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Key indicators

Single-crystal X-ray study
T = 160 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.042
wR factor = 0.108
Data-to-parameter ratio = 16.3

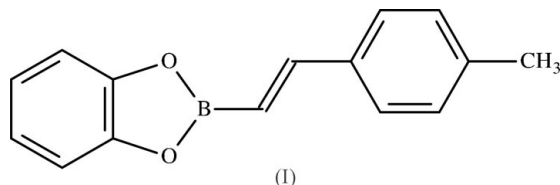
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

(E)-2-[2-(4-Methylphenyl)ethenyl]-1,3,2-benzodioxaborole

Molecules of the title compound, $\text{C}_{15}\text{H}_{13}\text{BO}_2$, are essentially planar with a high degree of conjugation. Pairs of molecules related by inversion symmetry show π -stacking interactions, and the overall packing is a herring-bone pattern. The molecular geometry is similar to that of closely related analogues.

Comment

The title compound, (I), is one of a series of 2-styrylboronate esters prepared in a study of hydroboration reactions of alkynes, with a variety of *para* substituents (Wiesauer, 1997). We have previously reported the structure of the parent compound with no substituent in the *para* position (Clegg *et al.*, 2001). The title compound is the methyl analogue. Structures have also been determined for the SMe (Yuan *et al.*, 1990), OMe (Nguyen *et al.*, 2002) and CF_3 (Clegg *et al.*, 2004) derivatives.



The molecule of the title compound (Fig. 1) is essentially completely planar except for the H atoms of the methyl group, with a high degree of conjugation. The r.m.s. deviation of all non-H atoms from their mean plane is 0.071 Å. All torsion angles for non-H atoms are close to 0 and 180°, the largest corresponding to a twist of about 7° around the B—C bond linking the alkene double bond to the benzodioxaborole (Bcat) group (Table 1). This almost completely planar arrangement is found also for the other derivatives mentioned above.

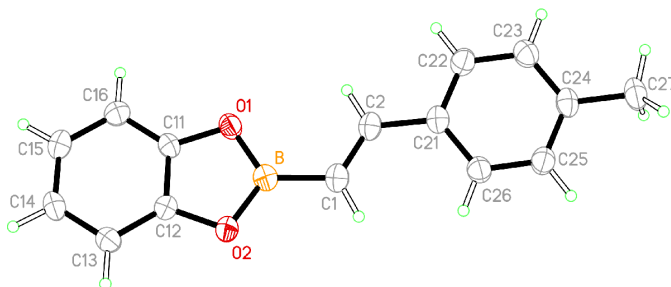
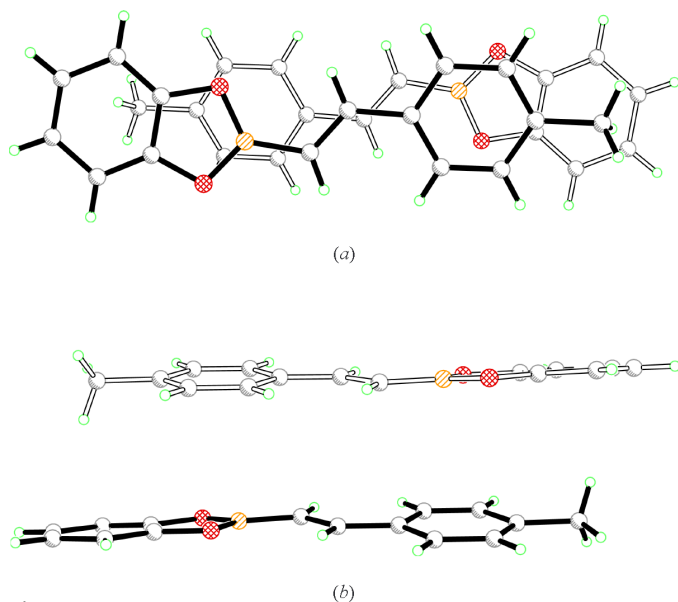
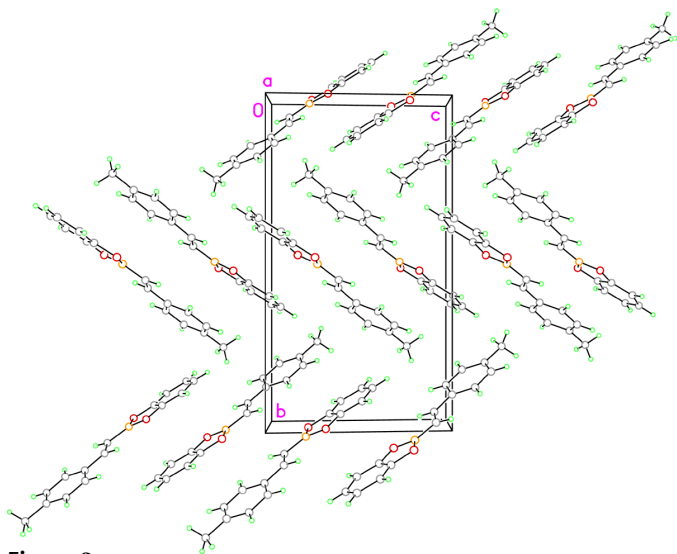


Figure 1
The molecular structure, with atom labels and 50% probability ellipsoids for non-H atoms.

