

# Weak Intermolecular Interactions in the Crystal Structures of Molecules with Tetrahedral Symmetry: Diamondoid Nets and Other Motifs

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**ABSTRACT:** Motif-forming characteristics of weak intermolecular interactions ( $\text{Br}\cdots\text{Br}$ ,  $\text{C}\equiv\text{CH}\cdots\text{C}\equiv\text{C}$ , and  $\text{C}\equiv\text{CBr}\cdots\text{C}\equiv\text{C}$ ) were examined in the solid state structures, determined by single-crystal X-ray diffraction, of tetraphenylmethane and 1,3,5,7-tetraphenyladamantane derivatives substituted at the four vertices with bromo, ethynyl, bromoethynyl, and 1,3-diethynyl groups. The crystals of the bromo- and ethynyl-substituted tetraphenylmethane derivatives exhibited triply interwoven diamondoid lattices sustained by weak interactions between bromo and ethynyl groups. It was observed that when bromo- and ethynyl groups are interchanged in these compounds, their solid-state structures did not change significantly. The crystals of tetrakis(4-bromoethynylphenyl)methane, as well as 1,4- and 1,3,5-bromoethynylbenzene, were sustained by rare, T-shaped  $\text{C}\equiv\text{CBr}\cdots\text{C}\equiv\text{C}$  contacts, but a comparison between these solid-state structures showed significant differences. All terminal 1,3-dienes were unstable compounds that decomposed rapidly. In general, it was observed that tetrahedral building blocks with a larger tetrahedral core, such as adamantane, formed disordered structures or fragile, highly solvated crystals.

## Introduction

Research aimed at understanding the factors that control the packing of molecules in crystals has grown exponentially in recent years.<sup>1</sup> An area of great interest in this field is the synthesis of organic crystals with large and dimensionally fixed cavities, which could lead to porous materials possessing useful catalytic, optical, or magnetic properties.<sup>2</sup> As part of this effort, research groups worldwide have prepared two- and three-dimensional networks by linking organic and inorganic molecules with strong and highly directional interactions, for example, hydrogen bonding<sup>3</sup> and metal–ligand coordination.<sup>4</sup>

More recently, a significant body of work has focused on weak solid-state interactions,<sup>5,6</sup> such as  $\pi\cdots\pi$  stacking, halogen–halogen,  $\text{C}\equiv\text{CH}\cdots\pi$ ,  $\text{C}\equiv\text{CH}\cdots\pi$ (phenyl),  $\text{C}-\text{H}\cdots\text{O}$ , and  $\text{NO}_2\cdots\text{I}$  contacts. Although their effects on the topology of crystals are subtle, and the rationalization of their motif-forming characteristics is more difficult than with strong interactions, the study of weak interactions is of great significance for the development of crystal engineering, and their utilization in crystal design has increased. For instance, weak interactions have been successfully employed to prepare two-dimensional crystals with useful solid-state properties.<sup>6n,1b</sup> Second, whereas weak interactions cannot form host frameworks that are rigid and robust, recent work has shown that hosts that are flexible and adaptable have useful properties.<sup>7</sup> Finally, there is a wide variety of

functional groups that form weak solid-state interactions, and the number of building blocks that can be employed in crystal design is now considerably expanded.

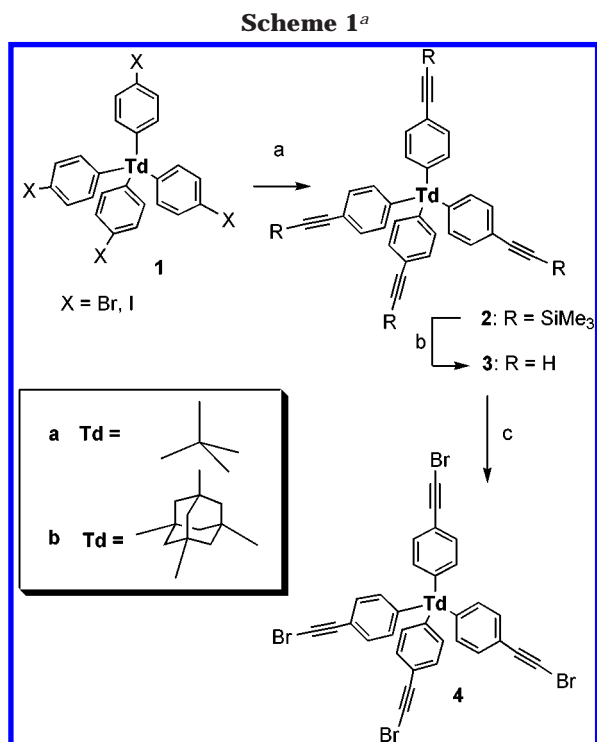
Here we report the synthesis and crystallographic study of a series of tetrahedral molecules substituted with groups that form weak interactions in the solid state. We were interested in understanding whether weak interactions can be used to form three-dimensional packing motifs and host networks that are commonly observed through hydrogen bonding. One of the most interesting three-dimensional crystal motifs that possesses large cavities interconnected by channels<sup>8</sup> is that which mimics the solid-state structure of diamond and is termed diamondoid.<sup>9</sup> Tetrahedral molecules have been extensively employed as “supramolecular synthons”<sup>1b</sup> to prepare diamondoid networks by strong hydrogen bonding or coordination to metals.<sup>9b</sup> However, examples involving weak intermolecular interactions are scarce. Desiraju has reported the formation of diamondoid nets sustained by  $\text{N}\cdots\text{Br}$  interactions in cocrystals of 1,3,5,7-tetrabromoadamantane or  $\text{CBr}_4$  and hexamethylenetetramine, and  $\text{Br}\cdots\text{Br}$  interactions in crystals of 1,3,5,7-tetrakis(4-bromophenyl)adamantane.<sup>1b</sup> More recently, an example of a diamondoid network sustained by  $\text{C}\equiv\text{CH}\cdots\text{C}\equiv\text{C}$  weak hydrogen bonding has been reported by us.<sup>10</sup>

