

C–H $\cdots\pi$ interactions in ethynylbenzenes: the crystal structures of ethynylbenzene and 1,3,5-triethynylbenzene, and a redetermination of the structure of 1,4-diethynylbenzene

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The crystal structures of 1,4-diethynylbenzene **1** and 1,3,5-triethynylbenzene **2** show similar packing principles with CH $\cdots\pi$ (triple bond)-zigzag networks; surprisingly, the packing motif of ethynylbenzene **3** is quite different.

Recent work has shown that the π -electrons of a C \equiv C triple bond can act as a hydrogen bond acceptor.^{1–6} In addition to the usual donor substituents, such as hydroxy and amino groups, it was shown that carbon-bonded hydrogen atoms can also display donor properties. Terminal alkynes represent one of the best CH $\cdots\pi$ hydrogen bond donors due to the acidity of the alkynyl hydrogen atom.⁷ This functional group has the advantage of providing simultaneously donor and acceptor properties for CH $\cdots\pi$ hydrogen bridges. Whereas the expected geometry for this type of intermolecular interaction is T-shaped,⁸ as in acetylene,⁹ this idealized motif with a CH $\cdots\pi$ angle of (180 \pm 10°) is rarely found in the solid state. We report herein the comparison of the CH $\cdots\pi$ interactions in the three title ethynylated aromatics.

Although already known,¹⁰ the structure of 1,4-diethynylbenzene **1** was redetermined under the same conditions as for 1,3,5-triethynylbenzene **2** and ethynylbenzene **3** for a better comparison and higher accuracy (mainly for the positions of the hydrogen atoms).[†] In the solid state **1** has a layer structure; the arrangement within the layers is shown in Fig. 1.

The molecules are connected by CH $\cdots\pi$ hydrogen bridges in a zigzag pattern along a mirror glide plane similar to that known for other compounds with terminal ethynyl groups, *e.g.* DL-prop-2-ynylglycine,⁷ but-3-ynoic acid¹¹ and 1,4-diethynylcubane.¹² Each molecule is fixed by four hydrogen bridges and the geometrical data indicate ideal conditions for relatively strong CH $\cdots\pi$ hydrogen bonds (Table 1). Between the layers there exist no herringbone interactions as in benzene, and only a staggering of the coplanar rings can be observed (plane–plane

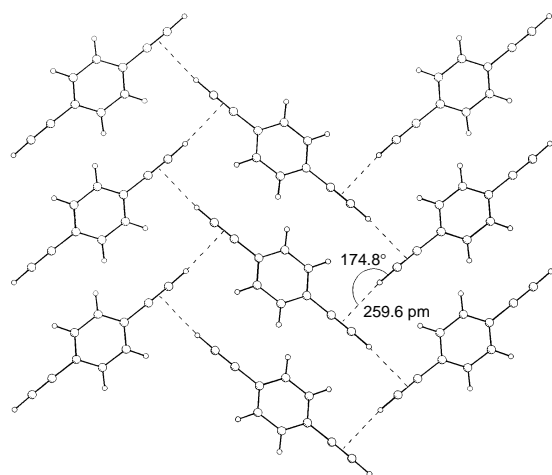


Fig. 1 Section of the layer structure of **1** in the 100 direction

Table 1 CH $\cdots\pi$ distances and angles for **1–3**

Compound	Bond geometry ^b	H \cdots M ^a distance/pm	CH \cdots M ^a angle/°
1	trip	259.6	174.8
2	trip	268.1	165.7
	trip	272.3	147.3
	trip	281.4	140.1
3	ring	260.2	143.6
	ring	268.3	160.5
	trip	257.7	174.3

^a M = centre of the π -system. The positions of the hydrogen atoms were normalized to a C–H distance of 108 pm. ^b Ring = bond to π -system of the phenyl group; trip = bond to π -system of the triple bond.

distance 353 pm). The CH \cdots M contacts (M is the centre of the triple bond) are among the shortest contacts found in the Cambridge Structural Database.¹³ The molecules are tilted by 25.0° to the 100 plane. Thus the major attractive forces which contribute to the lattice energy are the hydrogen bridges to the triple bonds, which form a two-dimensional network.

A similar packing principle can be observed in the crystal structure of **2**; however, because of the different molecular geometry the packing is more complex and can be described as a folded layer structure. The main attractive forces between the molecules of **2** are also hydrogen bond bridges from the ethynyl hydrogen atoms to the π -electrons of the triple bonds. Each molecule acts three times as an acceptor and as a donor, making six contacts per molecule with three distinct distances (Fig. 2). The connections of each molecule to its environment, however, are not symmetrical: the first ethynyl group acts only as a donor, the second acts as a donor and an acceptor and the third acts as a donor and a double acceptor. All of the contacts are rather short and the angles C_{ethynyl}H \cdots M lie between 140 and 180° and compare well with those in **1**.

