

Three bis-*ortho*-diynylarenes (BODA)K. Prasanna U. Perera,^a Khalil A. Abboud,^b Dennis W. Smith Jr^a and Mariusz Krawiec^{a*}^aDepartment of Chemistry, Clemson University, Clemson, SC 29634, USA, and^bDepartment of Chemistry, University of Florida, Gainesville, FL 32611, USA

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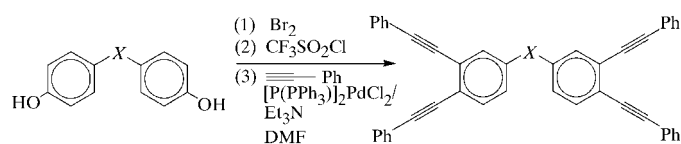
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The molecule of 3,3',4,4'-tetrakis(phenylethynyl)biphenyl, C₄₄H₂₆, is approximately planar and is located on a crystallographic inversion center. Bis[3,4-bis(phenylethynyl)phenyl] ether, C₄₄H₂₆O, has molecules located on twofold symmetry axes, whereas the molecule of 2,2-bis[3,4-bis(phenylethynyl)phenyl]propane, C₄₇H₃₂, does not exhibit any molecular symmetry.

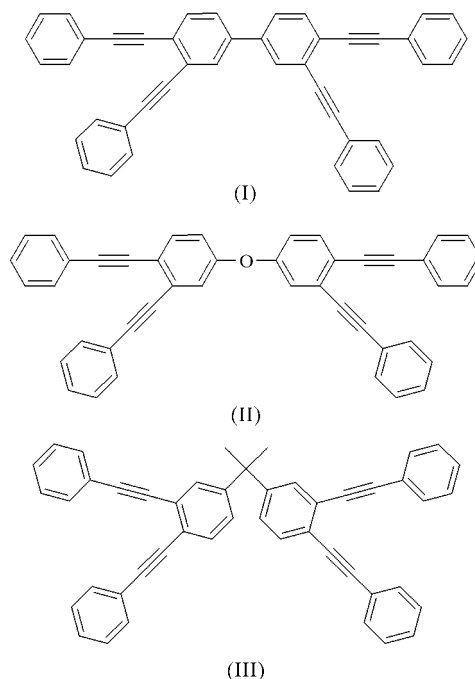
Comment

Bis-*ortho*-diynylarene (BODA) compounds are a new class of tetrayne monomers which undergo thermally induced Bergman cyclization (Bergman, 1973) to form processable precursors leading to polyarylene networks (Smith *et al.*, 1998). BODA-derived networks are targeted for applications such as high-temperature thin-film dielectrics, optoelectronic materials (Smith *et al.*, 1998), matrix composite resins, and precursors to glassy carbon microstructures (Shah *et al.*, 2000). Currently BODA monomers are polymerized in solution or melt. However, solid-state polymerization could occur with appropriate high-melting crystals. We report here the crystal structures of a series of BODA compounds with melting points below their polymerization temperatures (*i.e.* <473 K).



The molecule of compound (I) (Fig. 1) is located on an inversion center and is approximately planar, with an r.m.s displacement of the C atoms from the molecular plane of 0.131 Å and a maximum displacement of 0.230 (3) Å for atom C5. The molecules are stacked in the direction of the crystallographic *b* axis; the distances between benzene rings are reported in Table 4. The molecule of compound (II) (Fig. 2) is located on a twofold symmetry axis; both parts of the molecule are planar, with an r.m.s displacement for the non-H atoms of 0.174 Å and a maximum displacement from the least-squares plane of 0.352 (3) Å for atom C13. For BODA molecules with

terminal phenyl groups, π -stacking of the aromatic rings is an important factor in determining the crystal packing. The π -stacking distances of all molecules reported here are in a narrow range. The almost planar stacking of the molecules in (I) (as illustrated by the small value of the dihedral angle



between the stacked rings) indicates very efficient packing (Table 4). Rings C1–C6 of the two adjacent molecules of (II) are exactly parallel to each other. The other close contact between phenyl rings in the structure of (II) exhibits a slightly longer distance and a relatively large angle between the planes of the two interacting rings (Table 4). Reactivity-determining trans-alkyne distances are reported in Table 5 for the three title compounds. The variation of the distance in the molecule