In this paper, this idea is expanded to a series of tetrahedral building blocks substituted at the four vertices with groups that form weak interactions in the solid state and have linear, rodlike geometry.<sup>11</sup> These are the acetylenic, diacetylenic, bromo, and bromoalkynyl groups (a)–(f).

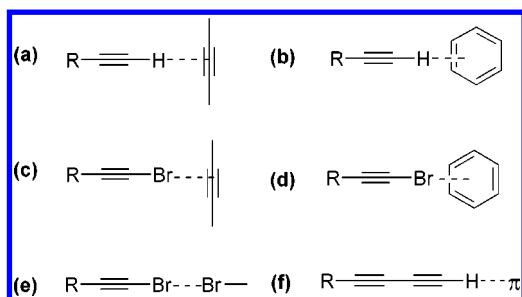
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<sup>a</sup> (a) Et<sub>3</sub>N, CuI, [Ph<sub>3</sub>P]<sub>2</sub>PdCl<sub>2</sub>, Me<sub>3</sub>SiC≡CH, reflux; (b) *n*-Bu<sub>4</sub>NF, CH<sub>3</sub>CN; (c) (1) MeLi, THF; (2) NBS.

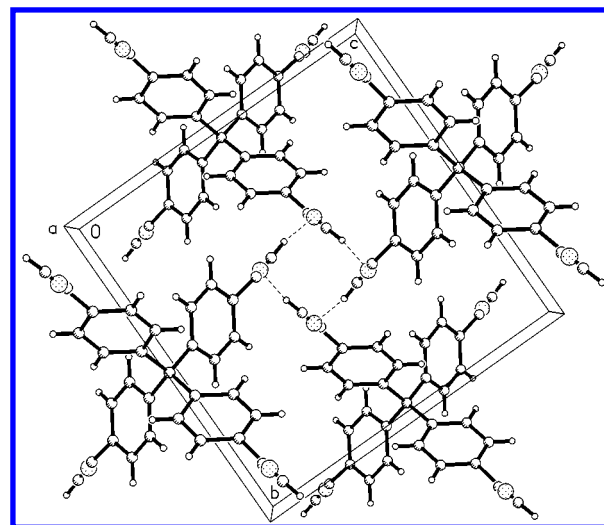


In theory, such tetrahedral building blocks should act as rigid scaffolds that maintain all functional groups at the four vertices in a fixed orientation. The absence of alternative conformations should decrease the degree of polymorphism in the crystals and should maximize the likelihood of formation of diamondoid nets.

## Results and Discussion

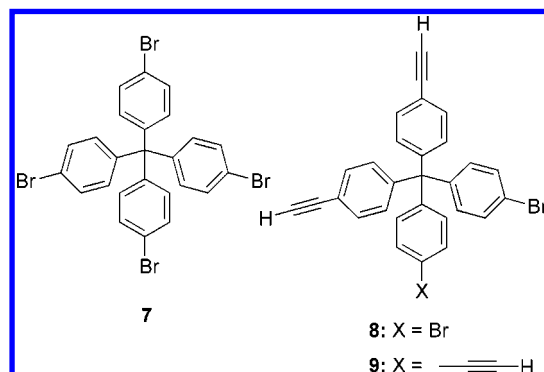
The synthesis of the tetrahedral building blocks from known halides **1a**<sup>12</sup> and **1b**<sup>13</sup> is shown in Scheme 1. Bromoethynes were obtained by treatment of the lithium acetylides with *N*-bromosuccinimide.<sup>11b</sup> All compounds prepared were soluble in many organic solvents and were easily purified and crystallized.

The DSC thermograms of **2a**, **2b**, **3a**, **3b**, **4a**, and **4b** showed thermal polymerization, presumably leading to highly cross-linked polymers. In each case, evidence for polymerization is provided by the presence of an exotherm in the first heating scan and the absence of any thermal transition when the sample was cooled and then heated a second time. This thermal behavior is different from that reported for other tetrahedrally substituted adamantane derivatives,<sup>13,14</sup> including ethynyladamantanes,<sup>15</sup> which exhibit melting and/or glass transitions.

