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Synthesis and Crystal Structures of Isolable Terminal Aryl Hexatriyne and Octatetrayne Derivatives: Ar−(C≡C)$_n$H (n = 3, 4)

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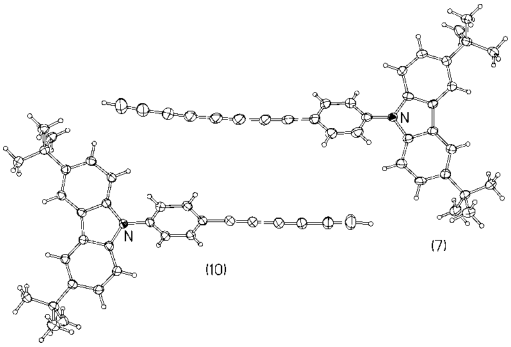
ABSTRACT



Unprecedented stability has been observed in terminal aryl hexatriyne and terminal aryl octatetrayne derivatives by judicious choice of a bulky, nonplanar headgroup [viz., 4-(3,6-di-*tert*-butyl-*N*-carbazolyl)phenyl] which hinders topochemical intermolecular interactions in the crystal lattice.

It is generally accepted that alkyl and/or aryl terminal oligoynes with more than two conjugated triple bonds are unstable to routine isolation and purification, and these compounds decompose quickly under ambient conditions.[1] Phenylhexatriyne was reported to explode at 0 °C in the absence of air during attempted isolation,[2] while the unsubstituted hexatriyne exploded violently upon exposure to air.[3] Kloster-Jensen et al. reported the isolation of the parent butadiyne, hexatriyne, octatetrayne, and even decapentayne [H−(C≡C)$_n$H] ($n = 2-5$). However, the only data to support the structures were UV−vis spectra and ^{1}H NMR spectra of mixtures.[4] Since the instability of oligoynes increases dramatically as the sp-carbon chain elongates, aryl terminal hexatriynes and higher homologues have normally been obtained as solutions rather than isolated as their pure forms.[5] Organometallic analogues are generally considered to be significantly more stable than their organic counterparts,[6] thus terminal organometallo-hexatriynes have been isolated and

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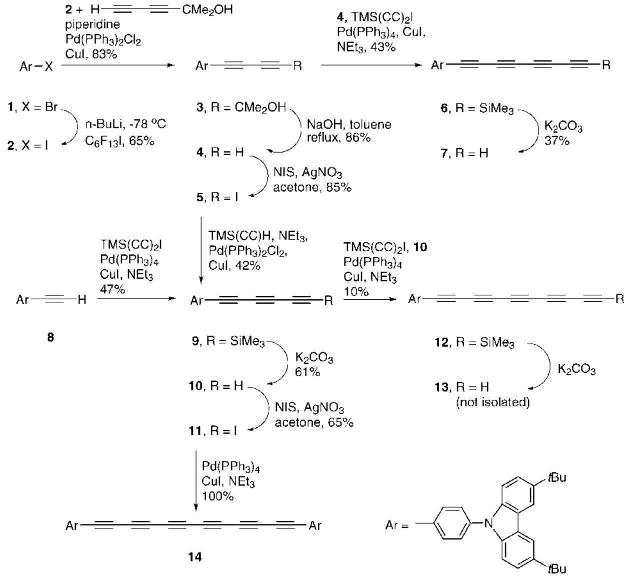
well characterized.[6,7] A Zn porphyrinylphenylhexatriyne has also been isolated.[8] Recently, we reported the synthesis and X-ray crystal structures of a series of terminal aryl/heteroaryl butadiynes which were stable to ambient isolation and characterization.[9] The crystal packing motifs of these molecules played important roles in their solid-state stability. Intermolecular cross-linking of triple bonds is a major pathway for the decomposition of oligoynes.[10] Bulky aryl head groups should stabilize longer sp homologues by hindering the topochemical intermolecular interactions in the crystal lattice, which are required for the head−tail $\pi-\pi$ cross-coupling.[11]

With the aim of synthesizing longer all-organic terminal oligoynes, we chose *N*-phenylcarbazole as a headgroup because the *N*-phenyl substituent cannot be coplanar with the carbazole moiety due to steric repulsion between *peri*-H atoms, as proven by AM1 calculations (showing potential minima at twist angles $\theta = 45°$ and 135° with a torsion barrier of 11 kcal/mol at $\theta = 0°$),[12] NMR data, and crystal structures of *N*-phenylcarbazole ($\theta = 78°$ and 55°),[12] *N*-(4-cyanophenyl)carbazole ($\theta = 48°$),[13] and **8** ($\theta = 47°$).[14]

