

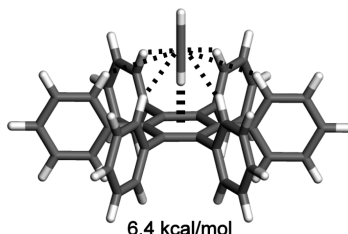
Hexaphenylbenzenes as Potential  
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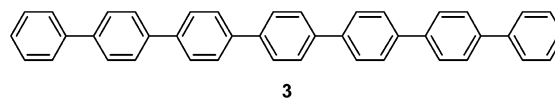
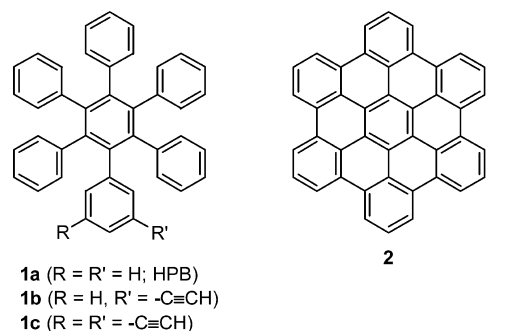
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## ABSTRACT



Acetylene sponges can be created by taking advantage of the nonplanar geometry of hexaphenylbenzenes and the special capacity of the central aromatic ring to engage in C(sp)–H... $\pi$  interactions reinforced by secondary C(sp<sup>2</sup>)–H... $\pi$  interactions, as revealed by X-ray crystallographic studies and DFT calculations.

Nonplanar aromatic compounds with multiple contiguous aryl substituents, represented by hexaphenylbenzene (**1a** = HPB), have special properties that make them widely useful in science and technology.<sup>1</sup> In particular, their complex topologies limit conjugation and disfavor extensive intermolecular  $\pi$ – $\pi$  and C–H... $\pi$  interactions.<sup>2,3</sup> As a result, these compounds can be expected to show higher HOMO–LUMO gaps, lower degrees of self-association, less efficient packing, and higher solubilities than planarized analogues such as hexa-peri-



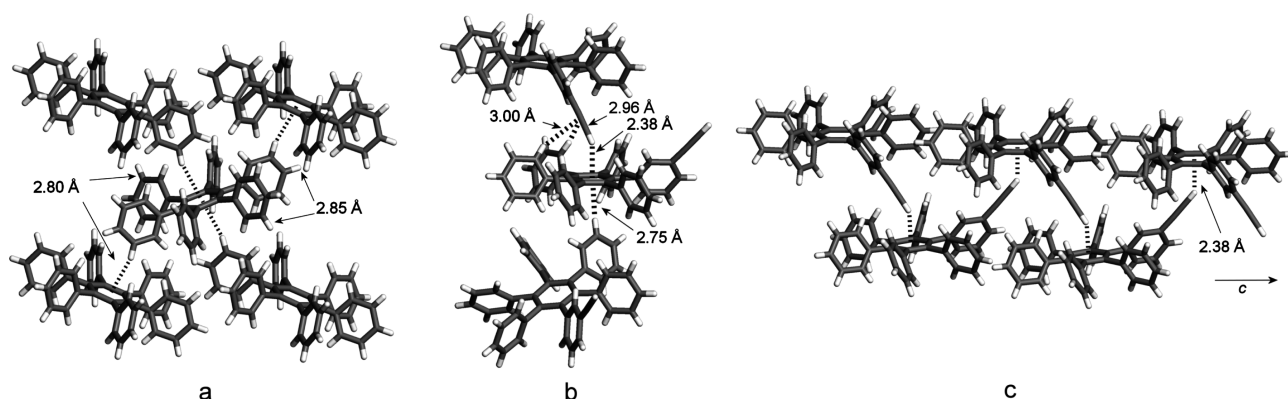
hexabenzocoronene (**2**) or linear analogues such as *p*-septiphenyl (**3**). These marked differences have been underscored by the results of a recent systematic crystallographic analysis of the structures of HPB (**1a**) and its relatives.<sup>4</sup> For example, the ratio of H...H contacts to C...H contacts in the structure of compound **1a** (67:32) greatly exceeds the ratio observed in the structure of linear isomer **3** (39:61).