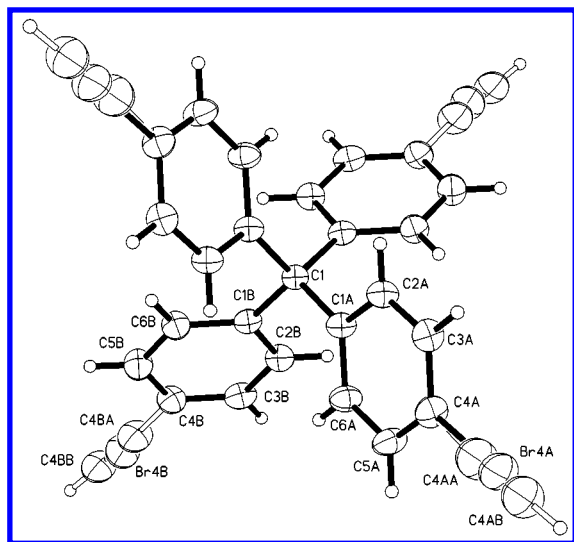


**Figure 1.** Packing and interactions in bis(4-bromophenyl)-bis(4-ethynylphenyl)methane (**8**), which packs with tetragonal symmetry. Each terminal site is occupied, on average, by one-half bromo and one-half ethynyl substituents.

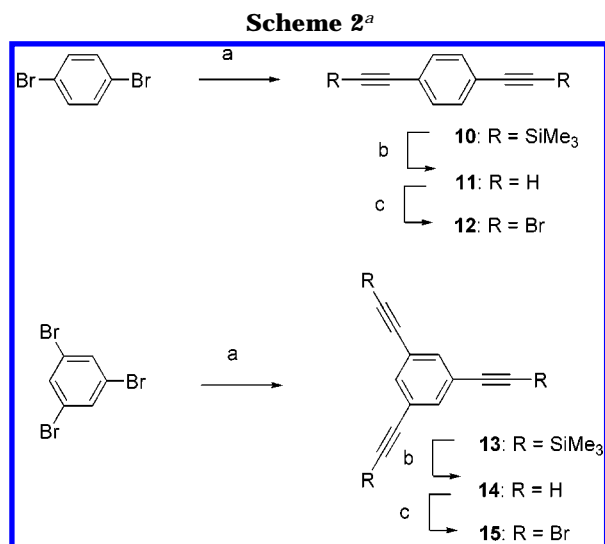
**Br...Br and C≡CH...C≡C Interactions.** It has been demonstrated, most notably by Philp and Boese,<sup>6</sup> that interactions between ethynyl and halogen (mostly Br and Cl) substituents in the solid-state structure of substituted benzenes are interchangeable, a result of similarities between alkynes and halogens (C≡CH...C≡C vs Br...Br) in polarization pattern and geometrical characteristics. This observation has been repeated by us in a preliminary crystallographic study of ethynyl-substituted tetrahedral building blocks.<sup>10</sup> We observed that tetrakis(4-ethynylphenyl)methane (**3a**) forms interwoven diamondoid lattices sustained by C≡CH...C≡C interactions identical to those observed in di- and trisubstituted benzenes.<sup>6c</sup> The geometry of the contacts (2.76 Å C≡CH...C≡C distance, 110.6° angle between lines passing through interacting ethynes)<sup>10</sup> and a 18 cm<sup>-1</sup> difference between the  $\nu_{C=CH}$  in the solid-state and solution FT-IR spectra of **3a**,<sup>16</sup> suggest that such interactions are weak hydrogen bonds. Interestingly, the structural topology of **3a** mimics closely that reported by Desiraju for tetrakis(4-bromophenyl)methane (**7**).<sup>1b</sup> We have now extended this observation to bifunctional compounds **8** and **9**, both byproducts isolated during the synthesis of **3a**.



Compounds **8** and **9** crystallized with essentially the same diamondoid motif, again of the same topological type as **3a** and **7**. Their average crystal structures,



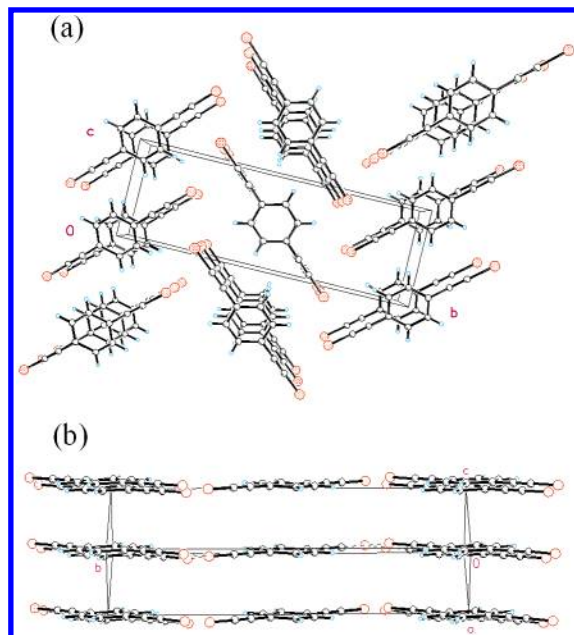
**Figure 2.** 4-Bromophenyl-tris(4-ethynylphenyl)methane (**9**). The molecular images and the packing interactions of **8** and **9** are very similar, but **9** displays slight deviations toward monoclinic symmetry. Each terminal site in **9** is occupied by approximately 1/4 bromo and 3/4 ethynyl substituents.



