Polyyne Structures

DOI: 10.1002/anie.200904145

Synthesis and Structural Analysis of One-Dimensional sp-Hybridized Carbon Chain Molecules**

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alkynes · carbynes · structure elucidation · cumulenes · polyynes

Carbyne, a hypothetical carbon allotrope, has been the subject of considerable debate and research in the scientific community.[1,2] Unlike other carbon allotropes such as diamond, fullerene, and graphite, carbyne is a one-dimensional infinite chain molecule that entirely consists of sp-hybridized carbon atoms. Carbyne is characterized by extremely high physical fragility and reactivity, which has thwarted attempts to isolate and fully study it. Thus, the existence and true structure of carbyne has been a controversial topic since it first appeared in the literature.

Carbyne is expected to have many interesting properties as it has unique structural and electronic features. In principle, carbyne could exist in two isomeric forms (Figure 1): one form consists of alternating single and triple C−C bonds (polyyne type) and the other form consists only of C−C double bonds (polycumulene type).[3] Theoretical calculations predicted that the polyyne type is the more stable of the two forms.[4] Although various studies have been published on the structure and properties of this hypothetical allotrope, the fundamental inaccessibility of carbyne has led researchers to examine its low-molecular-weight homologue, polyyne. It is expected that the structure and physicochemical properties of carbyne might be predicted based on those of polyyne.[5]

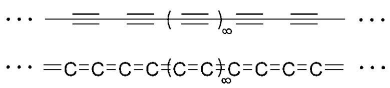
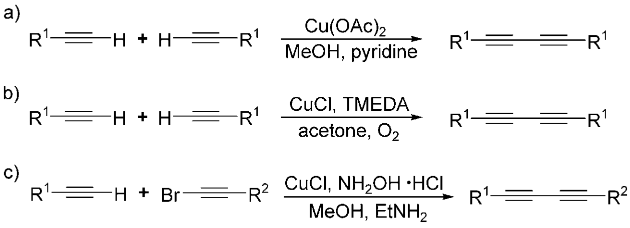


Figure 1. Two possible isomeric forms of carbyne.

Strictly speaking, polyynes are oligomers of acetylene rather than true polymers. The general structure of polyynes can be represented as $H-(C\equiv C)_n-H$. There are a number of ways to synthesize polyynes. The most popular methods remain the laser ablation of carbon solids along with arc discharge using carbon electrodes in organic solvents.[2] Polyynes are rather stable in dilute solutions but not in concentrated solutions or in the solid state. In general, the stability of polyynes drastically decreases as the number of acetylene units increases. The apparent instability of polyynes provides some explanation of why polyyne and carbyne remain difficult to identify and characterize experimentally.

The stability of polyynes can be improved by incorporating end groups at the termini of the chain.[6] These end groups provide either steric bulk or stabilizing electronic effects that prevent the reactive polyyne core from cross-linking or being oxidized. Various functional groups such as alkyl, aryl, trialkylsilyl, and even organometal groups, have been employed as end groups. With the aid of these end groups, researchers have been able to synthesize isolable polyyne molecules with chain lengths up to 32 carbon atoms.[2] A number of end-capped polyynes have been crystallographically characterized to reveal the properties of polyyne. A comprehensive analysis of X-ray crystallographic data for the hitherto reported polyyne structures was provided by Szafert and Gladysz in their recent review.[7]

A number of methods are currently used for the synthesis of end-capped polyynes, most of which have been well summarized in recent reviews.[8] One of the most popular synthetic methods is the copper-catalyzed oxidative homocoupling of terminal alkynes.[8,9] The history of the homocoupling of acetylene compounds dates back to 1869, when Glaser found that copper(I) phenylacetylide underwent oxidative dimerization in air under basic conditions.[9a] Since then, numerous modifications and improvements have been made. Eglinton and Galbraith generated the requisite copper(I) acetylide in situ for the oxidative homocoupling using excess $Cu(OAc)_2$ in methanolic pyridine (Scheme 1 a).[9b] Hay



Scheme 1. Commonly used homo- and heterocoupling reactions of alkynes for the synthesis of polyyne. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

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[**] This work was supported by the SRC/ERC program (R11-2007-107-02001-0) and the WCU program (R32-2008-000-10098-0) through KOSEF funded by MEST.

