of these molecules.

We report herein the successful synthesis of a series of aryl end-capped polyynes that have been constructed in order to explore their structural and nonlinear optical (NLO) properties. In several cases, traditional homocoupling methods were effective for formation of the desired polyynes. In other cases, an alternative method was exploited based on a modified Fritsch–Buttenberg–Wiechell (FBW) rearrangement.^{2a} A comparison of the two methods is briefly described.

The first two molecules in the series, diphenyl butadiyne (**1**) and octatetrayne (**2**), were synthesized on the basis of an adaptation of a known route.^{7,8} The synthesis of hexaynes

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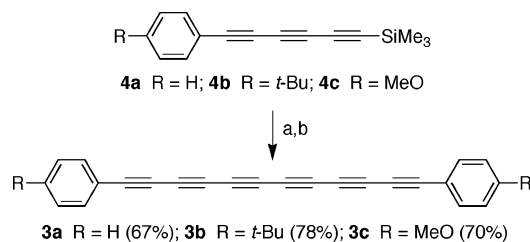
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(7) Armitage et al. have previously reported compounds **2**, **3a**, and **5**; see: Armitage, J. B.; Entwistle, N.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1954**, 147–154.

Scheme 1. Synthesis of Phenyl Hexaynes **3a–c**^a

^a Reagents and conditions: (a) K₂CO₃, MeOH/THF, rt; (b) CuCl, TMEDA, O₂, CH₂Cl₂, rt.

3a–c required triene precursors **4a–c** (Scheme 1), which were formed in good yields using a recently developed adaptation of the FBW rearrangement.^{2a,8} Protodesilylation of **4a–c** afforded the unstable terminal triynes,⁹ which were immediately carried on, following workup, to the subsequent homocoupling reaction under Hay conditions.⁴ The yields of hexaynes **3a–c** were surprisingly good in comparison to that previously reported for **3a**.^{10,11}

Although successful, the formation of hexaynes via this route was not ideal because of the instability of the deprotected triene intermediates. For example, Armitage and co-workers reported that attempted isolation of the phenyl-1,3,5-hexatriyne afforded a solid that exploded at 0 °C in the absence of air.⁷ Furthermore, attempts by the same group to extend this methodology to the next longer homologue, octayne **5**, afforded only 0.5% yield of an unstable orange solid. In an effort to avoid unstable polyyne intermediates and provide sufficient amounts of octayne **5** for study, an alternate approach was explored (Scheme 2). The known dibromoolefins **6a,b**^{2a} were desilylated and then subjected to Hay coupling conditions⁴ at low temperature¹² with an excess of the catalyst (2 equiv) in an effort to decrease reaction times. Despite their highly unsaturated structures, products **7a** and **7b** were isolated in excellent yields as relatively stable solids and survived for months under refrigeration.

Successful conversion of bromides **7a** and **7b** to the desired polyynes via a FBW rearrangement necessitated the use of a nonpolar solvent, typically hexanes.^{2a} Both **7a** and **7b** were, however, nearly insoluble in hexanes. After exploring a number of possible media, toluene was determined to provide

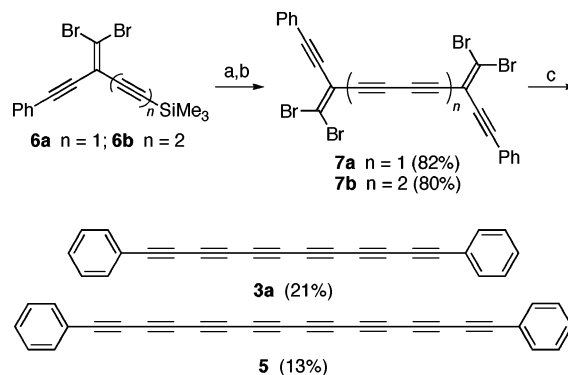
(8) Synthetic and characterization details are provided as Supporting Information.

(9) **Caution:** isolation of deprotected 1,3,5-hexatriynes should not be attempted as they can explode even at low temperature and in the absence of air; see ref 7.

(10) Selected spectral data. Compound **3a**: ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 7.5 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 4H); ¹³C NMR (75.5 MHz, CDCl₃, ATP) δ 133.5, 130.4, 128.7, 120.2, 77.5, 74.3, 67.3, 64.6, 63.6, 62.6. Compound **5**: ¹H NMR (300 MHz, THF-*d*₈) δ 7.32 (d, *J* = 7.6 Hz, 4H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 4H); ¹³C NMR (75.5 MHz, THF-*d*₈, ATP) δ 134.4, 131.8, 129.7, 120.3, 79.1, 74.1, 67.9, 64.6, 63.8, 63.75, 63.72, 63.4.

(11) A 30% yield for **3c** had been reported by Armitage and co-workers; see ref 7.