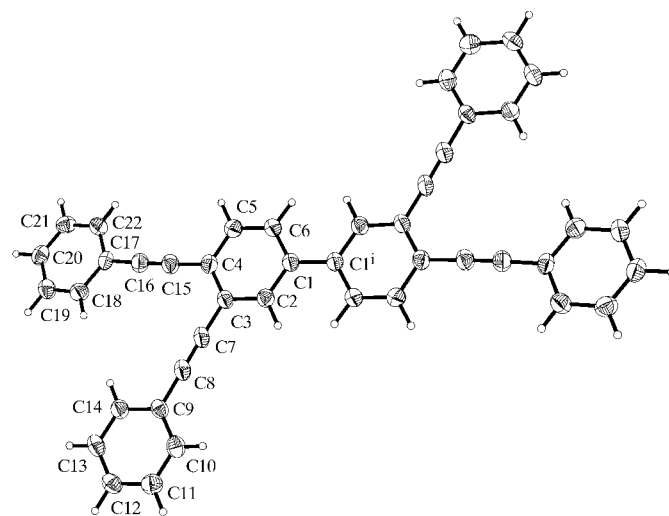


Figure 1

A view of molecule (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as circles of arbitrary radii. [Symmetry code: (i) $-x, 1 - y, 2 - z$.]

of (III) (Fig. 3) is comparable to the variations between different molecules. Thus, it seems that the packing plays an important role as the spacer group in determining the transalkyne distances in these BODA compounds in the solid state. Apart from their potential application for network polyarenes, the monomers are good candidates for crystal engineering as robust and versatile building blocks for supramolecular assemblies.

The 1,2-bis(phenylethynyl)phenyl fragment present in all three title compounds is relatively uncommon among structures reported in the Cambridge Structural Database (CSD; Allen, 2002). Most often, such fragments occur as part of a larger macrocycle consisting of alternating benzene rings and ethynylene bridges. Sometimes they also incorporate a transition metal atom in the center. There are only four structures reported in the CSD with a free-standing 1,2-bis(phenylethynyl)phenyl fragment, namely 1,2-bis[2-(3-hydroxyphenyl)ethynyl]benzene (refcode ECACEQ; Schmittel *et al.*, 2001), bis{2-[2-(trimethylsilylethynyl)phenylethynyl]phenyl}ethyne and bis[2-(2-ethynylphenylethynyl)phenyl]ethyne (GOPMIH and GOPMON, respectively; Baldwin *et al.*, 1998), and 1,2-bis[2-(2-ethynylphenyl)ethynyl]benzene (PIPYUI; Baldwin *et al.*, 1993). In GOPMIH and GOPMON, only two of the aromatic rings are coplanar, the rest of the molecules being twisted as a result of bulky substituents. The atomic

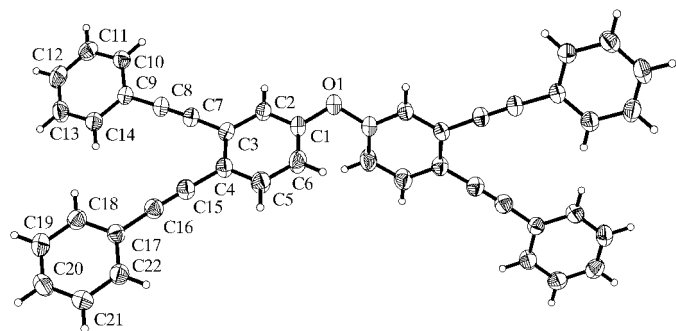


Figure 2
A view of the molecule of (II), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as circles of arbitrary radii.

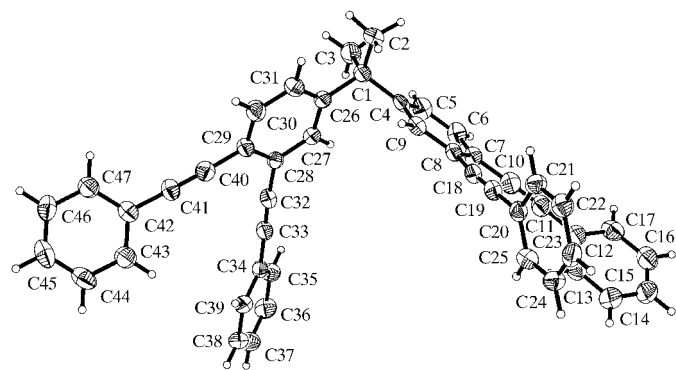


Figure 3
A view of the molecule of (III), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as circles of arbitrary radii.

coordinates of PIPYUI were not reported in the CSD. The molecule of the fourth structure, ECACEQ, is nearly planar, closely resembling the planar fragments in (I) and (II). ECACEQ forms a hemihydrate clathrate with two molecules encapsulating one water molecule.