We now report the successful synthesis, isolation, and X-ray structural analyses of the terminal aryl hexatriyne **10** and the terminal aryl octatetrayne **7** both of which are monocapped with an all-organic group, namely, 4-(3,6-di-*tert*-butyl-*N*-carbazolyl)phenyl. To the best of our knowledge, a pure terminal octatetrayne has not been reported previously. The trimethylsilyl (TMS) protected decapentayne homologue **12** has also been isolated, although the corresponding terminal pentayne **13** was unstable to isolation. **Caution:** The stability of terminal oligoynes is dependent on the nature of the end groups. Although no explosions were encountered during this work, great care should be taken when carrying out similar reactions.

Our synthetic strategy toward the terminal oligoynes (Scheme 1) was based on iterative cross-coupling reactions of terminal 4-(3,6-di-*tert*-butyl-*N*-carbazolyl)phenyl alkynes with 1-iodo-4-trimethylsilyl butadiyne (TMSBI)[15] under Sonogashira conditions, apart from the butadiyne derivative **4** which was prepared via precursor **3** using a 2-methyl-3,5-hexadiyn-2-ol protocol.[9,16] For the synthesis of the TMS-protected hexatriyne **9**, both methods, namely, the cross-coupling of the monoalkyne **8**[17] with TMSBI and the cross-coupling of the iodo-butadiyne **5** with trimethylsilylacetylene (TMSA), gave **9** in comparable yields. However, the former route was synthetically preferable as the cleaner reaction mixture facilitated purification. Furthermore, the monoalkyne **8** and its counterpart TMSBI are more readily available than the diyne homologue **5**. The terminal hexatriyne **10** was obtained by deprotecting **9** with potassium carbonate in MeOH-CH$_2$Cl$_2$ at room temperature. Similarly, the tetrayne **7** was obtained by cross-coupling of diyne **4** with TMSBI, followed by deprotection of **6**. However, the attempted cross-coupling of iodo-hexatriyne **11** with TMSA under Sonogashira conditions yielded exclusively the oxidatively self-coupled diaryldodecahexayne derivative **14**, as dark yellow crystals which could be stored at room temperature in the dark for 6 months without any change.[18] The same reaction under Hay conditions[7] resulted in decomposition of **11** and self-coupling of TMSA. We, therefore, abandoned this route.

Scheme 1. Synthesis of the Terminal Aryl Oligoynes



Following the successful isolation of the terminal tetrayne **7**, the synthesis of pentayne **13** was attempted. Terminal hexatriyne **10** was cross-coupled with TMSBI under Sonogashira conditions to afford TMS-capped pentayne **12** in 10% yield. The orange crystals of **12** were remarkably stable: a sample was stored at rt in a flask wrapped with Al foil for a week, then in a freezer (at ca. −20 °C) for several months without any observable color change. It is likely that the low yield of **12** was due to decomposition of **10** in the reaction mixture. A large amount of insoluble dark-brown solid was observed: this is characteristic of decomposed oligoynes. The

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attempted cross-coupling of tetrayne **7** with iodo-TMSA yielded a dark brown solid from which no product could be isolated. The attempted isolation of the terminal pentayne **13** from the deprotection of **12** was unsuccessful, although the UV−vis absorption spectrum (Figure 1b) obtained from a dilute solution of the reaction mixture was consistent with the formation of **13**. The deprotection resulted in an 18 nm blue shift in the oligoynic λ_{max} which is larger than that reported for a mesityl analogue ($\Delta\lambda_{max}$ 8 nm in MeOH).[5c] However, Maldi-Tof mass spectrometry could not detect any expected signal for **13** from the solution of deprotected **12**. Presumably, **13** decomposed too rapidly as the solvents were evaporated during the matrix preparation. Therefore, the synthesis of higher homologues was not attempted.

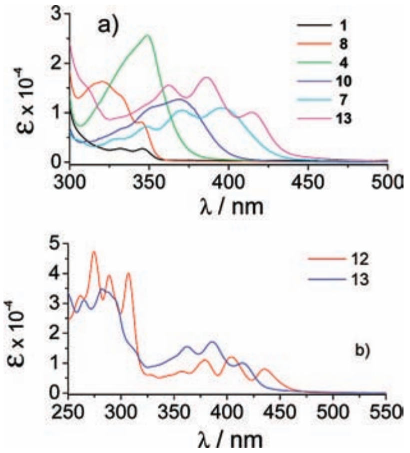

Figure 1. UV−vis absorption spectra: (a) **1**, terminal mono- (**8**), di- (**4**), tri- (**10**), tetra- (**7**), and penta- (**13**) ynes (1×10^{-5} M in dichloromethane); (b) comparison of the pentaynes **12** and **13**. The concentration of pentayne **13** is arbitrary.

