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## Third Polymorph of Phenylacetylene

Tejender S. Thakur, Ranganathan Sathishkumar, Amol G. Dikundwar,  
Tayur N. Guru Row,\* and Gautam R. Desiraju\*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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**ABSTRACT:** A third polymorph of phenylacetylene ( $Z' = 6$ ), which is obtained by quenching the liquid, shows some similarities to the two earlier known forms, and the adoption of a high  $Z'$  value in this crystal form is discussed.

This communication reports the third polymorph of phenylacetylene, which has  $Z' = 6$ . Weiss et al. reported the first crystal structure of phenylacetylene ( $\alpha$ -form;  $Z' = 2.5$ ,  $P\bar{1}$ ).<sup>1</sup> The structure contains two ordered full molecules and a half molecule disordered across an inversion center. Of the three symmetry independent ethynyl groups, one of the H-atoms points toward a triple bond and the two others to the  $\pi$ -systems of neighboring aromatic rings. Katrusiak and co-workers isolated a second polymorph ( $\beta$ -form) of the compound by application of pressure on the liquid in a diamond anvil cell.<sup>2</sup> These workers described their structure as being “nearly isostructural” to the  $\alpha$ -form. The space group remains the same, but the  $c$  parameter is increased by 20% and  $Z'$  increases concomitantly to 3. The two disordered molecules in the  $\alpha$ -form are replaced by two ordered molecules that are related by a center of inversion at a distance of 1.6 Å from each of the phenyl rings. All the other molecules are in the same relative orientations in  $\alpha$ - and  $\beta$ -forms. The structure of the  $\beta$ -form can be understood as arising from a lengthening of the  $c$ -axis in the  $\alpha$ -form so that there is enough space created for the disordered molecule to be replaced by two ordered molecules related by an inversion center.

