Carbon-rich molecules: synthesis and isolation of aryl/heteroaryl terminal bis(butadiynes) (HC≡C–C≡C–Ar–C≡C–C≡CH) and their applications in the synthesis of oligo(arylenebutadiynylene) molecular wires†

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The synthesis, isolation and characterisation are reported for a series of terminal aryl/heteroaryl bis(butadiynes) (HC≡C–C≡C–Ar–C≡C–C≡CH) **4a–e** including the X-ray molecular structure of the 2,5-pyridylene derivative **4d**; compound **4a** and the mono-protected analogue [HC≡C–C≡C–Ar–C≡C–C≡C–C(OH)Me_2] **5a** serve as convenient precursors for the synthesis of highly-conjugated oligo(arylenebutadiynylene)s.

Introduction

Conjugated diyne and oligoyne molecules are of great interest in contemporary acetylene chemistry[1] as a class of carbon-rich backbones.[2] They are of theoretical interest as probes of extended π-conjugation[3] and they can serve as active components in optoelectronic devices (wires, switches and nonlinear optics, *etc.*).[4] Recently, the synthesis and optoelectronic properties of oligo(aryleneethynylene) (OAE) systems, $(\mathrm{Ar{-}C{\equiv}C{-}})_n$, have been widely investigated.[5] For example, oligo-*p*-(phenylenethynylene)s (OPEs) serve as bridges to mediate photoinduced electron transfer [6] and the conductance of single OPE molecules has been determined in molecular device architectures.[7] Oligoyne systems $[\mathrm{R{-}(C{\equiv}C)}_n\mathrm{{-}R}]$ with internal carbyne fragments are also contemporary targets and many derivatives of nanoscale lengths end-capped with organometallic,[8] silyl[9] or aryl substituents[10] have been synthesised. Aryl end-capped derivatives beyond 1,6-diarylhexatriyne $[\mathrm{Ar{-}(C{\equiv}C)_3{-}Ar}]$ have proved challenging due to the instability of some of these systems and/or their precursors.[11]

Oligo(arylenebutadiynylene)s $(\mathrm{Ar{-}C{\equiv}C{-}C{\equiv}C{-}})_n$ are a class of carbon-rich backbones which have rarely been studied.[12] Encouraged by our recent work[13] on the isolation and unexpected stability[14] of a series of terminal aryl/heteroaryl butadiynes (Ar–C≡C–C≡CH) we postulated that analogous terminal bis(butadiynes) (HC–C≡C–C≡C–Ar–C≡C–C≡CH) might be isolable species[15] and, if so, they could be valuable precursors to oligo(arylenebutadiynylene)s. Herein we describe the synthesis and isolation of a series of aryl/heteroaryl bis(butadiynes) **4a–e** {Ar = 2,5-dimethoxy-1,4-phenylene, 4,4-biphenylene, [2,7-(9,9-dimethyl)fluorenylene], 2,5-pyridylene and 4,6-pyrimidylene} including the first crystal structure of a terminal aryl bis(butadiyne), compound **4d**.

