Communication

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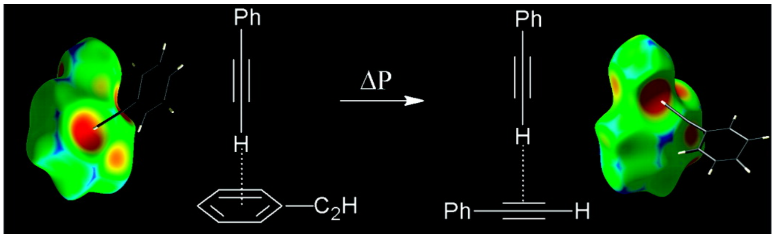
J. Am. Chem. Soc., **2007**, 129 (42), 12620-12621• DOI: 10.1021/ja074885r • Publication Date (Web): 27 September 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Nearly Isostructural Polymorphs of Ethynylbenzene: Resolution of ≡CH···π(arene) and Cooperative ≡CH···π(C≡C) Interactions by Pressure Freezing

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Ethynylbenzene (phenylacetylene, hereafter PA) is the prototypic aromatic hydrocarbon where cohesive forces are dominated by CH···π interactions. It is also a substrate for acetylenic coupling synthesis, yielding potential artificial receptors for molecular recognition,[1] or for obtaining polyphenylacetylene, a candidate material for electronic applications exhibiting interesting photo-induced semiconducting properties.[2−4] The role of weak hydrogen bonds, including CH···π interactions, for the molecular association and formation of crystal structures has been discussed for decades.[5] Although considerably weaker compared to OH···O hydrogen bonds or electrostatic interactions in ionic crystals, the contribution of CH···π contacts is commonly regarded to be crucial for dynamic interaction of phospholipid bilayers with proteins or pharmaceuticals, cotton dying, cohesion between graphite and hydrocarbons in rubber, and other molecular phenomena in biology and materials science.[2] The nature of weak CH···π bonds is still disputable, particularly, as only few crystal structures with undisturbed CH···π interactions were reported. Therefore, structures where the character of CH···π bonds is clearly manifested, like in polymorphs of compounds incapable of interacting via stronger forces, are particularly valuable. The reported low-temperature crystal structure of PA (denoted PAα) is triclinic, space group $P\bar{1}$.[3] In the unit cell, there are five molecules ($Z = 5$), of which one is head-to-tail disordered in two half-occupied coplanar orientations related by the inversion center (Figure 1). Moreover, the density ($\rho = 1.100$ g cm^{-3}) and mp (228.2 K) of PA are exceptionally low compared to those of 1,4-diethynylbenzene (1.202 g cm^{-3}, 369.5 K) and 1,3,5-triethynylbenzene (1.178 g cm^{-3}, 376−377 K); the mp of PA is even much lower than that of benzene (278.5 K).[6] These properties indicate inefficient crystal packing in PAα. In ethynylbenzenes, alkynyl hydrogens are acidic, and the ethynyl groups act as the potential H-donors in hydrogen bonds, while either triple bond or aromatic π-electrons can be H-acceptors. The structures of 1,4-diethynylbenzene and 1,3,5-triethynylbenzene are governed by ≡CH···π(C≡C) contacts and arene rings stacking, while that of highly symmetric benzene/acetylene 1:1 complex is dominated by ≡CH···π(arene) contacts.[7] PAα represents an intermediate structure, with both ≡CH···π(C≡C) and ≡CH···π(arene) interactions present (Figure 1), and the aromatic rings show edge-to-face arrangement[8] characteristic of benzene polymorphs.[9] This suggested that ≡CH···π(C≡C) interactions are stronger than ≡CH···π(arene).[10] In this study, we have shown that pressure freezing of PA favors the cooperative ≡CH···π(C≡C) over ≡CH···π(arene) interactions, and their changed balance results in a new ordered PAβ phase, in an unprecedented polymorphic relation to PAα.

