Synthesis and characterization of cross-conjugated polyenynes

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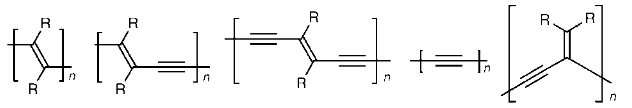
Extended, cross-conjugated polyenynes are reported as well as a description of their electronic (UV–VIS) characteristics and an X-ray crystallographic analysis of hexayne 9 that shows solid-state molecular alignment suitable for topochemical polymerization.

The sequential combination of sp and/or sp^2 hybridized carbons affords a series of wire-like π-conjugated carbon chains typified by the structures of polyacetylene (**1**),[1] polydiacetylene (PDA, **2**)[2,3] and polytriacetylene (PTA, **3**)[4] in a progression that ultimately concludes with the one-dimensional carbon allotrope, carbyne (**4**).[5–7]



1 **2** **3** **4** **5**

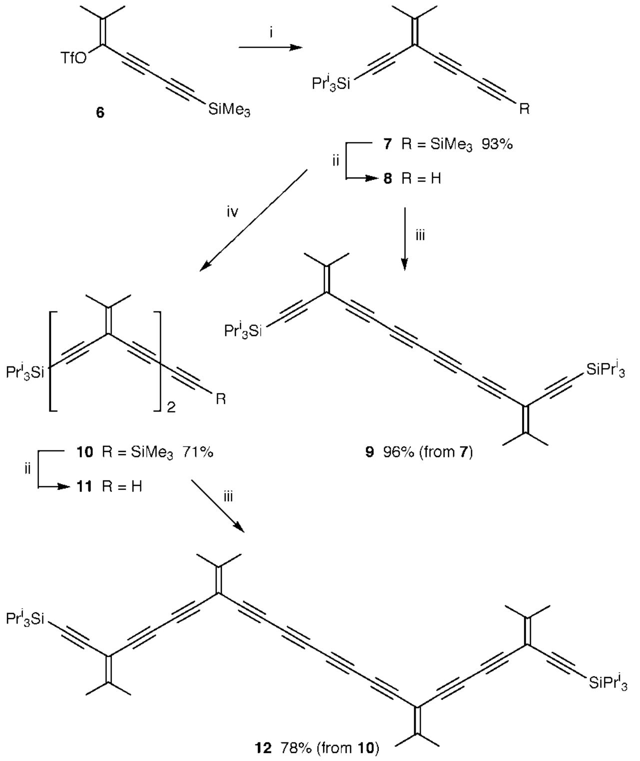
The most recent addition to this mélange of enyne oligomers is *iso*-polydiacetylene (*iso*-PDA, **5**),[8] the cross-conjugated isomer of **2**.[9] Studies of *iso*-PDAs have shown that π-electron communication is present along the cross-conjugated framework, albeit to a much lesser extent than for PDAs. To provide a better understanding of the physical and electronic characteristics of cross-conjugated enynes, we have extended the skeleton of **5** by inserting additional alkyne groups. Herein, we report the first synthesis of these cross-conjugated polyenynes and a preliminary description of their electronic, X-ray crystallographic and solid-state chemical characteristics.

The enyne oligomers were synthesized as outlined in Scheme 1. Vinyl triflate **6**[10] was coupled with triisopropylsilylacetylene in THF at ambient temperature. Work-up and flash column chromatography, gave the triyne **7** in 93% yield.† Protodesilylation of **7** gave terminal alkyne **8**, which was then oxidatively homocoupled[11] to hexayne **9** in 96% yield as a stable, light yellow solid.

Triyne **8** was also elaborated to pentayne **10** in 71% yield *via* reaction with vinyl triflate **6**, as described for the formation of **7**. Desilylation of **10** gave the terminal alkyne **11**, which afforded a good yield of decayne **12**. Notably, the ^{13}C NMR of **12** shows individual resonances for all 10 acetylenic carbons, as well as four unique signals for the alkylidene methyl carbons.‡

Yellow single crystals of hexayne **9** were grown by diffusion of MeOH into a CH_2Cl_2 solution at –20 °C, and the structure was determined by X-ray crystallographic analysis (Fig. 1).§ The π-framework of **9** is virtually planar, with a maximum deviation of 0.130(17) Å from the least-squares plane for the 16-carbon conjugated skeleton.¶ All six triple bonds are essentially the same length, suggesting little bond length alteration as a result of π-conjugation and contrasting results for PDA oligomers of similar size.[12] The eight tetrayne carbons are virtually linear, showing only a gradual curvature with bond angles deviating less than 3° from 180°.

