

## LETTER TO THE EDITOR

# Preferential Formation of $C\equiv C-H\cdots\pi(C\equiv C)$ Interactions in the Solid State

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**This paper probes the propensity for terminal alkynes to form  $C\equiv C-H\cdots\pi$  interactions in the solid state, by rationalization of the structural properties of molecular solids in which  $C\equiv C-H$  is the only recognized hydrogen bond donor group, but in which there are different possible  $\pi$  systems that may serve as the acceptor for  $C\equiv C-H\cdots\pi$  interactions. These  $\pi$  systems are the  $C\equiv C-H$  group itself and the arene ring  $\pi$  system. Thus, in the crystal structures of 1,4-diethynylbenzene (redetermined here) and 1,3,5-triethynylbenzene (reported for the first time here) there is competition between the  $C\equiv C-H$  groups and the arene rings as acceptors for  $C\equiv C-H\cdots\pi$  interactions. It is found that both structures contain chains of  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions—zig-zag chains in the case of 1,4-diethynylbenzene and helical chains in the case of 1,3,5-triethynylbenzene. Neither structure contains any  $C\equiv C-H\cdots\pi(\text{arene})$  interactions. Cooperativity in the formation of the chains of  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions is strongly implicated (although not directly proven) by the results reported here. The conclusions derived here concerning the preferences for the formation of  $C\equiv C-H\cdots\pi$  interactions have important implications with regard to the recognition and utilization of weak intermolecular interactions in the structural design of molecular solids.** © 1997 Academic Press

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### INTRODUCTION

The development of strategies for controlled aggregation of molecules in the solid state—so-called crystal engineering (1, 2)—has relied to a large extent on the use of conventional strong hydrogen bonds (such as  $O-H\cdots O$  and  $N-H\cdots O$ ) to give rise to the preferential construction of motifs with predictable structural properties. There is, however,

increasing emphasis on the exploitation of weaker intermolecular forces, such as  $C-H\cdots O$  (3) and  $X-H\cdots\pi$  (4) interactions, both of which may be described loosely as types of hydrogen bond. Recently, there has been some interest (5) in the acidic  $C-H$  group in terminal alkynes as a hydrogen bond donor and the alkyne  $C\equiv C$  bond as a hydrogen bond acceptor, and it has been suggested (6, 7) that cooperative effects are operative in arrays of  $C\equiv C-H\cdots C\equiv C-H\cdots$  interactions, similar to the mutual polarization found (8) in arrays of  $O-H\cdots O-H\cdots$  hydrogen bonds. In general, however, the  $C-H\cdots\pi$  interactions investigated so far have been secondary interactions in structures that contain much stronger hydrogen bonds as the dominant (structure-controlling) intermolecular force, and the role of the  $C-H\cdots\pi$  interactions in dictating the structural properties in these cases is therefore difficult to decipher.

In order to derive a deeper understanding of the nature of  $C\equiv C-H\cdots\pi$  interactions, we focus here on systems that allow competition between different possible types of  $C\equiv C-H\cdots\pi$  interactions, in the absence of any other intermolecular interactions that would traditionally be regarded as strong (e.g., conventional hydrogen bonds). In particular, the systems selected for study allow the competition between different types of  $C\equiv C-H\cdots\pi$  interactions to be probed, with the  $\pi$  hydrogen bond acceptor being either the  $C\equiv C$  bond of an alkyne or the  $\pi$  system of an aromatic ring. All of these structural components are present in ethynyl substituted benzenes, and here we report and rationalize the structural properties of 1,4-diethynylbenzene and 1,3,5-triethynylbenzene, as determined by single crystal X-ray diffraction. These structures show  $C\equiv C-H\cdots\pi$  interactions to alkyne residues only, demonstrating *inter alia* that the  $C\equiv C-H\cdots\pi$  interaction between terminal alkynes can be a controlling intermolecular force in the solid state.

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## EXPERIMENTAL

1,4-Diethynylbenzene and 1,3,5-triethynylbenzene were synthesized by the Pd-catalyzed cross-coupling (9) of trimethylsilylacetylene to 1,4-dibromobenzene and 1,3,5-tri-bromobenzene, respectively, followed by the removal of the trimethylsilyl protecting groups under basic conditions.

Single crystals of 1,4-diethynylbenzene suitable for single crystal X-ray diffraction were grown by slow evaporation of acetone from a solution of 1,4-diethynylbenzene in acetone. Single crystals of 1,3,5-triethynylbenzene were grown by slow evaporation of toluene from a solution of 1,3,5-triethynylbenzene in toluene.