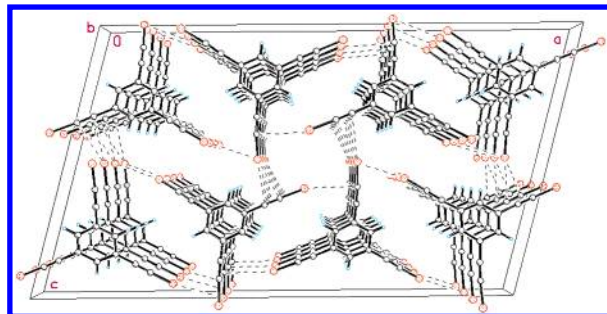
<sup>a</sup> (a) Et<sub>3</sub>N, CuI, [Ph<sub>3</sub>P]<sub>2</sub>PdCl<sub>2</sub>, Me<sub>3</sub>SiC≡CH, reflux; (b) *n*-Bu<sub>4</sub>NF, CH<sub>3</sub>CN; (c) (1) MeLi, THF; (2) NBS.

shown in Figures 1 and 2, respectively, show superimposed positions for the bromine atoms and ethynyl groups, which is due to random interchange of Br and C≡CH group orientations that occurs on going from one unit cell to another.<sup>17</sup> This could only be modeled in the structural refinement by allowing for an occupational disorder.

**Interactions between Bromoalkynes.** The X-ray analysis of propargyl-2-bromo-3-nitrobenzoate by Calabrese and co-workers<sup>18</sup> is the only report describing weak interactions between bromoalkyne units. Interestingly, the crystal structure reported by Calabrese shows bromoalkyne units approaching with C≡CBr⋯C≡C interactions that have geometrical characteristics similar to those described for alkynes and halogens. In theory, therefore, bromoethynyl derivatives of tetrahedral molecules, such as **4a** and **4b**, may form diamondoid nets analogous to those observed for **3a**, **8**, and **9**. For a comparison, we first synthesized 1,4-bromoethynyl



**Figure 3.** Two views of **12**. (a) Top view of planar sheets. The molecules are not parallel to the plane of the paper but are actually parallel to inclined diagonal (−101) crystal planes. (b) Edge-on view to the set of parallel sheets, showing how they pass through the unit cell diagonally.



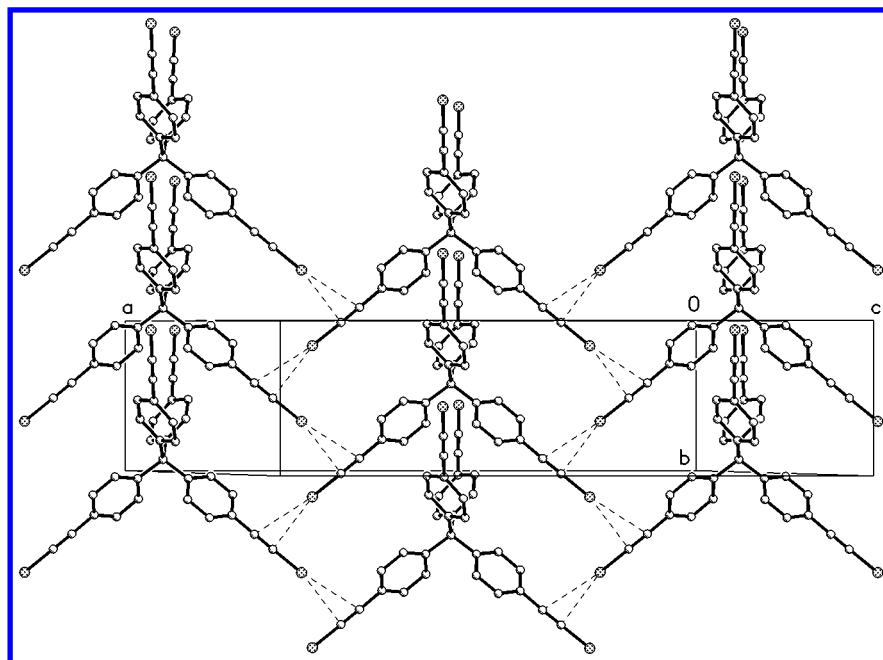
**Figure 4.** Top view of planar sheets in the crystal structure of **15**. Each molecule acts as an acceptor and a donor, making four contacts per molecules.

Ⓜ A 3D rotatable image of the packing structure in CIF format is available.

benzene (**12**) and 1,3,5-bromoethynylbenzene (**15**), Scheme 2.

The crystal structure of **12** in Figure 3 shows that C≡CBr⋯C≡C interactions form a zigzag ladder, the same motive found for interactions between ethynyl and/or halogen substituents in the solid-state structure of di- and trisubstituted benzenes.<sup>6</sup> The only contact less than vdW (vdW C⋯Br = 3.55 Å) is the bromine to the alkyne C8 atom (3.438 Å). The network observed for **12** is a set of parallel, almost planar sheets that are 3.405 Å apart and is two-dimensional: there are close contacts between all of the molecules in each sheet, but there are no interactions (such as π–π stacking, for instance) between the sheets as there is an in-plane shift between layers.