Analysis of the crystal packing of **9** down the *b*-axis shows the molecules are aligned in a parallel fashion (Fig. 1). The intermolecular proximity of the tetraynes in the crystal suggests the potential for topochemical polymerization as is well established for suitably aligned butadiynes and hexatriynes.[2,13,14a] The solid-state polymerization of octatetraynes has also been previously described, albeit in much less detail.[14]



Scheme 1 *Reagents and conditions*: i, triisopropylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, Pr^i_2NH, THF, room temp; ii, K_2CO_3, wet MeOH–THF (1 : 1), room temp; iii, CuI, TMEDA, O_2, CH_2Cl_2 room temp; iv, **6**, $PdCl_2(PPh_3)_2$, CuI, Pr^i_2NH, THF, room temp.

The parameters describing the intermolecular relationship of molecules **9** are depicted in Fig.1(*c*).[2,13a,14a] Polymerization of **9** *via* 1,2- or 1,4-addition, as described for tetrayne systems,[14] is unlikely considering that $R_{1,2}$ (6.7 Å) and $R_{1,4}$ (4.7 Å) are both considerably more than the ideal distance of 4 Å between reacting carbon atoms. The angle ϕ between the tetrayne rod and the stacking axis at *ca*. 28° is significantly less than the optimum value of 45° determined for 1,4-addition in di-, tri- and tetraynes.[2,13a,14a] Thus, two alternative addition patterns might occur for **9**, namely 1,6-addition ($R_{1,6}$ = 3.6 Å) and 1,8-addition ($R_{1,8}$ = 4.2 Å). The stacking angle ϕ is nearly identical to the value of 27° that denotes highest 1,6-reactivity in triacetylenes, and the stacking distance between monomer units at 7.7 Å is quite near the desired value of 7.5 Å.[13a] In view of these values, 1,6-addition is the expected mode of reaction for **9**.

Differential scanning calorimetry showed that crystals of **9** have a well-defined melting point at 103–104 °C that is followed by decomposition at 145 °C. Attempts to thermally effect polymerization of single crystalline **9** were conducted at 90 °C. Over the course of 8 h, the crystals darken slightly to yield an opaque solid. A loss of crystal integrity for the resultant material was confirmed by the absence of any X-ray diffraction pattern. To date, the product(s) of this thermal reaction has not been identified.

Photochemical polymerization of a single crystal of **9** was attempted by monochromatic irradiation at 280 nm.[15,16] After

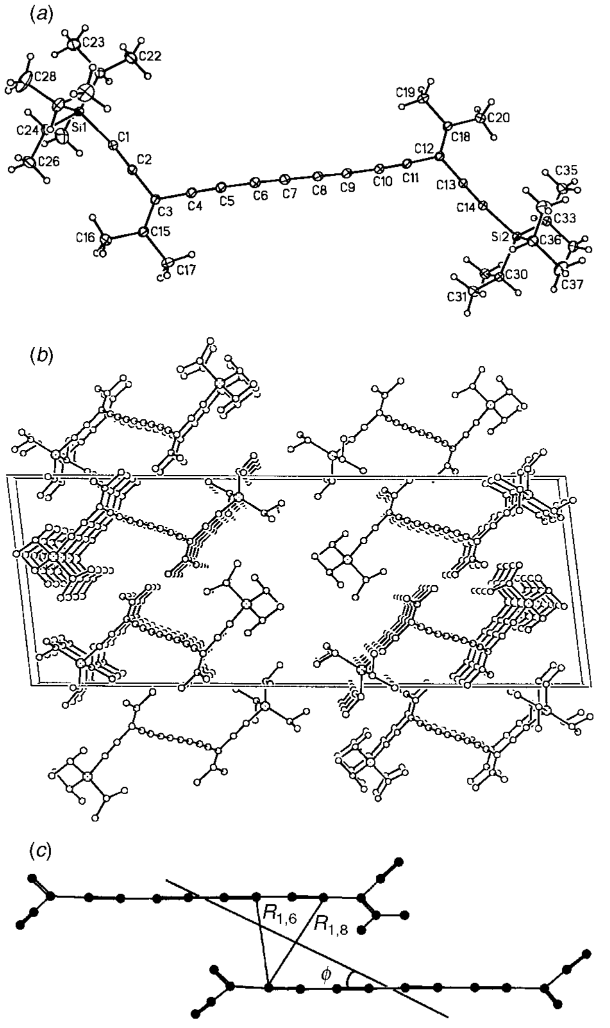


Fig. 1 (*a*) ORTEP drawing (20% probability level) of **9**, (*b*) crystal packing of **9** as viewed along the *b*-axis, and (*c*) crystal packing parameters for **9**.