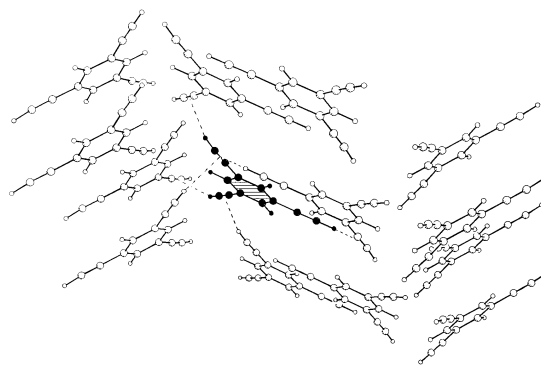


Fig. 2 Folded layers of **2**; one highlighted molecule shows the six hydrogen bridges

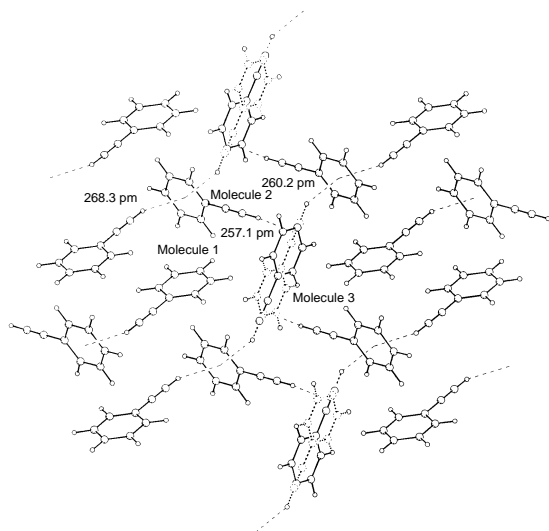


Fig. 3 Packing of **3**; molecule **3** is disordered (additional dotted molecule)

Surprisingly, the parent ethynylated benzene derivative **3** exhibits a very different packing in the crystal lattice. Five molecules are found in the unit cell (space group $P\bar{1}$) with two and a half in the asymmetric unit; consequently the half molecule is disordered. One of the ethynyl hydrogen atoms points to a triple bond and the other two point to the π -systems of two surrounding phenyl rings.

In contrast to **1** and **2** the molecules in **3** show benzene-type edge-to-face interactions.^{14,15} The angles between the planes of the rings lie between 80 and 90°, and the shortest CH \cdots M contact is 282.2 pm (276.4 pm for benzene¹⁴). The crystal structure of **3** represents a compromise between the herringbone packing of benzene and the coplanar stacking, as found for **1**, with CH \cdots π_{trip} interactions. The respective intermolecular distances and angles for **1–3** are summarized in Table 1.

Comparison of the physical properties of molecules **1–3** and benzene (Table 2) sheds light on the stability of the compromise packing of **3**. The melting point of **3** is abnormally low—over 50 °C lower than that of benzene. The calculated densities of the solids show a similar tendency: **1** and **2** have significantly higher densities than **3**. For **3** one would expect a higher density than for benzene, as its molecular mass is between those of benzene and **1**; however, the densities are approximately the same. These data clearly indicate that the lattice energy of **3**

Table 2 Melting points and calculated densities^a for **1–3** in the solid state

Compound	mp/°C	$\rho_{\text{calc}}/\text{Mg m}^{-3}$
Benzene ^b	5.5 ^c	1.094
1	96.5 ^d	1.202
2	103–104 ^e	1.178
3	–44.8 ^c	1.100

^a Measured at –183 °C for benzene and –148 °C for **1–3**. ^b Ref. 14. ^c Ref. 16. ^d Ref. 17. ^e Ref. 18.

must be substantially less and that the compromise packing is not as efficient as that of benzene or of **1** and **2**.

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Footnotes and References

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† Crystal data for **1** (ref. 17): C₁₀H₆, crystals obtained by sublimation (20 mbar, water cooled), space group $P2_1/c$, $a = 3.887(1)$, $b = 5.931(2)$, $c = 15.114(6)$ Å, $\beta = 90.84(3)^\circ$, $V = 348.4(2)$, $Z = 4$, $D_c = 1.20$ g cm^{–3}, 719 unique reflections, $F_o > 4\sigma(F_o)$, 58 parameters, $2\theta_{\text{max}} = 60^\circ$, $R1 = 0.054$.

For **2** (ref. 18): C₁₂H₆, crystals obtained by sublimation (1 mbar, water cooled) space group $C2/c$, $a = 19.048(9)$, $b = 3.947(2)$, $c = 23.692(11)$ Å, $\beta = 108.04(3)^\circ$, $V = 1693.3(13)$, $Z = 8$, $D_c = 1.18$ g cm^{–3}, 665 unique reflections, $F_o > 4\sigma(F_o)$, 110 parameters, $2\theta_{\text{max}} = 50^\circ$, $R = 0.058$.

For **3**: C₈H₆ (Aldrich), crystallized *in situ* on the diffractometer (ref. 19), space group $P\bar{1}$, $a = 5.763(3)$, $b = 9.099(5)$, $c = 15.332(8)$ Å, $\alpha = 77.31(4)^\circ$, $\beta = 81.25(5)^\circ$, $\gamma = 80.62(4)^\circ$, $V = 768.1(7)$, $Z = 5$, $D_c = 1.10$ g cm^{–3}, 2541 unique reflections, $F_o > 4\sigma(F_o)$, 219 parameters, $2\theta_{\text{max}} = 55^\circ$, $R1 = 0.069$.

All measurements were performed on a Nicolet R3m/V X-ray four circle diffractometer at –148 °C, using Mo-K α X-rays ($\lambda = 0.71073$), a graphite monochromator and the program SHELXTL (ref. 20); H-atom positions were refined isotropically. CCDC 182/560.

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