(12) Low temperature was necessary to prevent side reactions that likely arise from Castro–Stephens chemistry at the dibromoolefin groups: Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313–3315.

Scheme 2. Synthesis of Hexayne **3a** and Octayne **5**^a

^a Reagents and conditions: (a) K₂CO₃, MeOH/THF, rt; (b) CuCl, TMEDA, O₂, CH₂Cl₂, 0 °C; (c) BuLi, PhCH₃, –78 °C (**3a**) or –100 °C (**5**).

the best solubility, leading as well to the best yield of polyyne **3a** and **5**. Thus, 2.4 equiv of BuLi was added to the respective tetrabromide in toluene at low temperature, and the reaction was warmed to approximately –20 °C over a period of 30 min, and then quenched. As the least polar product of the reaction, crude polyyne **3a** and **5** could be readily purified by flash chromatography. Although the yield of **3a** was somewhat lower for the final step of the FBW reaction than for the Hay homocoupling, the FBW route remains quite attractive because of the stability of the immediate precursors, facile purification, and its success for longer derivatives such as **5**.

Hexaynes **3a–c** were isolated as kinetically stable orange solids, whereas octayne **5** was typically a less stable dark orange/red solid. Surprisingly, when **5** was crystallized from THF, the resulting rust colored solid showed substantially increased kinetic stability, surviving for over a year if kept under refrigeration. It is unclear whether the improved stability derives from a more stable polymorph or from increased purity in comparison to other samples.¹³

Crystals of **3a** suitable for X-ray crystallography were obtained by vapor diffusion of hexanes into a solution of **3a** in CH₂Cl₂/hexanes (1:1).¹⁴ The molecular geometry and solid-state packing as viewed down the crystallographic *a*-axis are shown in Figure 1. The structure of **3a** is nearly linear, with all sp–sp carbon bond angles between 177° and 180°. Molecules of **3a** are aligned in a parallel fashion as pairs of symmetry related dimers. Although intermolecular distances between sp-hybridized carbons are sufficiently short (e.g., C(2)–C(12') = 3.5 Å and C(1)–C(5') = 3.7 Å) to support topochemical polymerization, the arrangement and stacking angle suggest that an ordered polymerization would

(13) It is worth noting that octayne **5** was previously reported to be stable as a solid for only a period of hours when crystallized from ethyl acetate, perhaps the result of impurities remaining in the sample.

(14) Crystal data for **3a**: C₂₄H₁₀, *M* = 298.32, monoclinic space group *P*2₁/*n* (an alternate setting of *P*2₁/*c* [No. 14]), *D*_c = 1.194 g cm^{–3}, *a* = 7.7266(9), *b* = 12.4682(14), *c* = 17.2826(19) Å, β = 94.797(2)°, *V* = 1659.1(3) Å³, *Z* = 4, μ = 0.068 mm^{–1}. Final *R*(*F*) = 0.0534, *wR*₂(*F*²) = 0.1305 for 217 variables and 3404 data with *F*_o² ≥ –3σ(*F*_o²) (1612 observations [*F*_o² ≥ 2σ(*F*_o²)]); CCDC 249138.

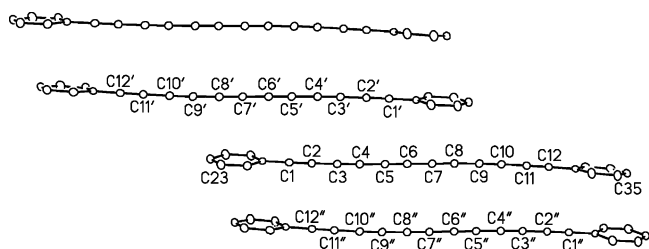


Figure 1. ORTEP drawing of compound **3a** showing several parallel-oriented symmetry-related molecules (20% probability level; hydrogen atoms omitted for clarity).¹⁷

not be favored.¹⁵ Surprisingly, differential scanning calorimetry (DSC) of **3a** shows no melting point but a rather sharp exotherm at 142 °C ($T_{\text{onset}} = 133$ °C, $T_{\text{max}} = 142$ °C), implying that a topochemical reaction may have resulted.¹⁶

Slow diffusion of hexanes into a CH_2Cl_2 solution of **3b** provided X-ray quality crystals.¹⁸ The unit cell shows two crystallographically unique molecules, which face each other about a pseudo center of inversion (Figure 2). Molecule B

