C12	0.4610 (2)	0.7161 (1)	−0.03500 (2)	0.0504 (7)
C13	0.3834 (2)	0.6750 (1)	0.01930 (2)	0.0446 (6)
C14	0.3286 (2)	0.5931 (1)	−0.03040 (2)	0.0436 (6)
C15	0.3618 (2)	0.5473 (1)	−0.13910 (2)	0.0501 (7)
C16	0.3114 (2)	0.4704 (1)	−0.18420 (3)	0.0582 (8)
C17	0.2238 (3)	0.4362 (1)	−0.12390 (3)	0.0630 (8)
C18	0.1893 (2)	0.4797 (1)	−0.01510 (3)	0.0610 (8)
C19	0.2426 (2)	0.5558 (1)	0.03080 (2)	0.0518 (7)
O20	0.4658 (2)	0.8365 (1)	0.10530 (2)	0.0638 (7)
Cl	0.1966 (1)	0.6067 (1)	0.17020 (1)	0.0808 (3)

Table 2. *Geometric parameters (Å, °)*

C1—C2	1.379 (3)	C11—C12	1.477 (2)
C1—C10	1.410 (3)	C11—O20	1.222 (3)
C2—C3	1.424 (2)	C12—C13	1.313 (3)
C2—C11	1.491 (3)	C13—C14	1.470 (2)
C3—C4	1.360 (3)	C14—C15	1.401 (3)
C4—C5	1.403 (3)	C14—C19	1.396 (3)
C5—C6	1.423 (3)	C15—C16	1.375 (2)
C5—C10	1.427 (2)	C16—C17	1.383 (4)
C6—C7	1.366 (4)	C17—C18	1.389 (4)
C7—C8	1.393 (2)	C18—C19	1.372 (2)
C8—C9	1.369 (3)	C19—Cl	1.751 (2)
C9—C10	1.422 (3)		
C2—C1—C10	121.3 (2)	C2—C11—O20	120.1 (2)
C1—C2—C11	122.7 (2)	C2—C11—C12	118.9 (2)
C1—C2—C3	118.9 (2)	C12—C11—O20	120.9 (2)
C3—C2—C11	118.2 (2)	C11—C12—C13	121.2 (2)
C2—C3—C4	120.8 (2)	C12—C13—C14	126.3 (2)
C3—C4—C5	121.0 (2)	C13—C14—C19	121.8 (2)
C4—C5—C10	119.1 (2)	C13—C14—C15	122.0 (2)
C4—C5—C6	123.4 (2)	C15—C14—C19	116.1 (2)
C6—C5—C10	117.4 (2)	C14—C15—C16	121.9 (2)
C5—C6—C7	121.7 (2)	C15—C16—C17	120.3 (2)
C6—C7—C8	120.1 (2)	C16—C17—C18	119.4 (2)
C7—C8—C9	121.1 (2)	C17—C18—C19	119.5 (2)
C8—C9—C10	119.9 (2)	C14—C19—C18	122.7 (2)
C5—C10—C9	119.7 (2)	C18—C19—Cl	117.1 (2)
C1—C10—C9	121.6 (2)	C14—C19—Cl	120.1 (1)
C1—C10—C5	118.6 (2)		
O20—C11—C12—C13	−21.4 (3)	C11—C12—C13—C14	−175.6 (2)
C2—C11—C12—C13	153.6 (2)		

H atoms were located in ΔF maps.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SDP* (Frenz, 1978). Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976), *PLUTO* (Motherwell & Clegg, 1978). Geometrical calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: AB1316). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(μ_2-Pinacolato-*O*,*O*′)-bis(pinacolato-*O*,*O*′)-diboron

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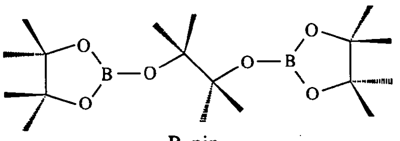
Abstract

The title compound, 2,2′-(2,3-dimethyl-2,3-butanediyldioxy)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane, $C_{18}H_{36}B_2O_6$, B_2pin_3, has two trigonal planar B atoms, each chelated by one pinacolato group, linked by a third pinacolate. The molecule is centrosymmetric, with an exactly *anti* conformation for the bridging pinacolate, and the two Bpin five-membered rings have a twist conformation with torsion angle O—C—C—O =

−27.39 (13)°. The B—O bonds to the bridging pinacolate [1.353 (2) Å] are slightly shorter than the chelate B—O bonds [1.367 (2) and 1.373 (2) Å].