Experimental

Bis-*ortho*-diynylarylene (BODA) derivatives can be synthesized as described previously (Smith *et al.*, 1998). The title monomers were prepared in three steps *via ortho*-bromination and trifluoromethylsulfonate (trifluoromethanesulfonate) esterification, followed by Pd-catalyzed coupling of phenylacetylene (Sonogashira *et al.*, 1975) to give the tetrayne (see reaction *Scheme* above). The solvents used for recrystallization were hexane-ethyl acetate (1:1) for (I) and (II), and hexane for (III).

Compound (I)

Crystal data

$C_{44}H_{26}$
 $M_r = 554.65$
Monoclinic, $P2_1/c$
 $a = 13.299$ (7) Å
 $b = 5.229$ (3) Å
 $c = 21.196$ (11) Å
 $\beta = 92.540$ (15)°
 $V = 1472.4$ (14) Å³
 $Z = 2$

$D_x = 1.254$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 3530 reflections
 $\theta = 1.0$ – 26.5°
 $\mu = 0.07$ mm⁻¹
 $T = 300$ (2) K
Platelet, colorless
 $0.30 \times 0.15 \times 0.10$ mm

Data collection

Rigaku Mercury CCD diffractometer
 ω scans
Absorption correction: multi-scan (Jacobson, 1998)
 $T_{\min} = 0.987$, $T_{\max} = 0.993$
14 417 measured reflections

3021 independent reflections
1664 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.091$
 $\theta_{\text{max}} = 26.5^\circ$
 $h = -16 \rightarrow 16$
 $k = -6 \rightarrow 6$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.079$
 $wR(F^2) = 0.182$
 $S = 1.15$
3021 reflections
200 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0608P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

C1–C1 ⁱ	1.486 (6)	C8–C9	1.430 (4)
C3–C7	1.430 (4)	C15–C16	1.198 (4)
C4–C15	1.435 (4)	C16–C17	1.413 (4)
C7–C8	1.207 (4)		
C2–C1–C6	117.1 (3)	C7–C8–C9	179.5 (4)
C2–C1–C1 ⁱ	121.4 (4)	C10–C9–C14	118.8 (3)
C6–C1–C1 ⁱ	121.6 (3)	C10–C9–C8	122.3 (3)
C2–C3–C4	118.6 (3)	C14–C9–C8	118.9 (3)
C2–C3–C7	120.2 (3)	C16–C15–C4	175.3 (4)
C4–C3–C7	121.1 (3)	C15–C16–C17	177.4 (4)
C5–C4–C3	118.9 (3)	C18–C17–C22	118.6 (3)
C5–C4–C15	118.8 (3)	C18–C17–C16	121.1 (3)
C3–C4–C15	122.3 (3)	C22–C17–C16	120.2 (3)
C8–C7–C3	178.3 (3)		

Symmetry code: (i) $-x, 1 - y, 2 - z$.

Compound (II)

Crystal data

$C_{44}H_{26}O$	$D_x = 1.209 \text{ Mg m}^{-3}$
$M_r = 570.65$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4736 reflections
$a = 35.483 (10) \text{ \AA}$	$\theta = 0.6\text{--}26.5^\circ$
$b = 5.8875 (15) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 15.919 (5) \text{ \AA}$	$T = 300 (2) \text{ K}$
$\beta = 109.932 (6)^\circ$	Block, colorless
$V = 3126.4 (14) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Rigaku Mercury CCD diffractometer	3203 independent reflections
ω scans	1964 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Jacobson, 1998)	$R_{\text{int}} = 0.051$
$T_{\text{min}} = 0.983$, $T_{\text{max}} = 0.986$	$\theta_{\text{max}} = 26.5^\circ$
15 387 measured reflections	$h = -44 \rightarrow 44$
	$k = -7 \rightarrow 7$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.184$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.15$	$\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$
3202 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$
204 parameters	
H-atom parameters constrained	