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**Figure 1.** (a) View of the structure of crystals of HPB (**1a**) grown from  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_2\text{Br}_2$ .<sup>5</sup> (b) View of the structure of crystals of analogue **1b** grown from  $\text{CH}_2\text{Cl}_2$ . (c) View of molecules of analogue **1b** enchainment along the *c* axis by multiple  $\text{C}-\text{H}\cdots\pi$  interactions. In all views, carbon atoms are shown in light gray and hydrogen atoms in white.  $\text{C}-\text{H}\cdots\pi$  interactions are represented by broken lines, with key distances indicated. In (c), only the primary  $\text{C}(sp)-\text{H}\cdots\pi$  interactions are shown.

Even though the characteristic nonplanar topology of HPB (**1a**) appears to set severe limits on access to the faces of all seven aromatic rings, intermolecular  $\text{C}-\text{H}\cdots\pi$  interactions are not entirely eliminated in the structure of its crystals.<sup>4,5</sup> Surprisingly, the fully substituted central aromatic ring serves as a double acceptor of  $\text{C}-\text{H}\cdots\pi$  interactions, one on each face (Figure 1a). This unexpected feature is also found in the structures of many related compounds with multiple contiguous phenyl groups.<sup>4</sup> We now report the results of an integrated experimental and theoretical study that reveals the particularly strong tendency of hexaphenylbenzenes to form  $\text{C}-\text{H}\cdots\pi$  interactions with alkynes. Their association defines a new supramolecular synthon that can be used predictably to engineer molecular crystals.<sup>6</sup>

By the route summarized in Scheme 1,<sup>7</sup> we made compound **1b**, in which a hexaphenylbenzene core and an ethynyl group are present within a single molecule. Compound **1b** was crystallized by slow evaporation of a solution in  $\text{CH}_2\text{Cl}_2$ . Routine analysis of disorder in the ethynyl group yielded a structure with noteworthy features.<sup>7,8</sup> As expected, the core adopts a nonplanar conformation similar to those of other derivatives of HPB (**1a**), with large torsional angles between the central and peripheral aromatic rings.<sup>4,9,10</sup> As shown in Figure 1b, one face of the central aromatic ring serves as acceptor in an unusually short  $\text{C}(sp)-\text{H}\cdots\pi$  interaction involving the ethynyl group as donor (2.38

Å/140°).<sup>11</sup> The other face engages in a  $\text{C}(sp^2)-\text{H}\cdots\pi$  interaction with a second neighboring molecule (2.75 Å/164°). A special feature in the structure is reinforcement of the primary  $\text{C}(sp)-\text{H}\cdots\pi$  interaction by secondary  $\text{C}(sp^2)-\text{H}\cdots\pi$  interactions in which the ethynyl group acts as acceptor (2.96 Å/140° and 3.00 Å/153°).<sup>12</sup> Overall, the resulting structure consists of supramolecular chains along the *c* axis maintained by multiple  $\text{C}-\text{H}\cdots\pi$  interactions (Figure 1c).

In the structure of compound **1b**, the acetylenic  $\text{C}-\text{H}$  bond competes successfully with a total of 29 other  $\text{C}-\text{H}$  bonds for access to the faces of the central aromatic ring. We reasoned that supramolecular organization could be better controlled in analogue **1c**, in which two  $\text{C}(sp)-\text{H}$  donors are available for both faces of the central ring. Compound **1c** was synthesized as shown in Scheme 1,<sup>7</sup> and crystals of composition **1c**·1 toluene were grown from toluene/hexanes.<sup>8,13</sup> As planned, the molecules are linked exclusively by short  $\text{C}(sp)-\text{H}\cdots\pi$  interactions (2.47 Å/135° and 2.46 Å/138°), creating chains along the *c* axis reinforced by additional  $\text{C}(sp^2)-\text{H}\cdots\pi$  interactions in which the ethynyl groups serve as acceptors (Figure 2).

