Olefin Metathesis

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Helical (5*Z*, 11*E*)-Dibenzo[*a*,*e*]cyclooctatetrene: A Spring-Loaded Monomer**

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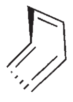
The introduction of a kink into an annulene cycle through having one of its double bonds in the *trans* configuration has severe consequences on the structure and stability of the resulting annulene. Modeling indicates that the π systems of either the [6]-annulene **1** or [8]-annulene **2** should wind into a helical conformation. The computed strain energy for **1** is circa 107 kcal mol^{-1}, and for **2** is approximately 21 kcal mol^{-1}.[1] Molecule **1** is probably too unstable at room temperature to allow it to be isolated and studied.[2] Herein we present a method to create the [8]-annulene **3**, a benzannulated version of **2**. Single crystal X-ray diffraction analysis of **3** reveals that it is a helix.[3] The strain of this ring structure makes it functional as a monomer for ring opening metathesis polymerization (ROMP), yielding a new type of living, regioregular oligophenylene vinylene.



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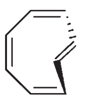

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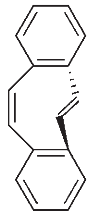

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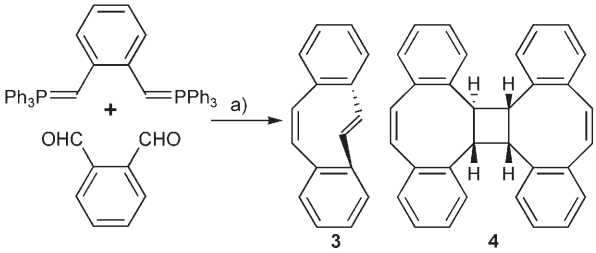
Scheme 1 shows the method used to prepare **3**, in which *o*-phthaldehyde reacts with the 1,2-bis(triphenylphosphonium ylide) at room temperature.[4] The isolated yield of **3** on a 20 mmol scale is about 20 %. Annulene **3** is stable for weeks. The strain energy we calculate using density functional theory (DFT) for **3** relative to the *cis*,*cis*-dibenzo[*a*,*e*]cyclooctatetraene is about 18 kcal mol^{-1}.[5] The stabilization owing to benzannulation, along with the steric protection provided by the aromatic rings, allows us to isolate **3**.[6] Previous studies on the synthesis of dibenzo[*a*,*e*]cyclooctatetraene have not reported the presence of **3**, and focus exclusively on the *cis*,*cis* isomer.[7] Using ^{1}H NMR spectroscopy, we observe only a trace amount of *cis*,*cis*-dibenzo[*a*,*e*]cyclooctatetraene. The only compounds we could isolate from the reaction mixture[8] were annulene **3**, a small amount of isomerized *cis*,*cis*-dibenzo[*a*,*e*]cyclooctatetraene, and a substance which has been difficult to characterize and that we tentatively assign as the dimer **4**[4] (Scheme 1). We suspect that earlier published work also likely produced **3**, but in those experiments **3** had isomerized during workup and/or purification. Emphasizing both the kinetic stability and the thermodynamic instability of **3**, we found that either UV irradiation, iodine, or traces of acid readily (and quantitatively) convert **3** into the more stable *cis*,*cis*-dibenzo[*a*,*e*]cyclooctatetraene.



Scheme 1. Double Wittig reaction to produce **3** and **4**. Reaction conditions: a) LiOEt in EtOH, DMF, slow addition over 6 h.

Wittig and co-workers synthesized dibenzo[*a*,*e*]cyclooctatetraene by a synthetic route that involved multiple Hofmann eliminations, and found that the material contained anomalous IR stretches.[9] These resonances would be reasonable for a strained, *trans* double bond, such as the one found in *trans*-cyclooctene,[10,11] but the structure was assigned to the more stable *cis*,*cis*-dibenzo[*a*,*e*]cyclooctatetraene. Subsequent studies, which prepared dibenzo[*a*,*e*]cyclooctatetraene by different methods, did not observe these anomalous IR stretching vibrations.[12,13] Further com-

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Supporting information for this article (synthesis of **3**, ROMP, and hydrogenation of poly-**3**; IR, ^{1}H NMR, ^{13}C NMR, and UV/Vis spectra, cif file, DFT optimized geometry for **3**; and ^{13}C NMR spectrum of poly-**3**) is available on the WWW under http://www.angewandte.org or from the author.

