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A Set of Homologous Hetarylenediyne Macrocycles by Oxidative Acetylene-Acetylene Coupling

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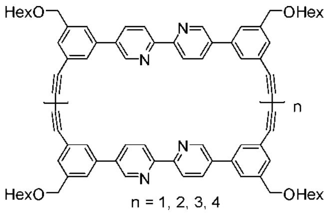
ABSTRACT



The synthesis of a set of bipyridine-containing macrocycles by oxidative acetylene−acetylene dimerization is described. The cycles are separated by preparative GPC, and the smallest homologue is analyzed by single-crystal X-ray diffraction, which shows a layered structure with channels that are partially filled with parts of the flexible chains of adjacent macrocycles. The cyclic trimer has a D_{3h} symmetry and is a possible candidate for the formation of metal organic supramolecular assemblies on surfaces.

Shape-persistent macrocycles are presently an intensely researched target in both organic and materials chemistry.[1] The interest is spurred by fascinating potential properties/applications that include host−guest interactions,[2] organization into and transport through porous materials,[3] and 2D pattern formation on surfaces.[2c,4] They may also serve as constituents for the construction of novel 3D structures.[5] A number of synthetic routes have been developed, and cycles with diameters of up to several nanometers were obtained.[6] The oxidative acetylene dimerization has often been used in ring closure reactions[7] as well as for the preparation of open chain linear oligomers.[8] Homo- and heteroaromatic macrocycles with different sizes and substitution patterns have been

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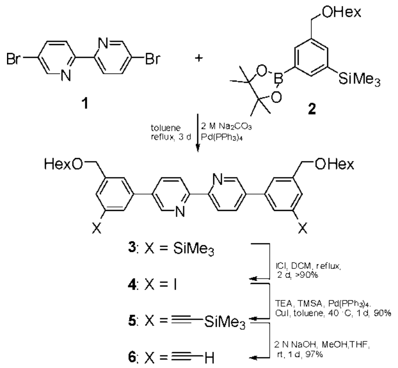
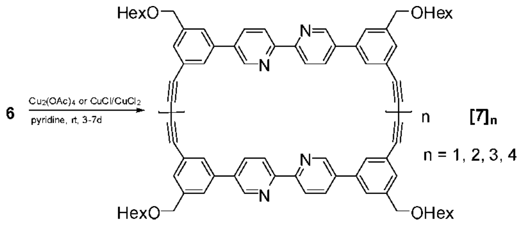
prepared using this reaction. We are presently looking for shape-persistent compounds with D_{3h} symmetry as constituents for the synthesis of two-dimensional networks,[9] and our attention was drawn to the cyclic trimer **[7]$_2$**. This cycle has three bipyridine (bipy) units with a 120° angle between their main axes and could thus be ideally suited for obtaining extended structures through square planar metal complexation. We describe herein the synthesis of bipy **6**, which is related to earlier studies on bipy building blocks from this group and the oligomerization of **6** to a series of macrocycles **[7]$_n$** as well as some open-chain zigzag products. The structure of **[7]$_1$** was elucidated by single crystal X-ray diffraction.

The synthetic sequence to macrocycles **[7]$_n$** is outlined in Schemes 1 and 2. The symmetrically substituted bipy **3** was prepared using a Suzuki−Miyaura cross-coupling reaction between 5,5′-dibromo-2,2′-bipyridine[10] (**1**) and the silylated benzene derivative **2**[11] in almost quantitative yield. Both silyl groups of **3** were then exchanged to iodo using ICl to give the diiodide **4** nearly quantitatively.[12] Compound **4** was prepared on a 10 g scale. Sonogashira reaction of **4** with trimethylsilyl acetylene (TMSA) gave **5**[13] whose hydrolytic treatment with NaOH furnished **6** with its two unprotected acetylene functions required for oligomerization.

Scheme 1. Synthesis of Macromonomer **6**



Scheme 2. Macrocyclization of **6**[a]



[a] Yields for $n = 1, 2, 3, 4$: 5%, 12%, 9%, 5%, respectively.

This compound was easily purified by column chromatography through silica gel and obtained as analytically pure material on a 3 g scale. The cyclization of **6** was performed on a 150 mg scale by oxidative acetylene−acetylene dimerization[14] using two different reaction conditions (Scheme 2). The first synthesis was done in a degassed pyridine solution of $Cu_2(OAc)_4$ to which a solution of **6** in pyridine was added slowly over 5 h followed by stirring at room temperature for 14 d. In the second, a pyridine solution of **6** was added over a period of 92 h to a solution of a large amount of CuCl and $CuCl_2$ in the same solvent followed by stirring for an additional 2 d at room temperature. To isolate the oligomer mixture the Cu salts had to be removed, parts of which were complexed to the bipy units. The decomplexation/removal was done with a solution of KCN in water. The emulsion that formed led to considerable losses of organic material (approximately 35%). The raw product was analyzed by analytical GPC (Waters 150-c Alc using Waters Styragel HR columns, Waters 410 RI and 484 UV−vis detectors, THF, PS standards), which showed three sharp peaks and a broad one (Figure 1). The corresponding products were separated by preparative GPC, which afforded them in almost pure form so that an additional column chromatographic step was sufficient to obtain reasonably pure (by NMR spectroscopy) compounds. Their structures were established as **[7]$_1$** (cyclic dimer, 8 mg, 5%), **[7]$_2$** (cyclic trimer, 10 mg, 12%), and **[7]$_3$** (cyclic tetramer, 14 mg, 9%) on the basis of mass spectrometric and ^{1}H and ^{13}C NMR spectroscopic studies. In a repetition of this experiment also the cylic pentamer **[7]$_4$** could be isolated (7 mg, 5%). Both reactions gave practically the same yields. Additionally some higher molecular weight, linear material was found. Figure 1 contains the molecular ion peaks of the cycles' MALDI-TOF mass spectra.

