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An unusual oligomerization/oxidation reaction of a 3-boron-substituted 1-phenylbuta-1,3-diene produces 6,9,16,19-tetraphenyl-5,15-distyryl-3,13,25,26-tetraoxa-2,12-dibora-pentacyclo[16.2.2.$2^{8,11}$.$1^{2,5}$.$1^{12,15}$]-hexacosa-1(20),7,10,17-tetraene

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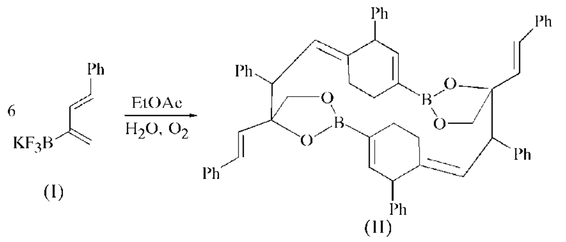
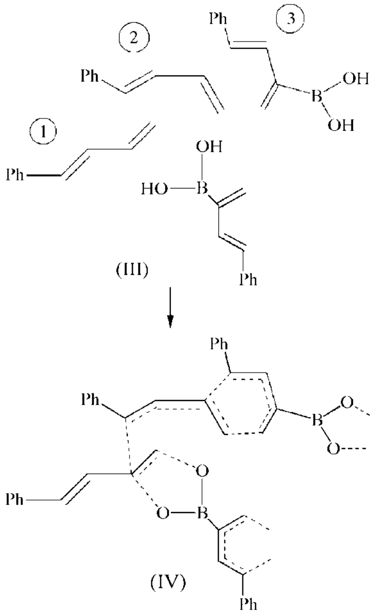
The unusual title macrocyclic structure, $C_{60}H_{54}B_2O_4$, has been isolated from exposure of 3-BF_3-1-phenylbuta-1,3-diene to both air and moisture in an attempt to obtain crystals of the starting butadiene compound. Formation of the macrocycle from six molecules of the starting butadiene material is rationalized and its structural features are compared with those of other $B(OR)_2$-substituted cyclohexane and benzene ring containing structures. Molecules reside on crystallographic centers of inversion and there are no intermolecular interactions of note in the crystal structure.

Comment

We have recently begun to prepare 2-boron- (De & Welker, 2005) and 2-silicon-substituted 1,3-dienes and to investigate their Diels–Alder/cross-coupling reactions (Pidaparthi *et al.*, 2007). Most recently, we reported the preparation of several halogen-substituted phenylbutadienes and their conversion into boron-substituted dienes (De *et al.*, 2007). To our surprise, when we attempted to grow crystals of a BF_3-substituted diene, *viz.* (I) (3-BF_3-1-phenylbuta-1,3-diene), in ethyl acetate/acetone under atmospheric conditions, a symmetrical structure, (II), derived from six molecules of (I), was isolated and characterized.



We can rationalize the formation of (II) through the reactive units (III) and (IV). The rationalization requires protonolysis of some of the B—C bonds in (I) to generate 1-phenylbuta-1,3-diene. The terminal double bond of one 1-phenylbuta-1,3-diene molecule (labeled '1' in the first scheme below) appears to have been oxidized and to have participated in an electrophilic addition reaction with the internal alkene of a second molecule of 1-phenylbuta-1,3-diene ('2' in the scheme below). The terminal double bond of this second molecule of 1-phenylbuta-1,3-diene has taken part in a Diels–Alder reaction with a boron-substituted diene (depicted as the boronic acid-substituted diene '3' in the scheme below). This rationalization also requires a hydrolysis of the starting dienyl trifluoroborate (I). Organotrifluoroborates are known to hydrolyze easily in mildly basic acetone/water mixtures (Yuen & Hutton, 2005). We suspect that there may still be traces of methoxide present after the preparation of (I), and this catalyzes the hydrolysis required by the production of (II).



The molecular structure of (II) is depicted in Fig. 1 and selected geometric parameters are given in Table 1. Bond lengths and angles in or near the B-atom coordination environment are normal (Table 1). The B1—C3 bonds in (II) are similar to other B—Csp^2 bonds in boronate ester compounds that have been reported recently, for example, 1.555–1.588 Å in (V) (Coghlan *et al.*, 2005), (VI) (Darwish *et al.*, 2004) and (VII) (Pohl *et al.*, 2004). Likewise the B—O and C—O bond lengths here are in the range of those reported for (V)–(VII) (1.35–1.38 and 1.45–1.47 Å, respectively). The O—B—O angles in (II) and (V)–(VII) are all 113 ± 1°, the C—C—B angles are all 119 ± 1° and the C—B—O angles are all 123 ± 1°.

