

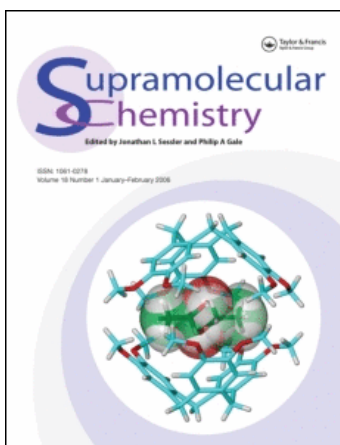
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### What have We Learned about Topochemical Diacetylene Polymerizations?

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# What have We Learned about Topochemical Diacetylene Polymerizations?

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**A series of five polydiacetylenes have been synthesized via topochemical polymerizations of the corresponding monomers. The requisite structural parameters for the polymerization were achieved by the use of a host–guest co-crystal strategy. The atom trajectories of the polymerization reactions are discussed.**

*Keywords:* Polydiacetylenes; Topochemical polymerizations; Crystal design; Host–guest chemistry; Hydrogen bonding

One of the more powerful applications of supramolecular chemistry is the preparation of specific molecules via precise preorganization of the reactants. This is the role of many catalysts and such preorganization is exemplified in its most elegant form by Nature's many enzymes. Another form of natural organization is the near-perfect order of a crystal. This form of organization can also lead to the synthesis of specific molecules via precise preorganization of reactants. Such reactions are called topochemical reactions. Topochemical reactions are well known to solid state chemists and have been studied extensively since the 1960s [1].

If we can use the principles of supramolecular chemistry to design a new catalyst or perhaps an artificial enzyme, then we should be able to use supramolecular chemistry to design and carry out a new topochemical reaction. This has been the goal of our research. We have targeted various previously unknown polymer systems, polymers that cannot be prepared in solution but are in reach via topochemical polymerizations. This work has led us to new forms of polydiacetylenes [2,3], including the first known terminal polydiacetylene [4], the first

polytriacetylenes [5] and the first topochemical polymerization of a triene [6]. In this paper we review some of the highlights of our work on the polydiacetylenes.

The basics of topochemical diacetylene polymerizations were first formulated by Wegner [7] and Baughman [8] over thirty years ago. They recognized the precise geometric requirements that were needed for such reactions to occur. Both a good match of the molecular repeat distance of the monomers to the repeat the polymer product and a close approach of the reacting atoms are needed (Fig. 1). A certain degree of molecular flexibility that will allow the necessary conformational changes is also needed.

Of course, knowing the precise geometric requirements and achieving them are two different things. Some diacetylenes crystallize in a manner consistent with these geometric requirements and a polymer can be formed upon heating or irradiation. In some cases the geometric match is near perfect and a crystal-to-crystal polymerization takes place. But in most cases, a given diacetylene does not crystallize properly. When a single molecule does not crystallize in the way we 'want' it to, there is little we can do about it. 'Wishing' for a second polymorph seldom works.

This is the problem that we have addressed in our work. How do you take a diacetylene that does not crystallize 'properly' and bring it into a new crystalline environment where the geometric requirements are met? Our solution has been a Host–guest co-crystal approach. We have used the principles of supramolecular chemistry to design host systems that can provide the necessary precise

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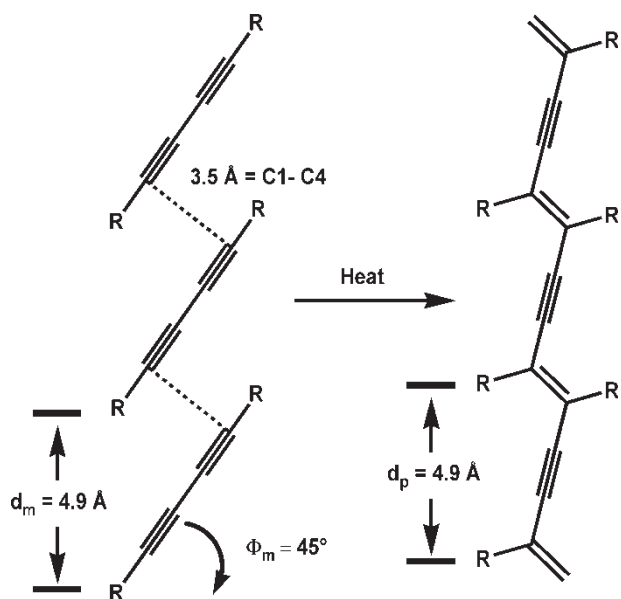
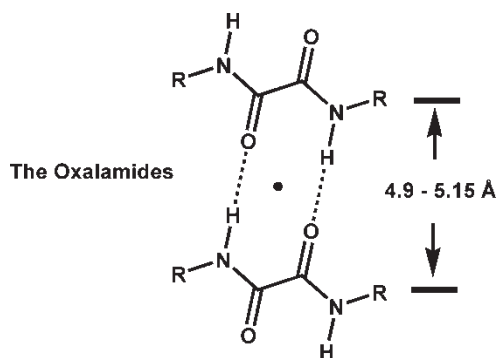