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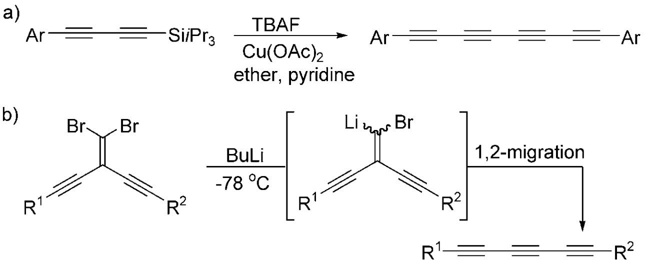
achieved oxidative homocoupling of acetylenes by using a catalytic amount of CuCl in the presence of TMEDA and O_2 (Scheme 1 b).[9c] Recently, palladium has been employed as a catalyst for the homocoupling of acetylenes instead of the traditional copper catalyst system.

One problem that plagues the oxidative homocoupling of alkynes is that this reaction is not suitable for the synthesis of polyynes with different end groups at the termini (unsymmetrical polyynes) or with an odd number of acetylene units. One solution to this problem is the Cadiot–Chodkiewicz coupling reaction: the Cu^I-catalyzed cross-coupling of terminal alkynes with 1-haloalkynes in the presence of a suitable amine (Scheme 1 c).[10] A number of variations have been developed, including several palladium-catalyzed reactions.[8a]

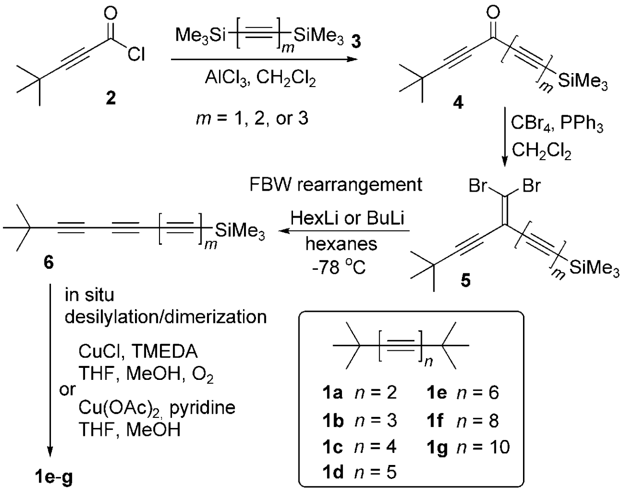
While these metal-catalyzed homo- and heterocoupling reactions have been used successfully to synthesize various extended polyynes, the major limitation of these reactions is that the vast majority of terminal polyynes required as coupling partners are unstable. Many elegant alternative methods have been developed to circumvent this limitation.[8] One notable strategy involves the in situ deprotection and direct utilization of an unmasked terminal alkyne. This approach eliminates the need for the isolation of unstable terminal alkynes during the reaction sequence. For example, treatment of silyl-protected diynes with a fluoride source followed by an in situ one-pot homocoupling reaction of the resulting terminal alkyne successfully provided the corresponding tetraynes (Scheme 2 a).[11] Another strategy involves the formation of a disubstituted alkynyl unit from other functional groups. One typical example is the use of the Fritsch–Buttenberg–Wiechell (FBW) rearrangement of alkylidene carbenoids (Scheme 2 b).[12] The alkylidene carbenoid generated in situ collapses to an internal triple bond to generate a C≡C unit through 1,2-migration of a pendent alkynyl group to efficiently provide a polyyne system.



Scheme 2. The formation of polyynes by a) in situ desilylation/oxidative dimerization and b) FBW rearrangement. TBAF = tetrabutylammonium fluoride.

Until now, one particular question that remained regarding the structures of polyyne was whether the triple and single bond lengths converge to one value as the length of the polyyne increases. Recent theoretical studies predicted that the triple bond becomes longer and the single bond shorter as the polyyne chains lengthen in order to reduce the bond length difference between them.[2,7] However, the bond length alternation (BLA) is expected to be finite and reach its limiting value once the polymer is at least a decayne ($n = 10$).[13] Although this hypothesis has been evaluated experimentally by several methods, including X-ray crystallography, there has not yet been compelling experimental evidence to confirm it. Previous characterization of end-capped polyynes by X-ray analysis did not fully provide the information necessary for comparison of individual bond lengths or the relationship between bond length and polymer length. This deficiency is primarily a result of "end-group effects" on the electronic properties of sp-hybridized carbon chains.

Although hydrogen or even a methyl end group would exert a minimal effect on the structure of polyynes,[14] the synthesis of polyynes with such end groups would be difficult because of their inherent instability. Thus, the *t*Bu group was chosen by Tykwinski and his co-workers to strike a balance between the polyyne stability and the conservation of the structure of polyyne. They have recently reported the successful synthesis of a series of *t*Bu-end-capped polyynes **1a–g** (Scheme 3) having up to 10 acetylene units.[15] The obtained polyynes are reasonably stable under ambient conditions, which has allowed for X-ray analysis of several derivatives. It is noteworthy that decayne **1g** is the longest polyyne that has ever been characterized by X-ray analysis.