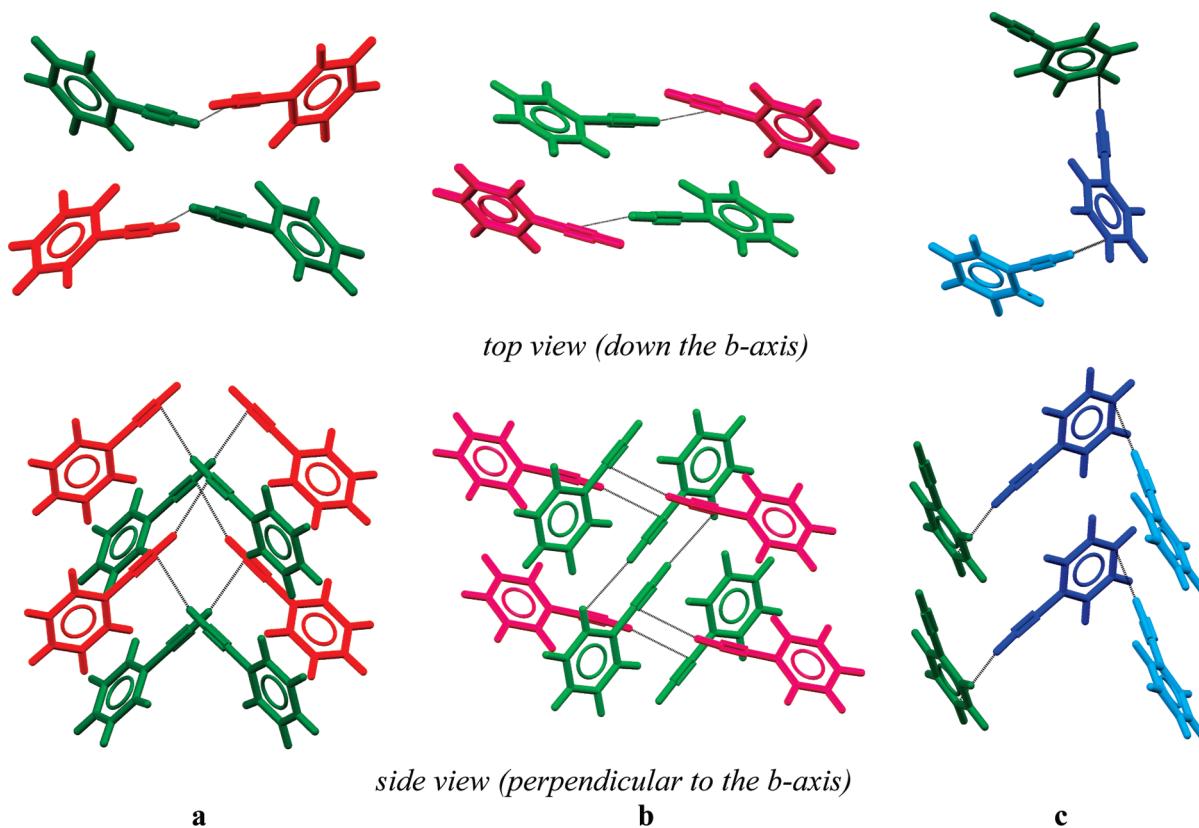
The new polymorph of phenylacetylene ( $\gamma$ -form) was obtained by us by quenching the compressed liquid. The neat liquid was taken in a Lindemann capillary tube and sealed. This sealing (from both ends, decreasing the length of the air gap in the capillary) produces the compression. The sealed capillary was maintained in a hot water bath at around 90–95 °C. The capillary was quickly inserted into liquid N<sub>2</sub>. This procedure mostly resulted in a breaking of the capillary. Occasionally, the capillary did not break and the quenched mass inside was almost completely the  $\gamma$ -form. Slight changes in the experimental conditions produced the two other forms. For example, if the capillary (sealed without compression) was heated only until about 60–75 °C in the water bath and then quenched suddenly, the  $\beta$ -form resulted. The  $\alpha$ -form was produced when the sample was cooled under controlled conditions without a preheating in the water bath. It was not easy to obtain the  $\gamma$ -form. Careful analysis of the reciprocal lattice images was necessary in order to identify the domains of the new form. The  $\gamma$ -form takes the monoclinic space group  $C2/c$  with  $Z' = 6$ . The crystal packings in all three phenylacetylene polymorphs are characterized by a number of T-shaped  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) and  $\equiv\text{C}-\text{H}\cdots\pi$  (aryl) contacts<sup>3–5</sup> (Scheme 1). These contacts are particularly common in this group of compounds. These weak  $\equiv\text{C}-\text{H}\cdots\pi$  interactions form supramolecular synthons,<sup>6</sup> for example the cyclic tetramer (Scheme 1b) found in the  $\alpha$ - and  $\beta$ -forms or the  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) zigzag chain found in the  $\gamma$ -form (Scheme 1a).

These  $\equiv\text{C}-\text{H}\cdots\pi$  patterns are very common in the crystal structures of terminal acetylenes. The Cambridge Structure Database<sup>7</sup> (CSD v5.31, update May 2010) gave 41 hits for pure hydrocarbons (containing C and H only) with a terminal ethynyl group (Supporting Information). Among these 41 hits, 32 structures are aromatic compounds. Analysis of the crystal packing of these 32 compounds allows an assessment of the competition between the aryl and ethynyl donor/acceptor functionalities in determining the overall crystal packing. The patterns in Scheme 1 are the most common. This analysis indicates a full exploitation of the hydrogen bond donor and acceptor capabilities in terminal ethynyl aromatics with an equal propensity for both aryl and ethynyl donors/acceptors. A slight preference toward the  $\equiv\text{C}-\text{H}\cdots\pi$  (aryl) interactions was seen over the  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) and C(aryl)–H $\cdots\pi$  (aryl) interactions.