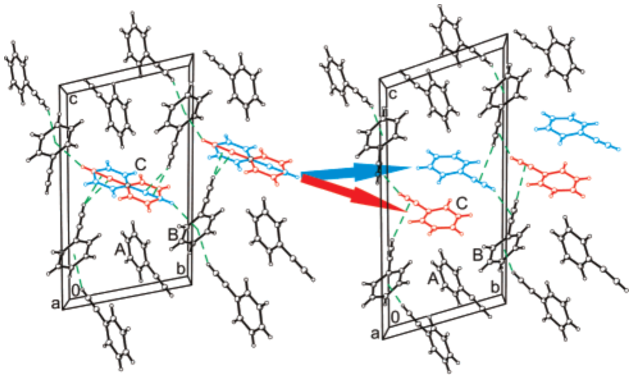

Figure 1. Crystal structure of PAα (left) and PAβ (right) viewed along axis ***a***. Two sites of disordered molecule C in PAα and two corresponding displaced molecules in phase PAβ are indicated in red and blue. The ≡CH···π interactions are represented by the green dashed lines.

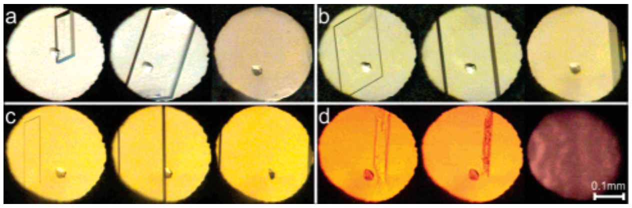

Figure 2. Stages of the single-crystal PAβ growth inside the DAC chamber: (a) from crystal seed to single crystal filling the chamber at 0.40 GPa; (b) at 0.43 GPa; (c) at 0.51 GPa; (d) PA in most of the chamber volume polymerized, except for the remains of PAβ single crystal slowly disintegrating at pressure >0.51 GPa. The last picture shows the polymerized sample in transmission mode. A small ruby chip for pressure calibration is placed close to the chamber center.

We performed a single-crystal diffraction study on PA, in situ pressure-frozen in a diamond anvil cell (DAC). The new high-pressure PAβ phase has been found to be the stable phase of PA from its freezing pressure at 0.4 to 1.25 GPa,[11] preceding its polymerization at ca. 395 K (Figure 2). Low-T and high-P polymorphs α and β are nearly isostructural: they crystallize in the same space group $P\bar{1}$ with very similar unit-cell dimensions, except for parameter c by ca. 1/5 longer in PAβ.[12] The density of PAβ at 0.4 GPa of 1.131 g cm^{-3} is only slightly higher than that of PAα, but still lower than that in other analogous compounds.

The arrangement of two ordered molecules in PAα, labeled A and B, remains almost unchanged in PAβ, while the disordered molecule C in PAα is replaced in PAβ with two fully ordered molecules. These two ordered molecules are related through the inversion center located between them at about 1.6 Å to the phenyl rings (Figure 1). Thus Z of the polymorphs is different: 5 in PAα and 6 in PAβ. The molecular arrangement in PAβ clearly favors the ≡CH···π(C≡C) over ≡CH···π(arene) interactions, compared to phase PAα (Table 1).

The predicted course of pressure-induced transformation in phase PAα and PAβ[13] was that the disorder of the molecule C would be eliminated and space group symmetry would lower to $P1$. Presently, only two $P1$ symmetric structures with $Z = 5$ are known, and the ordered PA crystal was a candidate for yet another exceptional

10.1021/ja074885r CCC: $37.00

Table 1. The Number of H-Donors (D) and H-Acceptors (A) in ≡CH···π(C≡C) and ≡CH···π(arene) Bonds Formed by Symmetry-Independent Molecules A, B, and C in Polymorphs α and β

interaction	≡CH···π(C≡C)		≡CH···π(arene)	
	phase α	phase β	phase α	phase β
molecule A	−/−	−/−	1D/−	1D/−
molecule B	$^{1}/_{2}$D/−	1D/1A	$^{1}/_{2}$D/1$^{1}/_{2}$ A	−/1A
molecule C	−/1A	1D/1A	1D/−	−/−
total	1$^{1}/_{2}$ $^{1}/_{2}$D/1A	4 2D/2A	4 2$^{1}/_{2}$ D/1$^{1}/_{2}$ A	2 1D/1A