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

O1—C1	1.395 (3)	C8—C9	1.429 (3)
C3—C7	1.434 (3)	C15—C16	1.197 (3)
C4—C15	1.433 (3)	C16—C17	1.440 (3)
C7—C8	1.196 (3)		
C1—O1—C1 ¹	118.1 (3)	C5—C4—C15	119.9 (2)
C2—C1—C6	121.3 (2)	C3—C4—C15	121.6 (2)
C2—C1—O1	117.5 (2)	C14—C9—C10	118.8 (2)
C6—C1—O1	121.1 (2)	C14—C9—C8	119.4 (2)
C2—C3—C4	120.0 (2)	C10—C9—C8	121.9 (2)
C2—C3—C7	120.7 (2)	C18—C17—C22	118.7 (2)
C4—C3—C7	119.4 (2)	C18—C17—C16	122.3 (2)
C5—C4—C3	118.5 (2)	C22—C17—C16	119.0 (2)
C1 ¹ —O1—C1—C2	−142.0 (2)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Compound (III)

Crystal data

$C_{47}H_{32}$	$Z = 2$
$M_r = 596.73$	$D_x = 1.187 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.323 (3) \text{ \AA}$	Cell parameters from 54 reflections
$b = 14.575 (4) \text{ \AA}$	$\theta = 2.0\text{--}25.0^\circ$
$c = 19.776 (4) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$\alpha = 69.53 (3)^\circ$	$T = 173 (2) \text{ K}$
$\beta = 81.20 (4)^\circ$	Needle, colorless
$\gamma = 79.14 (4)^\circ$	$0.50 \times 0.06 \times 0.05 \text{ mm}$
$V = 1669.3 (10) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	5860 independent reflections
ω scans	3266 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Blessing, 1995)	$R_{\text{int}} = 0.048$
$T_{\text{min}} = 0.924$, $T_{\text{max}} = 0.997$	$\theta_{\text{max}} = 25.0^\circ$
12 148 measured reflections	$h = -7 \rightarrow 7$
	$k = -17 \rightarrow 15$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.150$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
5860 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
427 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.0095 (14)

Table 3

Selected geometric parameters (\AA , $^\circ$) for (III).

C1—C3	1.528 (4)	C18—C19	1.197 (4)
C1—C4	1.534 (4)	C19—C20	1.432 (4)
C1—C26	1.536 (4)	C28—C32	1.448 (4)
C1—C2	1.539 (4)	C29—C40	1.436 (4)
C7—C10	1.436 (5)	C32—C33	1.193 (4)
C8—C18	1.438 (4)	C33—C34	1.432 (4)
C10—C11	1.194 (4)	C40—C41	1.192 (4)
C11—C12	1.434 (5)	C41—C42	1.435 (4)
C3—C1—C4	112.4 (3)	C10—C11—C12	172.8 (4)
C3—C1—C26	107.3 (3)	C19—C18—C8	175.0 (3)
C4—C1—C26	109.6 (2)	C18—C19—C20	179.0 (3)
C3—C1—C2	107.9 (3)	C33—C32—C28	175.6 (3)
C4—C1—C2	108.1 (2)	C32—C33—C34	177.6 (3)
C26—C1—C2	111.6 (3)	C41—C40—C29	177.9 (3)
C11—C10—C7	174.9 (4)	C40—C41—C42	178.0 (4)

Table 4

Selected perpendicular π -stacking distances (\AA) and dihedral angles ($^\circ$) in the title BODA compounds.

The distances are measured from the centroid of the first ring to the least-squares plane of the second ring.

	Ring 1	Ring 2	Distance 1→2	Distance 2→1	Dihedral angle
(I)	C1—C6	C9—C14	3.451	3.429	2.1 (2)
(I)	C17—C22	C9—C14	2.630	3.416	9.7 (2)
(II)	C1—C6	C1—C6	3.519	3.519	
(II)	C9—C14	C17—C22	3.848	3.714	15.5 (2)

Table 5

Trans-alkyne distances (\AA) in the title BODA molecules.

	C11...C19 (C8...C16)	C33...C41 (C8...C16)
(I)	4.262 (5)	4.262 (5)
(II)	4.061 (3)	4.061 (3)
(III)	3.844 (4)	4.159 (6)

All H atoms, except those on atoms C22 and C23 of (III), were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.98 and 0.99 \AA were used for methyl and

secondary C atoms, respectively. A distance of 0.93 Å was used for the C_{sp^2} atoms in (I) and (II), and a distance of 0.95 Å was used for (III). H-atom displacement parameters were set at $1.5U_{eq}$ of the parent C atom for the methyl groups and at $1.2U_{eq}$ for all other C atoms.

For compounds (I) and (II), data collection: *CrystalClear* (Rigaku, 1998–2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). For compound (III), data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*. For all compounds, program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: FR1389). Services for accessing these data are described at the back of the journal.

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