plicating matters, an attempt to resolve the disagreement concluded erroneously that the material prepared by Wittig contained an exocyclic olefin.[14] The IR spectrum we obtained for **3** (Supporting Information, Figure S1) agrees with the spectrum from Wittig's reaction. The reduced symmetry of **3** make its ^{1}H- and ^{13}C NMR spectra (Supporting Information, Figure S2 and S3) easily distinguishable from those of *cis,cis*-dibenzo[*a*,*e*]cyclooctatetraene.[7]

We were able to grow crystals of **3** that were suitable for X-ray diffraction.[15] Figure 1 shows three different views of the crystal structure of **3**. In Figure 1 A, the helical nature of the backbone of the molecule is emphasized, with the purple ribbon wound into a left-handed *M*-helix. Both enantiomers of **3** are present within the unit cell of the crystal. The molecule has C_2-symmetry; it is noteworthy that the π system is nearly perpendicular to the π system of the rest of the molecule, and is thereby isolated from conjugation. We have not yet been able to resolve this material into its enantiomers using chiral silver salts,[11] but we are confident that it is configurationally stable and ultimately could be resolved.

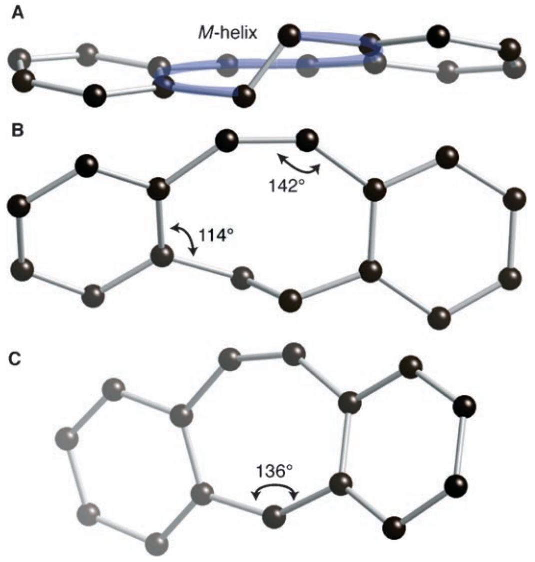
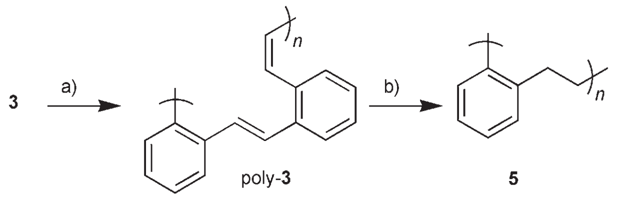


Figure 1. Different views of one of the molecules taken from the crystal structure of **3**. The black spheres represent carbon atoms. A) View facing towards the *trans* double bond. The purple ribbon traces the *M*-helix of the backbone. B) Face-on view of the molecule. C) View along the *trans* double bond, showing the deviation of the double bond from planarity (C–C=C–C dihedral angle = 136°).

The strain in the cycle is evident from the structural deviations from ideality. The plane defined by the substituents of the *trans* olefin are twisted away from planarity by circa 44° (Figure 1 C). The near planarity of the *cis*-stilbene portion of the molecule is reflected in the 66-nm red-shift in its absorbance (Supporting Information, Figure S4) relative to *cis,cis*-dibenzo[*a*,*e*]cyclooctatetraene.[16] As a consequence of the planarity demanded by the *trans* olefin, the *cis* double bond is significantly strained; the angle at the sp^2 carbons on the *trans* side of the molecule are compressed to an angle of about 114° and are expanded to an angle of approximately 142° on the *cis* half of the molecule (see Figure 1 B).

The strain energy in this cycle and the presence of both *cis* and *trans* double bonds makes **3** an interesting substrate for ring opening metathesis polymerization (ROMP).[17] We find that ROMP using well-known ruthenium-based catalysts[18] (see Scheme 2) does give poly-**3**. It should be noted that under these conditions *cis,cis*-dibenzo[*a*,*e*]cyclooctatetraene is unreactive. Figure 2 compares the downfield window of the ^{1}H NMR spectrum for the unreacted annulene **3** and the polymer. For **3**, there are two resonances (singlets at $\delta = 6.72$ and 6.37 ppm in Figure 2 A), one for each of the olefinic protons and additional downfield resonances arising from the aromatic rings.[19] ^{1}H NMR spectra of the polymers as they are



Scheme 2. Ring opening metathesis polymerization of **3**, and subsequent hydrogenation to **5**. Reaction conditions: a) [$Cl_2(PCy_3)_2Ru{=}CHPh$], CH_2Cl_2, RT. b) 10% Pd/C, H_2 3.7 atm, toluene.