FIGURE 1 For a topochemical diacetylene polymerization reaction the monomers should be aligned at 4.9 Å, the repeat distance in the final polymer. A close approach of the C1–C4 carbons is also desirable. This occurs when the monomer tilt angle,  $\Phi_m$ , is about 45°.

structural organization and impose it upon the reactive guest monomers.

In carrying out our investigations we have learned many things about topochemical polymerizations. In particular, we have greatly expanded the number of known crystal-to-crystal polymerizations. Such experiments are very valuable, because they give precise structural parameters for the monomers and the polymers and a view of reaction trajectories that is difficult to achieve any other way. This has allowed us to refine the geometric requirements for these reactions and to formulate new ideas and strategies that may lead us and others to new designs in the future.



The key to topochemical polymerizations is an alignment of the monomers into a linear array with an intermolecular repeat distance that matches the 4.9 Å repeat distance of the polymer (Fig. 1). We needed to design a host system that would reliably establish this distance. Fortunately, intermolecular hydrogen bonds between amides are of this magnitude. We have found that using two hydrogen bonds is best and that the simplest diamides, the oxalamides, work very well [9].

Oxalamides crystallize as one-dimensional  $\alpha$ -networks with repeat distances that average about 5.05 Å. The shortest we have found is 4.83 Å [10], while sterically hindered examples can be considerably longer. For a reliable host–guest interaction, complementary functional groups on the host and the guest are needed. As acid–base interactions lead to the most dependable intermolecular interactions, we have investigated diacetylenes with acidic (carboxylic acid or phenol) or basic (pyridine) substituents. Our best polymerization results have come from compounds 1–4. The simplest complementary oxalamide host molecules are the diacid 5 and the dipyridine 6.