The crystal structure of the  $\gamma$ -form contains six independent molecules in the asymmetric unit. The overall packing shows that the molecular units are rather randomly oriented. Two of the symmetry independent molecules (red and green in Figure 1a) are engaged in the formation of a parallel set of  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) zigzag chains related by 2-fold symmetry, giving an impression of a  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) tetramer when viewed down the 2-fold axis (Table 1). Another set of symmetry independent molecules (pink and light green in Figure 1b) also form  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) zigzag chains, but these are arranged in an antiparallel fashion around an inversion center; they too look like incipient tetramers. The two remaining symmetry independent molecules (blue and light blue in Figure 1c) are linkers between these columnar tetramer units and act through  $\equiv\text{C}-\text{H}\cdots\pi$  (aryl) and C(aryl)–H $\cdots\pi$  (aryl) interactions. The relationship between the  $\gamma$  and  $\beta$  forms can be envisaged as a transformation of the symmetry related incipient tetramer columns of  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) zigzag chains to a discrete  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) tetramer by compression of the cell along the  $a$ - and  $c$ -axes. A schematic depiction of such a transformation is given in Scheme 2. Considering the structural similarity and the negligible differences in the packing of the remaining parts of the crystal structures, a higher order common synthon ( $d$  in Scheme 2) can be proposed for all the forms of phenylacetylene. This synthon is made up of two tetramers linked with weak  $\equiv\text{C}-\text{H}\cdots\pi$  (aryl) interactions. Considering that it is a higher synthon,  $d$  may be termed as a long-range synthon aufbau module (LSAM), as recently defined by Ganguly and Desiraju.<sup>8</sup> A cartoon depiction of the transformation and the packing similarities in these forms is shown in Figure 2.

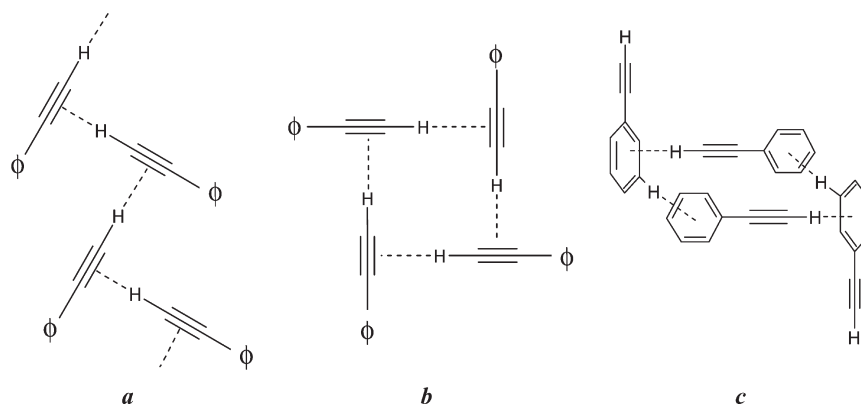
To obtain a further understanding of the packing similarities between the  $\gamma$ -form and the two other forms of phenylacetylene, the six symmetry independent molecules can be considered as being divided into two groups of three molecules each (Figure 2). The first group is comprised of pink, light green, and light blue molecules and represents a disoriented set with large deviations from the higher synthon  $d$ . The second group is made up of red,

\*Corresponding authors. T.N.G.: fax, (+91) 80-23601310; telephone, (+91) 80-23932796; e-mail, ssctng@sscu.iisc.ernet.in. G.R.D.: fax, (+91) 80-23602306; telephone, (+91) 80-22933311; e-mail, desiraju@sscu.iisc.ernet.in



**Figure 1.** C—H··· $\pi$  interaction patterns in the  $Z' = 6$   $\gamma$ -form of phenylacetylene: (a) parallel arrangement of  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) zigzag chains; (b) antiparallel arrangement of  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) zigzag chains; (c)  $\equiv\text{C}-\text{H}\cdots\pi$  (aryl) contacts. Symmetry independent molecules are color coded.