Surprisingly, reinforced  $\text{C}-\text{H}\cdots\pi$  interactions of the type observed in the structures of compounds **1b** and **1c** are strong enough to force the cocrystallization of suitable hexaphenylbenzenes and acetylenes.<sup>14</sup> Cooling a hot solution of HPB (**1a**) in  $\text{PhC}\equiv\text{CH}$  produced crystals that proved to belong to the monoclinic space group *Cc* and to have the composition **1a**·0.5  $\text{PhC}\equiv\text{CH}$ .<sup>13</sup> The resulting structure is maintained by multiple  $\text{C}-\text{H}\cdots\pi$  interactions (Figure 3), including the expected reinforced  $\text{C}(sp)-\text{H}\cdots\pi$  interaction involving  $\text{PhC}\equiv\text{CH}$  and the central aromatic ring of HPB (**1a**). In the

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(7) See the Supporting Information for details.

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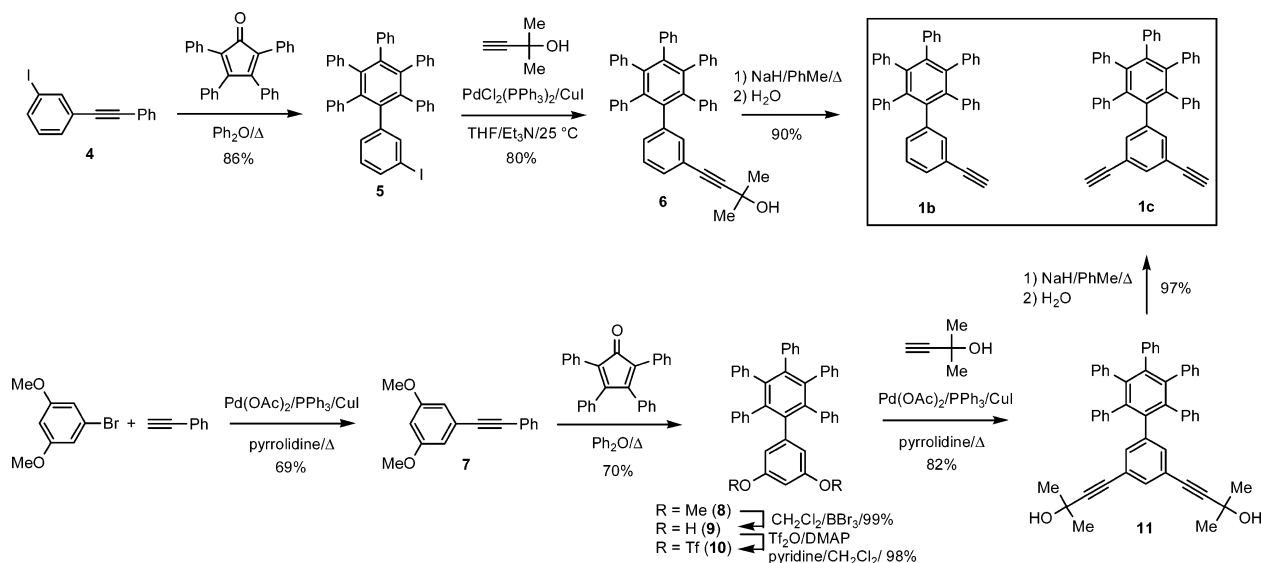
(11) The values correspond to the  $\text{H}\cdots$ centroid distance and the  $\text{C}-\text{H}\cdots$ centroid angle, respectively.

(12) The values correspond to (1) the distance from the hydrogen atom to the midpoint of the triple bond and (2) the  $\text{C}-\text{H}\cdots$ midpoint angle, respectively.