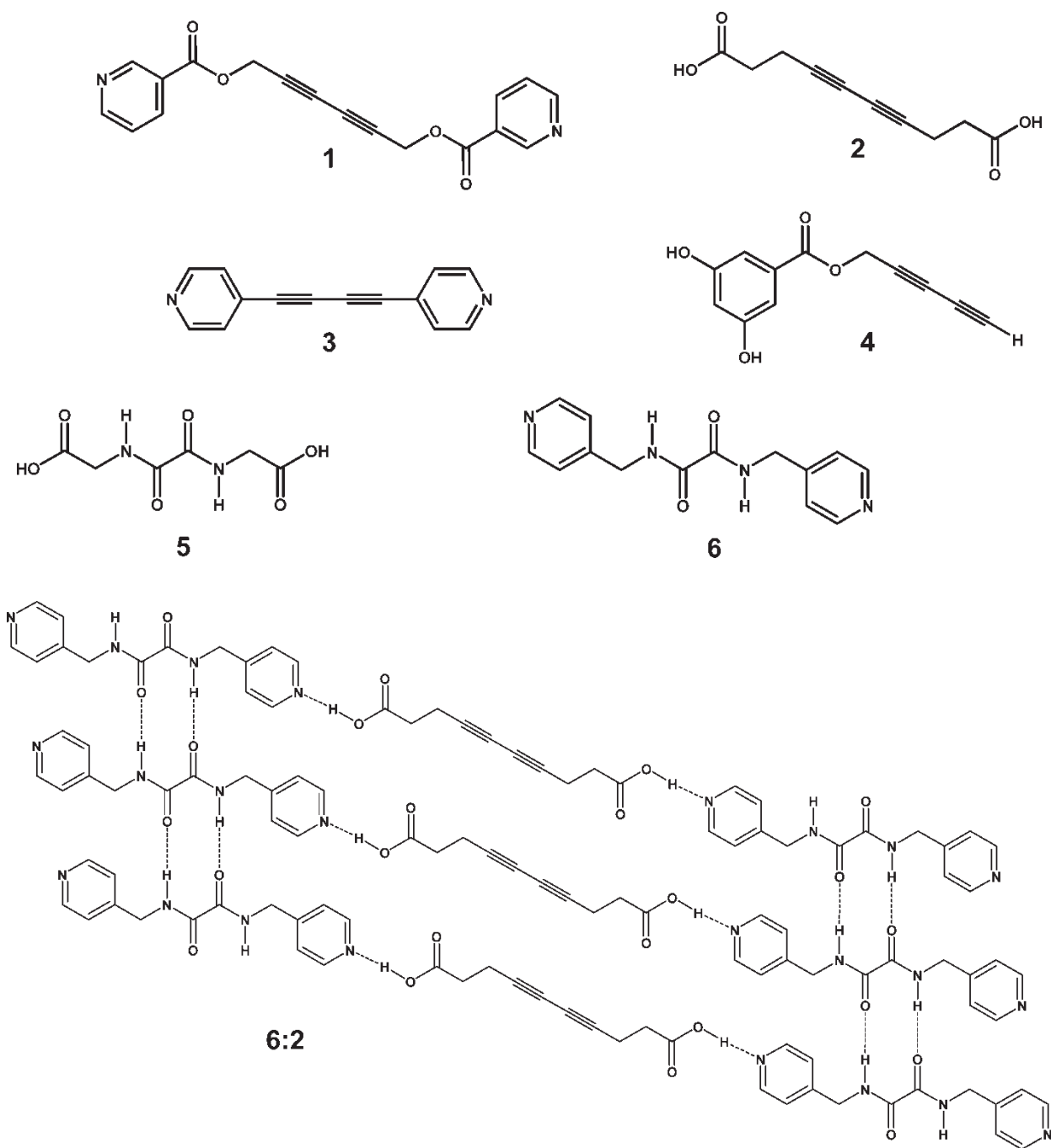
This combination of molecules gives us four host–guest pairs, 5:1<sup>†</sup> and 5:3<sup>‡</sup> with the acid host, and 6:2<sup>†</sup> and 6:4 [4] with the pyridine host. Three of the host–guest pairs led to co-crystals containing two-dimensional hydrogen-bonded  $\beta$ -networks. The fourth structure, the co-crystal 6:4 [4], has a similar network but it twists around to give a somewhat unique triple-helix structure. The oxalamide host still forms the expected hydrogen bonds and brings the diacetylene molecules into proper alignment.

In the course of preparing co-crystals of the resorcinol compound 4, we found that the molecule formed a hydrate, 4·H<sub>2</sub>O [4]. Quite fortuitously, the hydrate structure also met the requirements for diacetylene polymerization. Thus, in addition to the four designed crystals, we have a fifth crystal that we did not anticipate. All five crystals polymerize, four of them polymerize crystal-to-crystal, meaning that we can obtain full structures of the polydiacetylene products (Fig. 2). The 5:3 co-crystal does not polymerize crystal-to-crystal because the polymerization leads to crystal deterioration (Fig. 3).

<sup>†</sup>A preliminary account of this polydiacetylene has been given in Ref. [3]. A full publication will be submitted.

<sup>‡</sup>This host–guest pair is one of a series of eight bipyridine oxalamide co-crystals that we have prepared. A full publication will be submitted.

<sup>†</sup>Data for 6:2 were collected on a Bruker platform diffractometer with a Smart 1000 CCD detector using graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation at room temperature. Crystal data: C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>O<sub>6</sub>,  $M = 464.5$ , triclinic space group  $P1$ ,  $a = 4.908(7)$ ,  $b = 9.226(14)$ ,  $c = 12.922(19)$  Å,  $\alpha = 108.70(2)$ ,  $\beta = 96.783(18)$ ,  $\gamma = 96.30(2)^\circ$ ,  $V = 543.5(14)$  Å<sup>3</sup>,  $Z = 1$ ,  $d_{\text{cal}} = 1.42$  g/cm<sup>3</sup>. The poorly diffracting crystals gave only 496 data with  $F_o > 2\sigma(F_o)$ .  $R_1 = 0.078$ ,  $wR_2 = 0.1693$ . Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 244266.