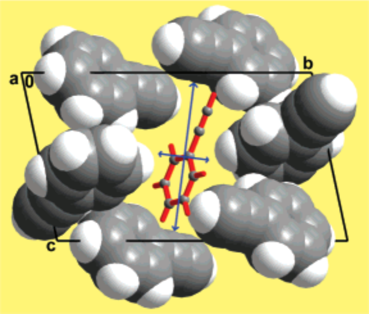

Figure 3. The cavity between van der Waals surfaces of ordered molecules A and B in phase PAα, containing molecule C (represented as small balls and red sticks) in one of its two positions. The size of the cavity is 8.0 × 3.3 Å along the directions indicated by blue arrows; the longest, medium, and shortest dimensions of the van der Waals model of the PA molecule are 9.5 × 6.5 × 3.4 Å, respectively.

structure of this type. To check this possibility, we redetermined the temperature-frozen PA structures at 225 and 100 K—in both temperatures, disordered phase PAα was obtained, the same as that previously determined at 125 K.[3] It occurs that the channel cavities outside the van der Waals surface of ordered molecules in PAα are too narrow to allow the PA molecules to rotate (Figure 3). Hence the disorder in phase PAα is static. On the other hand, due to the C_i-symmetric site of molecule C in the PAα structure, its ordering would not affect the balance of intermolecular interactions. Meanwhile, the formation of the PAβ polymorph increases the number of ≡CH···π(C≡C) bonds in the structure, and a cooperative system of four such bonds is formed as a cyclamer around the inversion center. The preference for the formation of cooperative arrangements of the ≡CH···π(C≡C) bonds was postulated by Steiner.[14]

Comparisons of polymorphs often reveal similarities in their structures extending in one, two, or locally in three dimensions.[15] Both polymorphs of PA are almost identical, except for the disordered molecule C in PAα and its two counterparts in PAβ, while the common space group $P\bar{1}$ and the pattern of molecular layers built of molecules A and B are retained.

The practical aspect of our investigations pertains to the solid-state thermal and pressure-induced polymerization of PA, studied by IR and Raman spectroscopy.[16] It leads to red organic glass of unknown structure. Our attempts to pressure polymerize PA isothermally at 295 K began by orange coloration of polycrystalline mass inside the DAC at about 4.0 GPa. Notably, single crystals of PAβ were considerably resistant to polymerization both by pressure and temperature. Polymerization of liquid PA was much easier and clearly observable by progressive color changes (Figure 2). Up to 1.25 GPa, the polymerization process activates at about 395 K and is hardly pressure-dependent. Once the polymerization was triggered in the liquid phase, it progressively "consumed" the PA crystal from its surface, as illustrated in Figure 2. After opening the DAC, the polymer was in the form of gel, which solidified on drying. This suggested that the polymerization was not complete, which was confirmed by the IR spectra recorded during the compression. A similar mixture was obtained by thermally induced polymerization at ambient pressure.[17]

In conclusion, the structure of pressure-frozen new polymorph β of PA, nearly fully isostructural with low-temperature form α, reveals a preference of PA molecules to form cooperative ≡CH···π(C≡C) contacts in a cyclic tetramer rather than ≡CH···π(arene) ones. This type of molecular association provides additional stability of PAβ compared to PAα, owing to which polymerization is achieved easier in liquid PA or in PAα by rising temperature; even pressure exceeding 1.5 GPa (ca. 1.5 × 10^4 atm) starts the polymerization process in PAβ from the crystal surface. It illustrates the stabilizing role of weak CH···π contacts, particularly at high pressure when their energy considerably increases compared to other interactions.

Acknowledgment. This study was supported by the Polish Ministry of Scientific Research, Grant No. N N204 1956 33.

Supporting Information Available: Details on crystallization, measurement techniques, additional microscopic images, IR spectra, Hirshfeld surfaces, structural dimensions, and a detailed description of molecular disorder in PAα. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary crystallographic data for this paper, CCDC-648809 and CCDC-648808 (PAα), CCDC-648803, CCDC-648804, CCDC-648805, CCDC-648806, and CCDC-648807 (PAβ), can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.

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JA074885R