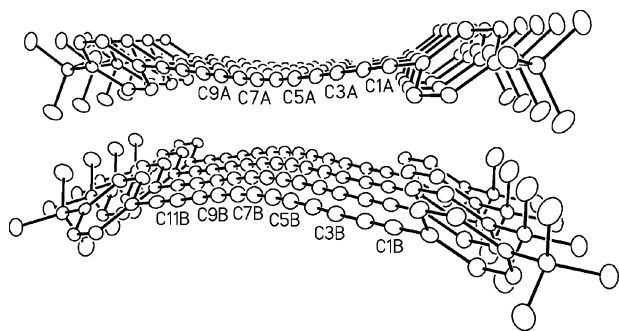


Figure 2. ORTEP drawing of compound **3b** showing several parallel-oriented molecules A and B (20% probability level; hydrogen atoms omitted for clarity).

on average shows somewhat more bending of the polyynyl framework than molecule A, with average C–C≡C bond angles of 177.4° and 177.9°, respectively. Rather than assuming a coplanar relationship, the terminal aryl groups of each molecule are nearly orthogonal. Neighboring molecules are stacked into rows, and packing parameters for both molecule A and B are near the range necessary for to-

(15) For an excellent review of solid-state characteristics of polyynes and parameters concerning topochemical polymerization, see: Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175–4205.

(16) See Supporting Information for details.

(17) Primed atoms are related to unprimed ones via the crystallographic inversion center (0, 0, 0); double-primed atoms are related to unprimed ones via the inversion center (0, 1/2, 0).

(18) Crystal data for **3b**: $\text{C}_{32}\text{H}_{26}$, $M = 410.53$, triclinic space group $P\bar{1}$ (No. 2), $D_c = 1.136$ g cm^{-3} , $a = 8.2179(9)$, $b = 16.7512(18)$, $c = 17.8407(19)$ Å, $\alpha = 90.584(2)^\circ$, $\beta = 91.395(2)^\circ$, $\gamma = 102.0395(19)^\circ$, $V = 2400.9(4)$ Å³, $Z = 4$, $\mu = 0.064$ mm⁻¹. Final $R(F) = 0.0703$, $wR_2(F^2) = 0.2027$ for 577 variables and 9710 data with $F_o^2 \geq -3\sigma(F_o^2)$ (4752 observations [$F_o^2 \geq 2\sigma(F_o^2)$]); CCDC 249139.

pochemical polymerization in a 1,6-manner.¹⁵ Several intermolecular close contacts exist along the polyynyl chains for both molecules A and B, and minima are observed for C(4)–C(9) in both (3.84 and 3.68 Å, respectively). In both cases, the stacking angle is 30° (optimal is ca. 27°) and the packing distance $d = 8.2$ Å (optimal is 7.4 Å). Similar to **3a**, DSC analysis of **3b** shows a narrow exotherm ($T_{\text{onset}} = 144$ °C, $T_{\text{max}} = 151$ °C) consistent with that expected of a topochemical polymerization process.¹⁹

The absorption spectra for compounds **1–3** and **5** are shown in Figure 3 and summarized in Table 1. The polyynes

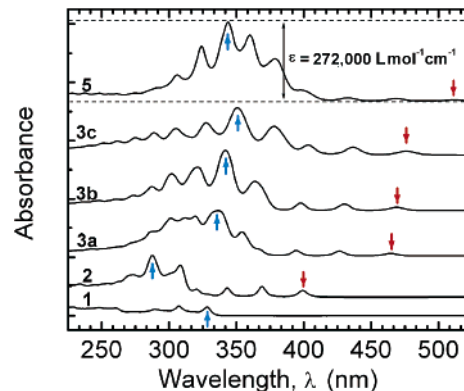


Figure 3. UV–vis absorption spectra for **1–3** and **5** (in THF). λ_{max} for region 2 is marked by an upward blue arrow, and λ_{max} for region 1 is marked by a downward red arrow. The highest molar absorptivity for the octayne is displayed.

display significant molar absorptivities for transitions at higher energy (region 2) and well-resolved vibronic structure for absorptions at lower energy (region 1). Increasing the electron density (**3c**) and conjugation length (**5**) affords

Table 1. Selected Optical Data for Polyynes **1–3** and **5**^a

compd	λ_{max} (nm) ^b ϵ (L mol ⁻¹ cm ⁻¹)	λ_{max} (nm) ^c ϵ (L mol ⁻¹ cm ⁻¹)	γ (10 ⁻³⁶ esu)
1	328 (30 000)		12 ± 2
2	288 (143 000)	399 (22 000)	49 ± 18
3a	337 (155 000)	465 (8 000)	217 ± 10
3b	342 (206 000)	469 (10 900)	300 ± 30
3c	351 (164 000)	476 (13 300)	n/a ^d
5	344 (272 000)	512 (3 600)	588 ± 36

^a THF solutions. ^b λ_{max} defined as the most intense absorption in region 2. ^c λ_{max} defined as the lowest energy absorption in region 1. ^d Sample **3c** was insufficiently soluble to reliably determine a γ -value.

bathochromic shifts for absorptions in both regions. It is interesting to note that with the exception of **3b** the molar absorptivities at λ_{max} in region 2 for **3** and **5** are somewhat

(19) Characterization of the product(s) from the heating of **3a** and **3b** is currently inconclusive, and further investigation is underway.

lower than those found for similar polyynes with aryl ether end-capping groups,^{2d} highlighting the effect of structure on oscillator strength for extended polyynes.