Crystals of 1,3,5-bromoethynylbenzene (**15**) were grown from benzene to form colorless, flat and very thin slates. Interestingly, although the same C≡CBr⋯C≡C zigzag interactions observed in **12** were present in the solid-state structure of **15**, the molecules did not pack in a



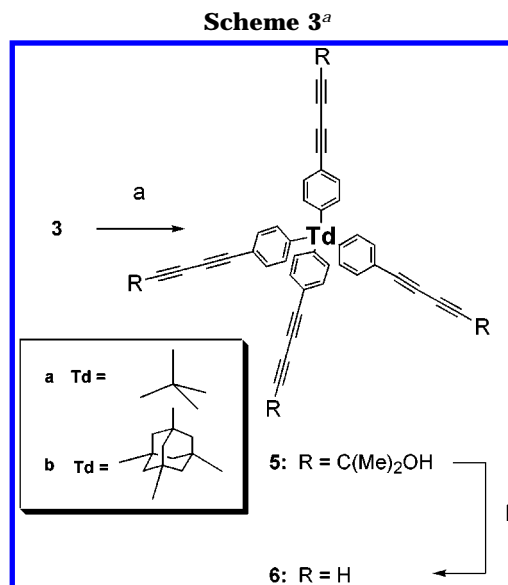
**Figure 5.** View of packing in the crystal of **4a**, viewed perpendicular to the *ab* plane (*a* horizontal, *b* vertical), which shows the ladders of  $\text{C}\equiv\text{CBr}\cdots\text{C}\equiv\text{C}$  interactions linking molecules in infinite planes parallel to the *ab* plane. Clusters of disordered solvent, ethyl ether, loosely bound in channels along *b* are not shown for clarity.

Ⓜ A 3D rotatable image of the packing structure in CIF format is available.

trigonal arrangement. The packing motif of trisubstituted **15**, shown in Figure 4, is quite different from that of the corresponding disubstituted compound. This is similar to what was observed by others in crystallographic studies of 1,4- and 1,3,5-triethynyl benzene.<sup>61</sup> In the structure of **15**, characterized by a set of slightly staggered parallel sheets, each of the three bromines has a different packing arrangement: two Br approach a neighboring alkyne with a close, almost perpendicular approach (but at different angles) and the third Br's closest contact is to another bromine atom. The result of the different packing geometry of the three  $\text{C}\equiv\text{CBr}$  groups is complex, asymmetrical packing within the layers.

The single-crystal X-ray analysis of **4a** shows an infinite two-dimensional network that is linked by  $\text{C}\equiv\text{CBr}\cdots\text{C}\equiv\text{C}$  interactions analogous to the ones observed in the crystals of **12** and **15**, but that it is not diamondoid, Figure 5. Each molecule of **4a** has a 2-fold axis and is in a monoclinic space group ( $C2/c$ ). The molecules of **4a** are ordered in rows in which the molecules are stacked like jacks. There are no distances less than vdW between these stacked molecules, while the rows are linked by  $\text{C}\equiv\text{CBr}\cdots\text{C}\equiv\text{C}$  interactions in which Br is almost perpendicular to the  $\text{C}\equiv\text{C}$  bond with 3.36 and 3.21 Å close contacts to the alkyne carbons. A cooperative pair of perpendicular approaches of Br to benzene rings were also observed:  $\text{Br}2\cdots\text{C}4\text{A}' = 3.44$  Å and  $\text{Br}2\cdots\text{H}6\text{B}' = 3.05$  Å (vdW  $\text{Br}\cdots\text{C} = 3.55$  Å and vdW  $\text{Br}\cdots\text{H} = 3.05$  Å).

**Diacetylenes.** Terminal 1,3-diyne **6a** and **6b**, Scheme 3, having long ( $\approx 8$  Å C(Ph) to C(alkyne)), rigid rod arms were prepared to study the geometry of weak interactions between diacetylenic groups and observe their relative orientation in the crystal. In rare cases, specifically in crystals where 1,3-diacetylenic groups are parallel and other very specific geometrical require-