All single crystal X-ray diffraction experiments were carried out using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å) on a Rigaku R-Axis II diffractometer equipped with an area detector and rotating anode source. The crystals used for data collection were placed in a capillary tube to reduce the rate of sublimation. Data collection for 1,4-diethynylbenzene comprised 36 frames, each recorded over an oscillation range of  $10^\circ$  with 10-min. exposure time per frame. Data collection for 1,3,5-triethynylbenzene comprised 45 frames, each recorded over an oscillation range of  $4^\circ$  with 22-min. exposure time per frame. The crystal to detector distance was 80 mm in both cases. No corrections were made for X-ray absorption. The structure was solved and refined by standard methods (TEXSAN (10), SHELXL93 (11)) and the positions of all nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. All hydrogen atom positions were fixed according to standard geometries.

## RESULTS AND DISCUSSION

The crystal structure of 1,4-diethynylbenzene was determined ( $R = 0.092$ ) many years ago (12), although the nature of the packing arrangement was not discussed in this earlier paper. With our present focus on intermolecular close contacts, it was desirable to improve the precision of this structure, and the structure was redetermined ( $R = 0.058$ ) as part of the present work (Table 1). In the structure of 1,4-diethynylbenzene (Fig. 1), the molecules are linked by  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions; there is only one type of  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction in this structure, with  $C\cdots M$  and  $H\cdots M$  distances of 3.74 and 2.68 Å, respectively (where  $M$  represents the midpoint of the  $C\equiv C$  bond), and a  $C-H\cdots M$  angle of  $176.1^\circ$ . Thus, the  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction is bifurcated almost symmetrically, with very similar  $H\cdots C$  distances (2.70 and 2.80 Å) to the two carbon atoms of the alkyne. These  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions create infinite zig-zag chains along the  $b$ -axis, and it is probable that these chains represent cooperative hydrogen bonding arrangements. The two  $C\equiv C-H$  groups in a given 1,4-diethynylbenzene molecule participate in two adjacent

TABLE 1  
Crystallographic Data for 1,4-Diethynylbenzene and 1,3,5-Triethynylbenzene

	1,4-Diethynylbenzene	1,3,5-Triethynylbenzene
Formula	C <sub>10</sub> H <sub>6</sub>	C <sub>12</sub> H <sub>6</sub>
$M_w$ (g mol <sup>-1</sup> )	126.15	150.17
Temperature (K)	295(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
$a$ (Å)	3.967(2)	19.0968(3)
$b$ (Å)	5.992(4)	4.0525(3)
$c$ (Å)	15.169(8)	23.815(3)
$\beta$ ( $^\circ$ )	91.199(14)	108.096(2)
$Z$	2	8
Crystal size (mm <sup>3</sup> )	0.50 × 0.30 × 0.10	0.50 × 0.25 × 0.10
Measured reflections	3599	4060
Independent reflections	634	1429
$wR(F^2)$ [for $F^2 > 2\sigma(F^2)$ ]	0.104	0.124
$R$ [for $F^2 > 2\sigma(F^2)$ ]	0.058	0.055

chains of  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions, and essentially a two-dimensional sheet is constructed, with the mean plane of these sheets parallel to the  $bc$  plane. These sheets are stacked by arene  $\pi\cdots\pi$  interactions (interplanar distance 3.71 Å) along the  $a$ -axis.

The structure of 1,3,5-triethynylbenzene (Tables 1 and 2) comprises double helical chains of  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions along the  $b$ -axis (Figs. 2 and 3), with the two helices related to each other by one unit cell translation