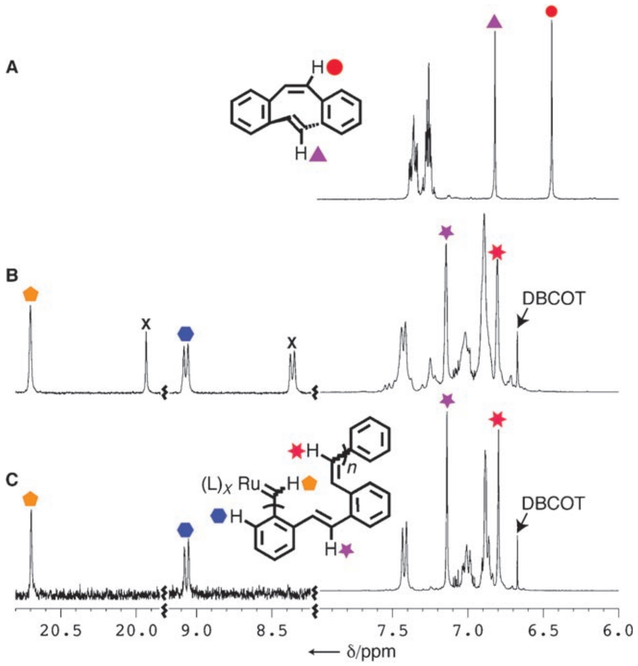


Figure 2. Downfield region of the 1H NMR spectra of: A) **3** in CD_2Cl_2;[19] B) [$Cl_2(PCy_3)_2Ru{=}CHPh$] (0.016 mmol) and **3** (0.13 mmol) in CD_2Cl_2 (1 mL), in which the intensity of the two most downfield segments of the spectrum are magnified 8 times; C) [$Cl_2(PCy_3)_2Ru{=}CHPh$] (0.012 mmol), PCy_3 (0.036 mmol), and **3** (0.22 mmol) in CD_2Cl_2 (1 mL), in which the intensity of the two most downfield segments of the spectrum are magnified 64 times. DBCOT refers to *cis,cis*-dibenzo[*a*,*e*]cyclooctatetraene, and × to unreacted starting ruthenium alkylidene complex.

growing are contained in Figure 2B,C. Figure 2B shows the spectrum of a mixture of **3** and the ruthenium-based olefin metathesis catalyst, $[Cl_2(PCy_3)_2Ru{=}CHPh]$,[20] at a mole ratio of 8:1 (monomer/catalyst). Despite the excess of the monomer, there are two types of alkylidene species present in solution. One of them is from the unreacted catalyst (marked with ×), and the other is from the growing polymer chain. We infer from this finding that the rate of chain propagation is faster than the rate of chain initiation for **3**.[21] Adding three molar equivalents of tricyclohexylphosphine relative to the catalyst slows propagation relative to chain initiation, and then we only observe the alkylidene species characteristic of a living polymer chain (Figure 2C).[21]

We have not been successful in measuring the molecular weights and polydispersity indices of poly-**3** using gel permeation chromatography, as the solubility profile of poly-**3** is incompatible with the typical polystyrene standards used for GPC. We were, however, able to fully hydrogenate the double bonds of poly-**3** to yield the polymer **5** (Scheme 2), which is very soluble in THF. Table 1 shows the range of polydispersities and molecular weights obtained for **5**. When its molecular weight reaches about 10000, poly-**3** becomes insoluble in the reaction medium; therefore it is difficult to achieve higher molecular weights. We can also estimate the molecular weight with ^1H NMR by integrating the resonance from the alkylidene end group of poly-**3** (at $\delta \approx 20.7$ ppm) relative to the resonance from either olefin in the growing polymer (Figure 2C). The molecular weights determined with GPC were in general about 20% lower than those determined by NMR. The polydispersity of the polymer is high (1.499) when no ancillary tricyclohexylphosphine is added; with the added tricyclohexylphosphine ligand, the polydispersity was as low as 1.067. We monitored the progress of the reaction, and once the monomer was consumed we added more monomer (**3**); this added monomer was subsequently consumed. After hydrogenation of the polymer, the GPC analysis of these samples (Figure 3) shows that for each aliquot the polydispersity remains below 1.1, and the molecular weights increase as more monomer is added. We infer from this data is that the polymerization is living.