(13) The composition was determined by X-ray diffraction.

(14) For a related crystallographic and theoretical study of the cocrystallization of benzene and acetylene, see: Boese, R.; Clark, T.; Gavezzotti, A. *Helv. Chim. Acta* **2003**, *86*, 1085–1100.

Scheme 1. Synthesis of hexaphenylbenzenes **1b** and **1c**

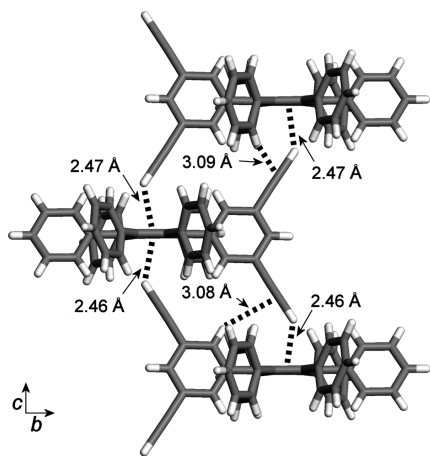


structure of the cocrystals of HPB (**1a**) and  $\text{PhC}\equiv\text{CH}$ , as well as in the crystals of hexaphenylbenzenes **1b** and **1c**, the thermal parameters of the  $-\text{C}\equiv\text{C}-\text{H}$  group are reduced,<sup>7</sup> presumably because the group is bound in a pocket and engages in strong  $\text{C}(\text{sp})-\text{H}\cdots\pi$  interactions.<sup>15</sup>

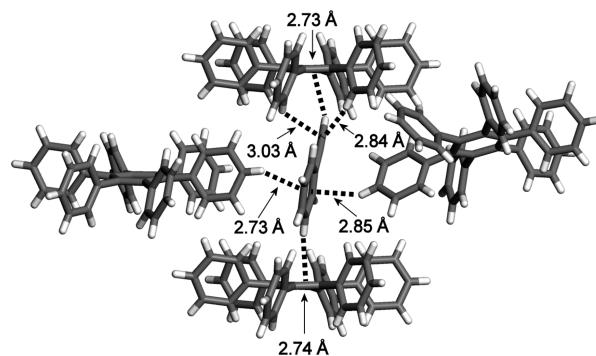
The pronounced tendency of hexaphenylbenzenes to engage in reinforced  $\text{C}(\text{sp})-\text{H}\cdots\pi$  interactions whenever possible suggests that such compounds can serve as sponges for acetylenes. To test this notion, we used DFT calculations to evaluate the association of acetylene with benzene, HPB (**1a**), and 1,3,5-triphenylbenzene held in three distinct conformations. The geometries were fully optimized at the B3LYP/6-31G\* level, with corrections for van der Waals

interactions and basis set superposition error.<sup>7</sup> The results are summarized in Figure 4. The complex of acetylene and benzene is calculated to favor an orthogonal geometry, with a short  $\text{C}(\text{sp})-\text{H}\cdots\pi$  interaction (2.31 Å), and the dissociation energy is estimated to be 3.5 kcal/mol, in good agreement with the conclusions of previous studies.<sup>14,16</sup> The addition of three phenyl groups does not increase this energy when they are forced to remain in the plane of the central ring; however, when they are orthogonal, the energy increases to 5.0 kcal/mol. Finally, the complex of acetylene with HPB (**1a**) is estimated to be stabilized by 6.4 kcal/mol, and the  $\text{C}(\text{sp})-\text{H}\cdots\pi$  interaction is linear and very short (2.18 Å/180°).