The successful isolation of the series of oligoynes **4**, **10**, and **7** has enabled for the first time an analysis of how the acetylenic ^{1}H NMR chemical shift changes with extending the sp-carbon chain length up to a C_8H system. In marked contrast to the red shifts of the UV−vis absorption spectra, which follow the Lewis−Calvin rule,[19] the additional shielding effects caused by extending a triple bond decreased dramatically as the chain length increased. The elongation from monoyne **8** ($\delta = 3.20$ ppm) to diyne **4** ($\delta = 2.54$ ppm) to triyne **10** ($\delta = 2.31$ ppm) to tetrayne ($\delta = 2.23$ ppm) resulted in 0.66, 0.23, and 0.08 ppm upfield shifts, respectively. This progressively reduced shielding effect of the additional triple bonds can also be seen from the ^{13}C chemical shifts of the TMS-protected oligoynes [di(*t*-butyl)carbazolylphenyl-$(C\equiv C)_n$-TMS], where the δ values of the methyl-C of the TMS group are 0.02 ($n = 1$),[20] −0.39 ($n = 2$, Figure S35), −0.51 ($n = 3$, Figure S20), −0.59 ($n = 4$, Figure S11), and −0.64 ($n = 5$, Figure S29), and thus the upfield shifts are 0.41, 0.12, 0.08, and 0.05, respectively. When the TMS protecting groups are removed, the ^{13}C chemical shifts of the terminal acetylenic carbons show the same trend, i.e., 77.9 (**8**, $n = 1$), 71.7 (**4**, $n = 2$), 69.2 (**10**, $n = 3$), and 68.2 (**7**, $n = 4$) ppm. This shielding effect is in agreement with the report of Ziessel et al. for pyridyl oligoynes[21] but is opposite to that reported for [H-$(C\equiv C)_n$-H] ($n = 1-4$) where the acetylenic protons were deshielded by additional triple bonds.[4]

The solution UV−vis absorption spectra of the terminal oligoynes are shown in Figure 1. Unlike their mesityl analogues,[4] the vibronic features of the low energy oligoynic bands for **4** and **10** were not clearly visible. In particular, butadiyne **4** exhibited a very intense single peak at $\lambda_{max} =$ 349 nm with a small shoulder on the high energy side. The loss of the fine structure could be due to overlap of the $n-\pi^*$ transition of the *N*-phenylcarbazole unit ($\lambda_{max} = 343$ nm for **1**, Figure 1a; and $\lambda_{max} = 343$ nm for *N*-phenylcarbazole in cyclohexane[22]) with the $\pi-\pi^*$ transitions of the oligoynic chromophores. For the tetrayne **7** and pentayne **13**, the vibronic fine structures with $\lambda_{max} = 348$, 371, and 395 nm (for **7**) and 362, 386, and 416 nm (for **13**), respectively, were well-defined. In addition, the carbazole-derived high intensity $\pi-\pi^*$ transitions below 300 nm for these two compounds also became vibronic (Figure 1b).

The stability of the crystalline butadiyne **4** is remarkable. A gram-scale sample was stored for many months at −20 °C without any noticeable color change. Triyne **10** decomposed faster in chloroform solution than **4**. Nonetheless, an NMR sample of **10** [ca. 5 mg in $CDCl_3$ (0.5 mL)] survived >6 h inside the spectrometer at 20 °C. A single crystal of **10** was obtained by an accelerated evaporation process. As expected, the tetrayne **7** was less stable than the triyne **10**. Crystals of **7** were stable in a freezer at −20 °C in the dark, although storage at 20 °C under standard room light resulted in darkening within ca. 10 min. Predictably, the pentayne homologue **13** was the least stable in the series.