Table 1: Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) for **5**.[a]

Entry	Ligand[b]	M_n	M_w	PDI
1	None	16273	24394	1.499
2	PCy_3[c]	1266	1391	1.099
3	PCy_3	1773	1905	1.074
4	PCy_3	2483	2735	1.101
5	PCy_3	7288	7773	1.067

[a] PDI $= M_n/M_w$. Compound **5** prepared by mixing $[Cl_2(PCy_3)_2Ru{=}CHPh]$ and **3** in CD_2Cl_2. Entries 2–5 are data from aliquots removed from the reaction mixture, which were then quenched with ethyl vinyl ether.[20] The double bonds were then hydrogenated as described in Scheme 2. [b] Additional tricyclohexylphosphine ligand added to the polymerization of **3**. [c] Tricyclohexylphosphine (8 mole equiv relative to the catalyst) added to reaction mixture.

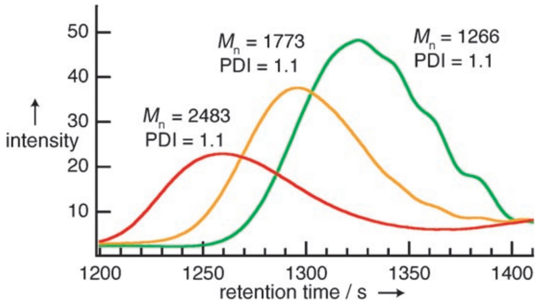


Figure 3. GPC data for aliquots taken from the reaction mixture. Each aliquot is hydrogenated to give **5**, and its number-average molecular weight M_n and polydispersity index (PDI) is determined. The first (green trace), second (yellow), and third (red) aliquot taken from the reaction are shown.

The ^1H NMR (Figure 2C) and ^{13}C NMR spectra (Supporting Information, Figure S5) of poly-**3** are remarkably simple. In both the ^1H and ^{13}C NMR spectra there are two olefinic resonances, one for the *cis* and one for the *trans* olefin, and the two resonances are of equal integrated intensity. We thus conclude that the phosphine-based catalysts yield a regioregular polymer with alternating *cis* and *trans* double bonds. It seems unlikely that a polymer that simply contains an equal number of *cis* and *trans* double bonds would have all of their ^{13}C and ^1H resonances at the same frequency. As support for this proposal, when we use ruthenium-based metathesis catalysts having N-heterocyclic carbene supporting ligands,[22] the ^1H NMR of the product polymer is much more complex, with multiple types of *cis* and *trans* double bonds (Supporting Information, Figure S6) implying that this catalyst gives ill-defined stereochemistry during polymerization.

The stereospecificity of this reaction is puzzling. Four possible metallocyclobutanes from the addition of a ruthenium alkylidene to the either the *cis* or *trans* olefin are given in the Supporting Information, Figure S7. Assuming that the metal alkylidene is selective and only reacts with either the *cis* or the *trans* double bond of **3**, only two of the adducts would produce a regioregular polymer. In view of the notable stereoregularity of the polymer, it is tempting to claim that the reaction of the ruthenium alkylidene ROMP active site with **3** is regioselective for either the *cis* or the *trans* double bond. We conducted DFT simulations to try to understand which of the two olefins is more susceptible.[23] These calculations gave an optimum geometry that was in good agreement with that found crystallographically (see the Supporting Information), and show an electronic structure that suggests that the *cis* double bond is the more reactive. The two highest-energy occupied and two lowest-energy unoccupied molecular orbitals of **3** were determined (Supporting Information, Figure S8). Both the highest-energy occupied and lowest-energy unoccupied orbitals are localized almost exclusively on the *cis* double bond, with a small amount of delocalization out onto the arenes. The *trans* double bond is also quite localized, as anticipated, but its orbital energy indicates that it is less strained than its *cis* sibling. This result is consistent with the molecular geometry;

whereas the presence of the *trans* olefin causes significant strain in the ring, the atomic disposition around the *trans* olefin is normal. The strain actually appears in the atomic disposition around the *cis* bond. For this reason, we believe that the ROMP occurs by opening at this latter bond.

In summary, we have described a method to create a new type of annulene in which one of its double bonds is kinked into a *trans* configuration. This strained structure is wound into a helical conformation, and is spring-loaded with circa 18 kcal mol^{-1} strain energy. It is an active partner in ROMP, forming living polymers. There are no prior examples of poly(phenylene vinylene)s with all-*ortho* linkages that formed in living polymerization, owing to the severe steric environment along the polymer backbone.[24] The method developed herein also appears to give regioregularity in the polymer backbone, which produces polymers with well-defined secondary structure. This secondary structure produces interior channels that can be exploited as a host for molecular guests. Moreover, these types of polymers have utility as electronic materials when oxidized into thin strips of graphene.[25–27]

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