Results and discussion

Our protocol (Scheme 1) is an extension of the route we have developed for arylbutadiynes.[13] The polar 2-hydroxy-2-propyl protecting group facilitates purification of the reaction mixtures. Reaction of the aryl/heteroaryl diiodides **1a–e** with 2-methyl-3,5-hexadiyn-2-ol **2**[16] (2.5–3.0 equiv.) under standard Sonogashira conditions[17] [triethylamine, CuI, $Pd(PPh_3)_2Cl_2$, 20 °C (for **1b**, **1e**) or 50 °C (for **1a**, **1c**, **1d**)] gave precursors **3a–e** (60–93% yields). For the crucial deprotection step (*i.e.* loss of acetone) the standard conditions were a catalytic amount of NaOH in refluxing toluene.[18] The optimum time for this deprotection was *ca.* 10 min: longer reaction times produced an increased amount of intractable black solid. In all cases a mixture was obtained of the di-deprotected **4a–e** and mono-deprotected products **5a–e**, which were cleanly separated by column chromatography. Pyridyl derivative **5d** was isolated as a mixture of regioisomers arising from deprotection of the substituent at C2 or C5. When refluxing benzene was used as the solvent for these reactions the yield of **4a** increased to 64%. The yields of **4b–e** were similar in either benzene or toluene. Compound **3d** was insoluble in benzene. However, the yield of **4d** was raised to 50% when the deprotection was carried out in refluxing THF.[19] The yields of **4a** and **5a** were unchanged when either NaOH, KOH or NaH was used as the base in refluxing toluene. All of the products in Scheme 1 were characterised by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Compounds **4a–e** have been stored as solids at −15 °C for several months without observable decomposition. At room temperature samples darkened in colour within *ca.* 24 h although they can be stored as dilute solutions for several days or even weeks.

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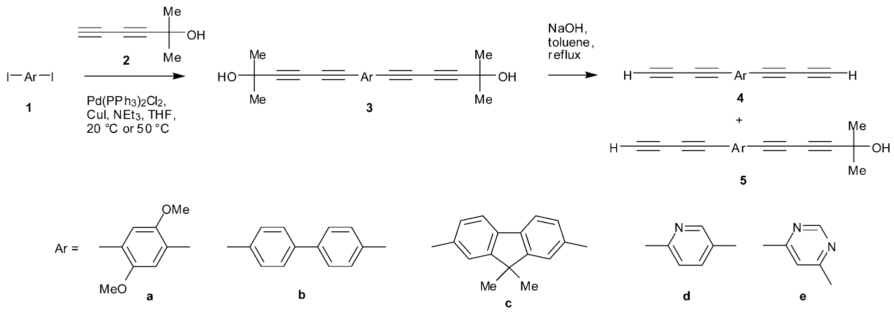
† Electronic supplementary information (ESI) available: Experimental details; characterisation data including crystallography; copies of UV–vis absorption and NMR spectra. CCDC reference numbers 675274–675276. See DOI: 10.1039/b802968g



Scheme 1 General scheme for the synthesis of aryl/heteroaryl bis(butadiynes). Isolated yields: **3a–e** (60–93%); **4a** 24% (64% from reaction in refluxing benzene); **4b** 65%; **4c** 62%; **4d** 27% (50% from reaction in refluxing THF); **4e** 22%; **5a** 52%; **5b** 30%; **5c** 37%; **5d** 20% (as a mixture of regioisomers); **5e** 15%.

X-Ray crystal structures‡ were obtained for the terminal bis(butadiyne) **4d** and the terminal mono(butadiyne) species **5a** and **5d** (notably **5d** crystallised as one regioisomer) (Fig. 1). The crystals of **4d**, **5a** and **5d** were sufficiently stable for routine X-ray analysis within a few days of their isolation. The molecular 'rod' in **4d** is essentially linear, whereas in **5a** it is S-shaped: C(9)≡C(10) and C(13)≡C(14) are nearly parallel, but deviate by 9.0° and 6.1° from the C(2) $\cdots$ C(5) direction. Compound **5d** shows a C-shaped bending, the C(9)≡C(10) and C(13)≡C(14) bonds forming an angle of 166.3°. The (localised) single and triple bonds in the butadiyne moieties have the usual lengths, not affected significantly by the 2-hydroxy-2-propyl group.

All three structures contain continuous hydrogen-bonded motifs (Fig. 2 and ESI†). Molecules of **4d** pack in a herringbone fashion to form layers parallel to the (010) plane. One acetylenic H group forms a nearly-linear C–H $\cdots$ N hydrogen bond, the other participates in a C–H $\cdots$ π(C≡C) interaction of rather awkward geometry. Molecules of **5d** are linked by ≡C–H $\cdots$ O hydrogen bonds into linear chains, whose periodicity is eminently suitable for cross-linking by O–H $\cdots$ N bonds. No such match is possible for the isomer with the N atom *ortho* to the protected butadiyne unit, which may be the reason why **5d** crystallised as one regioisomer.

