

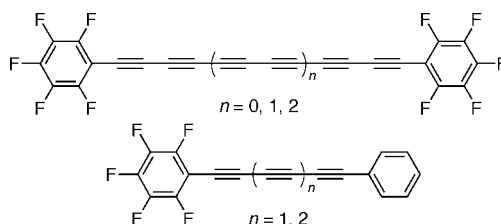
Synthesis and Solid-State Structure of
Perfluorophenyl End-Capped Polyynes

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ABSTRACT



Five new supramolecular building blocks have been synthesized on the basis of polyynes end-capped with pentafluorophenyl groups, including three symmetrical (16, 17, 18) and two unsymmetrical polyynes (7 and 12). The solid-state behavior of these molecules based on the attractive electrostatic interactions of the phenyl and perfluorophenyl groups has been examined by X-ray crystallographic analysis of 7, 12, and 16-25.

In 1960, Patrick and Prosser discovered that the admixture of benzene and hexafluorobenzene resulted in a room-temperature solid that was unique from either of its constituent parts.¹ It has subsequently been confirmed both experimentally and theoretically that benzene and perfluorobenzene have quadrupolar moments that are nearly equal in magnitude, but opposite in sign.² The result is a motif that allows one to realize supramolecular structures in which solid-state organization can be engineered based on the electrostatic interactions of phenyl and perfluorophenyl groups.³

In terms of the known acetylenic derivatives **1–6**,⁴ Grubbs and co-workers first established that attractive interactions between phenyl perfluorophenyl groups could also be used to direct the solid-state packing of diynes **3·4** and **6**.⁵ It has been suggested that this packing motif might lead to a productive topochemical polymerization reaction based on interatomic orientations that arise from close packing in molecular crystals derived from **3·4** or **6**,⁶ although this fact remains to be proven. It has also been recently established by Marder and co-workers that the packing for tolan derivatives **1·2** and **5** is also dominated by the same supramolecular forces found for diyne derivatives **3·4** and **6**.^{4e}

Our work with extended polyynes⁷ led us to consider why longer polyynes with perfluorophenyl units had not been synthesized and studied. It became clear quite quickly that the electrophilic nature of the perfluorophenyl group would likely make the assembly of such molecules a synthetic challenge.^{4e,8} Intrigued by this challenge, we sought to

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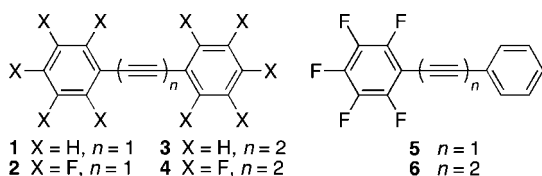
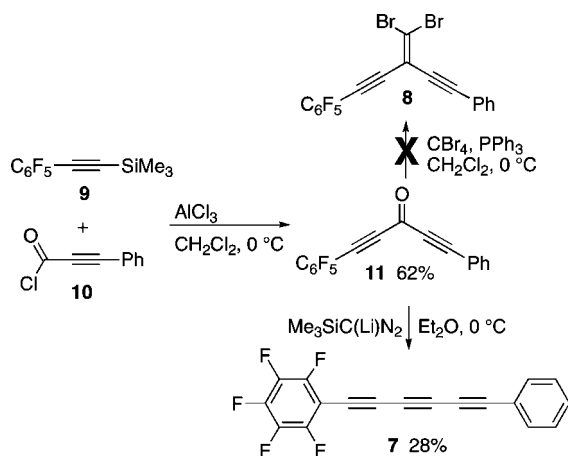


Figure 1. Known decafluoro- and pentafluorodiphenyl mono- and diynes.

construct perfluorophenyl polyynes and to determine if the solid-state behavior that had been observed for mono- and diynes **1–6** would extend to longer derivatives. We report herein the results of our efforts.

