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Macromolecular polyyne-containing benzoxazines for cross-linked polymerization

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ABSTRACT

A Mannich condensation of 2,4-di-*tert*-butylphenol, *p*-bromophenethylamine, and formaldehyde followed by a Sonogashira coupling of the resulting 3-(4-bromophenethyl)-6,8-di-*tert*-butyl-3,4-dihydro-*2H*-benz[1,3]oxazine (**1**-Br) with TMSC≡CH gave acetylenic benzoxazine **1**-C_2TMS which was a precursor for polyynic derivatives. Firstly, it was deprotected with K_2CO_3 in *i*PrOH/MeOH to give the terminal acetylene **1**-C_2H, which was subsequently dimerized to the symmetrical diyne **1**-C_4-**1**. Next, **1**-C_2H was transformed to **1**-C_4TMS via a Cadiot–Chodkiewicz coupling, and then **1**-C_4TMS was homocoupled with in situ deprotection to give octatetrayne **1**-C_8-**1**. X-ray diffraction studies of **1**-C_8-**1** showed distinctive chain bending and a packing analysis revealed the potential for 1,n-topochemical polymerization that implies a cross-linking opportunity.

1,3-Benzoxazines constitute a fast developing and sought-after class of heterocyclic monomers that upon thermal or catalytic curing produce thermosetting phenolic resins which possess many useful properties[1] including biological activity.[2] Among the most important properties of polybenzoxazines are near-zero shrinkage, high thermal stability, low water absorption, high UV retardance, and good mechanical performance.[1,3] Another factor, which makes benzoxazines an attractive target is their preparation accessibility. The majority of monomers are available via simple Mannich condensation from inexpensive and commercially available phenols, primary amines, and formaldehyde[1] although other synthetic approaches are also extensively utilized.[4–10]

In order to improve mechanical and other properties of polybenzoxazine resins further various monomer modifications have been developed. The introduction of a reactive functional group for further processing seems a natural strategy. Among many that have been tested, acetylenic benzoxazines have been targeted by several groups.[3a,11] Such functionalization has an additional advantage since the resulting acetylenic precursors can initially be polymerized at the C≡C bond in solution or in solid state (e.g. via 1,n-topochemical pathway) before polymerization at the benzoxazine moiety. The benzoxazine polymer can also be cross-linked through the acetylenic substituent. The resulting hyperbranched materials with improved mechanical and/or conductive properties possess extensive π delocalization and highly polarizable π-electron systems which introduce new characteristics. Compounds with unsaturated carbon chains (conjugated polymers) usually have unique properties, such as nonlinear optical responses (NLOs) or large molecular first- and second-order hyperpolarizabilities, β and γ, respectively.[12]

With this in mind, we initiated a project that started with the preparation and characterization of a series of novel acetylenic benzoxazine monomers that would constitute a group of precursors for highly-branched conductive polymers.

3-(4-Bromophenethyl)-6,8-di-*tert*-butyl-3,4-dihydro-*2H*-benz[1,3]oxazine (**1**-Br) was prepared by a routine Mannich condensation using a methanolic solution of 2,4-di-*tert*-butylphenol, *p*-bromophenethylamine, and formaldehyde, as shown in Scheme 1. The mixture was refluxed for 90 h and the final white crystalline product was obtained in a 64% yield as described in the experimental section in the Supplementary data.

Next, the acetylenic fragment was introduced to **1**-Br by a Sonogashira coupling using TMSC≡CH and the $Pd(PPh_3)_2Cl_2/Cu(OAc)_2/NEt_3$ catalytic system. Work-up gave analytically pure **1**-C_2TMS in a 68% yield as a beige solid. Deprotection of **1**-C_2TMS with K_2CO_3 in a *i*PrOH/MeOH mixture (v/v, 3/1) at room temperature gave after 24 h, the terminal acetylenic **1**-C_2H in a 95% yield that was dimerized to **1**-C_4-**1** and chain-extended to **1**-C_4TMS. Dimerization to the diyne was performed via oxidative coupling with $Cu(OAc)_2$ in pyridine yielding 97% of the target dimer. The chain extension was attained through the Cadiot–Chodkiewicz protocol with the use of IC≡CTMS, $Pd(PPh_3)_2Cl_2$, and CuI in the presence of iPr_2NH. **1**-C_4TMS was isolated in a 33% yield as a yellow solid and was subsequently dimerized to **1**-C_8-**1** with in situ deprotection by K_2CO_3 but without isolation of the terminal diacetylene **1**-C_4H as shown in