The products **[7]$_3$** and **[7]$_4$** can in principle consist of monocycles or catenanes (cycles **[7]$_3$** and **[7]$_4$** have the same mass as the catenanes from two **[7]$_1$** and **[7]$_1$**/**[7]$_2$**, respectively). It was difficult to differentiate between these two options by NMR or MS measurements. For simplicity we assume that both products are regular cycles. This is supported by the ^{1}H and ^{13}C NMR spectra of **[7]$_4$**, which give just one set of signals each, which would not to be

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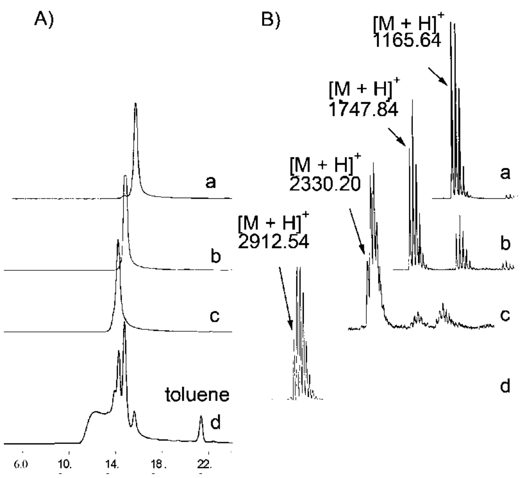

Figure 1. (A) GPC curves of purified **[7]**$_1$ (Aa), **[7]**$_2$ (Ab), **[7]**$_3$ (Ac), and the raw oligomerization mixture (Ad). (B) MALDI-TOF mass spectra of macrocycles **[7]**$_1$ (Ba), **[7]**$_2$ (Bb), and **[7]**$_3$ in a dithranol matrix (Bc) and **[7]**$_4$ (Bd, repetition experiment) in a DCTB matrix. Only the enlarged parts of the isotopically resolved [M + H]$^+$ signals are shown. The signals at higher masses correspond to the Na$^+$ and K$^+$ adducts, respectively.

expected for a compound consisting of intertwined **[7]**$_1$ and **[7]**$_2$. Unfortunately single crystals suitable for X-ray diffraction analysis could not be grown.

The unresolved part of the GPC elution curve was assigned to open chain oligomers with an average molar mass of M_{peak} = 10 600 g/mol based on polystyrene calibration.

Crystals of macrocycle **[7]**$_1$ were grown by slow diffusion of methanol into a solution of this cycle into chloroform. Its molecular structure is depicted in Figure 2 as an ORTEP representation. All ring atoms and the acetylenic carbon atoms exhibit normal thermal displacement parameters; those of the side chains differ drastically and reflect the differences in packing. The side chain attached to O1 fills the hole left in the center of another macrocycle and has very large thermal displacement parameters. The one at O2 shows normal thermal displacement parameters. The distance between opposite triple bonds within the cavity amounts to approximately 15.6 Å, and N1 and N1′ are about 8.0 Å apart from each other. The cycle is almost planar, with the bipyridine units are turned out of the plane with torsional angles of 35° (Figure 2). The cycles form a layer structure that gives rise to columns with channels (Figures 3). The distance between two cycles in the column is approximately 8.4 Å. Interestingly and in contrast to another bipyridine-containing macrocycle published by this group,[15] the X-ray analysis of **[7]**$_1$ does not reveal any solvent molecules in the crystal structure.

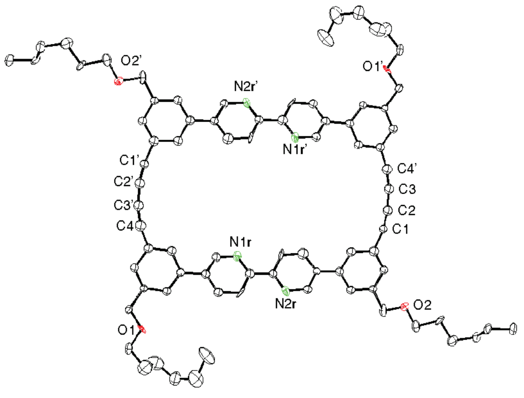

Figure 2. ORTEP plot of macrocycle **[7]**$_1$, viewed perpendicular to the macrocycle, 50% probability ellipsoids.

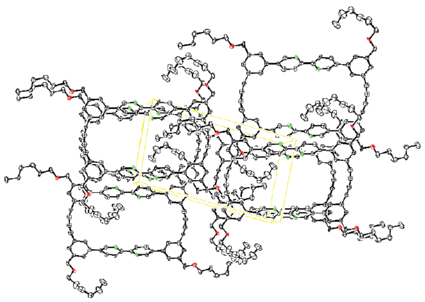

Figure 3. ORTEP plot of six molecules of **[7]**$_1$ showing the stacking of the aromatic rings.

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Supporting Information Available: Detailed descriptions of experimental procedures, characterization of compounds, spectra, and Crystallographic Information File (cif) of compound **[7]**$_1$. This material is available free of charge via the Internet at http://pubs.acs.org.

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