The synthesis of pentafluorodiphenyltriyne **7** (Scheme 1) proved to be more challenging than expected. As in previous

Scheme 1



triyne synthesis,⁷ a carbenoid Fritsch–Buttenberg–Wiechell (FBW) rearrangement⁹ with dibromoolefin **8** was planned to form the polyynyl core. Thus, the acylation reaction¹⁰ of trimethylsilylalkyne **9**^{8,11} with excess acid chloride **10** readily gave ketone **11** in good yield. All attempts toward forming **8** under typical dibromoolefination conditions were, however,

(7) For recent examples of polyynyl formation using the FBW rearrangement, see: (a) Chalifoux, W. A.; Tykwinski, R. R. *Chem. Rec.* **2006**, *6*, 169–182. (b) Luu, T.; Elliott, E.; Slepkov, A. D.; Eisler, S.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *Org. Lett.* **2005**, *7*, 51–54. (c) Eisler, S.; Slepkov, A. D.; Elliott, E.; Luu, T.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 2666–2676. (d) Eisler, S.; Tykwinski, R. R. In *Acetylene Chemistry: Chemistry, Biology, and Material Science*; Diederich, F.; Stang, P. J.; Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, Germany, 2005. (e) Eisler, S.; Chahal, N.; McDonald, R.; Tykwinski, R. R. *Chem. Eur. J.* **2003**, *9*, 2542–2550.

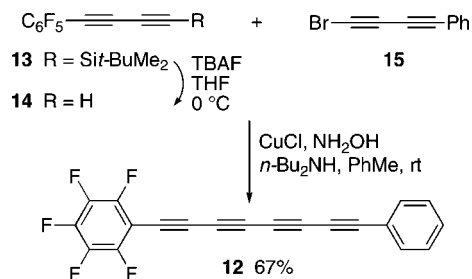
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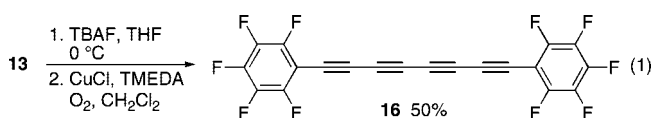
Scheme 2



frustratingly unsuccessful and resulted only in the formation of baseline material. Nevertheless, with ketone **11** in hand, the reaction with lithium trimethylsilyldiazomethane was attempted.¹² Satisfyingly, this provided for the desired carbenoid intermediate and subsequent rearrangement to form triyne **7**. To our knowledge, this is the first reported example of polyynyl formation using Colvin's reagent.¹²

As encountered in efforts toward triyne **7**, attempts to form the unsymmetrical tetrayne **12** via a FBW rearrangement from a dibromoolefinic precursor were not successful, even using methods successful for the formation of other tetraynes.⁷ Thus, an alternative approach was sought. The formation of diene **13** was readily developed from pentafluorobenzoyl chloride.¹³ Desilylation with tetrabutylammonium fluoride (TBAF) at 0 °C gave the deprotected diene **14**, and reaction with bromodiyne **15** (excess) under Cadiot–Chodkiewicz conditions¹⁴ gave **12** in good yield.

Diene **13** also, obviously, provided the basis for synthesis of symmetrical tetrayne **16** (eq 1). Thus, desilylation with TBAF at low temperature gave the terminal diene, which was immediately subjected to Hay oxidative homocoupling.¹⁵ The desired tetrayne **16** was isolated as a stable yellow solid in 50% yield over the two steps.



The synthesis of hexayne **17** and octayne **18** (Scheme 3) began from **9** and followed similar paths. A Friedel–Crafts

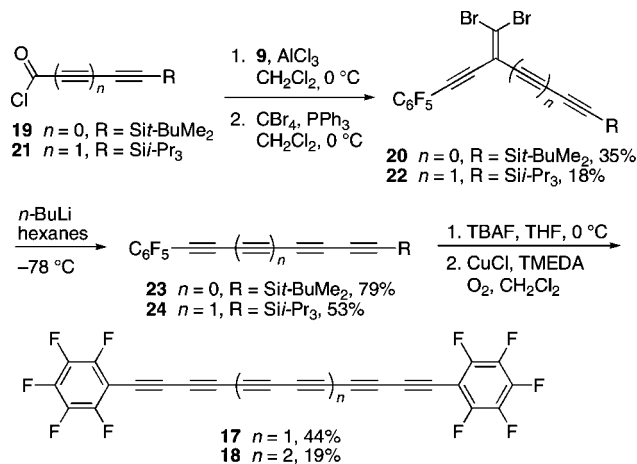
(12) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 869–874.

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(15) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321. For recent examples of polyynyl formation using the Hay and similar methods, see: de Quadras, L.; Bauer, E. B.; Mohr, W.; Bohling, J. C.; Peters, T. B.; Martín-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8296–8309. Simpkins, S. M. E.; Weller, M. D.; Cox, L. R. *Chem. Commun.* **2007**, 4035–4037. Zheng, Q.; Bohling, J. C.; Peters, T. B.; Frisch, A. C.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2006**, *12*, 6486–6505. Gibtner, T.; Hampel, F.; Gisselbrecht, J.-P.; Hirsch, A. *Chem. Eur. J.* **2002**, *8*, 408–432.

