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Tampering with Molecular Cohesion in Crystals of Hexaphenylbenzenes

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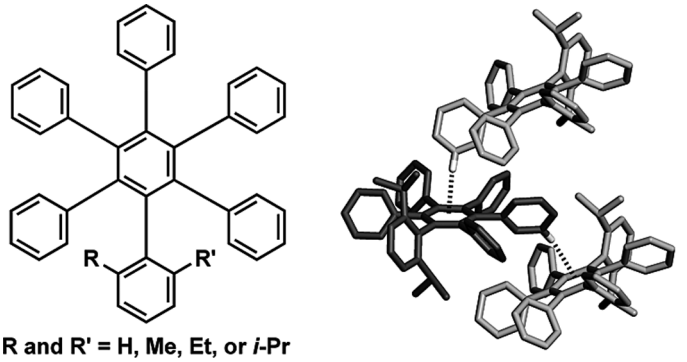

Hexaphenylbenzene (HPB) and analogous compounds have properties of broad utility in science and technology, including conformationally well-defined molecular structures, high thermal stability, high HOMO−LUMO gaps, little self-association, inefficient packing, and high solubilities. Previous structural studies of HPB and its analogues have revealed persistent involvement of the central aromatic ring in strong C−H···π interactions. These interactions can be blocked by adding simple ortho alkyl substituents to the peripheral phenyl groups. Comparison of the structures of HPB and a series of ortho-substituted derivatives has shown systematic changes in molecular cohesion and packing, as measured by packing indices, densities, solubilities, temperatures of sublimation, melting points, and ratios of H···H, C···H, and C···C contacts. These results illustrate how crystal engineering can guide the search for improved materials by identifying small but telling molecular alterations that thwart established patterns of association.

Introduction

Specialized aromatic compounds have found a niche in modern materials science and molecular electronics.[3] Their properties permit the fabrication of various devices, including light-emitting diodes, photovoltaic cells, field-effect transistors, lasers, sensors, RFID tags, and photorefractive systems. Among the most promising classes of aromatic compounds are acenes such as pentacene (**1**),[4,5] which are notable for high charge-carrier mobilities, and polynuclear aromatics such as hexa-*peri*-hexabenzocoronene (HBC, **2**),[6] which feature large π-surfaces. Unfortunately, compounds **1** and **2** cannot easily be used in thin-film molecular devices

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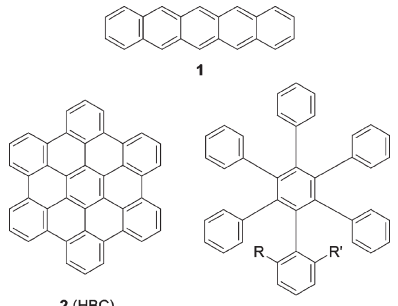
without significant structural modification. For example, the use of pentacene (**1**) itself is hampered by its ease of crystallization and by the existence of multiple polymorphic forms with different electronic properties.[7] Moreover, molecular packing in these polymorphs is guided by extensive C−H···π interactions, and the preferred structures have herringbone arrangements with minimal $\pi\cdots\pi$ overlap, which are considered unfavorable for conductivity. To increase orbital overlap in acenes, various strategies have been devised to favor $\pi\cdots\pi$ interactions at the expense of C−H···π interactions, such as by adding substituents or by modifying the surfaces on which thin films are grown.[4,5] Similarly, substituents have been attached to the periphery of HBC (**2**) to control the extent of π-stacking, increase solubility, and produce new functional materials.[8,9]



These examples show that many compounds with inherently attractive molecular properties, such as pentacene (**1**) and HBC (**2**), cannot achieve their full potential as components of materials without modifications specifically introduced to control packing and cohesion. Of particular value in the cases of compounds **1** and **2** are structural changes designed to alter the importance of C···H contacts (resulting from C−H···π interactions)[10,11] relative to C···C contacts (created by π-stacking). Identifying effective structural alterations requires insights about molecular packing and cohesion best drawn from the field of crystal engineering,[12] which is therefore poised to play a growing role in guiding the search for new functional materials. In particular, crystal engineering can reveal how classes of compounds prefer to crystallize and why those patterns are favored, thereby providing a blueprint for making subtle structural alterations that change how crystallization occurs or even prevent it from happening.[13]

A useful class of compounds related to acenes and polynuclear aromatics is defined by analogues of hexaphenylbenzene (**3a**, HPB), in which multiple contiguous aryl groups are attached to an aromatic core. Systematic structural studies of HPB (**3a**) and similar compounds have established that they are forced to adopt characteristic nonplanar conformations, with large torsional angles between the central and peripheral aromatic rings.[14] The resulting topology is propeller-shaped and toroidal. Its surface is rich in exposed C−H bonds, and access to the π-faces of the constituent aromatic rings is severely restricted. These conformational preferences have the predictable effect of limiting conjugation and disfavoring extensive intermolecular $\pi-\pi$ and C−H···π interactions,[14] leading to higher HOMO−LUMO gaps, lower degrees of self-association, less efficient packing, and higher solubilities than observed in planarized analogues such as HBC (**2**). These characteristic properties make derivatives of HPB (**3a**) increasingly useful in various areas of science and technology, particularly when poor molecular cohesion and inefficient packing are beneficial.[14]