## RESULTS

Figure 2 shows the crystal structures of the four polydiacetylenes that polymerized crystal-to-crystal. Table I gives some of the important structural results for the monomers and the polymers of the five co-crystals. An examination of the results reveals some interesting trends.

The first and most obvious result is the repeat distance,  $d_p$ , for a polydiacetylene. The repeat distances for the four polymer structures are all very close and average 4.90 Å. The 5:1 co-crystal is perhaps the best example of what might be called a classic

diacetylene polymerization. The monomer distance,  $d_m$ , of 4.93 Å is only slightly longer than the 4.90 Å of the final polymer. At 3.38 Å the C1–C4 distance is about as close as a nonbonded C–C distance can ever get. The crystals will polymerize at 100°C in 45 min. The reaction trajectory involves a rotation of the diacetylene unit by about 30° (Fig. 4a).

The 6:2 co-crystal also polymerizes readily; in fact it polymerizes so easily that we could never isolate a quality crystal of the monomer. Each crystal that we tried turned out to be at least partially polymerized. Presumably the monomer has structural parameters very close to the ideal.

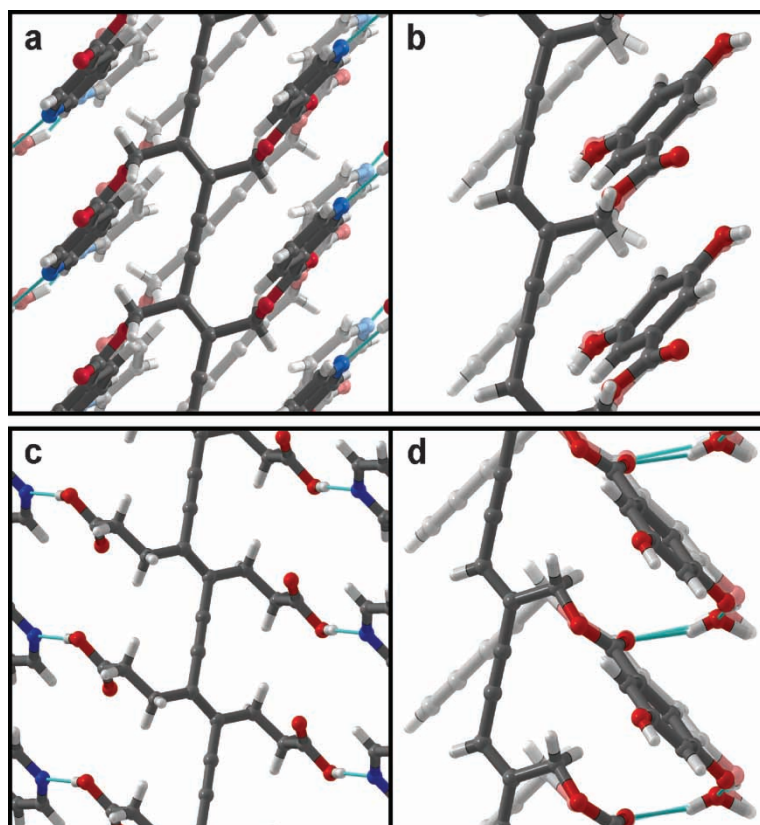


FIGURE 2 The crystal structures of four polydiacetylenes. In three cases the polymers are superimposed over the monomer structure, which appears in lighter color in the background. (a) The 5:1 co-crystal. (b) The 6:4 co-crystal. (c) The 6:2 co-crystal; in this case the monomer structure was too reactive for crystallographic studies. (d) The 4-H<sub>2</sub>O hydrate.