Scheme 3



acylation with **19** gave the corresponding ynone (not shown), which was purified and then readily converted to dibromoolefin **20**.¹⁶ The analogous reaction sequence of acylation and dibromoolefination starting with TIPS-protected **21** ultimately gave **22**, albeit in low yield over the two steps (using the TBDMS analogue of **21** failed to give product). FBW rearrangement of **20** and **22** then gave the triyne **23** and tetrayne **24**, respectively, in decent yields. Finally, desilylation and oxidative homocoupling under Hay conditions gave the desired polyynes **17** and **18**.

The characterization of extended polyynes **7**, **12**, and **16–18** by ¹⁹F NMR spectroscopy is particularly diagnostic, showing second order multiplets for the ortho and meta fluorine atoms at ca. -139 and -162 ppm (due to coupling with other magnetic nonequivalent F-atoms of the aryl ring). The signal of the para fluorine is typically observed as a triplet of triplets, centered at -153 ppm. The ¹³C NMR spectroscopic characterization of polyynes **7** and **12**, as well as many of their precursors, is complicated by an inability to effect both ¹H and ¹⁹F decoupling in a single NMR experiment. Nevertheless, all spectra and observed coupling patterns are consistent with the proposed structures.¹³ The MALDI MS analysis of octayne **18** is noteworthy. In addition to the signal observed at m/z 526 for M^+ , additional signals were found for the dimer ($2M^+ = 1052$), trimer ($3M^+ = 1578$), tetramer ($4M^+ = 2104$), and pentamer ($5M^+ = 2630$), showing aggregation or chemical cross-linking during the analysis.¹³

The observed melting points for phenyl and perfluorophenyl polyynes are summarized in Table 1, in comparison to several known molecules. In general, the decafluoro ($\text{Ph}_F\text{-(CC)}_n\text{-Ph}_F$) and pentafluoro ($\text{Ph-(CC)}_n\text{-Ph}_F$) polyynes show higher melting points than the analogous diphenyl polyynes. Likewise, for the two known systems, $n = 2$ and $n = 4$, the 1:1 cocrystals of $\text{Ph}_F\text{-(CC)}_n\text{-Ph}_F$ and $\text{Ph-(CC)}_n\text{-Ph}$ are higher melting solids than the corresponding $\text{Ph-(CC)}_n\text{-Ph}_F$ ana-

(16) (a) Ramirez, F.; Desai, N. B.; McKelvie, N. *J. Am. Chem. Soc.* **1962**, *84*, 1745–1747. (b) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769–3772.

Table 1. Melting Point (°C) Comparisons for Phenyl and Perfluorophenyl Polyynes

<i>n</i>	Ph-(CC) _{<i>n</i>} -Ph + Ph _F -(CC) _{<i>n</i>} -Ph _F			
	Ph-(CC) _{<i>n</i>} -Ph	Ph _F -(CC) _{<i>n</i>} -Ph _F	Ph _F -(CC) _{<i>n</i>} -Ph _F	Ph-(CC) _{<i>n</i>} -Ph _F
1	58.5–59 ¹⁷	123–123.5 ¹⁸	^a	104–105 ^{4e}
2	87 ⁵	114 ⁵	152 ⁵	124 ⁵
3	91–92 ¹⁷	n.a. ^b	n.a.	154–155
4	109–110 ¹⁹	174–176 ^c	133–134	125–126
6	133 ^{c,d}	133–134 ^c	n.a.	n.a.
8	85 ^{c,d}	99 ^c	n.a.	n.a.

^a The 1:1 cocrystal has been reported, but no melting point was provided, see ref 4e. ^b n.a.: not available. ^c Decomposition point. ^d Determined by differential scanning calorimetry.^{7b}

logues, even though the number of favorable phenyl–perfluorophenyl interactions is essentially identical in each case.