Analysis of the Hirshfeld surface derived from the structure of HPB (**3a**) suggests that cohesion is maintained primarily by diffuse H···H contacts, and well-defined directional forces such as C−H···π and $\pi\cdots\pi$ interactions are less important.[15−18] Specifically, the ratio of H···H to C···H contacts is 67:32, and C···C contacts are essentially absent. Close examination of C−H···π interactions in the structure of HPB (**3a**) reveals that none of the hindered peripheral phenyl groups serves as an acceptor, but both faces of the central aromatic ring are used in this way (Figure 1a).[14] This is not merely because potential pockets for binding are created above and below the central ring by the characteristic toroidal topology of HPB (**3a**). In fact, a primary driving force for association appears to be the ability of the central ring to act as an acceptor in C−H···π interactions, which can be reinforced by secondary interactions involving the ortho hydrogen atoms of the peripheral phenyl groups. This phenomenon is illustrated by the binding of a terminal acetylene in structure **4** (for clarity, only two of the six equivalent secondary C−H···π interactions are drawn).[19] DFT calculations have established that reinforced C−H···π interactions of this type can be as strong as

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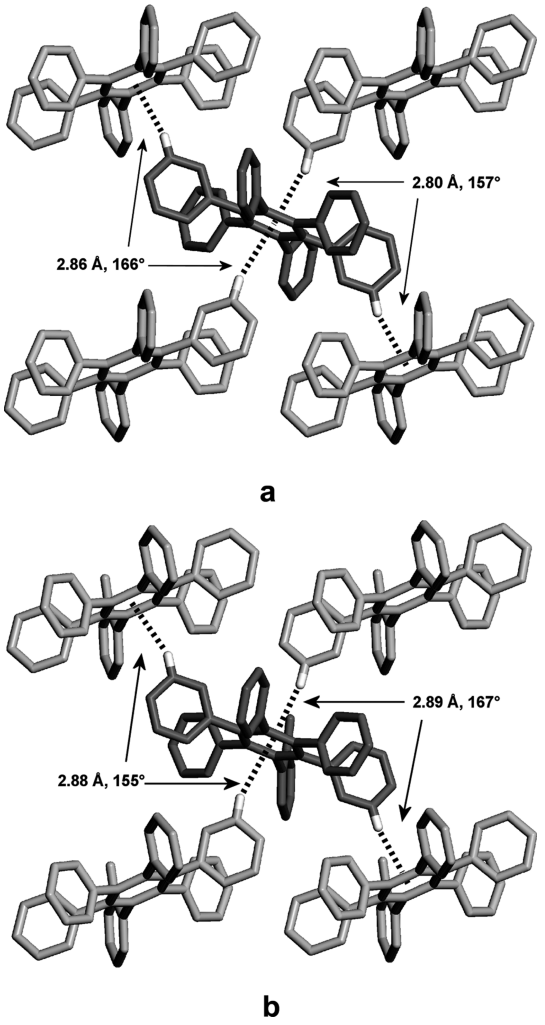
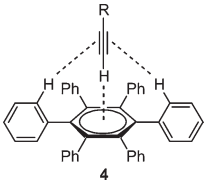


FIGURE 1. (a) View of the structure of crystals of HPB (**3a**) grown from CH_2Cl_2 or CH_2Br_2.[15] (b) View of the structure of crystals of monomethyl derivative **3b** grown from chlorobenzene. Both views show a central molecule (dark gray) and its primary neighbors (light gray). Carbon atoms are shown in gray, hydrogen atoms involved in C−H···π interactions appear in white, and the interactions are represented by broken lines. C−H···$\pi_{centroid}$ distances and angles are indicated.

normal hydrogen bonds, so they can make an important contribution to molecular cohesion.[19]



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Detailed understanding of cohesion and packing in the structures of HPB (**3a**) and related compounds allows crystal engineers to devise subtle yet potent structural alterations that can obstruct established preferences. We reasoned that preventing the central aromatic ring of HPB (**3a**) from engaging in reinforced C−H···π interactions would increase the ratio of H···H to C···H contacts and possibly lead to reduced molecular cohesion, increased volatility, and higher solubility. In principle, the C−H···π interactions of HPB (**3a**) can be blocked by adding suitable ortho substituents to the peripheral phenyl groups. In this paper, we describe the syntheses and structures of ortho-substituted derivatives **3b**−**e**. As planned, these compounds show substantial increases in the ratio of H···H to C···H contacts, as well as other properties that suggest decreased molecular cohesion.

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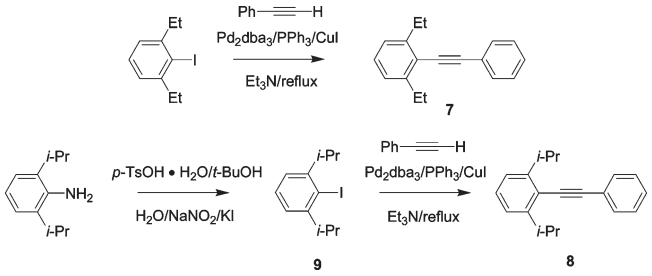
SCHEME 1



Results and Discussion

Synthesis of Ortho-Substituted Hexaphenylbenzenes 3b−e. The targets were prepared by an established general method for making hexaphenylbenzenes, using Diels−Alder reactions of suitably substituted tetraphenylcyclopentadienones with diphenylacetylenes, followed by extrusion of carbon monoxide (eq 1).[20] The required substituted diphenylacetylenes **5**[21] and **6**[22] were prepared by reported methods, and known compounds **7**[23] and **8**[24] were made by straightforward new procedures (Scheme 1). Diphenylacetylene **7** was synthesized in 71% yield by Sonogashira coupling of 1,3-diethyl-2-iodobenzene[25] with phenylacetylene, using Pd_2dba_3/PPh_3 and CuI as catalysts.[26] Compound **8** was prepared from 2,6-diisopropylaniline by the following two steps. A one-pot diazotization−iodination developed by Knochel and co-workers[25] provided the known 2-iodo-1,3-diisopropylbenzene (**9**)[24,27] in 57% yield, and then Sonogashira coupling[26] of intermediate **9** with phenylacetylene gave diphenylacetylene **8** in 71% yield. Diphenylacetylenes **5**−**8** were then allowed to react with tetraphenylcyclopentadienone to generate the desired ortho-substituted hexaphenylbenzenes **3b**−**e** in yields ranging from 52% to 77%. It is noteworthy that the high-temperature Diels−Alder reactions leading to hexaphenylbenzenes **3d** and **3e** were efficient despite very significant steric congestion. The success of these reactions demonstrates the broad scope

