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Polymerizations of a Terminal Diacetylene: Two Remarkable
Transformations Give the Same Conjugated Polymer**

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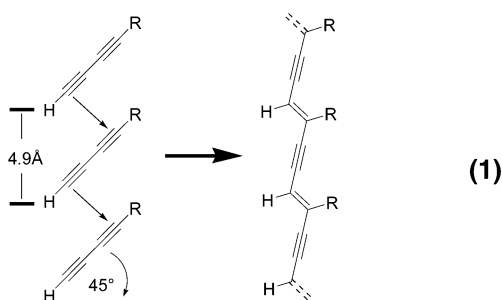
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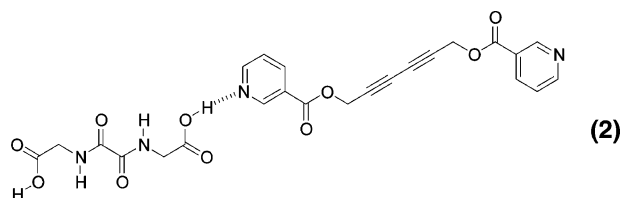
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The organization of reactants with the objective of selecting one reaction pathway among many is an important goal of chemistry. This process controls the structure of the product including absolute stereochemistry. Nature achieves this high level of specificity using enzymes. However, this goal is usually beyond our reach. The regularity and order of a crystalline lattice rival an enzyme with respect to molecular organization. Unfortunately, the application of a crystal lattice to organize molecules for a chemical reaction is a formidable problem. It requires a careful choice of the chemical reaction and a successful strategy for supramolecular assembly of the reactants. We have recently developed host-guest chemistry as a strategy for assembling monomers for topochemical polymerization. This approach has led to the first successful triacetylene and triene 1,6-polymerizations.^{1,2} We now report the application of this strategy to the first terminal diyne polymerization.

Polydiacetylenes have been known for about 35 years,³ resulting in the publication of over 2000 papers. Nearly all of this work has been carried out on fully substituted diacetylenes; indeed symmetrical diacetylenes are the most popular. Much rarer are studies of terminal diacetylenes. Little structural work has been carried out; the Cambridge Structural Database⁴ contains only four entries for terminal diacetylenes,⁵ none with the necessary structural parameters (eq 1) for a topochemical polymerization.⁶



How could one prepare such an array by design? In earlier work,⁷ we demonstrated that one could use a host-guest cocrystal to produce a network of hydrogen bonded oxalamide host molecules (2) that controlled the spacing and alignment of a diacetylene guest.



This host-guest approach works very well when both the host and the guest have matching end functionalities, that is, a dicarboxylic acid and a dipyridine. We envisioned that an analogous

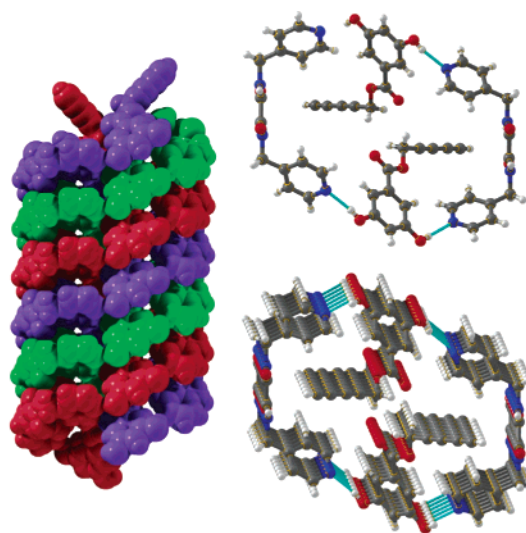
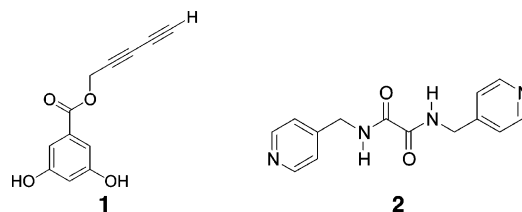


Figure 1. Three views of the crystal structure of the 1-2 cocrystal. If one focuses on the stronger phenol-pyridine hydrogen bond, the molecules form a hydrogen bonded chain in the form of a triple-helix of alternating molecules of **1** and **2**. The resorcinol headgroups are on the outer surface of the helix with the diacetylene tails in the center. The top drawing shows the four molecules of one turn of the helix. The left view shows that the helix is of order three. The lower right view shows the same structure from the top with the diacetylenes poised for topochemical polymerization.

motif could be achieved using a mono-substituted diacetylene with a difunctional headgroup such as resorcinol⁸ **1** and oxalamide⁹ **2**.



Resorcinol **1** was prepared and formed cocrystals with **2** from a methanol water solution. Figure 1 shows the structure, a beautiful triple-helical array. As designed, the diacetylene functionalities are arranged in a manner suitable for a topochemical reaction. The repeat distance is 5.090(4) Å, with an angle of 45.1°. The C1-C4' intermolecular distance is 3.638(4) Å. Heating the same single crystal to a temperature of 150 °C for 24 h gave the polymer structure shown in Figure 2. The polymerization motion is similar to the motion found in the various symmetrically substituted diacetylene polymerizations,¹⁰ a rotation about the diacetylene center with the C1 and C4 carbons each moving a similar distance with a pivot of the attached methylene group. The repeat distance shortens to 4.925(5) Å upon polymerization, Table 1.