Crystals of triyne **7** were grown from a solution of CHCl_3 at room temperature (Figure 2).²⁰ The individual molecules

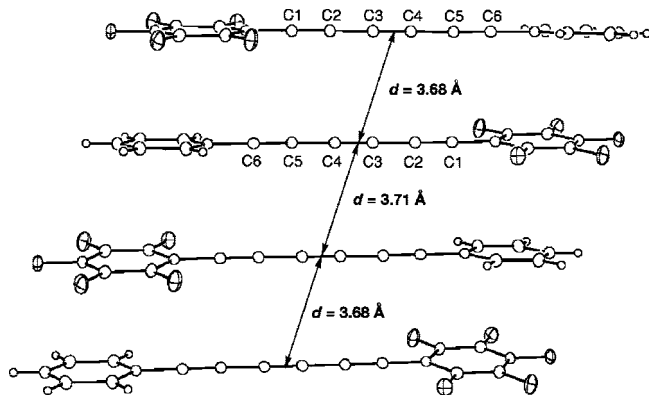


Figure 2. Solid-state orientation of **7** for four neighboring molecules; center-to-center distances d (20% probability level).

are essentially planar, with a dihedral angle between planes formed of terminal aryl rings of only $4.61(7)^\circ$. The triyne segment is nearly linear, with acetylenic bond angles that range from $178.8(2)$ to $179.8(3)^\circ$. Neighboring molecules stack to form centrosymmetric, dimeric pairs, separated by 3.46 \AA .²¹ The stacking of neighboring pairs is slightly offset, although still separated by 3.47 \AA . The center-to-center distances of $d = 3.68$ and $d = 3.71 \text{ \AA}$ are analogous to those

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(19) Armitage, J. B.; Entwistle, N.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1954**, 147–154.

(20) X-ray crystallographic data for **7**: $\text{C}_{18}\text{H}_3\text{F}_5$, $M = 316.22$, triclinic space group $P\bar{1}$ (No. 2); $a = 7.3722(6) \text{ \AA}$, $b = 7.9609(10) \text{ \AA}$, $c = 13.2604(12) \text{ \AA}$; $\alpha = 101.447(9)^\circ$, $\beta = 91.357(7)^\circ$, $\gamma = 114.541(7)^\circ$; $V = 688.93(12) \text{ \AA}^3$; $Z = 2$; $\rho_{\text{calcd}} = 1.524 \text{ g cm}^{-3}$, $\mu = 0.136 \text{ mm}^{-1}$; $T = -80 \text{ }^\circ\text{C}$. Final $R_1 = 0.0453$ (1881 observations [$F_o^2 \geq 2\sigma(F_o^2)$]); $wR_2 = 0.1266$ for 209 variables and 2838 data with [$F_o^2 \geq -3\sigma(F_o^2)$]; CCDC 677133.

found for **6**. Thus, the packing of **7** is very similar to the motif observed for the corresponding mono- and diyne analogues **5**^{4e} and **6**.⁵

Crystals of the next highest homologue of this series, tetrayne **12**, were grown from a mixture of CCl₄ and cyclohexane at room temperature (Figure 3).²² The conju-

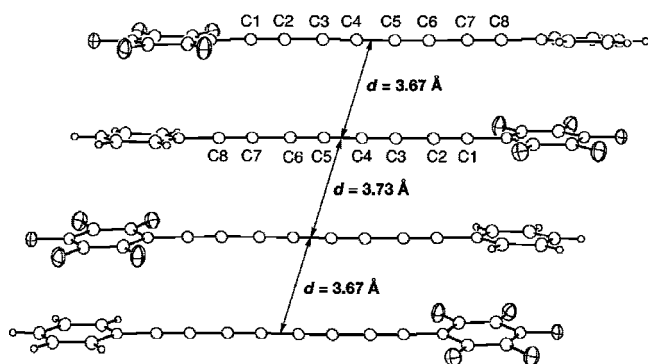


Figure 3. Solid-state orientation of **12** for four neighboring molecules; center-to-center distances d (20% probability level).

gated framework of **12** is nearly planar, with a dihedral angle between planes formed of terminal aryl rings of 4.67(12)°. The polyynic segment is basically linear, with acetylenic bond angles that range from 177.8(4) to 179.4(3)°. Two nearest neighbor molecules form a centrosymmetric dimeric pair separated by an interplanar distance of 3.46 Å, and successive pairs are stacked at the same distance of (3.47 Å). The center-to-center separation for the tetraynes is $d = 3.67$ and $d = 3.73$ Å, again comparable to **6** and **7**. Thus, the solid-state packing for polyynes **7** and **12**, in comparison to **5** and **6**, shows that polyynic length has a negligible effect on the supramolecular organization of these molecules in the solid state.