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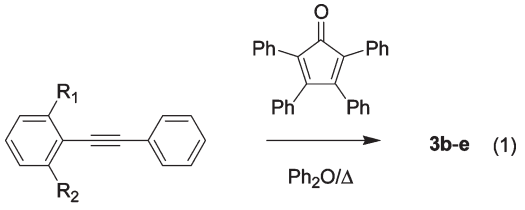
TABLE 1. Crystallographic Data for Ortho-Substituted Hexaphenylbenzenes 3b−e

	3b	3c	3d	3e
formula	$C_{43}H_{32}$	$C_{44}H_{34}$	$C_{46}H_{38}$	$C_{48}H_{42}$
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$Pna2_1$	$P2_1/n$	$P2_1$
a (Å)	12.3269(3)	12.3809(4)	12.3918(2)	12.8715(2)
b (Å)	11.6835(3)	11.7357(3)	11.7268(2)	10.8218(2)
c (Å)	20.8753(5)	21.3061(5)	23.2394(5)	13.1831(2)
α (Å)	90	90	90	90
β (Å)	90	90	98.217(1)	102.061(1)
γ (Å)	90	90	90	90
V (Å^3)	3006.49(13)	3095.74(15)	3342.39(11)	1795.78(5)
Z	4	4	4	2
ρ_{calcd} (g cm^{-3})	1.212	1.207	1.174	1.144
T (K)	150	150	150	150
μ (mm^{-1})	0.517	0.514	0.498	0.484
R_1, $I > 2\sigma$ (%)	4.85	6.42	5.29	3.22
R_1, all data (%)	4.99	6.49	5.54	3.23
ωR_2, $I > 2\sigma$ (%)	14.57	17.20	14.60	8.45
ωR_2, all data (%)	14.75	17.32	14.85	8.46
no. of measured reflections	46644	49197	55091	29219
no. of independent reflections	5275	5511	5529	5704
no. of obsd reflections, $I > 2\sigma(I)$	5078	5426	5193	5685

of the methodology employed, as well as the inherently high thermal stability of hexaphenylbenzenes.



5 (R_1= Me, R_2 = H)
6 (R_1= R_2 = Me)
7 (R_1= R_2 = Et)
8 (R_1= R_2 = *i*-Pr)

Structure of Crystals of Monomethyl Derivative 3b of HPB (3a). After substantial effort, we found that monomethyl derivative **3b** of HPB (**3a**) could be crystallized by slow evaporation of a solution in chlorobenzene. The resulting crystals proved to belong to the orthorhombic space group $Pna2_1$, and other crystallographic data are summarized in Table 1. The observed structure is essentially identical with that of HPB (**3a**), which has the same space group and closely similar unit cell parameters.[15,28] Comparison of parts a and b of Figure 1 reveals the striking overall similarity of the two structures. The failure of an added methyl group to alter the structure radically may result in part from inefficiencies in the packing of HPB (**3a**) itself. Its Kitaigorodskii packing index (67.1%)[29,30] and density (1.208 g cm^{-3}) are slightly lower than those of monomethyl derivative **3b** (67.3% and 1.212 g cm^{-3}), suggesting that the substituent simply fits into previously unoccupied voids, without disrupting the original lattice appreciably. Although the added methyl group does not eliminate C−H···π interactions, it makes them weaker, and the two C−H···$\pi_{centroid}$ distances rise from 2.80 and 2.85 Å in HPB (**3a**) to 2.88 and 2.89 Å in substituted derivative **3b**.[31,32]

Structure of Crystals of Dimethyl Derivative 3c of HPB (3a). Cooling a hot saturated solution of compound **3c** in toluene gave colorless crystals belonging to the orthorhombic space group $Pna2_1$, as previously observed for both HPB (**3a**) and monomethyl derivative **3b**. Additional crystallographic data are presented in Table 1, and the structure is shown in Figure 2a. The unit cell parameters are very similar to those of analogues **3a** and **3b**, with a slight increase in the lengths of the axes to accommodate the two methyl groups. In addition, the packing index (67.5%) and density (1.207 g cm^{-3}) are also close to those observed for compounds **3a** and **3b**. Molecular packing in the structure of dimethyl derivative **3c** (Figure 2a) resembles that of less-substituted analogues **3a** and **3b** (Figure 1). However, addition of a second methyl group allows the central aromatic ring to accept only one C−H···π interaction, instead of one on each face. In addition, the C−H···$\pi_{centroid}$ distance in the surviving interaction rises to 2.98 Å, whereas the average values in HPB (**3a**) and monomethyl derivative **3b** are 2.82 and 2.88 Å, respectively. These results (1) confirm that ortho substituents can alter the association of hexaphenylbenzenes by interfering with normal C−H···π interactions and (2) suggest that cohesion can be reduced to even lower levels by introducing larger ortho substituents.

(28) To facilitate comparison of the structures of hexaphenylbenzenes **3a**−**e**, all crystallographic data were collected at 150 K.

