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# Weak hydrogen bonding between acetylenic groups: the formation of diamondoid nets in the crystal structure of tetrakis(4-ethynylphenyl)methane†

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**The crystal structure of tetrakis(4-ethynylphenyl)methane 1 shows interwoven diamondoid lattices formed by weak hydrogen bonds between the acetylenic groups, while 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane 2 crystallizes in a non-symmetrical network.**

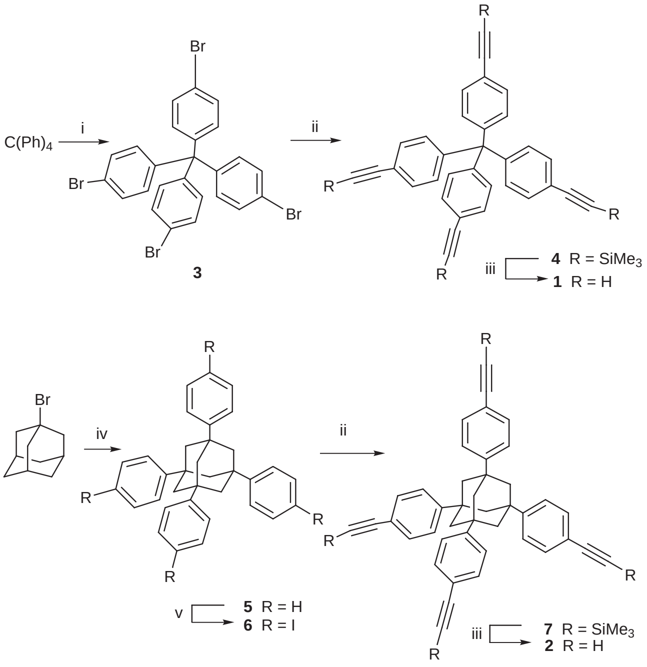
Organic crystals or polymers having large and dimensionally-fixed cavities are expected to exhibit unprecedented structural and physical properties.[1] A particularly attractive kind of network with a regular array of cavities can be obtained, in theory, by connecting the four vertices of tetrahedral organic molecules.[1e,2] This mode of assembly has been termed diamondoid due to its resemblance to the lattice structure of diamond.

Tetraphenylmethane and adamantane are useful building blocks for diamondoid networks. We are studying a series of derivatives bearing acetylenic groups on all four vertices. Ethynes are versatile functional groups for connecting building blocks because they possess rigid-rod geometry, complex with metals and undergo coupling and polymerization reactions.[3]

Fortuitously, the crystal structure‡ of the first model compound, tetrakis(4-ethynylphenyl)methane **1**, contained highly symmetric diamondoid networks formed by van der Waals association, or weak hydrogen bonding, between acetylenic groups. Crystal structures reported by others for a series of terminal alkynes show that the acidic C≡CH groups act as hydrogen donors and form close contacts with hydrogen bonding groups and also with π-systems, including ethynyl and phenyl groups.[4] These kinds of interactions possess the properties of weak (1–2.2 Kcal mol$^{-1}$) hydrogen bonds and are called C(alkyne)H··π hydrogen bonds.[4a]

While numerous examples exist of diamondoid networks formed by strong hydrogen bonding groups, such as carboxylic acids[1e] and pyridones,[1c] or by metal complexes,[1d] only a few involve van der Waals interactions, such as Br···N and Br···Ph.[1a] To the best of our knowledge, the crystal structure of **1** is the first diamondoid network sustained by C≡CH···C≡C close contacts. Interestingly, C≡CH···Ph interactions, often observed in the crystal structures of phenylsubstituted alkynes,[4a] were not observed in **1**.

Compound **1**§ was prepared in two steps and 67% yield from the known tetrabromide **3**[5] (Scheme 1). Compound **1** crystallizes in a body-centered space group, $I\bar{4}$, and molecules sit on unit cell center and corner sites that require $S_4$ symmetry (Fig. 1). A three-dimensional network is formed by weak hydrogen bonds between the alkynyl groups from four separate molecules that meet (*i.e.* come close) at nodes in the network that are also $S_4$ in their local symmetry. The molecule at the center of the cell forms linkages only to molecules that are 1.5 unit cells up and down in the *c* axis direction; they, in turn, link to other molecules that are 3.0 *c* axis translations above and below the origin molecule, and in so doing form cages that resemble super-adamantane models, which are outlined in Fig. 2. The super-adamantane cages are distorted, with a cross-cage distance of 21.7 Å (3 unit cell lengths) in the *c* direction, and two equal cross-cage distances of only 18.3 Å perpendicular to the *c* axis. The structural topology mimics closely that of tetrakis(4-bromophenyl)methane,[1a] which crystallizes in the same space group, and has nodes where four bromine atoms approach one another.



