

A 2-styrylboronate ester

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Key indicators

Single-crystal X-ray study

$T = 160\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.037

w R factor = 0.095

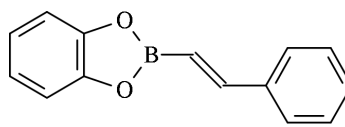
Data-to-parameter ratio = 16.6

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

Molecules of the title compound, (*E*)-2-(2-phenylethenyl)-1,3,2-benzodioxaborole, $\text{C}_{14}\text{H}_{11}\text{BO}_2$, are essentially completely planar with a high degree of conjugation. They pack with a herring-bone pattern in the crystal structure. The compound is synthesized with high regioselectivity by hydroboration of phenylacetylene with catecholborane.

Comment

Alkenylboronic esters and acids are versatile synthetic intermediates (Lane & Kabalka, 1976) for products such as *cis*-alkenes and haloalkenes, and they have important applications in palladium-catalysed cross-coupling reactions and the formation of organometallic compounds (Suzuki, 1985, 1998; Ohe *et al.*, 1988; Larock *et al.*, 1972; Pappo & Collins, 1972). The title compound, (I), was obtained by a hydroboration reaction of phenylacetylene with catecholborane (Brown & Gupta, 1972, 1975; Brown & Chandrasekharan, 1983). The first reported preparation of this compound (Joy *et al.*, 1966) involved treatment of cyclooctatetraene with boron trichloride, followed by reaction of the resulting (*E*)-styrylboron dichloride with catechol. In order to study the influence of electron-donating and electron-withdrawing substituents at the *para*-position of the phenyl ring on the reactivity of the double bond in catalysed hydroborations of styrylboronate esters, a series of *para*-substituted analogues has been prepared (Wiesauer, 1997).



(I)

The molecule (Fig. 1) is essentially completely planar, with an r.m.s. deviation of 0.071 \AA from the least-squares plane through all atoms. All torsion angles are close to 0 and 180° , the largest corresponding to a twist of about 6° about the C2—C21 bond linking the phenyl group to the central alkene unit. Bond lengths and angles are normal, with B—C somewhat shorter and C=C longer than generally observed for single and double bonds, respectively (Allen *et al.*, 1992); together with the planarity of the molecule, they indicate extensive delocalization.

It is instructive to compare the title compound with two closely related styryl bis(boronate) esters, (*Z*)-[(4-NC-C₆H₄)-C(Bcat)=CH(Bcat)] [(II); Bcat is 1,3,2-benzodioxaborole; cat = 1,2-O₂C₆H₄; Clegg *et al.*, 1996] and (*Z*)-[(4-MeO-C₆H₄)-

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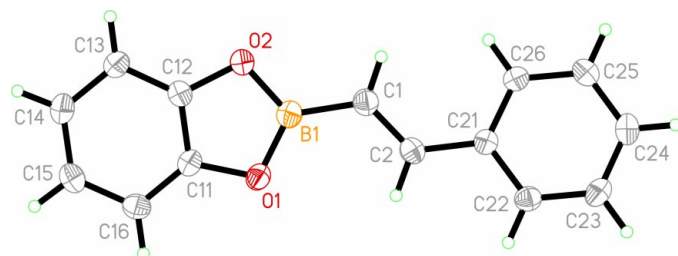


Figure 1
The molecular structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms.

C(Bcat)=CH(Bcat)] [(III); Lesley *et al.*, 1996]. These differ from (I) in having either a π -acceptor or π -donor substituent at the *para*-position of the phenyl ring attached to the α -carbon of the alkene and also a second Bcat moiety at C_α . In (II) and (III), the Bcat at the β -position is approximately coplanar (dihedral angles approximately 9 and 7°, respectively) with the alkene unit, as in (I), whereas the Bcat groups at C_α in (II) and (III) are roughly perpendicular (80 and 84°, respectively) to the alkene plane. In both (II) and (III), the C_β –B distances [1.535 (2) and 1.526 (2) Å] are significantly shorter than their C_α –B distances [1.569 (2) and 1.566 (2) Å] and are consistent with the C_β –B distance in (I) of 1.5321 (17) Å. Presumably this is a reflection of the delocalization present when the Bcat group is coplanar with the alkene and *trans* to the aryl moiety. The C=C distance in (I) [1.3368 (16) Å] is shorter than the corresponding distance in either (II) or (III) [1.349 (2) and 1.348 (2) Å, respectively] and is probably a result of less steric repulsion in the less substituted alkene.