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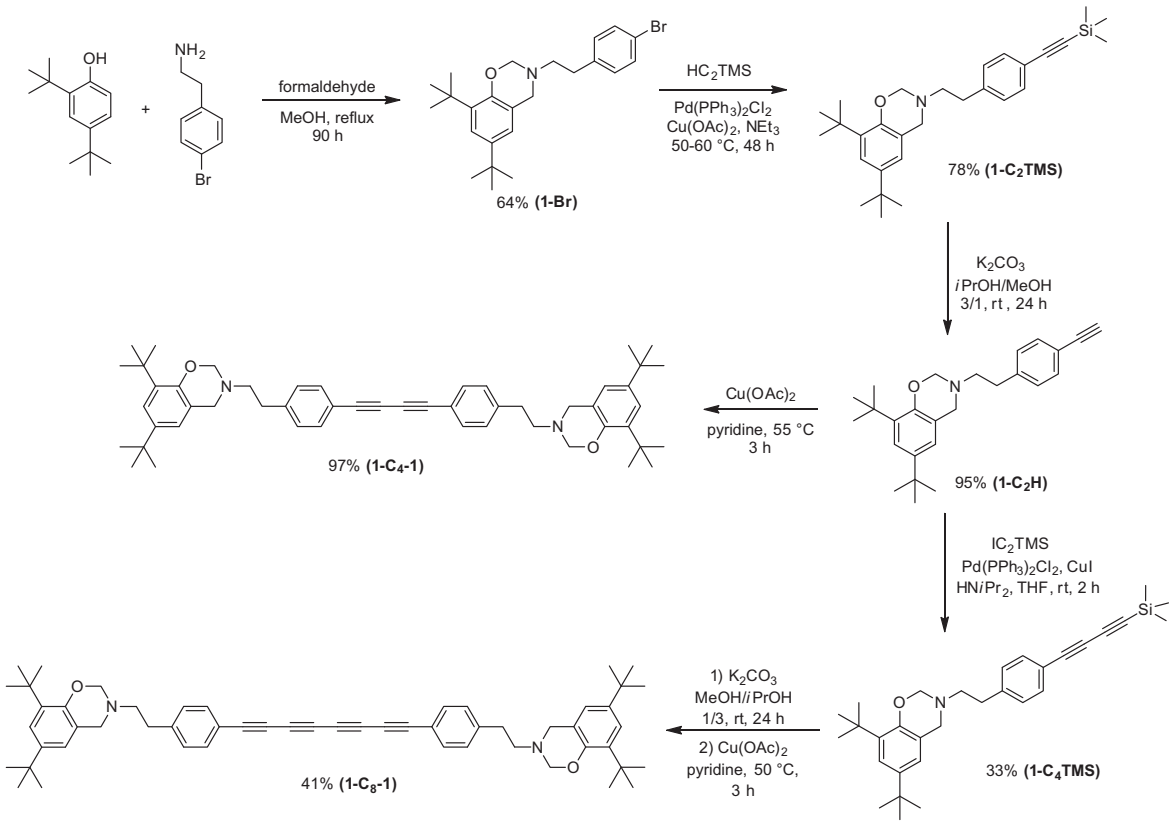

Scheme 1. Synthesis of **1**-C_4-**1** and **1**-C_8-**1**.

Scheme 1. Workup on a silica gel column gave the tetrayne **1**-C_8-**1** in a 41% yield as a yellow solid.