The dipyrindine crystal 5:3 is different. Although the structural parameters,  $d_m = 4.94 \text{ \AA}$ , C1–C4 =  $3.69 \text{ \AA}$ , look good, the crystals show no sign of thermal polymerization. If the crystals are irradiated

with UV light or  $\gamma$ -rays, polymerization takes place, but the crystals fall apart. So what is the problem? Most likely there is too little molecular flexibility. The direct pyridine substituent is too rigid. Examine Fig. 1. The angle to the R group is  $180^\circ$  for the  $sp$  hybridized diacetylene monomer. In the product the angle to the R group is  $120^\circ$  for the  $sp^2$  hybridized polymer. The diacetylenes pivot by  $30^\circ$  from about  $45^\circ$  to about  $15^\circ$  in the polymer. The R group must also pivot by  $30^\circ$  to achieve the necessary  $60^\circ$  of total movement. This pivot is easily accommodated by the adjoining methylene groups of the polymers of compounds 1, 2 and 4, but a pyridine has no pivot point. The crystals are thermally stable, the polymerization takes place with UV or  $\gamma$  irradiation, but the required massive movement of the pyridine ring

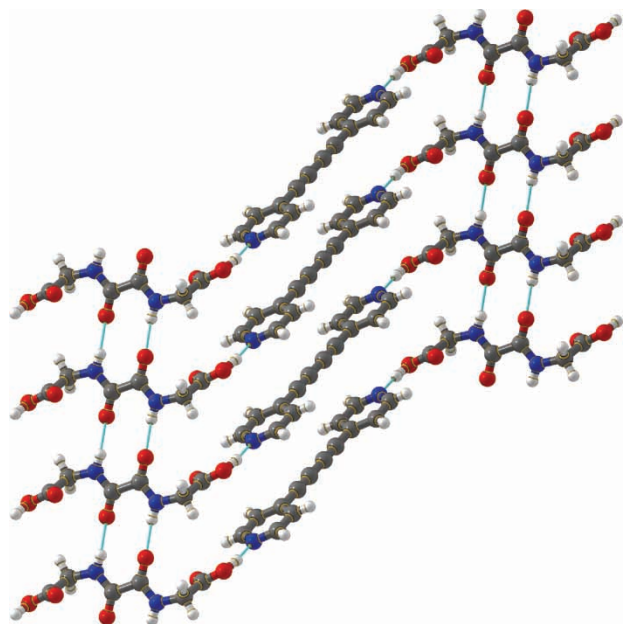


FIGURE 3 The crystal structure of the 5:3 co-crystal.

TABLE I Structural results for the diacetylene monomers and polymers

|              | 5:1  | 5:3        | 6:2        | 6:4  | 4-H <sub>2</sub> O |
|--------------|------|------------|------------|------|--------------------|
| $d_m$ (Å)    | 4.93 | 4.94       | No crystal | 5.09 | 4.72               |
| C1–C4 (Å)    | 3.38 | 3.69       | No crystal | 3.61 | 3.95               |
| $\Phi_m$ (°) | 42.9 | 48.0       | No crystal | 45.2 | 54.3               |
| $d_p$ (Å)    | 4.90 | No crystal | 4.91       | 4.91 | 4.87               |

<sup>a</sup> The various structural parameters are defined in Fig. 1.

