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1,4-Bis(*p*-tolylethynyl)benzene

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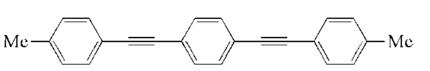
The rod-like molecule of the title hydrocarbon, $C_{24}H_{18}$, is centrosymmetric, with the centroid of the central benzene ring residing on an inversion center. The molecules display a planar conformation of the benzene rings and aggregate into stacks along the [010] direction *via* $Csp^3—H\cdots\pi$(arene) interactions, thus forming a stair-like pseudo-two-dimensional network. Each molecule acts as both a C—H hydrogen donor and a π-arene acceptor, forming four hydrogen bonds per molecule.

Comment

The present work forms part of our studies focused on the structures and reactivities of planar and curved polyaromatic hydrocarbons (Petrukhina *et al.*, 2004). Molecules showing π-extended conjugation attract special attention since they exhibit interesting electroconductive, magnetic and optical properties (Bunz, 2000; Delaire & Nakatani, 2000; Kawase *et al.*, 2003). Knowledge of the intermolecular interactions determining solid-state packing is required in order to understand the influence of crystal structure on the above properties. We present here the structural characterization of 1,4-bis(*p*-tolylethynyl)benzene, (I), the synthesis of which has been reported previously by Nguyen *et al.* (1994).



(I)

The present X-ray structural analysis shows that all three benzene rings are coplanar in the centrosymmetric molecule of (I) (Fig. 1), with an r.m.s. displacement of the C atoms from the molecular plane of 0.012 Å and a maximum displacement of 0.020 (1) Å for atom C10. The C—C bond lengths within the phenyl rings are very similar and are consistent with values typical for *para*-substituted aryls. The C≡C bond length [1.199 (2) Å; Table 1] is virtually identical to that reported for diphenylacetylene (C_6H_5–C≡C–C_6H_5), (II) [1.198 (3) Å; Mavridis & Moustakali-Mavridis, 1977].

In the current study, *ab initio* calculations have been performed on (I) at the HF/6-31G(*d,p*) level (Frisch *et al.*, 1998) in order to estimate the rotation barriers of the benzene rings. The potential minimum (−918.9296 a.u.) corresponds to the planar conformation. This contrasts with (II), where a conformation with perpendicular benzene rings is favoured (Liberles & Matlosz, 1971). The rotation barrier for the peripheral benzene rings in (I) (0.73 kcal mol^{-1}; 1 kcal mol^{-1} = 4.184 kJ mol^{-1}) is comparable with the rotation barrier in (II) (*ca* 0.6 kcal mol^{-1}). The rotation barrier for the central benzene ring located between the two C≡C triple bonds is only *ca* 1.6 times greater (1.14 kcal mol^{-1}) than for the terminal benzene rings, which are constrained by one triple bond.

In the crystal structure of (I), molecules are aligned along the [010] direction in a regular fashion but show a chain slippage of *ca* 3.45 Å, thus preventing π–π stacking of the phenyl rings of neighbouring molecules (Fig. 2). By contrast, the packing motif for (II) is based on a face-to-face coplanar stacking. The most probable reasons for such a difference in the solid-state structures of (I) and (II) are repulsive interactions of the methyl groups, forcing the molecules of (I) to slip, and the formation of intermolecular hydrogen bridges by means of the $Csp^3—H\cdots\pi$(arene) bonds, forming a pseudo-two-dimensional stack.

It has been shown previously that methyl groups can function as hydrogen-bond donors towards aromatic π systems (Desiraju, 2002). In the structure of (I), each linear hydrocarbon molecule serves as a two-site hydrogen-bond acceptor using two peripheral benzene rings, and as a two-site hydrogen-bond donor provided by the methyl groups. The $H\cdots A$ distance for these hydrogen bonds [2.605 (19) Å] is noticeably short (estimated as the distance between the H atom and the centroid, *Cg*1, of the benzene ring defined by atoms C2–C7), and is comparable with the distances for the more activated C—H donors, such as those containing ethylene or acetylene moieties (*ca* 2.5–2.7 Å; Weiss *et al.*, 1997; Gobius du Sart *et al.*, 2004). The angle formed by $Csp^3—H\cdots Cg1$ tends toward linearity and is 164°. It is worth mentioning that the H atom lies almost exactly over the centre of the accepting phenyl ring, with the H—*Cg*1—C*n* angles (C*n* is C2–C7) ranging from 86.3 (4) to 93.4 (4)°. Hence, it does not exhibit a preferential interaction with any C atoms.