Scheme 3. Synthesis of hexayne **1e**, octayne **1f**, and decayne **1g**.

The synthesis of the *t*Bu-end-capped higher polyynes **1e–g** developed by Tykwinski et al. involves a FBW rearrangement and an in situ deprotection/dimerization protocol as shown in Scheme 3. The synthesis is similar to their previous synthesis of triisopropylsilyl-end-capped polyynes.[16] Friedel–Crafts acylation of acid chloride **2** with the bissilyl-protected short polyyne **3** produced conjugated ketone **4**. Reaction of the crude ketone **4** under Corey–Fuchs conditions gave dibromide **5**. A FBW rearrangement was induced with an alkyl lithium reagent to give the corresponding polyynes end-capped at each terminus with a silyl or *t*Bu end group. The obtained compounds **6** were subjected directly to in situ desilylation/dimerization to afford the desired *t*Bu-end-capped hexayne **1e**, octayne **1f**, and decayne **1g** in modest to good yields.

Crystal structures were obtained for diyne **1a**, triyne **1b**, tetrayne **1c**, octayne **1f**, and decayne **1g** by X-ray diffraction methods. The crystal structures of the higher polyynes **1f** and **1g** are shown in Figure 2. Interestingly, decayne **1g** has been found in two different conformations: unsymmetrical **1gA** and centrosymmetric **1gB** (Figure 2). The polyyne chains of this series were revealed to be nearly linear and composed of conjugated triple bonds rather than cumulated double bonds.

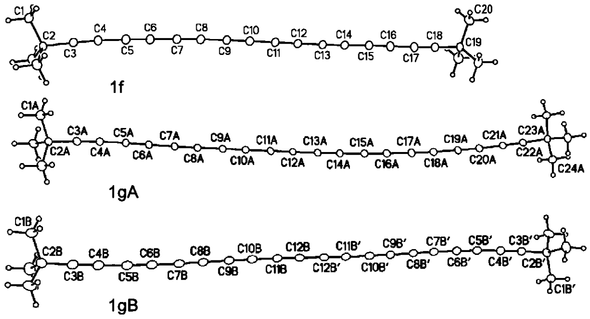


Figure 2. ORTEP drawings (ellipsoids at the 20% probability level) for **1f** and **1gA** and **1gB**. Reproduced from reference [15] with permission.

The crystal structures of a series of *t*Bu-end-capped polyynes are in close agreement with the theoretically predicted structures of uncapped polyynes. This data, summarized in Table 1, also provides the relevant information and trends necessary for comparison of bond lengths between chain lengths. For instance, the experimental BLA and BLA_{avg} values[17] for octayne **1f** and decayne **1g** deviate from the predicted values for $H-(C{\equiv}C)_9-H$ by only about 0.01 Å. The BLA value of decayne **1g** is also close to the theoretically predicted value for an infinite polyyne chain (Table 1, entries 7 and 8). The bond length analysis shows that the BLA and BLA_{avg} values decrease steadily as the polyyne chain is lengthened and reach its limiting value at ten repeating acetylene units (decayne), which matches the theoretical prediction.[13]

Tykwinski's synthesis and X-ray crystallographic analysis of a series of *t*Bu-end-capped polyynes provide strong evidence for reduced bond length alternation and support the theoretical prediction that the triple and single bond lengths of polyyne do not converge even as the polyyne chain becomes very long. These results also provide more insight into the structure of carbyne, since polyyne might be regarded as a relevant model of this hypothetical allotrope. Further studies on the characterization of linear and nonlinear optical properties of his "end group effect minimized" polyyne compounds are eagerly awaited. This work will add further impetus to the study of polyyne and carbyne. Although many challenges still lie ahead, we are one step closer to understanding the true structure and properties of carbyne. One might envisage a direct comparison of *t*Bu-end-capped higher polyynes with the polycumulenes containing the same number of carbon atoms and the same end groups in order to better understand carbyne and sp-hybridized carbon chains. This could be very interesting and useful. However, these latter compounds would be extremely difficult, if not impossible, to synthesize by current synthetic technologies because of their kinetic instability.

Table 1: Summary of experimental and theoretical BLA data.[a]

Entry	Polyyne	BLA [Å]	$C-C_{avg}$ [Å]	$C{\equiv}C_{avg}$ [Å]	BLA_{avg} [Å]	Ref.
1	**1a**	0.184	1.382	1.199	0.183	[15]
2	**1b**	0.164	1.368	1.202	0.166	[15]
3	**1c**	0.151	1.365	1.204	0.161	[15]
4	**1f**	0.140	1.356	1.209	0.147	[15]
5	**1g**[b]	0.139	1.352	1.206	0.146	[15]
6	$H-(C{\equiv}C)_9-H$	0.1291[c]	1.36175	1.2254	0.13675	[13a]
7	$H-(C{\equiv}C)_\infty-H$	0.1276[c]	–	–	–	[13a]
8	$H-(C{\equiv}C)_\infty-H$	0.133[d]	–	–	–	[13c]

[a] Table reproduced from reference [15] with permission. [b] Average values of **1gA** and **1gB**. [c] Calculated at the CCSD(T)/cc-PVTZ level of theory. [d] Results from the BHHLYP functional.