This structure was recently used as a test of crystal structure prediction methods (Lommerse *et al.*, 2000), and proved to be a considerable challenge to the currently available software systems, with only one prediction reasonably close to the experimentally observed structure.

Experimental

In a nitrogen-filled glove-box, phenylacetylene (4.0 g, 39 mmol) and catecholborane (4.7 g, 39 mmol) were heated at 343 K for 2 h in a scintillation vial. On cooling, an orange solid was formed. The pure product was obtained as a colourless crystalline material by recrystallization from diethylether/hexane by solvent diffusion at 238 K, in 70% yield. Analysis calculated: C 75.73, H 4.99%; found: C 75.30, H 4.98%. ^1H NMR (200 MHz): δ 6.48 (*d*, J = 18.5 Hz, 1H, CH=CHB), 7.08 (*m*, 2H, C_6H_4), 7.26 (*m*, 2H, C_6H_4), 7.38 (*m*, 3H, C_6H_5), 7.58 (*m*, 2H, C_6H_5), 7.77 (*d*, J = 18.5 Hz, 1H, CH=CHB). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz): δ 112.3 (2C, C_3 and C_6 of C_6H_4), 122.6 (2C, C_4 and C_5 of C_6H_4), 127.4 (2C, Ph), 128.7 (2C, Ph), 129.6 (1C, C_4 of Ph), 136.9 (1C, C_1 of Ph), 148.3 (2C, C_1 and C_2 of C_6H_4), 152.0 (1C, CH=CHB), resonances of C bonded to B too broad to be observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (64 MHz): δ 31.3. MS: 222 (M^+ , 100), 207 (26), 196 (52), 179 (30), 178 (30), 144 (68), 136 (78), 129 (21), 120 (84), 111 (60), 110 (79), 102 (77), 92 (48%).

Crystal data

$\text{C}_{14}\text{H}_{11}\text{BO}_2$
 M_r = 222.04
Monoclinic, $P2_1/c$
 a = 6.8351 (9) Å
 b = 7.6342 (10) Å
 c = 21.422 (3) Å
 β = 96.447 (3)°
 V = 1110.8 (3) Å³
 Z = 4

D_x = 1.328 Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 5221 reflections
 θ = 2.8–28.6°
 μ = 0.09 mm⁻¹
 T = 160 (2) K
Block, colourless
0.62 × 0.50 × 0.40 mm

Data collection

Bruker SMART 1K CCD diffractometer
 ω rotation with narrow frames
6709 measured reflections
2571 independent reflections
2326 reflections with $I > 2\sigma(I)$

R_{int} = 0.022
 θ_{max} = 28.6°
 h = -9 → 8
 k = -6 → 10
 l = -28 → 28

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.037
 $wR(F^2)$ = 0.095
 S = 1.06
2571 reflections
155 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.3966P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.001
 $\Delta\rho_{\text{max}}$ = 0.26 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.15 e Å⁻³
Extinction correction: *SHELXTL*
Extinction coefficient: 0.021 (2)

Table 1

Selected geometric parameters (Å, °).

C1–C2	1.3368 (16)	B1–O2	1.3909 (15)
C1–B1	1.5321 (17)	B1–O1	1.3910 (15)
C2–C21	1.4692 (15)		
C2–C1–B1	124.72 (11)	O1–B1–C1	125.50 (11)
C1–C2–C21	126.86 (11)	C11–O1–B1	104.82 (9)
O2–B1–O1	111.54 (10)	C12–O2–B1	105.06 (9)
O2–B1–C1	122.96 (11)		
B1–C1–C2–C21	-178.83 (11)	C1–C2–C21–C22	173.52 (11)
C2–C1–B1–O2	179.17 (11)	C1–C2–C21–C26	-6.08 (18)
C2–C1–B1–O1	-1.22 (19)		

The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . H atoms were placed geometrically and refined with a riding model (including free rotation about C–C bonds), and with U_{iso} constrained to be $1.2U_{\text{eq}}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: local programs; data reduction: *SAINTE* (Siemens, 1995); program(s) used to solve and refine structure: *SHELXTL* (Sheldrick, 1994); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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