**Figure 2**

The overlap of two parallel molecules related by inversion symmetry, seen (a) from above and (b) from the side. One molecule is shown with filled bonds, and the other with hollow bonds.

**Figure 3**

The crystal packing, viewed along the *a* axis.

Bond lengths and angles are typical of compounds in which Bcat is attached to an alkene double bond; these include not only the derivatives with different *para* substituents, but also the compounds (Bcat)CH=C(*R*)(Cl), where *R* is either Me or Et (Bayer *et al.*, 2002), the symmetrically substituted alkene (Bcat)₂C=C(Bcat)₂ (Gu *et al.*, 2001), two Bcat-substituted cyclopentadienes (Avent *et al.*, 2003), and several alkenes and dialkenes with two or more Bcat groups (Lesley *et al.*, 1996; Clegg *et al.*, 1996). Steric interaction, particularly between Bcat groups, forces some of these molecules to adopt non-planar forms, which has minor effects on the degree of conjugation and hence on some bond lengths.

Centrosymmetric pairs of molecules of the title compound show extensive overlap (Fig. 2) and a separation of about 3.57 Å, indicating some π -stacking interaction. These dimeric

units are further assembled into a herring-bone pattern in the overall crystal packing (Fig. 3), as is commonly found for planar organic molecules.

Experimental

4-Methylphenylethyne (0.565 g, 4.86 mmol) and catecholborane (0.643 g, 5.36 mmol) were heated at 343 K for 2 h in a scintillation vial under a nitrogen atmosphere. The resulting yellow solid was recrystallized twice from *n*-hexane, in a final yield of 67%. Analysis calculated: C 76.32, H 5.55%; found: C 76.78, H 5.41%. Mass spectrum: 236 (*M*⁺, 100%), 221 (12.7%), 209 (6.3%), 143 (7.7%), 118 (27.6%), 117 (29.2%), 116 (26.3%), 115 (29.3%), 105 (10.6%), 91 (27.8%). ¹H NMR (200 MHz): δ 2.36 (*s*, 3H, CH₃), 6.41 (*d*, *J* = 18.5 Hz, 1H, H2), 7.07 (*m*, 2H, two of H13–H16), 7.18 (*d*, *J* = 7.9 Hz, 2H, H23 and H25), 7.24 (*m*, 2H, two of H13–H16), 7.47 (*d*, *J* = 7.9 Hz, 2H, H22 and H26), 7.74 (*d*, *J* = 18.5 Hz, 1H, H1) (using the crystallographic numbering scheme of Fig. 1). ¹³C{¹H} NMR (50 MHz): δ 21.4 (1C, C27), 112.3 (2C, C13 and C16), 122.6 (2C, C14 and C15), 127.4 and 129.5 (2 × 2C, C22, C23, C25, C26), 134.3 (1C, C24), 139.9 (1C, C21), 148.4 (2C, C11 and C12), 152.0 (1C, C2), resonance of C1 too broad to be observed. ¹¹B{¹H} NMR (64 MHz): δ 31.7.

Crystal data

C₁₅H₁₃BO₂
M_r = 236.06
 Monoclinic, *P*2₁/*n*
a = 6.4402 (9) Å
b = 18.455 (3) Å
c = 10.2790 (14) Å
 β = 96.901 (3)°
V = 1212.8 (3) Å³
Z = 4

D_x = 1.293 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5025 reflections
 θ = 2.0–28.4°
 μ = 0.08 mm⁻¹
T = 160 (2) K
 Block, colourless
 0.60 × 0.58 × 0.40 mm

Data collection

Bruker SMART 1K CCD diffractometer
 Thin-slice ω scans
 Absorption correction: none
 6815 measured reflections
 2697 independent reflections

2420 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.029
 θ_{\max} = 28.6°
h = -8 → 6
k = -14 → 24
l = -13 → 13

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.042
wR (*F*²) = 0.108
S = 1.06
 2697 reflections
 165 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.4808P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.0146 (18)

Table 1

Selected geometric parameters (Å, °).

C1–C2	1.3370 (19)	B–O1	1.3911 (17)
C1–B	1.5343 (19)	B–O2	1.3907 (17)
C2–C21	1.4709 (17)		
C2–C1–B	122.11 (12)	O1–B–O2	111.27 (11)
C1–C2–C21	127.71 (12)	B–O1–C11	105.17 (10)
C1–B–O1	123.97 (12)	B–O2–C12	105.16 (10)
C1–B–O2	124.75 (12)		
B–C1–C2–C21	177.86 (12)	C1–C2–C21–C22	-177.24 (13)
C2–C1–B–O1	6.1 (2)	C1–C2–C21–C26	3.2 (2)
C2–C1–B–O2	-172.12 (12)		

H atoms were positioned geometrically and refined with a riding model, including torsional freedom around the C–C bond, with C–

H = 0.95 (aromatic and olefinic) or 0.98 Å (methyl), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ($1.5U_{\text{eq}}$ for methyl groups).

Data collection: *SMART* (Bruker, 2001); cell refinement: local programs; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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