As a result of hydrogen bonding, the distance between the molecules of (I) in the stacks (3.52 Å) is similar to the intermolecular distance between 3,3′,4,4′-tetrakis(phenylethynyl)-

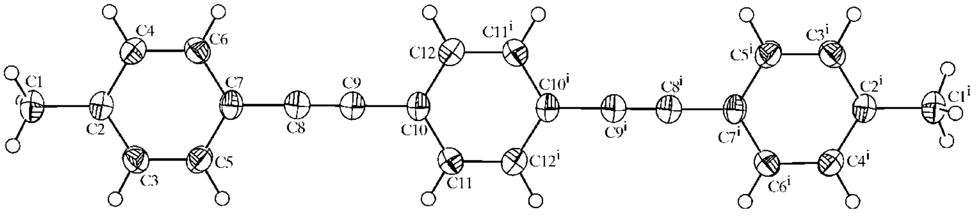


Figure 1
A view of the molecular structure of (I), showing displacement ellipsoids at the 70% probability level and H atoms as spheres of arbitrary radii. Atoms labelled with a symmetry code are symmetrically dependent *via* an inversion centre [symmetry code: (i) $2 - x, -y, -z$].

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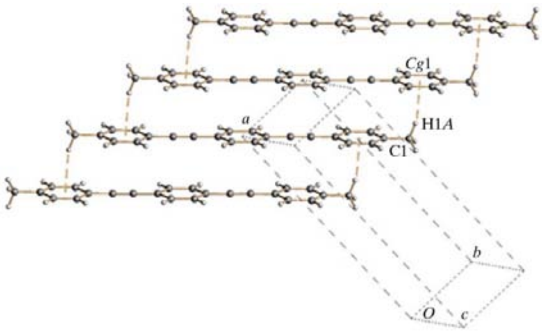

Figure 2
A fragment of the crystal structure of (I), showing the formation of a pseudo-two-dimensional network along the [010] direction *via* Csp^3—H$\cdots\pi$(arene) hydrogen bonds.

biphenyl molecules (3.45 Å), held by strong π–π interactions (Perera *et al.*, 2003). This may represent an additional verification for the existence of the hydrogen bridges that are responsible for the solid-state packing of (I).

In summary, an addition of methyl groups to rod-like π systems provides a source for C—H$\cdots\pi$(arene) hydrogen bonding, which results in a sliding of the chain of one linear polyaromatic molecule over another in the solid state. This effect can be used to direct the self-assembly of aromatic hydrocarbons and to control their crystal packing.

Experimental

1,4-Bis(*p*-tolylethynyl)benzene was synthesized according to the literature procedure of Nguyen *et al.* (1994). The crude product was purified by sublimation to yield a well defined crystalline powder, which was sealed under vacuum in a small glass ampoule and placed in an electric furnace that had a small temperature gradient along the length of the tube. The temperature was set at 428 K. After 2 d, the temperature was gradually lowered at a rate of 5 K h^{-1}. This resulted in the deposition in the coldest part of the ampoule of single crystals of (I) suitable for X-ray analysis.

Crystal data

$C_{24}H_{18}$
M_r = 306.38
Monoclinic, $P2_1/c$
a = 14.5478 (11) Å
b = 4.9229 (4) Å
c = 11.3006 (9) Å
β = 100.7110 (10)°
V = 795.22 (11) Å^3
Z = 2
D_x = 1.280 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3277 reflections
θ = 2.4–28.3°
μ = 0.07 mm^{-1}
T = 173 (2) K
Plate, colourless
0.27 × 0.12 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
0.3°-wide ω scans
6512 measured reflections
1863 independent reflections
1358 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.034
$\theta_{\rm max}$ = 28.3°
$h = -19 \rightarrow 19$
$k = -6 \rightarrow 6$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.144
S = 1.01
1863 reflections
145 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.0001$
$\Delta\rho_{\rm max}$ = 0.28 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.5054 (15)	C8—C9	1.1992 (15)
C7—C8	1.4378 (14)	C9—C10	1.4372 (14)
C7—C8—C9	179.10 (12)	C8—C9—C10	179.76 (14)

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the benzene ring defined by atoms C2–C7.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$A\cdots Cg$1$^{\rm i}$	1.000 (18)	2.605 (19)	3.578 (2)	164 (2)

Symmetry code: (i) $x, y + 1, z$.

All H atoms were refined independently; C—H = 0.964 (13)–0.992 (12) Å for aromatic and 0.974 (18)–1.000 (18) Å for methyl H atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1238). Services for accessing these data are described at the back of the journal.

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