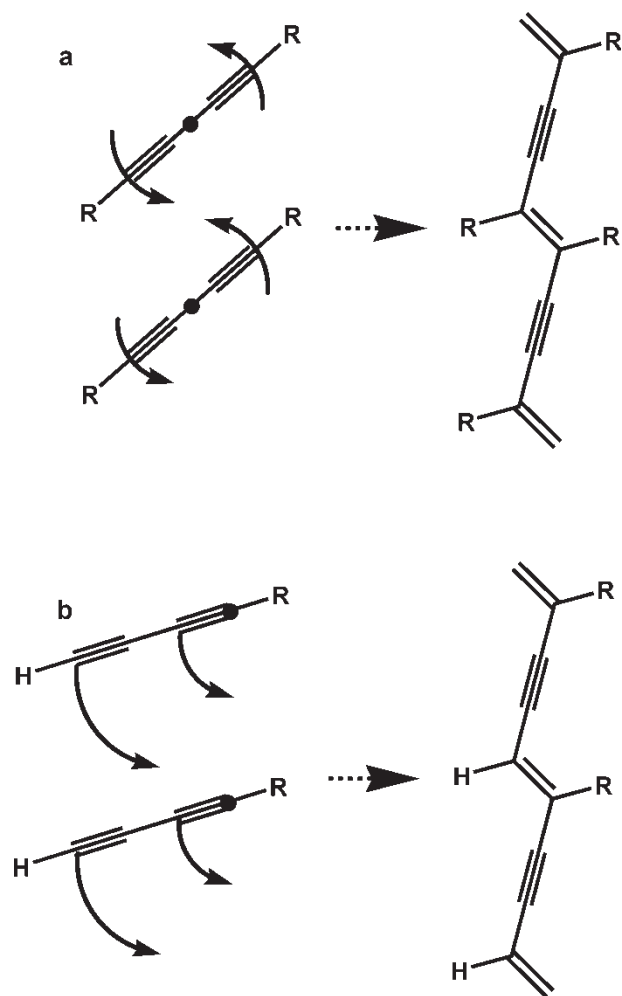


FIGURE 4 Two trajectories for diacetylene polymerizations. Mechanism **a** is the traditional mechanism. Each diacetylene rotates about its center point by  $30^\circ$ , bringing carbon atoms C1 and C4 together. In mechanism **b** the diacetylene bends by  $60^\circ$  at carbon atom C4.

seems to disrupt the lattice and brings about destruction of the crystal.

The polymer of resorcinol, **4**, a terminal diacetylene, has been prepared in two different crystalline environments. Prior to our work, no one had ever reported the topochemical polymerization of a terminal diacetylene. In the **6:4** host-guest co-crystal the monomers are spaced at  $5.09 \text{ \AA}$  and the repeat decreases to  $4.91 \text{ \AA}$  as the polymerization occurs. In the hydrate **4**· $\text{H}_2\text{O}$ , the monomers are spaced at only  $4.72 \text{ \AA}$  and the repeat distance increases to  $4.87 \text{ \AA}$  as the reaction proceeds. The two polymerizations approach the same polymeric repeat distance from opposite directions.

A detailed examination of the two sets of molecular movements is most informative. The **6:4** co-crystal behaves in the normal way following the traditional polymerization trajectory. With a  $d_m$  of  $5.09 \text{ \AA}$  and a C1–C4 distance of  $3.61 \text{ \AA}$  the crystals require a temperature of  $150^\circ\text{C}$  for 24 h for polymerize.

By contrast, the hydrate crystal **4**· $\text{H}_2\text{O}$  appears to have structural parameters unsuitable for a polymerization reaction. The repeat distance,  $d_m$ , is short at only  $4.72 \text{ \AA}$  and the C1–C4 distance is long at  $3.96 \text{ \AA}$ . Despite these less than ideal parameters the polymerization takes place very easily, polymerizing at only  $50^\circ\text{C}$ , a temperature  $100^\circ\text{C}$  lower than for the **6:4** co-crystal. An examination of Fig. 2d shows that the molecular trajectory is different. Instead of rotating about the midpoint of the diacetylene, the diacetylene bends at the C4 carbon atom. The end C1 carbon atom moves  $2.45 \text{ \AA}$ , while the C5 carbon atom moves only about  $0.40 \text{ \AA}$ . In the **6:4** co-crystal the movement was symmetrical with both atoms moving about  $1.35 \text{ \AA}$ .

This is a new reaction trajectory (Fig. 4b), not seen before. It is significant for two reasons. First, the atom movement of  $2.45 \text{ \AA}$  is large for any topochemical reaction. Second, this trajectory does not require a pivot of the single R group. The entire required  $60^\circ$  of movement can be taken up by the diacetylene. This suggests that a greater variety of terminal diacetylenes may be able to undergo polymerization reactions. Experiments to explore a variety of new terminal diacetylenes are under way.

## CONCLUSIONS

What have we learned about topochemical diacetylene polymerizations? First, we have learned that the reaction is not just a laboratory curiosity. Using the host-guest co-crystal approach it should be possible to polymerize a wide variety of diacetylenes. A substituent is needed to facilitate the host-guest interaction, and such things as sterics and molecular flexibility have to be taken into account, but we should be able to make many new polydiacetylenes using this methodology. These new polydiacetylenes are of interest because they totally conjugated polymers and they are highly organized. The optical and electrical properties of conjugated molecules are highly dependent upon organization. Finally, this work demonstrates that topochemical reactions are worthy of study for the insight they provide into reaction trajectories. Single-crystal X-ray studies give detailed structural information about both the preorganized reactants and the products. Such preorganization is very important throughout chemistry, but few other systems allow us to gather such precise structural information about reaction pathways.

## Acknowledgements

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