Whereas the linear optical characteristics of polyynes have been reported for a number of series of molecules, the third order NLO properties of polyynes are virtually unknown.^{20,21} The molecular third-order NLO susceptibilities (γ) for molecules **1–3** and **5** were evaluated using the DOKE technique,²² and the γ -values are listed in Table 1 and shown graphically in Figure 4 in comparison to their triisopropylsilyl

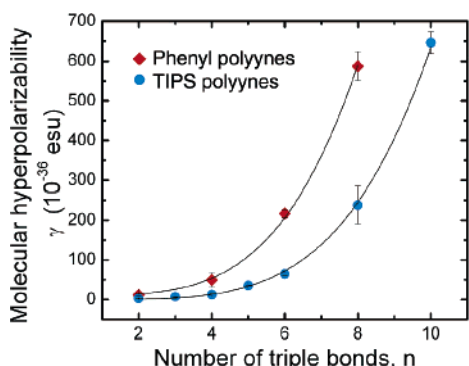
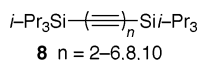


Figure 4. Graphical representation of γ -values for diphenyl polyynes **1–3a** and **5** in comparison to TIPS end-capped derivatives **8**. Curves are fit to a power-law of the form $\gamma = a + bn^c$, where a and b are constants.²⁰

(TIPS) end-capped cousins **8**.^{20,23} Hexayne **3b**, an alkylated derivative of **3a**, shows a γ -value that is modestly higher than the parent system **3a**. The donor-donor system **3c**, unfortunately, did not yield reliable results because of poor solubility in THF.



A comparison of the γ -values determined for polyynes **1–3a** and **5** to those of TIPS end-capped polyynes **8** shows

(20) Only one prior study of third-order NLO properties of extended polyynes has been reported; see: Slepko, A. D.; Hegmann, F. A.; Eisler, S.; Elliott, E.; Tykwinski, R. R. *J. Chem. Phys.* **2004**, *120*, 6807–6810.

(21) Polyynes have been widely studied theoretically, inter alia: (a) Nalwa, H. S.; Mukai, J.; Kakuta, A. *J. Phys. Chem.* **1995**, *99*, 10766–10774. (b) Archibong, E. F.; Thakkar, A. J. *J. Chem. Phys.* **1993**, *98*, 8324–8329. (c) Buma, W. J.; Fanti, M.; Zerbetto, F. *Chem. Phys. Lett.* **1999**, *313*, 426–430. (d) Kuzyk, M. G. *Phys. Rev. Lett.* **2000**, *85*, 1218–1221. (e) Kuzyk, M. G. *Opt. Lett.* **2000**, *25*, 1183–1185; corrigenda **2003**, *28*, 135.

(22) Slepko, A. D.; Hegmann, F. A.; Zhao, Y.; Tykwinski, R. R.; Kamada, K. *J. Chem. Phys.* **2002**, *116*, 3834–3840.

two significant features (Figure 4). First, the magnitude of the γ -values for the phenylated polyynes is higher than that of the silylated derivatives of equal length, which is perhaps not surprising because of the increased π -electron density afforded by the phenyl groups. Second, an analysis of γ -values as a function of length affords a power-law relationship $\gamma \sim n^c$ with an exponent of $c = 3.79 \pm 0.25$, (where n is the number of acetylene units). This exponent value is slightly lower than that determined for TIPS polyynes **8**, which display $\gamma \sim n^{4.28 \pm 0.13}$. The slightly lower exponent for **1–3a** and **5** might result from more significant end-group interaction between the polyyne framework and the conjugating phenyl groups relative to the more electronically inert silyl groups of **8**. If the influence of the end-groups were to diminish with length, however, inclusion of γ -values for longer members of this series could give a power-law relationship more in line with that observed for polyynes **8**. The synthesis and study of these longer derivatives is currently underway.

Although the power-law increase in γ -values for **1–3a** and **5** is slightly lower than that determined for the series of polyynes **8**, it is interesting to note that it is comparable to or higher than that determined experimentally for other conjugated oligomers, including polytriacetylenes ($c = 2.5$),²⁴ poly(arylene ethynylene)s ($c = 2.5$),²⁵ and polyenes ($c = 3.6$).²⁶ Extended polyynes thus remain an intriguing prospect for the realization of functional NLO materials.

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Supporting Information Available: Experimental procedures, spectroscopic data for new compounds, DSC traces, and crystallographic details for **3a** and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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