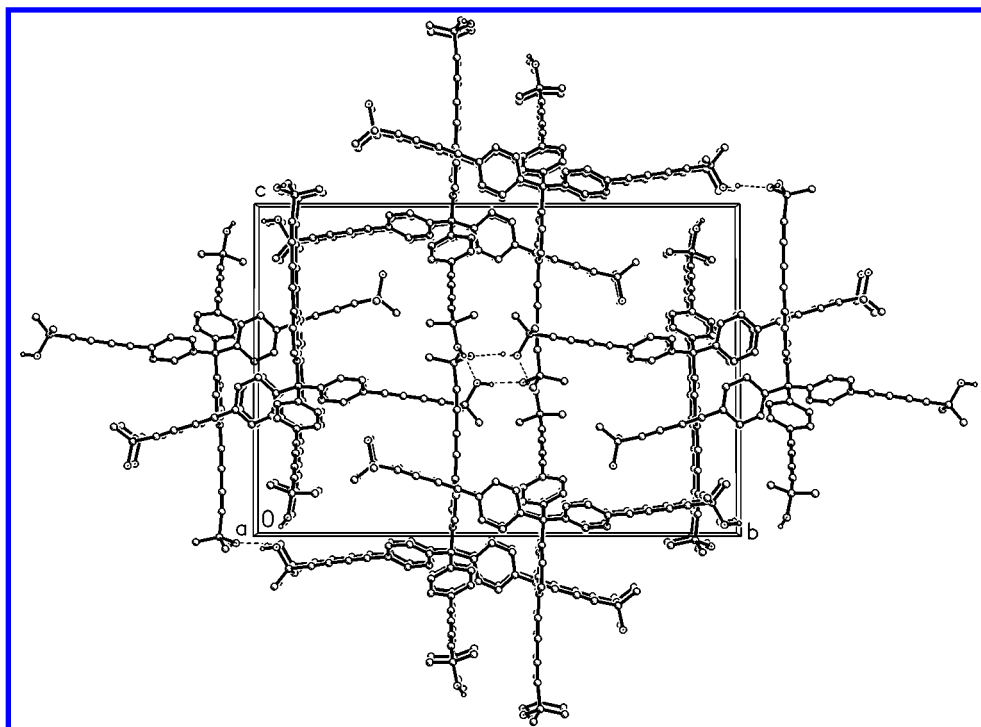
<sup>a</sup> (a) CuBr, pyridine,  $\text{HO}-\text{C}(\text{CH}_3)_2\text{C}\equiv\text{CBr}$ ; (b) NaH, THF.

ments are met, topochemical polymerization may occur upon exposure to UV or X-ray radiation.<sup>19</sup> Protected diynes **5a** and **5b** were synthesized in good yields by Cadiot-Chodkiewicz coupling<sup>20</sup> of **3a** and **3b** with 3-hydroxy-3,3-dimethyl-1-bromopropyne.<sup>21</sup>

Unfortunately, terminal 1,3-diyne **6a** and **6b** could not be isolated in their pure form and fully characterized. Both compounds slowly polymerized (in concentrated solutions or as solids) during attempts of purification and crystallization to afford an orange, insoluble powder, and decomposed when the ethyne deprotection step was performed in aqueous and strongly basic conditions (KOH or NaOH).

However, we were able to purify and crystallize diynes **5a** and **5b**, with all four 1,3-diyne units capped with





**Figure 6.** View of packing in the crystal of **5a**. Molecules link through hydrogen-bonded clusters of six hydroxyls from six different molecules. One full cluster is seen at the center of this view. One of the four arms of each molecule is not involved in hydrogen bonding, but projects into solvent channels at  $b, c = 1/4, 3/4$ . The 24 water sites used to model solvent in each unit cell are omitted for clarity.

Ⓜ A 3D rotatable image of the packing structure in CIF format is available.

**Table 1. Collection of X-ray Data and Refinement of Crystal Structures**

	<b>4a<sup>a</sup></b>	<b>8<sup>b</sup></b>	<b>9<sup>b</sup></b>	<b>12</b>	<b>15</b>
formula	C <sub>37</sub> H <sub>26</sub> Br <sub>4</sub> O	C <sub>29</sub> H <sub>18</sub> Br <sub>2</sub>	C <sub>31</sub> H <sub>19</sub> Br	C <sub>10</sub> H <sub>4</sub> Br <sub>2</sub>	C <sub>12</sub> H <sub>3</sub> Br <sub>3</sub>
F. W.	806.22	526.25	471.37	283.95	386.87
cryst system	monoclinic	tetragonal	monoclinic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>I-4</i>	<i>I2</i>	<i>P2(1)/n</i>	<i>C2/c</i>
<i>a</i> (Å)	28.075(5)	12.8335(14)	12.800(4)	3.9807(3)	32.902(3)
<i>b</i> (Å)	7.3840(17)	12.8335(14)	7.2452(15)	18.6350(8)	3.9832(6)
<i>c</i> (Å)	18.645(3)	7.2245(15)	12.950(3)	6.2083(5)	19.1281(18)
$\beta$ (deg)	116.026(19)		90.105(19)	90.804(8)	105.010(8)
<i>V</i> (Å <sup>3</sup> )	3473.3(12)	1189.9(3)	1200.9(5)	460.49(5)	2421.3(5)
<i>Z</i>	4	2	2	2	8
<i>D</i> <sub>calcd</sub> (mg mm <sup>-3</sup> )	1.542	1.469	1.304	2.048	2.123
temp (°C)	-50	21	21	21	-50
measured refl <sup>c</sup>	3549	1904	1869	1410	3233
unique refl	2152	822	905	633	1584
<i>R</i> (all refl.)	0.0759	0.0530	0.0684	0.0247	0.0326
w <i>R</i> 2 (all refl.)	0.1862	0.1279	0.1604	0.0639	0.0827