There are no accessible voids in the molecular structure of (II). Steric factors seem to dictate the orientation of the styryl (C15/C16/Ph) group. Some nonbonded contacts are notable, involving the styryl C=C H15 atom on C15 with neighboring HC atoms (H15···H18 = 2.21 Å, H15···H2*A* = 2.65 Å and H15···C30′ = 3.01 Å). Any rotation of the coplanar (to within 0.009 Å; atom C15 is displaced by 0.31 Å) C16/Ph group that

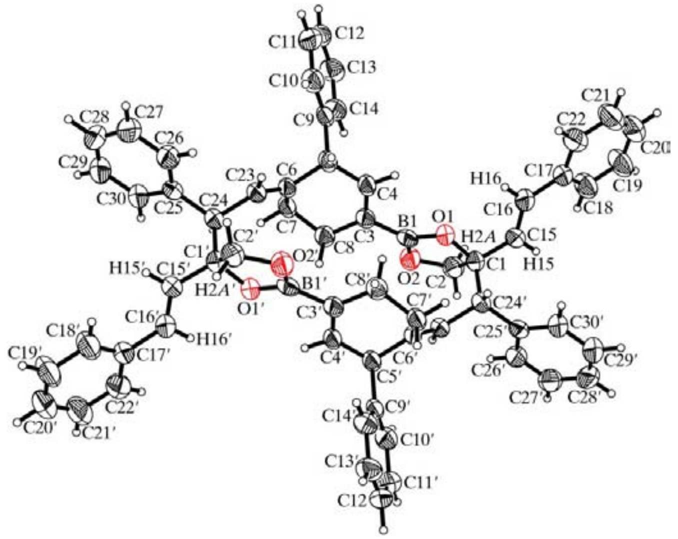
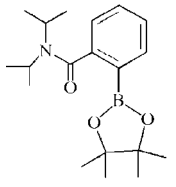
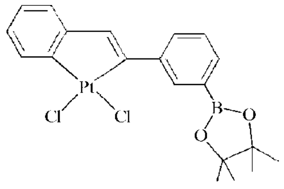


Figure 1
The molecular structure of (II), with non-H atoms depicted with 50% probability displacement ellipsoids. H atoms are represented by arbitrarily small spheres. Atoms labeled with a prime (′) are related to nonprimed atoms by a crystallographic inversion center.

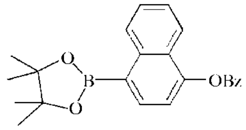
would elongate the 2.39 Å H16···O1 contact would simultaneously shorten the H15···H18, H15···H2*A* and H15···C2 contacts or the H15-to-aromatic ring (intramolecular) and H19-to-aromatic ring (intermolecular) contacts depending upon the direction of rotation. The styryl group is distorted from planarity by 17°, as determined by the angle between normals to the C15/C16/C17 and C17–C22 least-squares mean planes.



(V)



(VI)



(VII)

Experimental

Complex (I) (3-BF$_3$-1-phenylbuta-1,3-diene) was prepared as described previously (De *et al.*, 2007). Crystals of (II) were grown by evaporation of an ethyl acetate/acetone solution of (I) at 298 K with no precautions taken to exclude air or moisture.

Crystal data

$C_{60}H_{54}B_2O_4$	$V = 2289.4$ (9) Å^3
$M_r = 860.65$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.212$ (3) Å	$\mu = 0.08$ mm^{-1}
$b = 6.0975$ (13) Å	$T = 193$ (2) K
$c = 29.028$ (6) Å	0.37 × 0.09 × 0.03 mm
$\beta = 101.764$ (3)°	

Data collection

Bruker APEX CCD area-detector diffractometer	13447 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3260 independent reflections
$T_{\min} = 0.973$, $T_{\max} = 0.998$	1769 reflections with $I > 2\sigma(I)$
	$R_{\rm int} = 0.082$
	$\theta_{\max} = 23.3°$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	298 parameters
$wR(F^2) = 0.107$	H-atom parameters constrained
$S = 0.85$	$\Delta\rho_{\max} = 0.16$ e Å^{-3}
3260 reflections	$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—B1	1.361 (4)	O2—C2	1.455 (3)
O1—C1	1.454 (3)	B1—C3	1.553 (4)
O2—B1	1.369 (4)		
B1—O1—C1	108.2 (2)	O2—B1—C3	123.0 (3)
B1—O2—C2	106.6 (2)	O1—C1—C15	109.7 (2)
O1—B1—O2	113.3 (3)	C4—C3—B1	118.6 (3)
O1—B1—C3	123.7 (3)	C8—C3—B1	119.7 (3)

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

Crystals of (II) diffracted poorly and only 54% of the reflections with $2\theta < 46.5°$ were 'observed' [$I > 2\sigma(I)$]. The final structural model incorporated anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for all H atoms H atoms were included in the structural model as idealized atoms (assuming sp^2- or sp^3-hybridization of the C atoms and C—H bond lengths of 0.95–1.00 Å). $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); 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: GG3111). Services for accessing these data are described at the back of the journal.

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