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(31) The existence of significant intermolecular C−H···π aromatic interactions can be assessed in various ways. In the case of the structure of HPB (**3a**) itself (Refcode HPHBNZ03),[15] for example, the central aromatic ring engages in an intermolecular C−H···π interaction that can be characterized by various geometric parameters, including (1) the distance of the hydrogen atom to the mean-square plane of the central aromatic ring (2.76 Å), (2) the distance of the same hydrogen atom to the nearest carbon atom of the central aromatic ring (2.91 Å), and (3) the corresponding C−H···$\pi_{centroid}$ distance (3.00 Å). To avoid ambiguity, we consider that an intermolecular C−H···π aromatic interaction is present only when the C−H···$\pi_{centroid}$ distance is ≤3.05 Å, which is 1.05 times greater than the sum of the accepted van der Waals radii of hydrogen (1.20 Å) and carbon (1.70 Å). Similar criteria have been used previously in other studies of C−H···π interactions.[32]

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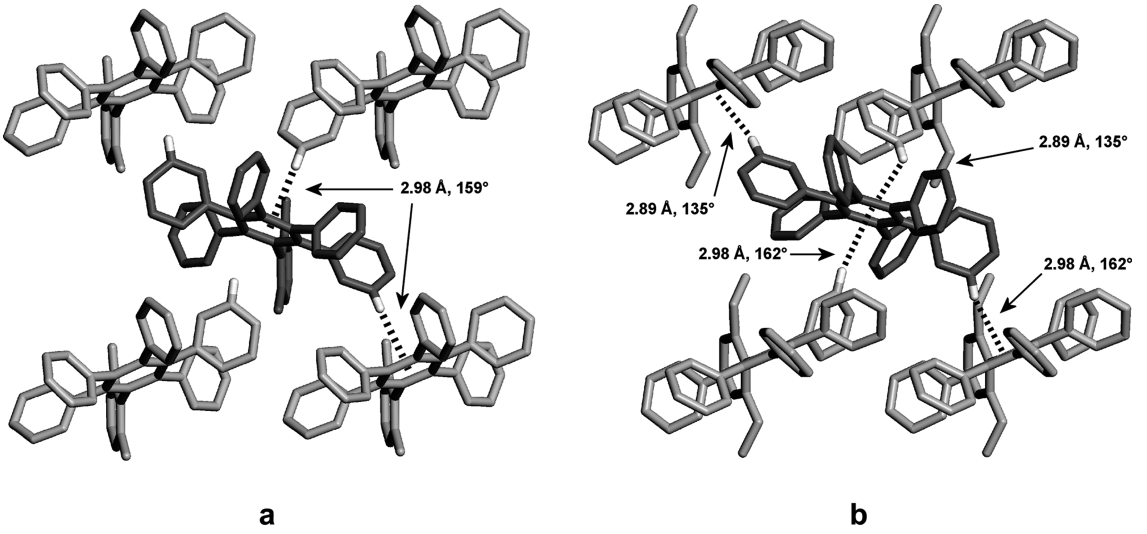

FIGURE 2. (a) View of the structure of crystals of dimethyl derivative **3c** grown from toluene. (b) View of the structure of crystals of diethyl derivative **3d** grown from toluene/hexanes. Both views show a central molecule (dark gray) and its primary neighbors (light gray). Carbon atoms are shown in gray, hydrogen atoms involved in C−H···π interactions appear in white, and the interactions are represented by broken lines. C−H···$\pi_{centroid}$ distances and angles are indicated.

Structure of Crystals of Diethyl Derivative 3d of HPB (3a). Hexaphenylbenzene **3d**, with two added ethyl groups, was significantly more soluble in typical organic solvents than less-substituted analogues **3a**−**c**. Crystals grown by cooling a hot saturated solution in toluene/hexanes were found to belong to the monoclinic space group $P2_1/n$, and additional crystallographic data are provided in Table 1. The introduction of two ethyl groups had the desired effect of lowering both the packing index (66.3%) and density (1.174 g cm^{-3}) relative to the values observed for analogues **3a**−**c**. Despite these differences, molecular organization in the structure remains largely unaltered (Figure 2b). The space group is different from those of the structures of less-substituted analogues **3a**−**c**, but the unit cell dimensions are still very similar, and the β angle remains close to 90° (Table 1). Comparison of the unit cell parameters observed for the structures of hexaphenylbenzenes **3b**−**d** (Table 1) shows nearly monotonic evolution in response to the increasing size of the ortho substituents. Despite evidence of poorer cohesion in the structure of diethyl derivative **3d**, both faces of the central aromatic ring engage in C−H···π interactions, with an average C−H···$\pi_{centroid}$ distance of 2.94 Å. The average distance is significantly longer than those observed in the crystal structures of HPB (**3a**) and monomethyl derivative **3b** (2.82 and 2.88 Å, respectively), but slightly shorter than that found in dimethyl derivative **3c** (2.98 Å).

Structure of Crystals of Diisopropyl Derivative 3e of HPB (3a). Like diethyl analogue **3d**, diisopropyl derivative **3e** showed higher solubility than less-substituted hexaphenylbenzenes **3a**−**c**. Crystals grown from toluene/hexanes proved to belong to the monoclinic space group $P2_1$, and additional crystallographic data are presented in Table 1. As expected, further decreases are observed in the packing index (65.1%) and density (1.144 g cm^{-3}). Moreover, the bulky substituents induce a major change in packing, and the consistent pattern observed in compounds **3a**−**d** is no longer favored by analogue **3e** (Figure 3). Only one face of the central aromatic ring participates in a C−H···π interaction, and the C−H···$\pi_{centroid}$ distance is 2.76 Å, the shortest observed in the series of compounds **3a**−**e**. The unexpected observation of the shortest C−H···$\pi_{centroid}$ distance in the most hindered derivative (**3e**) of HPB underscores the special difficulty of engineering predictable molecular crystals when no strong directional interactions are present. However, it is important to note that the unusually short contact appears to come at the cost of foregoing any C−H···π interaction involving the other face of the central ring. Indeed, no C−H···π contact involving the second face is shorter than 5.06 Å, and an empty pocket with a volume of approximately 13 Å^3 lies directly above the face.[33]