<sup>a</sup> This refinement revealed an unresolved disordered solvent near the center of a centric cavity. It was modeled as the superposition of two centric half-weight molecules of ethyl ether, the crystallization solvent, with tetrahedral constraints on the carbon atoms. <sup>b</sup> This structure was refined in triclinic (*I-1*), monoclinic (*I2*), and tetragonal (*I4*) symmetries to see if the bromine atoms were ordered, as they might be in a triclinic cell, or disordered.<sup>26</sup> (*I-1*), a nonstandard setting of *P(-1)*, was used in this trial refinement to avoid the transformation to a quite different unit cell required by *P(-1)*. <sup>c</sup> All data sets were measured with CuK $\alpha$  radiation ( $\lambda = 1.54178$  Å) out to  $2\theta = 115$  or  $115.5^\circ$ , the CuK $\alpha$  limit of the Bruker P4 diffractometer.

protecting groups, which are both stable compounds. Crystals of **5a** and **5b** were grown from 2-butanone, but the crystals of **5b** rapidly deteriorated during the X-ray data collection. Tetrahedral 1,3-diyne **5a** formed crystals that exhibited sparse diffraction patterns, limited to a low-resolution angular range, Figure 6. All reflections with *d* spacings less than 1.4 Å were essentially zero, with intensity values averaging only  $1.6 \times \sigma(\text{Int})$ . This is due to the presence of large channels filled with disordered, perhaps fluid, solvent. As expected, the refinement was difficult and led to much lower precision results than are usually reported for small molecules.<sup>22</sup>

**Adamantane Derivatives.** In general, we have observed a distinct difference between tetrahedral building blocks derived from tetraphenylmethane and those having adamantane as the core. All adamantane derivatives that we prepared crystallized in a disordered structure and different batches of crystals formed different polymorphs (**3b**)<sup>10</sup> or formed very fragile solvates that rapidly deteriorated (**4b** and **5b**). For instance, the crystals of tetraphenylmethane derivative **4a** were easily obtained and were of good quality, while crystals of **4b**, grown from several different solvents, either deteriorated during the X-ray data collection or were of

low quality. We observed the same behavior in at least one other instance. Our working hypothesis is that the phenyl substituents on the adamantane core are less crowded and become available for edge-to-face-type of interactions not possible with the more congested tetraphenylmethane frame. Indeed, we observed that additional interactions are present in crystals of **3b** which were never observed in the crystals of tetraphenylmethane derivatives:  $C\equiv CH\cdots\pi(Ar)$  and  $\pi(Ar)\cdots\pi(Ar)$ . The mixture of interactions involved may result in less efficient packing and more disordered structures.

**Conclusions.** Tetraphenylmethane derivatives substituted with bromo and/or ethynyl groups all showed triply interwoven diamondoid lattices sustained by  $Br\cdots Br$  contacts and  $C\equiv CH\cdots C\equiv C$  weak hydrogen bonding. Our observations are in agreement with previous reports noting that these two kinds of weak interactions are often exchangeable. A study of bromoethynyl derivatives of benzenes and tetraphenylmethane showed  $C\equiv CBr\cdots C\equiv C$  interactions, which have the same geometrical characteristics of  $Br\cdots Br$  and  $C\equiv CH\cdots C\equiv C$  interactions.