The November 2007 release of the CSD[23] contains no structure with a $(C\equiv C)_4H$ moiety and only two with a $(C\equiv C)_3H$, viz. $(^tBuNO)ClC_6H_3(C\equiv C)_3H$ (which polymerized under X-rays even at 220 K, hence only the lattice parameters were obtained)[24] and $(PhN-C_5H_4N)_4Ru_2(C\equiv C)_3H$, where the oligoyne chain may be stabilized by $p\pi-d\pi$ interaction with

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(25) X-ray experiments: SMART 6K CCD area detector diffractometer, graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), SHELXTL 6.14 software (Bruker AXS, Madison WI, USA, 2003). At room temperature, single crystals deteriorated rapidly, both in and out of mother liquor. The diffraction of **4** and **7** was weak, mean $I/\sigma(I) = 5.0$ and 4.3, respectively. Crystal data for $C_{30}H_{29}N$ (**4**), $C_{34}H_{29}N$ (**7**), and $C_{32}H_{29}N$ (**10**): $M = 403.54/451.58/427.56$, $T = 120$ K, monoclinic, space group $P2_1/c$ (no. 14), $a = 19.295(2)/21.065(3)/5.824(1)$, $b = 5.7668(9)/5.6665(8)/19.988(2)$, $c = 22.291(3)/22.090(4)/21.420(2)$ Å, $\beta = 107.45(1)/98.48(5)/96.61(1)°$, $V = 2366.2(5)/2607.9(7)/2476.9(5)$ Å^3, $Z = 4$, $D_c = 1.133/1.150/1.147$ g/cm, 13441/13239/24480 reflections measured, 5416/4588/6544 unique, of which 2698/2068/4950 with $I > 2\sigma(I)$, $R_{int} = 10.0/12.7/4.2\%$, $R_1[I > 2\sigma(I)] = 5.3/6.0/4.7\%$, $wR(F^2) = 11.8/10.5/12.8\%$ (all data). CCDC 679671 (**4**), 679672 (**7**), 679673 (**10**) contain the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

the σ-bonded Ru atom.[7b] Indeed, two-thirds (28 out of 41) of the $R(C\equiv C)_2H$ derivatives also have the R unit linked to the butadiyne unit through a (transition) metal atom.

X-ray structural studies of **4**, **7**, and **10** (Figure 2) showed the expected twisted conformation (θ = 58, 50, and 51°, respectively).[25] The oligoyne rods are slightly bent, the terminal bonds forming an angle of 172, 174, and 164°, respectively. In each structure, it is possible to discern arrays of parallel oligoyne rods, related by the *b* translations in **4** and **7** and by the *a* translation in **10**. The translation ("stacking") vectors of 5.77, 5.67, and 5.82 Å are inclined to the rod directions by 48, 42, and 45°, respectively. The packing does not favor polymerization. In **4** the, shortest inter-rod distances (C1···C4) of 4.30 Å exceed the threshold of 4 Å required for solid-state polymerization.[26] The shortest distances in **7**, viz., C1···C4, C2···C5, C3···C6, C4···C7, and C5···C8, of 3.73−3.88 Å, are within this limit but not topologically suitable for a regular polymerization without large displacements of entire molecules.[10] Such displacements, or even smaller (but still substantial) atomic displacement occurring during a "good" topotactic polymerization of butadiynes, would be seriously hindered by the bulky and nonplanar di(*t*-butyl)carbazolylphenyl substituent.[11a] Structure **10** has both problems simultaneously, the shortest contacts C1···C4, C2···C5, and C3···C6 being 4.06−4.17 Å.

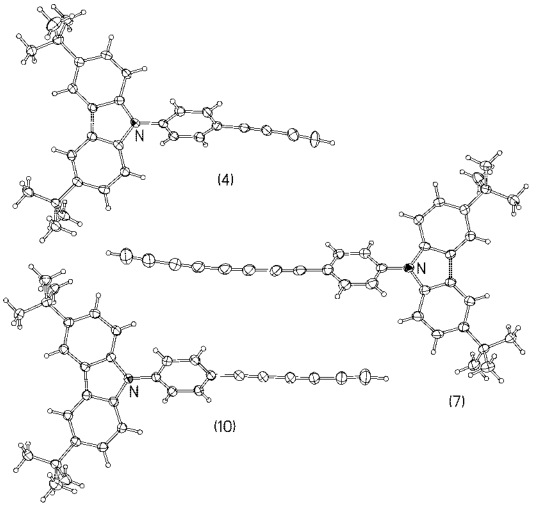

Figure 2. X-ray molecular structures of **4**, **7**, and **10**.

In summary, unprecedented stability has been observed in all-organic terminal aryl hexatriyne and octatetrayne derivatives by judicious choice of a bulky, nonplanar headgroup [viz., 4-(3,6-di-*tert*-butyl-*N*-carbazolyl)phenyl] which serves to hinder the topochemical intermolecular interactions in the crystal lattice which are required for the head−tail cross-linking of the oligoyne units. New acetylenic building blocks which are suitable for the assembly of polyyne chains and other carbon-rich scaffolds[27] have been synthesized.

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Supporting Information Available: Supporting Information for this article including synthetic details, NMR, and MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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