All compounds gave correct microanalyses and/or HRMS peaks and their structures followed from their NMR (^{1}H and ^{13}C) properties and X-ray analysis. For instance, in the proton spectrum of **1**-Br, the diagnostic signals of the methylene protons of the two –C**H**$_2$– groups from the newly formed heterocycle gave singlets at δ 4.86 and 4.02 ppm. The proton spectrum of **1**-C_2TMS revealed an additional singlet at δ 0.24 ppm assigned to the protons of the trimethylsilyl group. Also the ^{13}C NMR spectrum of **1**-C_2TMS showed two additional signals at δ 105.4 and 93.8 ppm assigned to the carbons from the acetylenic fragment and a signal at δ 0.2 ppm from the carbon atoms of the TMS fragment. Next, both the ^{1}H and ^{13}C NMR spectra of **1**-C_2H confirmed the successful removal of the TMS group showing the absence of the corresponding signals in both spectra. Instead, the singlet of the terminal proton appeared at δ 2.74 ppm. Both, the symmetric and unsymmetric C_4 compounds, **1**-C_4-**1** and **1**-C_4TMS, showed signals of chain carbons at δ 82.8 and 75.2 ppm for **1**-C_4-**1**, and at δ 90.6, 88.1, 77.1, and 74.0 ppm for **1**-C_4TMS. The terminal TMS group signals of the latter compound emerged at δ 0.23 ppm and at −0.18 ppm in ^{1}H and ^{13}C NMR spectra, respectively. Also the ^{13}C NMR spectrum of **1**-C_8-**1** showed all the carbon chain signals between δ 78.1 and 63.9 ppm.

Yellow plates of **1**-C_8-**1** were grown by slow evaporation of a $CHCl_3$ solution. The crystal structure was determined as described in the Supplementary data. As depicted in Figure 1, the molecule of **1**-C_8-**1** is non-centrosymmetric. Both phenyl rings are twisted by 8.1°. The triple bond distances within the carbon chain are 1.216(6), 1.216(6), 1.213(6), and 1.198(6) Å and are similar to those found for C≡C in ethyne[13] (1.2033 Å) and butadiyne (1.217–1.20964 Å).[14] The single bond distances are 1.355(6), 1.351(6), and 1.377(6) Å and are similar to those found for other tetraynes.[15a,b]

As can be noticed in Figure 1 the chain conformation is an unsymmetric bow with a C(11)–C(41) distance of 11.732 Å. The sum of all bonds within the carbon chain adds to 11.780 Å which accounts for a 0.41% contraction.[15] Similar deformations were observed in organic tetraynes TMS-C_8-TMS[16] (0.48%) and *t*Bu-C_8-*t*Bu[17] (0.34%) although they were much more pronounced in other organometallic compounds.[15] Also the average chain bond angle of 177.5° (the smallest for all organic tetraynes)[15] supports a distinctive deformation.

Searching for an alkyne polymerization potential, the packing analysis was next performed. The compound crystallizes in the P-1 space group, so the molecules form one set of parallel chains. The closest chain–chain distance in **1**-C_8-**1** is 3.880 Å that seems surprisingly short for such a bulky end-group. The ϕ angle, which is a measure of the chain–chain translation[15] equals 50.2°, which accounts for the offset value of 3.162 Å and the fractional offset of 0.27.[15] It is noteworthy, that the ideal values of the ϕ angle and the chain–chain separation to ensure the highest possibility of topochemical polymerization are 45° and ca. 3.5 Å (for the 1,4-polymerization).

The oxazine rings in the benzoxazine end-caps crystallize in a preferred (also for further polymerization) distorted half-chair conformation with θ and φ parameters of 127.3(5)° and 272.1(6)°, respectively, for the O(1), C(22), N(1), C(21), C(31), C(36) ring and 50.6(6)° and 98.0(6)° for the ring defined by the O(2), C(52), N(2), C(51), C(61), and C(66) atoms.[18] The corresponding within-the-oxazine-ring torsion angles at both ends of **1**-C_8-**1** are: 13.5(5)° for C(31)–C(36)-O(1)-C(22) and −12.5(5)° for C(61)–C(66)-O(2)-C(52), 49.3(4)° for C(36)-O(1)-C(22)-N(1) and −46.2(5)° for C(66)-O(2)-C(52)-N(2), 65.8(4)° for O(1)-C(22)-N(1)-C(21) and −64.4(4)° for O(2)-C(52)-N(2)-C(51), 46.3(4)° for C(22)-N(1)-C(21)-C(31) and −48.9(5)° for C(52)-N(2)-C(51)-C(61), −14.7(5)° for N(1)-C(21)-C(31)-C(36) and 19.3(6)° for N(2)-C(51)-C(61)-C(66), and −2.8(6)° for C(21)-C(31)-C(36)-O(1) and