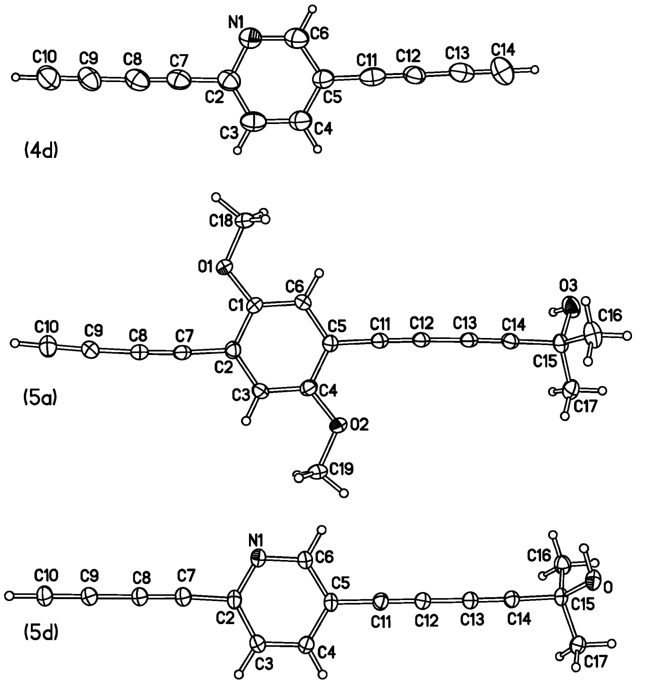


Fig. 1 X-Ray molecular structures of **4d**, **5a** and **5d** (50% probability thermal ellipsoids).

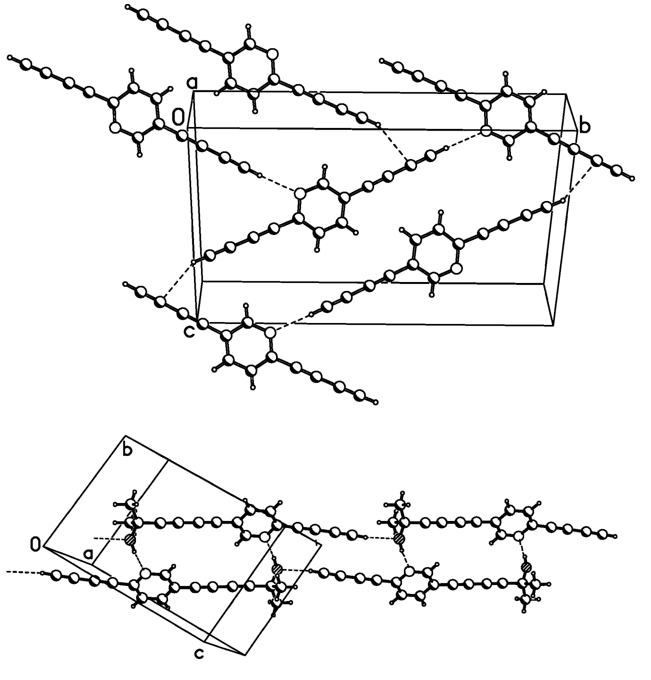


Fig. 2 Hydrogen bonds (dashed lines) in the structures of **4d** (top) and **5d** (bottom).