## Experimental Section

**Single-Crystal X-ray Diffraction Analyses.** Crystal X-ray data were obtained by gluing crystals to the ends of thin glass fibers and observing them on a Bruker P4 diffractometer equipped with Cu K $\alpha$  radiation and a graphite monochromator. Cell dimensions and orientations were obtained from least-squares refinements of the setting angles of 35–50 accurately centered reflections. Crystal structures were solved by direct methods using the SHELXTL suite of computer programs.<sup>23</sup> Neutral atom scattering factors were used,<sup>24</sup> corrected for real and imaginary anomalous dispersion.<sup>25</sup> Full-matrix least squares refinement, based on  $F^2$  differences, was used on all unique data for all structures, with the aid of the SHELXL program.<sup>23</sup> Additional crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publications CCDC 158160–158164 and 159157. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Characterization Data** (for synthetic procedures see Supporting Information). **4a:** DSC: exotherm 155 °C;  $^1H$  NMR  $\delta$ : 7.33 (8H, d,  $J = 8.5$ ), 7.01 (8H, d,  $J = 8.5$ ).  $^{13}C$  NMR  $\delta$ : 145.96, 131.52, 130.80, 120.89, 79.55 ( $C\equiv C-Br$ ), 63.50 (C), 50.30 ( $C\equiv C-Br$ ). HRMS (FAB): calcd for  $C_{33}H_{16}^{79}Br_3^{81}Br_1$ : 729.7966, found 729.8012; calcd for  $C_{33}H_{16}^{79}Br_2^{81}Br_2$ : 727.7949, found 731.7972. **4b:** DSC: exotherm at 153 °C;  $^1H$  NMR  $\delta$ : 7.43 (8H, d,  $J = 9$ ), 7.39 (8H, d,  $J = 9$ ), 2.10 (12H, s,  $CH_3$ );  $^{13}C$  NMR  $\delta$ : 149.45, 132.06, 125.03, 120.65, 79.61 ( $C\equiv C-Br$ ), 49.54 ( $C\equiv C-Br$ ), 46.66 ( $C(Ph)_4$ ), 39.28 ( $CH_3$ ); HRMS (FAB): calcd for  $C_{42}H_{28}^{79}Br_3^{81}Br_1$ : 849.8906, found 849.8886; calcd for  $C_{42}H_{28}^{79}Br_2^{81}Br_2$ : 851.8890, found 851.8865. **5a:**  $^1H$  NMR  $\delta$ : 7.37 (8H, d,  $J = 8.5$ ), 7.09 (8H, d,  $J = 8.5$ ), 1.57 (24H, s,  $CH_3$ );  $^{13}C$  NMR  $\delta$ : 146.34, 132.12, 130.74, 119.91, 86.92, 78.21, 73.66, 76.01, 65.78, 64.17, 31.10. **5b:**  $^1H$  NMR  $\delta$ : 7.46 (8H, d,  $J = 8.5$ ), 7.38 (8H, d,  $J = 8.5$ ), 2.18 (12H, s), 1.58 (24H, s,  $CH_3$ );  $^{13}C$  NMR  $\delta$ : 149.96, 132.69, 125.13, 119.51, 86.68, 78.60, 73.07, 67.02, 65.71, 39.31, 31.24, 30.92. **8:** DSC: exotherm at 254 °C;  $^1H$  NMR  $\delta$ : 7.38 (8H, dd,  $J = 8.5$ ,  $J = 8.5$ ), 7.11 (6H, d,  $J = 8.5$ ), 7.03 (2H, d,  $J = 8.5$ ), 3.06 (3H, s,  $C\equiv CH$ );  $^{13}C$  NMR  $\delta$ : 146.13, 144.51, 132.49, 131.66, 131.00, 130.68, 120.68, 120.30, 83.12 ( $C\equiv CH$ ), 77.66 ( $C\equiv CH$ ), 64.48 ( $C(Ph)_4$ ). **9:** DSC exotherm at 275 °C;  $^1H$  NMR  $\delta$ : 7.38 (8H, dd,  $J = 8.5$ ,  $J = 8.5$ ), 7.11 (4H, d,  $J = 8.5$ ), 7.02 (4H, d,  $J = 8.5$ ), 3.05 (2H, s,  $C\equiv CH$ );  $^{13}C$  NMR  $\delta$ : 146.09, 144.47, 132.43, 131.67, 131.02, 130.62, 120.71, 120.35, 83.08 ( $C\equiv CH$ ), 77.71 ( $C\equiv CH$ ), 64.18 ( $C(Ph)_4$ ). **10:**  $^1H$  NMR  $\delta$ : 7.39 (4H, s, ArH), 0.24 (18H, s,  $CH_3$ );

$^{13}C$  NMR  $\delta$ : 131.73, 123.10, 104.52 ( $C\equiv CSi$ ), 96.28 ( $C\equiv CSi$ ),  $-0.11$  ( $CH_3$ ). **11:**  $^1H$  NMR  $\delta$ : 7.44 (4H, s, ArH), 3.17 (2H, s,  $C\equiv CH$ );  $^{13}C$  NMR  $\delta$ : 131.99, 122.52, 83.00 ( $C\equiv CH$ ), 79.07 ( $C\equiv CH$ ). **12:** DSC: exotherm at 169 °C;  $^1H$  NMR  $\delta$ : 7.38 (s, ArH);  $^{13}C$  NMR  $\delta$ : 131.88, 122.95, 79.52 ( $C\equiv CBr$ ), 52.19 ( $C\equiv CBr$ ); GC/MS ( $m/z$ ) 285.8 (48), 283.8 (100), 281.8 (52), 204.9 (4), 202.9 (4), 141.9 (12), 124.0 (83), 98.0 (26), 74.0 (30). **13:** DSC: exotherm at 142 °C;  $^1H$  NMR  $\delta$ : 7.383 (3H, s, ArH), 0.121 (27H, s,  $CH_3$ );  $^{13}C$  NMR  $\delta$ : 134.91, 123.62, 103.13 ( $C\equiv CSi$ ), 95.59 ( $C\equiv CSi$ ),  $-0.17$  ( $CH_3$ ). **14:**  $^1H$  NMR  $\delta$ : 7.57 (3H, s, ArH), 3.11 (3H, s,  $C\equiv CH$ );  $^{13}C$  NMR  $\delta$ : 135.63, 122.91, 81.58 ( $C\equiv CH$ ), 78.68 ( $C\equiv CH$ ). **15:** DSC: exotherm at 142 °C;  $^1H$  NMR  $\delta$ : 7.46 (s);  $^{13}C$  NMR  $\delta$ : 135.23, 123.52, 78.08 ( $C\equiv C-Br$ ), 52.07 ( $C\equiv C-Br$ ); GC/MS ( $m/z$ ) 389.7 (33), 387.7 (95), 385.7 (100), 383.7 (37), 308.8 (4), 306.8 (8), 304.8 (4), 227.9 (31), 225.9 (32), 147.0 (25), 146.0 (13), 98.0 (19), 85.0 (6), 73.7 (6), 73.3 (6).

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**Supporting Information Available:** X-ray structural information on **4a**, **8**, **9**, **12**, **15**, and **5a**, including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and six figures, DSC diagrams of **3a** and **4a**, and synthetic procedures for **4a**, **4b**, **5a**, **5b**, **8–15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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