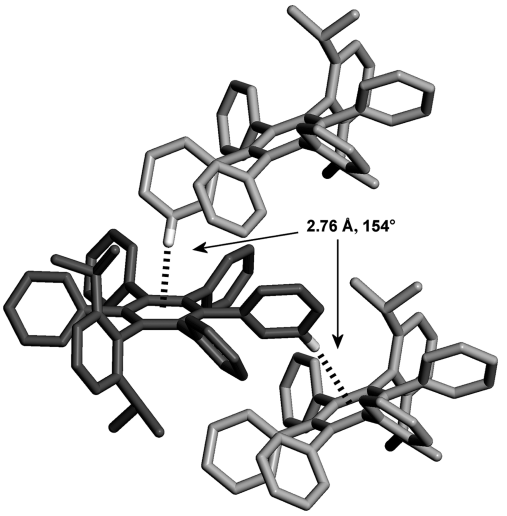

FIGURE 3. View of the structure of crystals of diisopropyl derivative **3e** grown from toluene/hexanes, showing a central molecule (dark gray) and its principal neighbors (light gray). Carbon atoms are shown in gray, hydrogen atoms involved in C−H···π interactions appear in white, and the interactions are represented by broken lines. C−H···$\pi_{centroid}$ distances and angles are indicated.

(33) The value was obtained by using the command VOID in the program PLATON.[30]

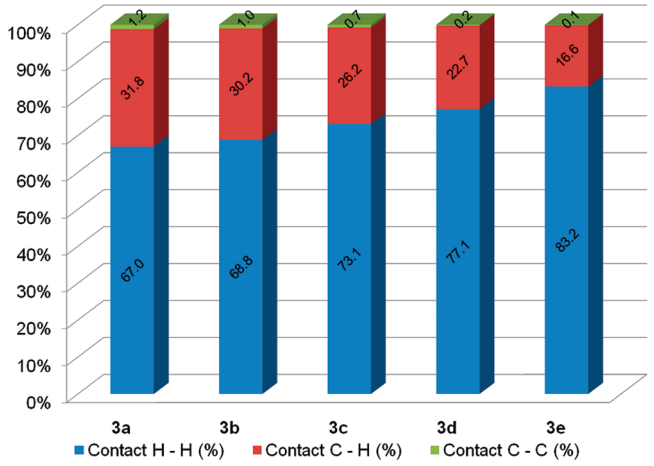

FIGURE 4. Bar graph showing the nature of intermolecular contacts in crystals of hexaphenylbenzenes **3a**−**e**, as determined by analyses of Hirshfeld surfaces.

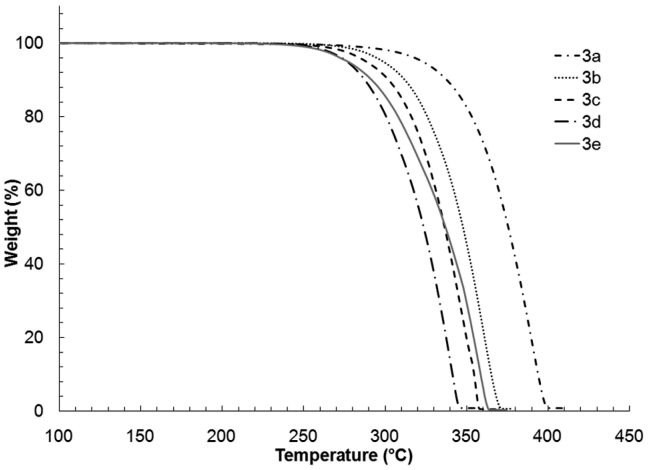

FIGURE 5. Thermogravimetric analyses of crystalline samples of hexaphenylbenzenes **3a**−**e**, carried out under N_2 at a rate of heating of 10 deg/min.

Comparison of Structural Features Exhibited by Hexaphenylbenzenes 3a−e. Analysis of the structures of compounds **3a**−**e** confirms that the central aromatic ring of hexaphenylbenzenes is strongly predisposed to engage in intermolecular C−H···π interactions. However, the number and strength of these interactions can be controlled rationally by the simple expedient of placing alkyl groups at the ortho positions of a single peripheral phenyl group. As planned, adding substituents of increasing size reduces the efficiency of packing, as demonstrated by progressively lower packing indices, lower densities, and longer average C−H···$\pi_{centroid}$ distances. When the substituents reach a critical size, the characteristic packing observed in HPB (**3a**) and simple derivatives can no longer be sustained.

The series of compounds **3a**−**e** is designed to show increasing resistance to the formation of intermolecular C−H···π interactions, so the ratio of H···H to C···H contacts should increase systematically. To test this hypothesis, we used standard analyses of Hirshfeld surfaces to decipher and quantify intermolecular contacts in the structures of hexaphenylbenzenes **3a**−**e** (Figure 4).[16−18] These analyses confirm that progressively larger ortho substituents cause a monotonic increase in H···H contacts at the expense of C···H and C···C contacts. HPB (**3a**) itself has an impressively high ratio of H···H to C···H contacts (67:32), but the value reaches an even higher level in diisopropyl derivative **3e** (83:17).

It is remarkable that the cohesion of compounds with largely aromatic surfaces can be so thoroughly dominated by diffuse H···H contacts. The growing utility of hexaphenylbenzenes in science and technology is based in part on properties associated with poor molecular cohesion, such as inefficient packing and high solubility. Our results suggest that these valuable properties can be enhanced by astute structural alterations, without simultaneously changing other useful features of hexaphenylbenzenes, such as their well-defined topologies and high HOMO−LUMO gaps.