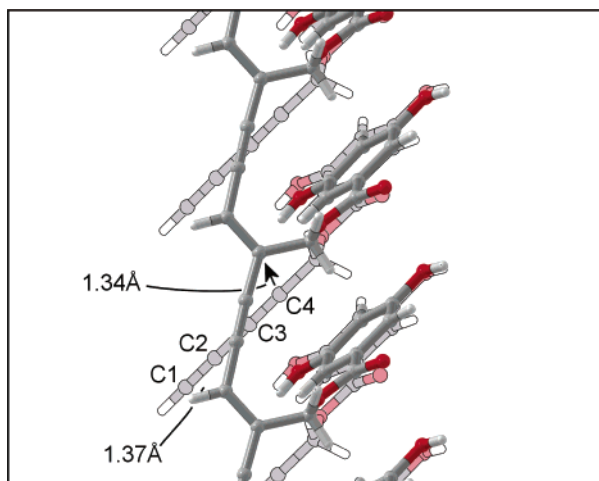


Figure 2. The pale background drawing shows the structure of the **1·2** cocrystal diacetylene monomers. The bold foreground drawing shows the structure of the resulting polydiacetylene. The main motion is a rotation of the diacetylene accompanied by a pivot of the methylene group. The C1 and C4 atom movements are similar, 1.37 and 1.34 Å.

Table 1. Crystallographic Data

	1·H₂O monomer	1·H₂O polymer	1·2 monomer	1·2 polymer
<i>a</i> (Å)	4.725(1)	4.876(2)	14.345(1)	14.607(1)
<i>b</i> (Å)	7.878(2)	7.814(3)	5.090(4)	4.925(5)
<i>c</i> (Å)	30.482(8)	27.407(9)	33.38(3)	33.14(3)
α (deg)	90	90	90	90
β (deg)	90.502(5)	87.203(7)	94.83(1)	91.92(1)
γ (deg)	90	90	90	90
vol (Å ³)	1134.5(5)	1043.0(6)	2450(4)	2382(4)
den. g/cm ³	1.371	1.491	1.318	1.356
space grp.	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>

We were pleased with our designed structure, but in carrying out the synthesis we found an unexpected bonus. When pure resorcinol **1** is recrystallized from a methanol water mixture, large single crystals formed that showed an unexpected reddish brown color. These crystals turned black at 85 °C and showed no melting point up to 300°. A well-formed crystal was selected, and a structure determination revealed that the molecule had crystallized as a monohydrate with alignment of the diacetylene functionalities in reasonable agreement with the requirements for a topochemical polymerization, Figure 3.

The all important repeat distance is a bit short at 4.725(1) Å with a declination angle of 54.3°; the C1–C4' intermolecular contact is 3.95 Å. These parameters are at the fringe of the range normally associated with crystal-to-crystal polymerizations, but upon heating the same single crystal at a relatively low temperature of 50 °C for 20 h a smooth single-crystal-to-single-crystal polymerization took place.

The polymerization of **1·H₂O** is accompanied by a significant change in both unit cell constants and crystal density. The polymerization occurs along the short *a* axis. This axis lengthens from 4.725(1) Å in the monomer crystal to 4.876(1) Å in the polymer crystal. At the same time, the long *c* axis of 30.482(8) Å dramatically contracts to a value of 27.407(8) Å in the polymer crystal. The density increases by 8.8%. The extreme motion of the terminal diacetylene groups causes this 3 Å shrinkage of the *c* axis. There is a bend at C4 with C1 moving inward by an unprecedented 2.45 Å to approach the C4' atom of the molecule below.

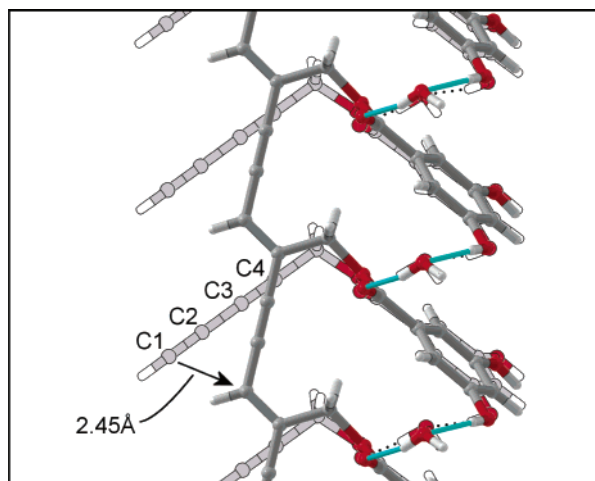


Figure 3. The pale background drawing shows the structure of the **1·H₂O** terminal diacetylene monomer structure. The bold foreground drawing shows the structure of the resulting polydiacetylene. The main motion is an inward swing of the diacetylene unit with a bend at C4. Atom C1 moves inward 2.45 Å. This inward motion of the diacetylene causes a shrinkage of the unit cell *c* axis and a 9% increase in crystal density.

It is interesting to note that the repeat distance in the **1:2** structure decreases from 5.090(4) Å for the monomer to 4.925(5) Å for the polymer. The **1·H₂O** structure starts short at 4.725(1) Å and lengthens to 4.876(1) Å. The polymer repeat distances approach the ideal 4.9 Å from opposite directions.

In conclusion, molecule **1** has turned out to be an interesting molecule. It undergoes the first structurally characterized polymerization of terminal diacetylene, and it does it twice. In the hydrate, the diacetylene functionality is “free”, and there is a dramatic 2.45 Å swinging movement of C1. In the designed structure, the diacetylene polymerization takes place in a triple-helix “cage”, and the diacetylene movement is much more constrained. A detailed comparison of these two sets of structural changes offers an interesting insight into the precise trajectories of polymerization reactions.

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Supporting Information Available: Details of the synthetic procedures and tables of X-ray diffraction data (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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