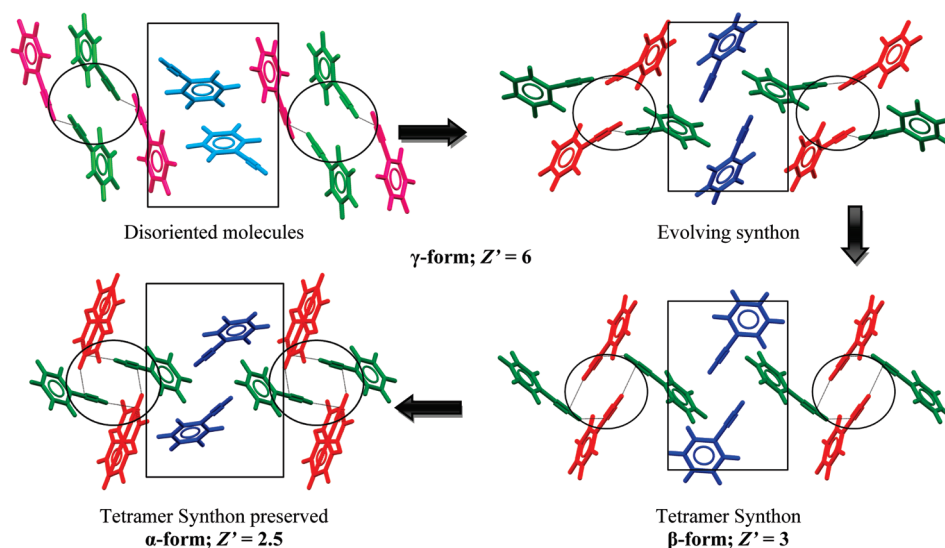
**Scheme 1**



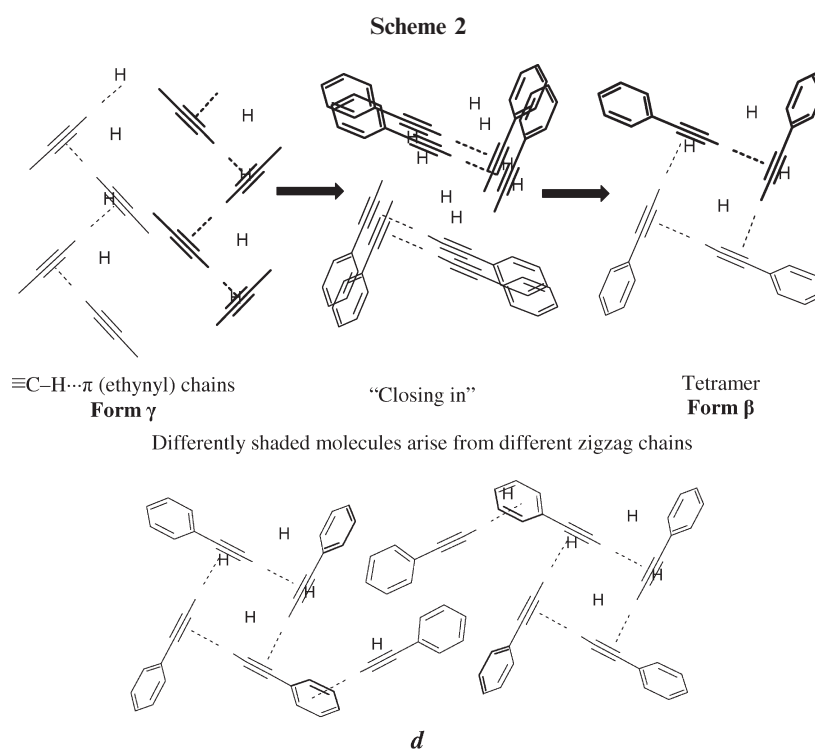
**Table 1.** C—H··· $\pi$  Interactions in the  $\gamma$ -Form of Phenylacetylene<sup>a</sup>