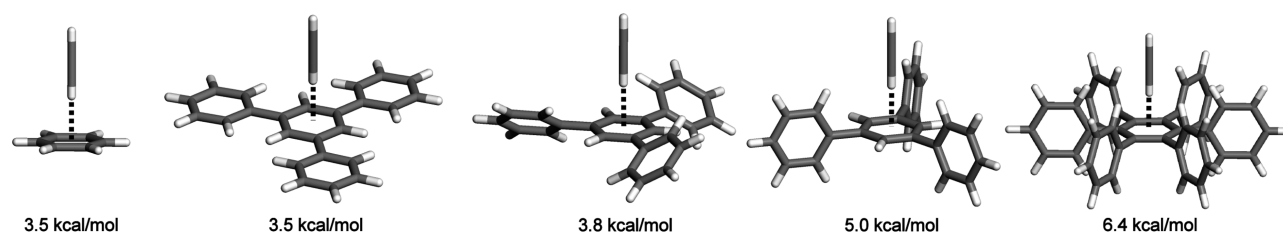
Together, these results suggest that the central  $\text{C}(\text{sp})-\text{H}\cdots\pi$  interaction contributes 3.5 kcal/mol, and each cofacial ortho  $\text{C}-\text{H}$  bond of an orthogonal phenyl group adds a reinforcing  $\text{C}(\text{sp}^2)-\text{H}\cdots\pi$  interaction worth 0.5 kcal/mol.



**Figure 2.** View of the structure of crystals of compound **1c** grown from toluene/hexanes, with guest molecules of toluene omitted for clarity. Carbon atoms are shown in light gray and hydrogen atoms in white.  $\text{C}-\text{H}\cdots\pi$  interactions are represented by broken lines, with key distances indicated.



**Figure 3.** View of the structure of 2:1 cocrystals of HPB (**1a**) and  $\text{PhC}\equiv\text{CH}$ . Carbon atoms are shown in light gray and hydrogen atoms in white.  $\text{C}-\text{H}\cdots\pi$  interactions are represented by broken lines, with key distances indicated.



**Figure 4.** Structures and dissociation energies of complexes formed when acetylene is bound by benzene, 1,3,5-triphenylbenzene (in three conformations), and HPB (**1a**), as estimated by DFT calculations.

Simple  $C(sp)-H\cdots\pi$  interactions are well-known, but they account for only about half of the overall stabilization of the acetylene-HPB (**1a**) complex. Moreover, the reinforcing secondary interactions help draw the bound acetylene closer to the  $\pi$ -acceptor. For both reasons, it is clear that acetylene-hexaphenylbenzene complexes have unique features not previously noted. Careful examination of electron densities in the calculated acetylene-HPB (**1a**) complex shows reductions on the cofacial ortho hydrogens,<sup>7</sup> thereby confirming the importance of the secondary reinforcing interactions. Furthermore, these interactions appear to be strong enough to slightly distort the geometry of HPB (**1a**) in a way that brings the ortho hydrogens closer to the bound acetylene.<sup>7</sup> Although theory suggests that the reinforced  $C(sp)-H\cdots\pi$  interactions of hexaphenylbenzenes should be linear, competing intermolecular interactions and geometric constraints in crystals can induce significant deformations, as observed in the structures formed by compounds **1a–c**.

The characteristic nonplanar topology of hexaphenylbenzenes creates sites on both faces of the central aromatic ring

that are ideal for binding acetylenes by  $C(sp)-H\cdots\pi$  interactions reinforced by secondary  $C(sp^2)-H\cdots\pi$  interactions. The importance of this new associative motif is revealed by its persistent presence in the structures described above. Moreover, calculations show that its strength is nearly twice that of normal  $C(sp)-H\cdots\pi$  interactions, making it similar to hydrogen bonds in its ability to direct molecular association with predictable directionality. If so, it should be possible to observe the binding of acetylenes by hexaphenylbenzenes in solution; however, compounds **1a–c** are too poorly soluble in suitable solvents to permit such tests, and we are currently preparing derivatives with higher solubility. We believe that such compounds can be engineered for new applications in supramolecular chemistry, such as the creation of sponges for the selective sorption of acetylene itself.<sup>17</sup>

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**Supporting Information Available:** Detailed experimental procedures, spectroscopic data for all new compounds, and additional crystallographic and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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