Compounds **4a** and **5a** served as building blocks for the synthesis of oligo(arylenebutadiynylene) derivatives using standard Sonogashira cross-coupling protocols. Compound **4a** was

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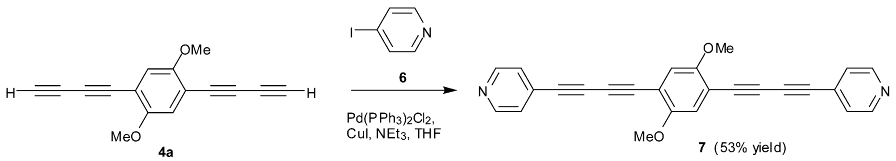
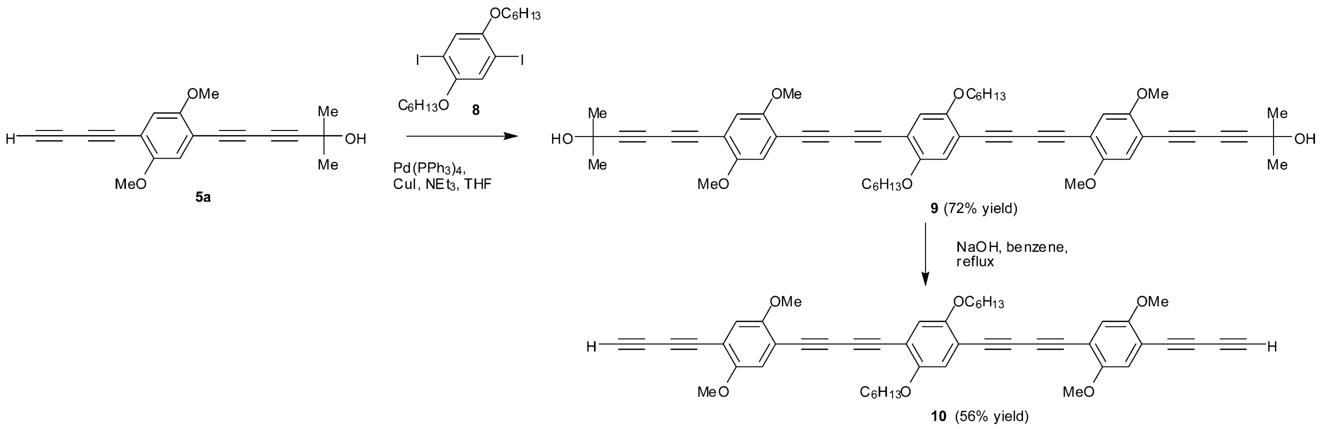
‡ Crystal data: **4d**, $C_{13}H_5N$, $M = 175.18$, monoclinic, $P2_1/c$, $a = 3.7926(8)$, $b = 20.217(4)$, $c = 12.385(3)$ Å, $\beta = 94.91(1)°$, $U = 946.2(3)$ Å^3, $Z = 4$, $D_c = 1.230$ g cm^{-3}, $\mu = 0.073$ mm^{-1}, 8467 reflections ($2\theta \leq 50°$), $R_{int} = 0.1512$, $R(F) = 0.0686$ [683 data with $I \geq 2\sigma(I)$], $wR(F^2) = 0.2080$ (1685 unique data); **5a**, $C_{19}H_{16}O_3$, $M = 292.32$, monoclinic, $C2/c$, $a = 17.555(2)$, $b = 9.126(1)$, $c = 19.831(2)$ Å, $\beta = 101.46(1)°$, $U = 3113.7(6)$ Å^3, $Z = 8$, $D_c = 1.247$ g cm^{-3}, $\mu = 0.084$ mm^{-1}, 11371 reflections ($2\theta \leq 55°$), $R_{int} = 0.0676$, $R(F) = 0.0444$ [1987 data with $I \geq 2\sigma(I)$], $wR(F^2) = 0.0945$ (3571 unique data); **5d**, $C_{16}H_{11}NO$, $M = 233.26$, triclinic, $P\text{-}1$, $a = 5.7609(7)$, $b = 9.0756(10)$, $c = 12.6163(14)$ Å, $\alpha = 87.79(1)$, $\beta = 77.87(1)$, $\gamma = 77.99(1)°$, $U = 630.77(12)$ Å^3, $Z = 2$, $D_c = 1.228$ g cm^{-3}, $\mu = 0.077$ mm^{-1}, 7737 reflections ($2\theta \leq 60°$), $R_{int} = 0.0236$, $R(F) = 0.0436$ [2626 data with $I \geq 2\sigma(I)$], $wR(F^2) = 0.1171$ (3464 unique data).