| donors →    | red <sup>b</sup>                                    | green   | blue  | pink  | light green   | light blue               |
|-------------|---|---|---|---|---|--------------------------|
| acceptors ↓ |   |   |   |   |   |                          |
| red         |   | I (3.67 Å)<br>III ( <i>o</i> , 3.89 Å)<br>IV ( <i>m</i> , 3.83 Å) | III ( <i>p</i> , 3.69 Å)<br>IV ( <i>m</i> , 3.68 Å) |   |   |                          |
| green       | I (3.55 Å)<br>III ( <i>o</i> , 3.81 Å)              |   |   |   |   | III ( <i>p</i> , 3.54 Å) |
| blue        | II (3.53 Å)   |   |   | III ( <i>p</i> , 3.70 Å)<br>IV ( <i>m</i> , 3.72 Å) |   | III ( <i>m</i> , 3.52 Å) |
| pink        | III ( <i>p</i> , 3.78 Å)<br>IV ( <i>m</i> , 3.84 Å) |   |   |   | I (3.80 Å)<br>IV ( <i>m</i> , 3.62 Å)               |                          |
| light green |   | III ( <i>m</i> , 3.67 Å)<br>IV ( <i>p</i> , 3.78 Å)               |   | I (3.74 Å)<br>IV ( <i>o</i> , 3.56 Å)               |   |                          |
| light blue  |   |   | II (3.52 Å)   |   | IV ( <i>m</i> , 3.73 Å)<br>III ( <i>o</i> , 3.95 Å) | IV ( <i>p</i> , 3.64 Å)  |

<sup>a</sup> I,  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl); II,  $\equiv\text{C}-\text{H}\cdots\pi$  (aryl); III, C(aryl)—H··· $\pi$  (ethynyl); IV, C(aryl)—H··· $\pi$  (aryl). <sup>b</sup> Color codes represent symmetry independent molecules (see Figure 2). The numbers given in parentheses correspond to the C··· $\pi$  (centroid) distances; *o*, *m*, *p* signify the particular H-atom that is involved in the interaction.



**Figure 2.** Cartoon depiction of the relationship between the three crystalline forms of phenylacetylene. Symmetry independent molecules are color coded.



blue, and green molecules; this group shows close similarities with the  $\alpha$  and  $\beta$  forms and represents a more evolved stage of synthon *d*.

A comparison of the crystallization conditions for the three polymorphs of phenylacetylene further reconfirms their positions in the crystal energy landscape. We were able to crystallize all the three forms of phenylacetylene by means of *in situ* cryocrystallization. A slow cooling rate of 20–1000 K/h (OXFORD N<sub>2</sub> cryosystem) always resulted in the formation of the  $\alpha$ -form. A faster cooling rate obtained by sudden quenching of the liquid gave the  $\beta$ - and  $\gamma$ -forms. When the quenching was done from around 60–75 °C, the  $\beta$ -form predominates. Such quenching is equivalent to the high pressure conditions employed by Katrusiak and co-workers.<sup>2</sup> When the quenching was done from around 90–95 °C (with compression), the  $\gamma$ -form is obtained. In other words, the  $\gamma$ -form is obtained under the most extreme kinetic conditions. Accordingly, it is postulated to figure earlier in the

crystallization reaction coordinate, as manifested by its higher value of  $Z'$ . The most controlled crystallization conditions produced the  $\alpha$ -form, which has the lowest  $Z'$  value. So, we may state that the crystallization profile for the compound proceeds in the sequence  $\gamma \rightarrow \beta \rightarrow \alpha$ .

In summary, the  $\gamma$ -form of phenylacetylene ( $Z' = 6$ ), which is obtained by quenching the liquid, would appear to be a metastable kinetic phase. The molecule does not possess any strong hydrogen bonding functionality, and thus, the overall crystal packing in all the polymorphs relies substantially on weak interactions of the C–H $\cdots\pi$  and  $\pi\cdots\pi$  type.<sup>9</sup> Compared to the  $\gamma$ -form, there is an increased importance of the  $\equiv\text{C}-\text{H}\cdots\pi$  (ethynyl) hydrogen bonds in the  $\alpha$  and  $\beta$  forms. This work shows that, to some extent, the crystal structures of polymorphs with higher values of  $Z'$  may provide some clues as to how the lower  $Z'$  forms evolve during crystallization.

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**Supporting Information Available:** CSD refcodes of crystal structures of compounds containing a terminal ethynyl group (Table S1), analysis of the C–H··· $\pi$  interactions present in the crystal structures of compounds containing a terminal ethynyl group (Table S2), and CIF-file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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