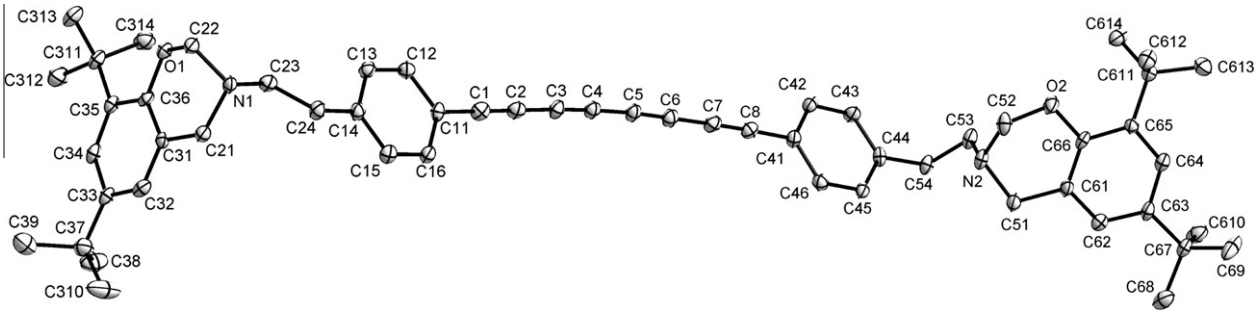

Figure 1. The molecular structure of **1**-C_8-**1** with atom-labeling.

−0.1(6)° for C(51)-C(61)-C(66)-O(2) and they do not differ significantly. Consequently, the positions of the methylene carbon C(22) and nitrogen N(1) as well as the carbon C(52) and N(2) in relation to the planes defined by C(31) to C(36) and C(61) to C(66) atoms, respectively, are also similar. The position of both atoms on the opposite sides of the plane of the phenyl ring is believed to be an important factor that promotes polymerization. In **1**-C_8-**1**, the C(22) atom deviates from the phenyl plane by −0.3402 Å while the nitrogen N(1) is 0.4525 Å above it. These values for the other end of **1**-C_8-**1** are −0.2859 and 0.4543 Å.

One of the most important reactions of benzoxazines is their thermal ring opening polymerization (ROP).[19] In 2000, Wang and Ishida discussed two different mechanisms for such a process depending on the position of substituents in the aromatic ring of the phenolic moiety that resulted in two kinds of polymers.[20] Lately, also Schönfeld, Marquet, and Sebastián presented elegant mechanistic studies on the subject.[21]

In order to establish the potential of the new benzoxazines in the ROP process their thermal analysis was performed. TGA-DSC was employed to monitor the thermal behavior of the compounds and measurements were performed in N_2 and in an oxidative atmosphere at a speed of 20 °C/min from 50° C to 500–700 °C. Figure 2 shows the resulting curves (in N_2) and the melting points are summarized in Table 1.

Each compound exhibits a main thermal transition of the endothermal type that was assigned to the melting process. Only in case of the dimer **1**-C_4-**1**, does the process begin at a much higher temperature that exceeds 238 °C. There are basically no differences