approximately 2 h, a darkening of the crystal to yellow–orange was observed. Irradiation was continued for another 4 h with little additional darkening. X-Ray analysis of the crystal afforded a diffraction pattern and cell parameters identical to that of pure **9**, indicating little change in the solid beyond that which may have occurred at the outer surface of the crystal.

The electronic absorption spectra of **9**, **12** and 1,8-bis(4-*tert*-butylphenyl)-octa-1,3,5,7-tetrayne **13**, are shown in Fig. 2. The lower energy region is dominated by the absorption pattern of the tetrayne moiety and is remarkably similar to that of **13**.[17] Each compound displays three absorptions at *ca*. 405, 374 and 348 nm. Whereas the UV spectra of elongated *iso*-PDAs show evidence of π-electron communication *via* cross-conjugation,[8] this effect is absent in **9** and **12**, as the three lowest energy absorptions of **12** are each red-shifted by only 1 nm *versus* those of **9**.

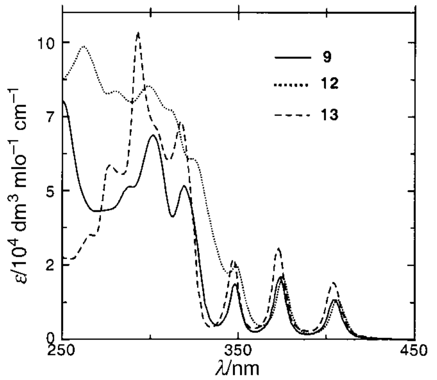


Fig. 2 UV–VIS spectra in $CHCl_3$ comparing polyynes **9**, **12** and **13**.

In conclusion, cross-conjugated polyenynes **7**–**12** can be synthesized in high yields as relatively stable solids. The UV–VIS spectra of **9** and **12** show a minimal contribution from cross conjugation. The solid state organization of **9** is suitable for topochemical polymerization, although initial attempts to effect thermal and photochemical polymerization have been unsuccessful. Further studies on **9** and **12** are currently underway.

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Notes and references

† The purity and structure of all new compounds were confirmed by ^{1}H and ^{13}C NMR, IR, UV, MS and either EA or HRMS.

‡ *Selected data* for **9**: yellow solid, mp 103–104 °C; δ_H(300 MHz, $CDCl_3$) 2.07 (s, 6H), 2.05 (s, 6H), 1.07 (s, 42H); δ_C(75 MHz, $CDCl_3$) 162.3, 101.2, 100.9, 94.9, 76.3, 75.0, 67.8, 64.1, 23.4, 23.2, 18.7, 11.3. For **12**: yellow solid, decomposition begins at *ca*. 80 °C; δ_H(300 MHz, CD_2Cl_2) 2.11 (s, 12H), 2.09 (s, 6H), 2.06 (s, 6H), 1.10 (s, 42H); δ_C(125 MHz, CD_2Cl_2) 166.6, 160.8, 102.3, 101.2, 99.7, 94.3, 80.2, 77.5, 77.0, 76.9, 75.4, 74.4, 68.1, 64.2, 23.7, 23.6, 23.3, 23.1, 18.8, 11.7.

§ *Crystal data* for **9**: $C_{38}H_{54}Si_2$, $M = 566.99$, monoclinic space group $P2_1/c$ (No. 14), $Dc = 1.018$ g cm^{-3}, $Z = 4$, $a = 13.5571(8)$, $b = 7.7132(5)$, $c = 35.616(2)$ Å, $\beta = 96.5990(10)°$, $V = 3699.7(4)$ Å^3, $\mu = 0.118$ mm^{-1} Final $R(F) = 0.0472$, $wR_2(F^2) = 0.1366$ for 365 variables and 7039 data with $F_o^2 \geqslant -3\sigma(F_o^2)$ (4842 observations $[F_o^2 \geqslant 2\sigma(F_o^2)]$). CCDC 182/1485.

¶ The known X-ray structures of tetraynes and a pentayne have been summarized in refs. 7(*b*) and 7(*c*).

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