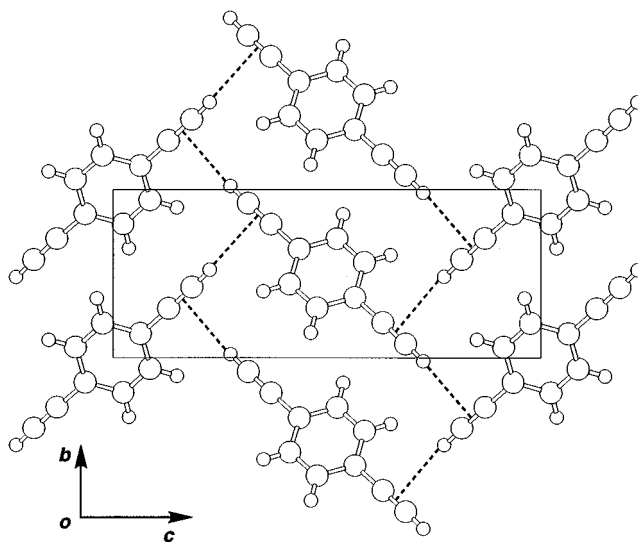
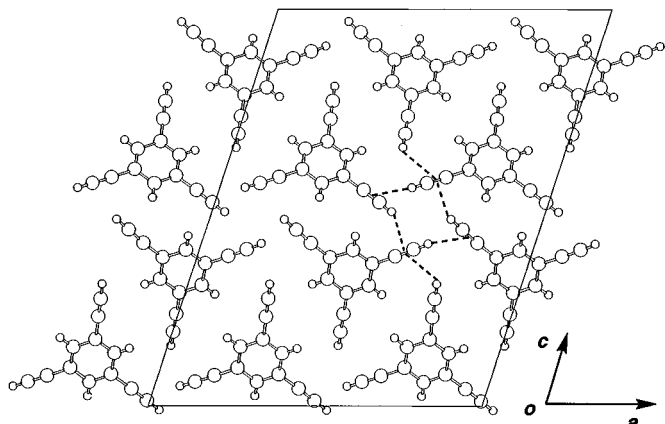
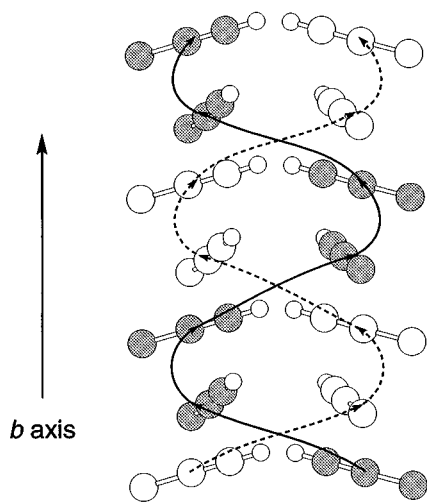


FIG. 1. Ball and stick representation of the crystal structure of 1,4-diethynylbenzene viewed along the  $a$ -axis. The projection of the unit cell is represented by the solid lines. Selected hydrogen bonds are shown as dashed lines.

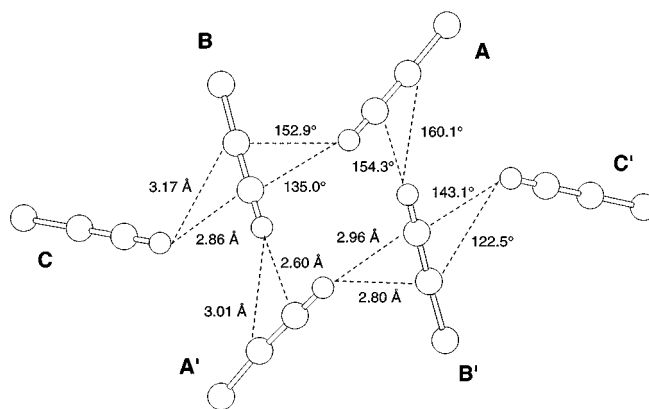


**FIG. 2.** Ball and stick representation of the crystal structure of 1,3,5-triethynylbenzene viewed along the *b*-axis. The projection of the unit cell is represented by the solid lines. Selected hydrogen bonds are shown as dashed lines.

along the *b*-axis. The pitch of each helix is therefore  $2b$ . As for 1,4-diethynylbenzene, the arrangement of the infinite  $C\equiv C-H\cdots C\equiv C-H\cdots$  chains within the helix may be proposed as a co-operative hydrogen bonding arrangement. Within one helix, the repeating unit contains four  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions, comprising two crystallographically independent types of  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction. As shown in Fig. 4, the two types of interaction have similar  $C\cdots M$  separations, with average  $C\cdots M$  distance 3.76 Å, average  $H\cdots M$  distance 2.79 Å, and average  $C-H\cdots M$  angle 152.5°. The two different  $C\equiv C-H\cdots\pi(C\equiv C)$



**FIG. 3.** Ball and stick representation of the double helices formed by infinite chains of  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions in the crystal structure of 1,3,5-triethynylbenzene. For clarity, only the  $C-C\equiv C-H$  fragments of each molecule of 1,3,5-triethynylbenzene are shown. The helix represented by unshaded fragments is related to that represented by shaded fragments by translation of one unit cell along the *b*-axis.