**Scheme 1** *Reagents and conditions*: i, Br$_2$, Fe (ref. 5); ii, Et$_3$N, CuI, [Ph$_3$P]$_2$PdCl$_2$, Me$_3$SiC≡CH, reflux, 81%; iii, TBAF, MeCN, 85%; iv, AlCl$_3$, C$_6$H$_6$, reflux, 50% (ref. 7); v, (CF$_3$CO$_2$)$_2$IPh, I$_2$, CHCl$_3$, 70% (ref. 7).

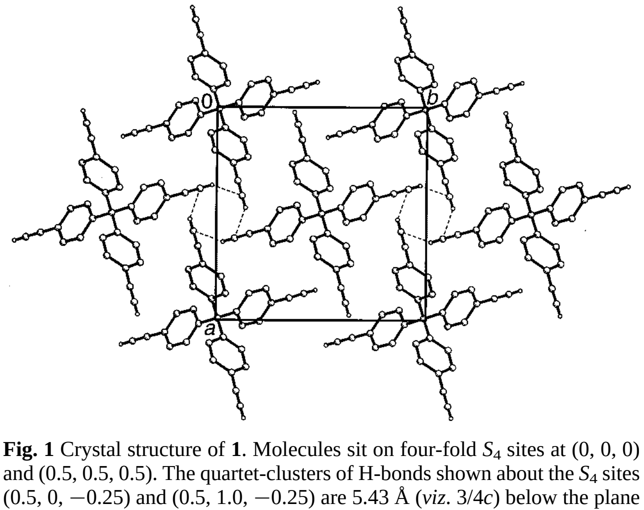


**Fig. 1** Crystal structure of **1**. Molecules sit on four-fold $S_4$ sites at (0, 0, 0) and (0.5, 0.5, 0.5). The quartet-clusters of H-bonds shown about the $S_4$ sites (0.5, 0, −0.25) and (0.5, 1.0, −0.25) are 5.43 Å (*viz.* 3/4*c*) below the plane passing through the central atom. The C≡CH···C≡C distance is 2.76 Å, and the H-bond makes an angle of 152° with CH and 86° with C≡C.

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† Experimental details and extra crystallographic views are available from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/173/

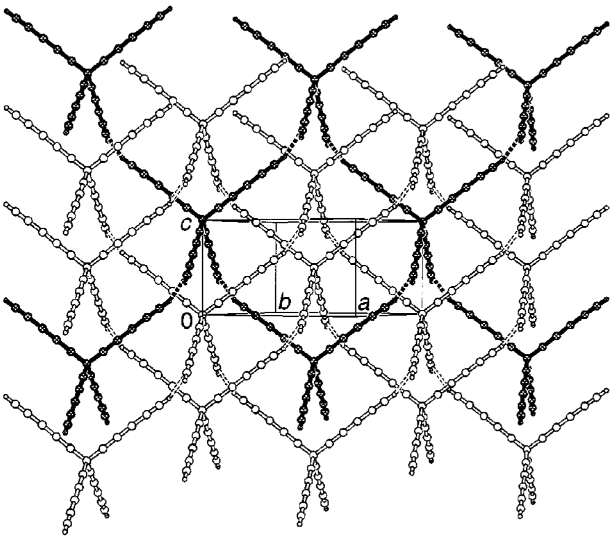

**Fig. 2** A schematic view of the three interwoven diamondoid nets, one of which is accented in bold. For clarity, the phenyl groups have been replaced by three 'atoms' in a straight line.

The repetition of a single linked cage by crystal lattice translations produces a three-dimensional network, but origin molecules located at +*c* and +2*c* serve as generators of two more networks which penetrate the holes of the first network, and coexist without (close) interaction. The assembly is thus comprised of three identical interwoven diamondoid networks (Fig. 2). The hydrogen bonded alkyne moieties are neither perpendicular (inter-line angle of 90°) nor antiparallel (180°), but approach at an intermediate inclination, with an inter-linear angle of 110.6° between lines passing through the ethynes of H-bonded neighbors in the cluster. The inter-alkyne hydrogen bond H4B···C4B′ (2.76 Å), is the only intermolecular distance less than the expected van der Waals' contact (2.90 Å).[6] Hydrogen atom positions were normalized to give linear 1.08 Å C–H bonds before calculating all H-bond parameters. The closest C–H approach is to the terminal C atom; distances to the other alkyne C atom and to the midpoint of the alkyne bond are greater.

To assess whether a diamondoid motif would occur upon changing the tetrahedral core, we prepared 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane **2**§ (Scheme 1.)[7] In the crystal structure‡ of **2**, both C≡CH···C≡C and C≡CH···Ph interactions are present, but the lattice is not diamondoid. Compound **2** crystallizes from benzene–hexane in a monoclinic packing arrangement (*C*2/*c*), with two molecules of **2** and a half-molecule of benzene in the asymmetric unit of the crystal (Fig. 3). Crystals of **2** grown from a few solvents other than benzene also showed asymmetric lattices.