Thermal Analyses of Hexaphenylbenzenes 3a−e. Thermogravimetric analyses of crystalline samples of hexaphenylbenzenes **3a**−**e** demonstrated that all five compounds have high thermal stability (Figure 5). Heating the samples above 250 °C led to a 100% weight loss due to complete sublimation, as confirmed visually. It is noteworthy that the temperatures at which sublimation begins decrease as the size of the ortho substituents increases. This observation is consistent with the notion that the substituents decrease overall molecular cohesion by increasing diffuse H···H contacts at the expense of directional C···H contacts. In the case of diisopropyl derivative **3e**, subsequent loss of weight is less rapid than in the cases of analogues **3a**−**d**, possibly because their packing is markedly different.

Hexaphenylbenzenes **3a**−**e** also show systematic differences in their melting points, which tend to decrease as the ortho substituents increase in size. HPB (**3a**) is reported to melt at 454−456 °C,[34] and monomethyl derivative **3b** also melts above 400 °C; however, dimethyl, diethyl, and diisopropyl derivatives **3c**−**e** melt at 364−365, 282−283, and 285−287 °C, respectively. Enthalpies of sublimation and lattice energies are directly related,[35] but melting points do not provide a reliable measure of molecular cohesion; nevertheless, the observed values are consistent with the notion that ortho substituents reduce cohesion as they increase in size.

Conclusions

A traditional pursuit of crystal engineers is the systematic structural analysis of a series of related compounds to discern characteristic patterns of crystallization, which then allow the behavior of other compounds to be predicted. An exciting new thrust in crystal engineering is to use accumulated structural knowledge in a contrary way, by identifying small but telling molecular alterations that can foil established patterns of association, thereby preventing crystallization or forcing it to occur in different ways. We have tested the power of this strategy by examining the representative case of hexaphenylbenzenes, which have properties of broad utility in science and technology, including conformationally well-defined molecular structures, high thermal stability, high HOMO−LUMO gaps, low degrees of self-association, inefficient packing, and high solubilities.

(34) Fieser, L. F. *Org. Synth.* **1966**, *46*, 44–48. Fieser, L. F. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 604−608.
(35) Ouvrard, C.; Mitchell, J. B. O. *Acta Crystallogr.* **2003**, *B59*, 676–685.

Previous structural studies of hexaphenylbenzene (**3a**) and related compounds have revealed persistent involvement of the central aromatic ring in strong C−H···π interactions.[14,19] In principle, these key cohesive forces can be blocked by adding simple ortho substituents to the peripheral phenyl groups. Comparison of the structures of HPB (**3a**) and ortho-substituted derivatives **3b**−**e** has shown systematic changes in molecular cohesion and packing, as measured by packing indices, densities, solubilities, temperatures of sublimation, melting points, and ratios of H···H, C···H, and C···C contacts. As planned, adding ortho substituents to hexaphenylbenzene (**3a**) has the beneficial effect of altering molecular cohesion without necessarily changing other properties of value.

Our work has focused on the particular case of hexaphenylbenzenes, but it illustrates a potentially general strategy for using principles of crystal engineering to guide the search for improved molecular materials. At the core of this strategy is the ability to control association by making astute molecular alterations based rationally on systematic crystallographic analyses.

Experimental Section

2,6-Diisopropylaniline was purified by distillation from CaH_2 prior to use. 2-Methyl-(1-phenylethynyl)benzene (**5**),[21] 1,3-dimethyl-2-(phenylethynyl)benzene (**6**),[22] tetraphenylcyclopentadienone,[36] and 1,3-diethyl-2-iodobenzene[25] were prepared according to reported procedures. Anhydrous and oxygen-free solvents were obtained by passage through columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). All other reagents and solvents were purchased from commercial sources and used without further purification unless otherwise indicated.

In studies of single crystals by X-ray diffraction, data were collected at 150 K with a Bruker Microstar diffractometer with Cu Kα radiation. The structures were solved by direct methods with SHELXS-97 and refined with SHELXL-97.[37,38] Nonhydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and refined as riding atoms. In all structural studies, calculated X-ray powder diffraction patterns closely matched those obtained experimentally by analysis of bulk crystalline samples.[39]

1,3-Diethyl-2-(phenylethynyl)benzene (7).[23] Pd_2dba_3 (0.352 g, 0.384 mmol), CuI (0.073 g, 0.38 mmol), and PPh_3 (0.403 g, 1.54 mmol) were combined under N_2. Triethylamine (10 mL) was added, followed by 1,3-diethyl-2-iodobenzene (1.00 g, 3.84 mmol) and phenylacetylene (0.84 mL, 0.78 g, 7.6 mmol), and a stream of N_2 was bubbled through the mixture for 10 min. The mixture was heated at reflux for 18 h under N_2 and then allowed to cool to 25 °C. Removal of volatiles by evaporation under reduced pressure left a dark residue, which was dissolved in CH_2Cl_2 (75 mL). The solution was washed with 1 N aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried with anhydrous $MgSO_4$ and filtered through a small pad of silica gel, using CH_2Cl_2 as eluent. Removal of volatiles from the eluent by evaporation under reduced pressure left a residue, which was purified by flash chromatography (silica gel, hexanes) to give 1,3-diethyl-2-(phenylethynyl)benzene (**7**; 0.64 g, 2.7 mmol, 71%) as a colorless liquid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57−7.53 (m, 2H), 7.41−7.31 (m, 3H), 7.23 (AK_2 system,[40] 1H, ^3J = 7.6 Hz), 7.11 (AK_2 system,[40] 2H, ^3J = 7.6 Hz), 2.92 (q, 4H, ^3J = 7.6 Hz), 1.33 (t, 6H, ^3J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.7, 131.5, 128.5, 128.4, 128.2, 125.5, 124.1, 121.6, 97.0, 86.8, 28.3, 15.0; HRMS (APCI-TOF) calcd for $[C_{18}H_{18} + H]^+$ *m*/*e* 235.14812, found 235.14768.