**FIG. 4.** Ball and stick representation of the intermolecular contacts of the ethynyl groups within a helix in the crystal structure of 1,3,5-triethynylbenzene. For clarity, only the  $C-C\equiv C-H$  fragments of each molecule of 1,3,5-triethynylbenzene are shown. The residue **A** forms a short contact with **B**, **B** with **A'**, **A'** with **B'**, and **B'** forms a short contact with the residue **A** in the next repeat unit of the helix. The geometric parameters have been determined assuming ideal positions of H atoms, based on  $C-H$  bond lengths of 1.06 Å and  $C=C-H$  bond angles of 180°.

interactions that alternate along the helix have different orientational characteristics—each of these  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions is clearly biased toward one of the two carbon atoms, in one case involving the carbon atom attached to the arene ring and in the other case involving the carbon atom of the  $C-H$  unit. Experimental (13) and computational (14) evidence suggests that the potential energy surface for the  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction between terminal alkynes is relatively insensitive to the position of the hydrogen atom along the  $C\equiv C$  bond vector. Therefore, the energy difference between a symmetrically bifurcated motif and a motif in which the direction is biased toward an individual carbon atom is small. This feature creates the opportunity for considerable geometrical flexibility (as observed in the structures discussed here) in the formation of  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions.

Within a given double helix, each molecule has an alkyne residue participating in an adjacent helix, thus creating slabs of interlocked double helices which lie parallel to the *ab*-plane; the helices in a given slab are either only left-handed or only right-handed, with the chirality alternating between adjacent slabs. The third alkyne residue of each 1,3,5-triethynylbenzene molecule participates in a longer  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction ( $C-H\cdots M$  distance 2.86 Å,  $C-H\cdots M$  angle 143.1°) with a  $C\equiv C$  group within the helix of an adjacent slab. This third alkyne group does not act as an acceptor in any  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction (Fig. 4).

In conclusion, we have demonstrated that the  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction is a robust motif which can serve as a controlling intermolecular interaction in the solid state, but nevertheless offers considerable geometrical

**TABLE 2**  
**Atomic Coordinates and Equivalent Isotropic Atomic Displacement Parameters for 1,3,5-Triethynylbenzene**

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
C(1)	0.1474(1)	− 0.2121(4)	− 0.4413(1)	0.057(1)
C(2)	0.2185(1)	− 0.2937(4)	− 0.4067(1)	0.057(1)
C(3)	0.2302(1)	− 0.4579(4)	− 0.3533(1)	0.054(1)
C(4)	0.1704(1)	− 0.5441(4)	− 0.3346(1)	0.056(1)
C(5)	0.0991(1)	− 0.4638(4)	− 0.3691(1)	0.057(1)
C(6)	0.0878(1)	− 0.2984(4)	− 0.4223(1)	0.059(1)
C(7)	0.1352(1)	− 0.0426(5)	− 0.4967(1)	0.066(1)
C(8)	0.1250(1)	0.0972(6)	− 0.5418(1)	0.085(1)
C(9)	0.3032(1)	− 0.5472(5)	− 0.3169(1)	0.061(1)
C(10)	0.3613(1)	− 0.6262(6)	− 0.2848(1)	0.075(1)
C(11)	0.0374(1)	− 0.5563(5)	− 0.3496(1)	0.065(1)
C(12)	− 0.0125(1)	− 0.6342(6)	− 0.3338(1)	0.080(1)

diversity. The combination of robustness and geometrical flexibility offers considerable scope for the construction of a range of different (but predictable) molecular packing arrangements based on  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions. It is significant that, in the structures investigated here, the  $C\equiv C-H\cdots\pi(C\equiv C)$  interaction is preferred over the possible competing  $C\equiv C-H\cdots\pi$  interaction to the available arene  $\pi$  systems. We may tentatively extrapolate from these observations and suggest that these conclusions are generally applicable when a sufficient number of  $C\equiv C-H$  groups are present in the system. When there is a deficit of  $C\equiv C-H$  groups, other competing intermolecular interactions may exert a controlling influence. Indeed it is significant that the structure of 1,3,5-triethynylbenzene can be rationalized on the basis of  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions alone, whereas

the structure of 1,4-diethynylbenzene relies on arene  $\pi\cdots\pi$  stacking in one direction in the crystal, in addition to the  $C\equiv C-H\cdots\pi(C\equiv C)$  interactions that control the structural properties in the other directions.

#### ACKNOWLEDGMENTS

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