Scheme 2 Synthesis of **7**.



Scheme 3 Synthesis of **10**.

end-capped by two-fold reaction with 4-iodopyridine to give **7** in 53% yield (Scheme 2).[20] Compound **5a** (2 equiv.) reacted with reagent **8** to give **9** in 72% yield. Hexyloxy chains were attached to **8** to enhance the solubility of the products. Bis-deprotection of **9** gave compound **10** which was isolated as an amorphous yellow solid in 56% yield and identified by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Both compounds **9** and **10** are shelf-stable at room temperature for at least several months, which suggests that they will prove to be a valuable building block in this series. Clearly, further cross-coupling reactions of **10** to yield longer oligo(arylenebutadiynylene)s can be envisaged.

UV–vis absorption spectra in chloroform solution provide evidence that there is increased conjugation in the bis-butadiyne series, compared to their mono-butadiyne analogues. For example, 2,5-bis(buta-1,3-diynyl)pyridine **4d** shows a 34 nm red shift for the lowest energy peak compared to 3-(buta-1,3-diynyl)pyridine[13b] (Fig. 3). Similarly, the biphenyl system **4a** shows a 21 nm red shift compared to its mono(butadiyne) analogue (see ESI†).

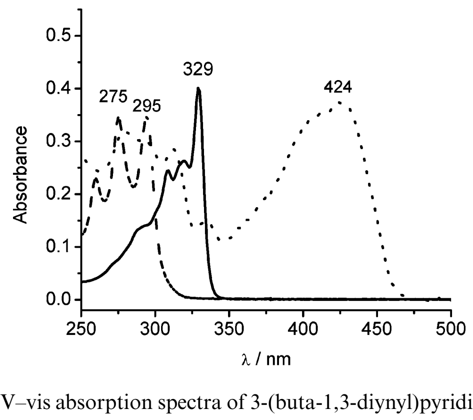


Fig. 3 UV–vis absorption spectra of 3-(buta-1,3-diynyl)pyridine (dashed line), **4d** (solid line) and compound **10** (dotted line) in chloroform solution.

The terminal 2-hydroxy-2-propyl groups have no significant effect on the absorption spectra of this series of compounds as shown by a comparison of the protected compounds **3a–e** and their deprotected counterparts **4** and **5**, and a comparison of **9** and **10** (see ESI†). Extended π-conjugation in the oligo(*p*-phenylenebutadiynylene) derivatives **9** and **10** (Scheme 3) is clearly evident from their substantially red-shifted absorptions, especially of the lowest energy band, compared to the segments **3a** and **4a** (**4a**: λ_{max} 293, 310, 379 nm; see ESI†). The numerous absorption peaks in the spectra of **9** and **10** are typical of oligo(*p*-phenyleneethynylene) derivatives bearing alkoxy substituents: the absorptions at λ_{max} 427 (**9**) and 424 nm (**10**) can be assigned to a HOMO–LUMO transition.[21]

In summary, the synthesis and isolation of a range of terminal aryl- and heteroaryl-bis(butadiynes) (HC–C≡C–C≡C–Ar–C≡C–C≡CH) have been achieved for the first time. These compounds are sufficiently stable for characterisation by ^{1}H NMR, ^{13}C NMR and UV–vis spectroscopy and mass spectrometry, and in one case (compound **4d**) an X-ray crystal structure has been obtained. Furthermore, we have established an expedient route to oligo(arylenebutadiynylene) derivatives, which are an essentially unexplored class of carbon-rich molecules.

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