2-Iodo-1,3-diisopropylbenzene (9).[24,27] 2,6-Diisopropylaniline (15.1 mL, 14.2 g, 80.1 mmol) was added to a suspension of *p*-TsOH·H_2O (68.5 g, 360 mmol) in a mixture of *t*-BuOH (480 mL) and water (20 mL), and the mixture was cooled to 10 °C. A solution of sodium nitrite (16.6 g, 240 mmol) and potassium iodide (49.8 g, 300 mmol) in water (70 mL) was then added dropwise during 2.5 h, without allowing the temperature of the mixture to rise above 10−15 °C. The temperature was then allowed to rise to 25 °C, and the mixture was stirred for an additional 1.5 h. Solid $NaHCO_3$ (~30 g) was then added to bring the mixture to pH 9−10, followed by solid $Na_2S_2O_3$ (79 g). The resulting mixture was stirred vigorously for 30 min, giving rise to an orange solution that was poured into water (2.0 L). The mixture was extracted with Et_2O (4 × 100 mL), and the combined extracts were washed with water and brine, dried with anhydrous $MgSO_4$, and filtered. Removal of volatiles by evaporation under reduced pressure left a residue of dark red liquid, which was purified by distillation to give a slightly pink fraction boiling at 100−105 °C/1.5 mm Hg. The pink color was removed by passing the product through a plug of silica gel, using hexanes as eluent. Removal of solvent from the eluent by evaporation under reduced pressure gave 2-iodo-1,3-diisopropylbenzene (**9**; 13.1 g, 45.5 mmol, 57%) as a colorless liquid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (t, 1H, ^3J = 7.7 Hz), 7.08 (d, 2H, ^3J = 7.7 Hz), 3.41 (septet, 2H, ^3J = 6.8 Hz), 1.24 (d, 12H, ^3J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.2, 128.5, 123.9, 109.3, 39.5, 23.5; HRMS (ESI-TOF) calcd for $[C_{12}H_{17}I + H]^+$ *m*/*e* 289.04477, found 289.04513. Anal. Calcd for $C_{12}H_{17}I$: C, 50.02; H, 5.95. Found: C, 49.85; H, 5.90.

1,3-Diisopropyl-2-(phenylethynyl)benzene (8).[24] Pd_2dba_3 (0.636 g, 0.695 mmol), CuI (0.132 g, 0.693 mmol), and PPh_3 (0.728 g, 2.78 mmol) were combined under N_2. Triethylamine (20 mL) was added, followed by 2-iodo-1,3-diisopropylbenzene (**9**; 2.00 g, 6.94 mmol) and phenylacetylene (1.52 mL, 1.41 g, 13.8 mmol), and a stream of N_2 was bubbled through the mixture for 10 min. The mixture was then heated at reflux for 24 h under N_2 and allowed to cool to 25 °C. Volatiles were removed by evaporation under reduced pressure, and the residue was partitioned between CH_2Cl_2 (50 mL) and 1 N aqueous HCl (50 mL). The aqueous phase was discarded, and the organic phase was further washed with 1 N aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The solution was then dried with anhydrous $MgSO_4$ and filtered. Removal of volatiles by evaporation under reduced pressure left a residue that was purified by flash chromatography (silica gel, hexanes) to afford 1,3-diisopropyl-2-(phenylethynyl)benzene (**8**; 1.29 g, 4.92 mmol, 71%) as a colorless liquid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57−7.53 (m, 2H), 7.41−7.32 (m, 3H), 7.29 (t, 1H, ^3J = 7.7 Hz), 7.16 (d, 2H, ^3J = 7.7 Hz), 3.62 (septet, 2H, ^3J = 6.9 Hz), 1.32 (d, 12H, ^3J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.9, 131.4, 128.6, 128.5, 128.2, 124.2, 122.3, 121.0, 97.5, 86.8, 32.0, 23.4; HRMS (ESI-TOF) calcd for $[C_{20}H_{22} + H]^+$ *m*/*e* 263.17943, found 263.17871.

1-(2-Methylphenyl)-2,3,4,5,6-pentaphenylbenzene (3b). Tetraphenylcyclopentadienone (2.00 g, 5.20 mmol) and 2-methyl-(1-phenylethynyl)benzene (**5**; 1.00 g, 5.20 mmol) were combined in diphenyl ether (4 mL), and the mixture was heated at reflux for 4 days. The mixture was allowed to cool to 25 °C, and the resulting yellow crystalline precipitate was separated by filtration and washed with EtOH and hexanes. Recrystallization from

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(37) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structures and SHELXL-97, Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1997.

(38) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(39) See the Supporting Information for details.

(40) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; Wiley-VCH: Weinheim, Germany, 1998.

o-xylene yielded 1-(2-methylphenyl)-2,3,4,5,6-pentaphenylbenzene (**3b**; 1.49 g, 2.72 mmol, 52%) as a colorless solid. A sample for thermal analysis was prepared by crystallization from dioxane: mp (sealed capillary) >400 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95−6.70 (m, 29H), 2.03 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 140.79, 140.52, 140.43, 140.39, 140.35, 140.18, 139.84, 135.85, 132.15, 131.71, 131.62, 131.59, 131.50, 130.49, 128.95, 126.71, 126.65, 126.55, 126.43, 126.27, 125.42, 125.27, 124.08, 20.87;[41] HRMS (ESI-TOF) calcd for $[C_{43}H_{32} + H]^+$ *m*/*e* 549.25768, found 549.25640. Anal. Calcd for $C_{43}H_{32}$: C, 94.12; H, 5.88. Found: C, 94.01; H, 5.72.