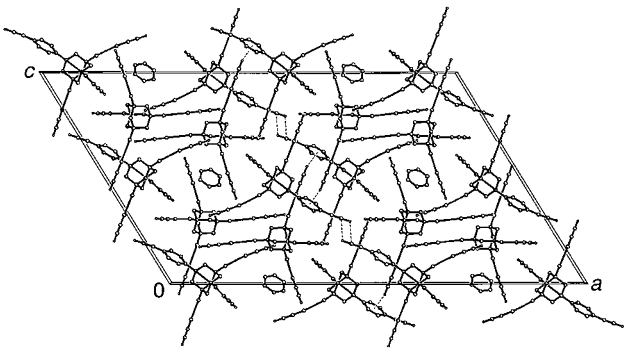

**Fig. 3** Crystal structure of **2**. Sixteen molecules of **2** and four benzene molecules occupy each cell; those on the bottom and top faces are shown twice. For clarity, the phenyl groups have been replaced by three 'atoms' in a straight line.

In contrast to **1**, where all alkynes are involved in extended CH··π networks, only two of eight independent alkyne termini of **2** participate in close contacts. One alkyne hydrogen atom points directly at the face of a neighboring near-perpendicular phenyl ring, with CH···C(Ph) approaches of 2.55, 2.60 and 2.75 Å, a typical CH··π interaction mode. The other close contact is an almost antiparallel (side-by-side) approach between two C≡CH termini related by a 2-fold rotation, with a C···H distance of 2.60Å and a C···C distance of 3.17Å (expected[6] van der Waals contacts are 2.9 and 3.4 Å). Similar alkynyl contacts of both types have been reported before.[2a,8]

In summary, the crystal structure of **1** is the first example of a diamondoid packing motif formed by weak hydrogen bonding between acetylenic groups. We are currently investigating hydrogen bonding of **1** and **2** with other compounds and expanding the family of ethynyl-substituted tetrahedral building blocks.

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## Notes and references

‡ Intensity data for **1** and **2** were measured on a Bruker diffractometer with Cu-K$\alpha$ radiation ($\lambda$ = 1.54178 Å) at $T$ = 293 K. Structures were solved by direct methods, aided by program XS, and refined with full-matrix least-squares program XL, from SHELXTL (ref. 9). *Crystal data* for **1**: $C_{33}H_{20}$, $M$ = 416.49, tetragonal space group $I\bar{4}$; $a = b$ = 12.9197(4), $c$ = 7.2357(5) Å, $V$ = 1207.8(1) Å$^3$, $Z$ = 2, and $D$(X-ray) = 1.145 mg mm$^{-3}$. Clear colorless 0.54 × 0.26 × 0.17 mm crystal; 1204 data measured to a 2$\theta$ max of 116°. Absorption correction by integration over crystal volume ($\mu$ = 0.493 mm$^{-1}$). Least-squares refinement on $F^2$ differences; $R$-factors: $R$ = 0.0367, $wR2$ = 0.0993 for all 848 unique refl. For **2**: $C_{42}H_{32}\cdot 1/4(C_6H_6)$, $M$ = 556.20, monoclinic space group $C2/c$, $a$ = 48.460(4), $b$ = 10.5467(13), $c$ = 28.759(3) Å, $\beta$ = 121.896(4)°, $V$ = 12479(2) Å$^3$, $Z$ = 16, and $D$(X-ray) = 1.184 mg mm$^{-3}$. Clear colorless 0.48 × 0.11 × 0.05 mm crystal; 8609 data measured to 2$\theta$ = 90°[$<I>$ was measured to be $< 2\sigma(I)$ at higher angles]. Absorption correction by integration over crystal volume ($\mu$ = 0.504 mm$^{-1}$). Least-squares refinement on $F^2$ differences varied a total of 785 parameters. $R$ factors were $R$ = 0.0574 for 2985 unique reflections with [$I > 2\sigma(I)$], and $R$ = 0.1141, $wR2$ = 0.1376 for all 5051 unique reflections. CCDC 182/1111. The crystallographic data is available in CIF format from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/173/

§ *Selected data* for **1**: $\delta_H$ NMR (500 MHz, $CDCl_3$) 7.36 (d, *J* 4.5, 8H), 7.32 (d, *J* 4.5, 8H), 3.04 (s, 4 H, C≡C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 146.17, 131.64, 130.72, 120.25, 83.13 (*C*≡CH), 77.60 (C≡C*H*), 64.77 (*C*Ph$_4$). HRMS (FAB): calc. for $C_{33}H_{20}$: 416.1565, found 416.1565. For **2**: $\delta_H$ (500 MHz, $CDCl_3$) 7.46 (d, *J* 8.5, 8H), 7.39 (d, *J* 8.5, 8H), 3.03 (s, 4 H, C≡C*H*), 2.10 (br s, 12H, C*H*$_2$); $^{13}C$ $\delta_C$ (125 MHz, $CDCl_3$) 149.65, 132.23, 124.99, 120.06, 83.43 (*C*≡CH), 76.90 (C≡*C*H), 46.70 [*C*(ad)-Ph], 39.27 (*C*H$_2$) HRMS (FAB): calc. for $C_{42}H_{32}$: 536.2504, found 536.2504.

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