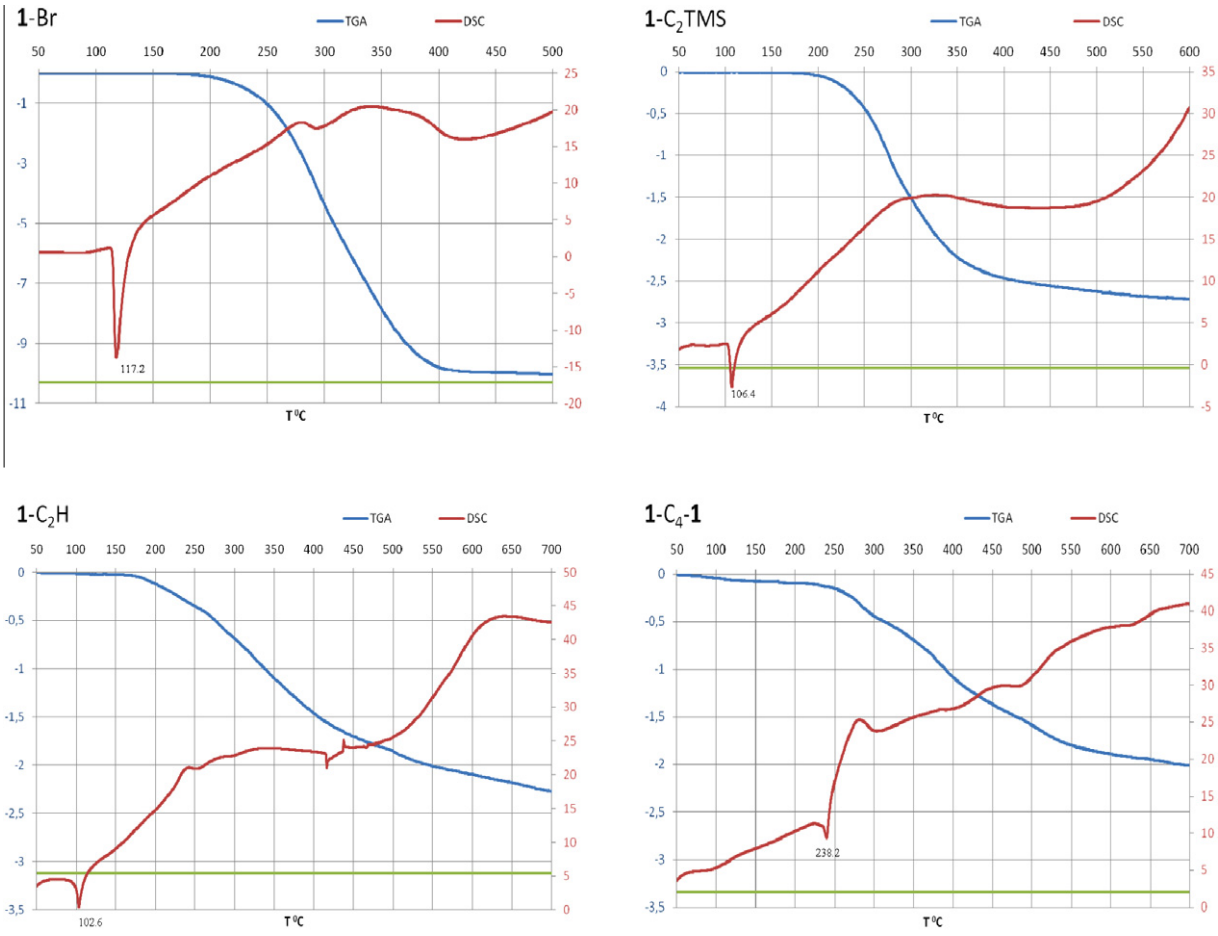

Figure 2. DSC for benzoxazines: **1**-Br (top, left), **1**-C_2TMS (top, right), **1**-C_2H (bottom, left), and **1**-C_4-**1** (bottom, right).

Table 1
Melting point of benzoxazines and the temperatures of initiation of mass loss process

Compound	mp (°C)	Temp. of mass loss (°C)
1-Br (N_2)	117	197
1-Br (air)	116	199
1-C_2TMS (N_2)	106	215
1-C_2TMS (air)	106	200
1-C_2H (N_2)	103	195
1-C_2H (air)	103	199
1-C_4-**1** (N_2)	238	257
1-C_4-**1** (air)	—	217

depending on the atmosphere in which the process is conducted (N_2 vs air).

In each case, another endothermal process occurs around 250 °C, but it is associated with the initiation of mass loss as visualized by the TGA curves. Hence, based on these results, and the ^{1}H NMR spectra of the resulting material, we conclude that instead of polymerization a decomposition process starts to occur at this point.

In summary, we have demonstrated an effective synthetic strategy to approach benzoxazine end-capped polyynes with different lengths of the carbon chain. The compounds were characterized by spectroscopic methods and by X-ray crystallography which showed the C_8 chain with a substantially bent conformation. The packing analysis of **1**-C_8-**1** showed one set of parallel chains that were separated by 3.880 Å. This and the value of the ϕ angle of 50.2° revealed a significant potential of the compound for topochemical polymerization. **1**-Br, both C_2 compounds and the butadiynic dimer **1**-C_4-**1** were subject to thermal analysis showing an endothermal process (above the melting point) that was associated with mass loss. This most probably excludes the thermal polymerization of the benzoxazine, although a catalytic polymerization cannot be disqualified.

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Supplementary data

Supplementary data (synthetic procedures, materials and methods, ^{1}H and ^{13}C NMR spectra, and X-ray data for **1**-C_8-**1** (CCDC-872155)) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.07.141.

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