1-(2,6-Dimethylphenyl)-2,3,4,5,6-pentaphenylbenzene (3c). 1,3-Dimethyl-2-(phenylethynyl)benzene (**6**; 0.568 g, 2.75 mmol) and tetraphenylcyclopentadienone (1.06 g, 2.76 mmol) were combined in diphenyl ether (2 mL), and the mixture was heated at reflux for 44 h. The mixture was allowed to cool to 25 °C and diluted with MeOH (5 mL). The resulting precipitate was separated by filtration and dried to give 1-(2,6-dimethylphenyl)-2,3,4,5,6-pentaphenylbenzene (**3c**; 1.19 g, 2.11 mmol, 77%) as an off-white solid. A sample for thermal analysis was prepared by crystallization from toluene: mp (sealed capillary) 364−365 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.89−6.78 (m, 25H), 6.75 (AK_2 system,[40] 1H, ^3J = 7.6 Hz), 6.64 (AK_2 system,[40] 2H, ^3J = 7.6 Hz), 2.10 (6H, s); ^{13}C NMR (benzene-d_6, 175 MHz) δ 141.58, 141.35, 141.33, 141.27, 140.87, 140.77, 140.36, 139.34, 136.10, 132.12, 132.06, 130.85, 127.28, 127.26, 127.23, 127.09, 126.90, 126.22, 125.80, 125.78, 21.79; HRMS (ESI-TOF) calcd for $[C_{44}H_{34} + H]^+$ *m*/*e* 563.27333, found 563.27245. Anal. Calcd for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.81; H, 5.97.

1-(2,6-Diethylphenyl)-2,3,4,5,6-pentaphenylbenzene (3d). 1,3-Diethyl-2-(phenylethynyl)benzene (**8**; 0.500 g, 2.13 mmol), tetraphenylcyclopentadienone (0.820 g, 2.13 mmol), and diphenyl ether (2 mL) were combined, and the mixture was heated at reflux for 48 h under N_2. The mixture was allowed to cool to 25 °C and diluted with MeOH (30 mL). The resulting precipitate was collected by filtration, washed with a small amount of MeOH, and dried to yield 1-(2,6-diethylphenyl)-2,3,4,5,6-pentaphenylbenzene (**3d**; 0.828 g, 1.40 mmol, 66%) as a colorless solid. A sample for thermal analysis was prepared by crystallization from toluene: mp (sealed capillary) 282−283 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.92 (t, 1H, ^3J = 7.6 Hz), 6.88−6.74 (m, 27H), 2.46 (q, 4H, ^3J = 7.5 Hz), 1.06 (t, 6H, ^3J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 175 MHz) δ 140.99, 140.90, 140.84, 140.73, 140.40, 140.34, 140.28, 139.14, 138.26, 131.76, 131.73, 130.74, 126.86, 126.66, 126.65, 126.33, 125.57, 125.22, 125.20, 123.33, 26.13, 13.36; HRMS (ESI-TOF) calcd for $[C_{46}H_{38} + H]^+$ *m*/*e* 591.30463, found 591.30381. Anal. Calcd for $C_{46}H_{38}$: C, 93.52; H, 6.48. Found: C, 93.46; H, 6.35.

1-(2,6-Diisopropylphenyl)-2,3,4,5,6-pentaphenylbenzene (3e). 1,3-Diisopropyl-2-(phenylethynyl)benzene (**8**; 0.750 g, 2.86 mmol) and tetraphenylcyclopentadienone (1.10 g, 2.86 mmol) were combined in diphenyl ether (2 mL), and the mixture was heated at reflux for 24 h under N_2. The mixture was allowed to cool to 25 °C and diluted with MeOH (30 mL). The resulting precipitate was collected by filtration, washed with MeOH (20 mL), and dried to give 1-(2,6-diisopropylphenyl)-2,3,4,5,6-pentaphenylbenzene (**3e**; 1.37 g, 2.21 mmol, 77%) as a colorless solid. A sample for thermal analysis was prepared by crystallization from toluene/hexanes: mp (sealed capillary) 285−287 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (t, 1H, ^3J = 7.7 Hz), 6.89−6.73 (m, 27H), 2.83 (septet, 2H, ^3J = 6.7 Hz), 0.86 (d, 12H, ^3J = 6.7 Hz); ^{13}C NMR (benzene-d_6, 175 MHz) δ 146.89, 141.96, 141.84, 141.65, 141.55, 141.30, 140.44, 138.16, 137.26, 132.77, 132.43, 132.01, 128.72, 127.27, 127.22, 126.94, 126.16, 125.74, 125.69, 123.44, 30.76, 25.13; HRMS (ESI-TOF) calcd for $[C_{48}H_{42} + H]^+$ *m*/*e* 619.33593, found 619.33432. Anal. Calcd for $C_{48}H_{42}$: C, 93.16; H, 6.84. Found: C, 93.16; H, 6.70.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **3b**−**e** and **7**−**9** and additional crystallographic details, including ORTEP views, X-ray powder diffraction patterns, and tables of structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(41) In hexaphenylbenzene **3b**, rotation of the *o*-tolyl group about the biphenyl bond is expected to be slow at 25 °C.[42] As a result, compound **3b** possesses 28 aromatic carbon atoms that are unique but spectroscopically very similar. We could not entirely resolve these signals by ^{13}C NMR, even at 175 MHz using a cryoprobe.

(42) Gust, D. *J. Am. Chem. Soc.* **1977**, *99*, 6980–6982.