Received: July 27, 2009
Published online: September 10, 2009

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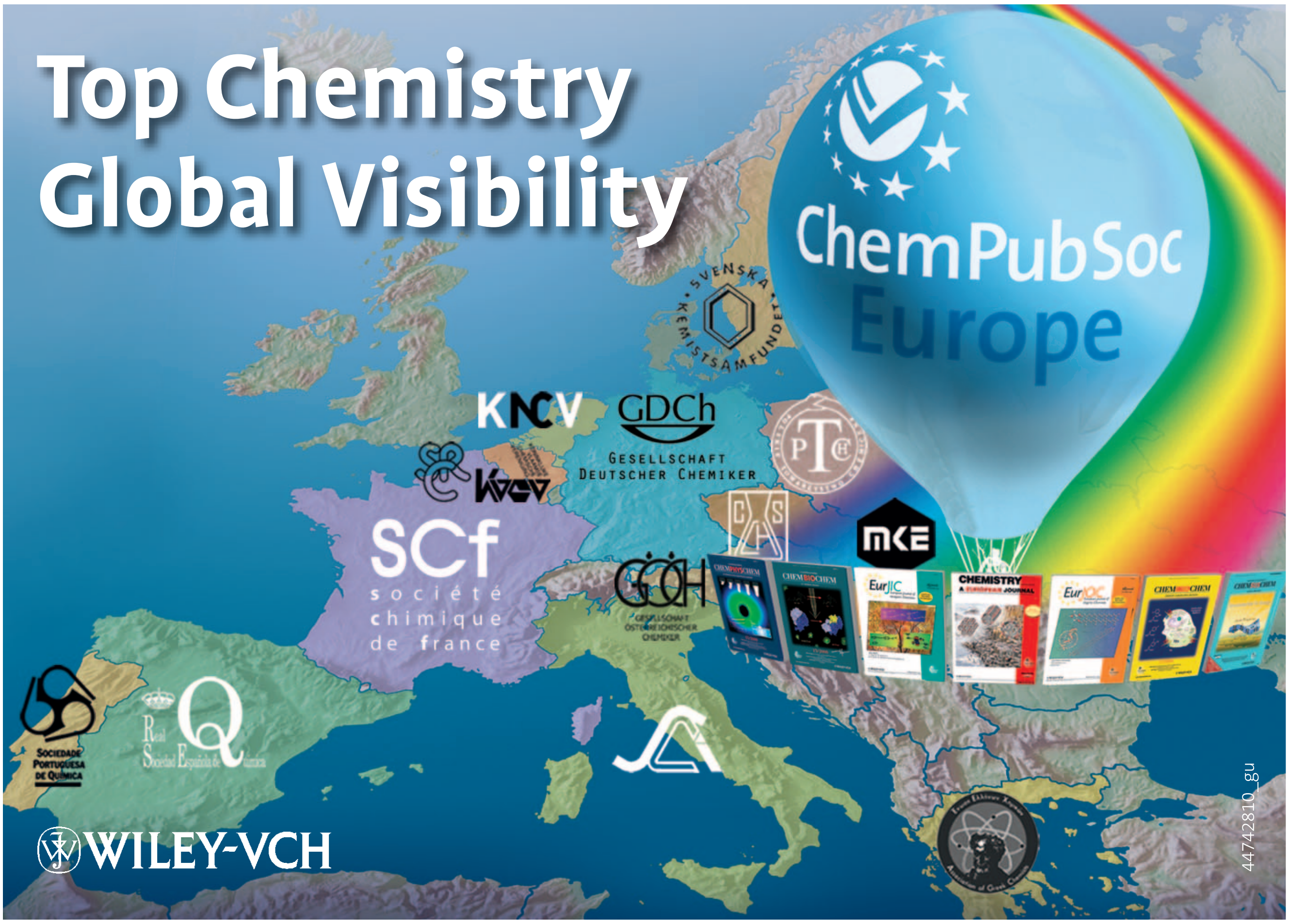
[17] BLA = the difference in the bond length between the central single and triple bonds; BLA_{avg} = the difference between the average length of all single and triple bonds except the terminal $C-C(CH_3)_3$ bond.



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