Cocrystals of **16** and diphenyl-1,3,5,7-octatetrayne (**25**)^{7b,19,23} were grown from a 1:1 mixture of the two compounds in MeOH at room temperature (Figure 4).²⁴ Both

(21) Intermolecular distances are based on the separation of planes generated from all non-hydrogen atoms of neighboring molecules using Mercury 1.3; see the Supporting Information for more details.

(22) X-ray crystallographic data for **12**: C₂₀H₅F₅, $M = 340.24$; triclinic space group $P\bar{1}$ (No. 2); $\rho_c = 1.470$ g cm⁻³; $a = 7.3896(12)$ Å, $b = 7.9448(13)$ Å, $c = 14.452(2)$ Å; $\alpha = 91.906(3)^\circ$, $\beta = 94.375(3)^\circ$, $\gamma = 114.390(2)^\circ$; $V = 768.5(2)$ Å³; $Z = 2$; $\mu = 0.128$ mm⁻¹. Final $R(F) = 0.0710$ (1522 observations [$F_o^2 \geq 2\sigma(F_o^2)$]); $wR_2 = 0.2125$ for 226 variables and 2702 data with [$F_o^2 \geq -3\sigma(F_o^2)$]; CCDC 677134.

(23) Haley, M. M.; Bell, M. L.; Brand, S. C.; Kimball, D. B.; Pak, J. J.; Wan, W. B. *Tetrahedron Lett.* **1997**, 38, 7483–7486.

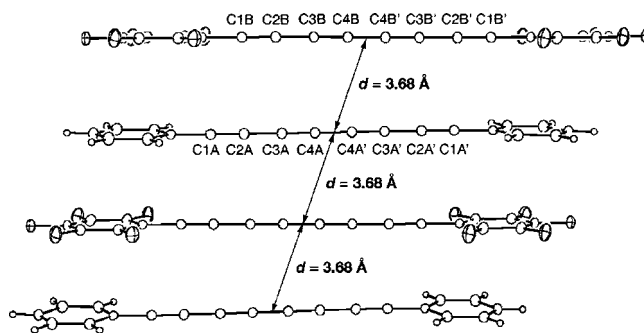


Figure 4. Solid-state orientation of **16:25** for four neighboring molecules; center-to-center distances d (20% probability level).

16 and **25** are nearly linear, with all acetylenic bond angles between 177.5(2) and 179.6(3)°. The alternate stacking of **16:25** mirrors that found in 1:1 mixtures of both **1:2**^{4e} and **3:4**,⁵ and the center-to-center distances for the tetraynes of $d = 3.68$ Å is nearly identical to those observed for **3:4** ($d = 3.69$ Å).⁵ Thus, the length of the acetylenic linker appears to play little role in the packing found in these cocrystalline pairs **1:2**, **3:4**, and **16:25**.

In conclusion, five new perfluoroaryl polyynes have been synthesized and the solid-state packing examined by X-ray crystallography for three examples. These crystallographic analyses show that the supramolecular packing motif documented previously for the shorter mono- and diacetylenic derivatives is maintained almost identically in the longer analogues (**7**, **12**, and **16:25**) studied here.

Acknowledgment. This work has been generously supported by the University of Alberta and the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Discovery Grant program.

Supporting Information Available: Experimental procedures, spectroscopic data, and copies of NMR spectra for new compounds. Copies of mass spectra for polyynes **7**, **12**, and **16–18**. CIF file for crystallographic structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(24) X-ray crystallographic data for **16:25**: C₄₀H₁₀F₁₀, $M = 680.48$; triclinic space group $P\bar{1}$ (No. 2); $\rho_c = 1.483$ g cm⁻³; $a = 7.3625(10)$ Å, $b = 7.8987(11)$ Å, $c = 14.684(2)$ Å; $\alpha = 82.017(2)^\circ$, $\beta = 80.119(2)^\circ$, $\gamma = 65.267(2)^\circ$; $V = 761.97(18)$ Å³; $Z = 1$; $\mu = 0.129$ mm⁻¹. Final $R(F) = 0.0413$ (1910 observations [$F_o^2 \geq 2\sigma(F_o^2)$]); $wR_2 = 0.1386$ for 226 variables and 2969 data with [$F_o^2 \geq -3\sigma(F_o^2)$]; CCDC 677135.