Comment

The compound (pin)B(μ-pin)B(pin), B_2pin_3 (pin = $OCMe_2CMe_2O$), was observed as an impurity in the reaction of $B_2(NMe_2)_4$ with pinacol and HCl, a procedure used for the preparation of B_2pin_2, bis(pinacolato-*O*,*O*′)diboron (Nöth, 1984). The compound B_2pin_2 is of interest with regard to the recently developed metal-catalysed diboration of alkynes (Ishiyama, Matsuda, Miyaura & Suzuki, 1993; Iverson & Smith, 1995, 1996; Ishiyama *et al.*, 1996; Lesley *et al.*, 1996) and alkenes (Baker, Nguyen, Marder & Westcott, 1995) and the palladium-catalysed synthesis of (aryl)B(pin) compounds (Ishiyama, Murata & Miyaura, 1995). It appears that B_2pin_3 is also formed in reactions of pinacol with BH_3.thf (Lesley *et al.*, 1996) or BCl_3 (Herberich & Fischer, 1996). Although studies of the reactivity of B_2pin_3 with metal complexes have not yet been carried out, the recently observed reactions (Lesley *et al.*, 1996) of the analogous compound B_2cat_3 (cat = 1,2-$O_2C_6H_4$, catecholato-*O*,*O*′) with [$(PPh_3)_2Pt(\eta$-$C_2H_4)$], a catalyst precursor for alkyne diboration, suggest that due care should be taken to remove any B_2pin_3 impurity that may exist in batches of B_2pin_2 to be used for diboration reactions.



B_2pin_3

Initial attempts to determine the crystal structure of B_2pin_3 at room temperature were unsatisfactory, with a rapid decline in intensity at higher Bragg angles and with very high displacement parameters, especially for methyl groups, but the structure is qualitatively similar to that determined at low temperature and reported here. The molecule is centrosymmetric in the solid state. Each of the two B atoms is chelated by one pinacolato group and the two B atoms are linked by a third pinacolate. The boron displays characteristic trigonal planar coordination, with a distortion of the angles from 120° because of the chelate ring formation [O1—B1—O2 reduced to 113.56 (12)°] and steric hindrance by the methyl groups of the bridging pinacolate [O1—B1—O3 expanded to 126.79 (12)°]; B1 lies essentially in the plane of its three bonded O atoms [deviation 0.003 (2) Å].

The BO_2C_2 five-membered boronate ester rings have a twist conformation, with one C atom on one side [by 0.244 (2) Å] and one on the other side [by 0.214 (2) Å] of the BO_2 plane, and with a O—C—C—O torsion angle of −27.39 (13)°. A very similar conformation has been found in other Bpin units, with torsion angles (ignoring sign) of 28.68 (12) and 29.27 (12)° (Clegg, Scott, Lesley, Marder & Norman, 1996; this paper discusses a wide range of *X*pin ring conformations), 26.9 (2) and 29.5 (2)° (Deloux, Skrzypczak-Jankun, Cheesman & Srebnik, 1994), and 33.0 (4)° (Seeger & Heller, 1985), but almost planar rings occur in B_2pin_2, with a torsion angle of only 1.6° (Nöth, 1984). The bridging pinacolate in B_2pin_3 has an *anti* conformation with an exactly 180° O—C—C—O torsion angle. The difference in the conformation of the chelating and bridging units does not significantly affect the C—O and C—C bond lengths and the angles at the C atoms. The B—O bonds to the bridging pinacolate are slightly shorter than those within the chelate rings. A similar but larger difference [*ca* 0.030 (4) Å] was found in the structure of B_2cat_3 (Westcott, Blom, Marder, Baker & Calabrese, 1993). The main difference between the structures of B_2pin_3 and B_2cat_3 is the enforced *cis* geometry of the bridging catecholate in contrast to the *anti* conformation of the bridging pinacolate, resulting in near-orthogonality of the two BO_3 planes in the catecholate compound because of steric interactions, while these two are almost coplanar in the pinacolate compound, for which the central $B_2O_6C_2$ core is close to planar [r.m.s. deviation 0.081 Å].

The crystal structure of B_2pin_3 has no notably short intermolecular contacts.

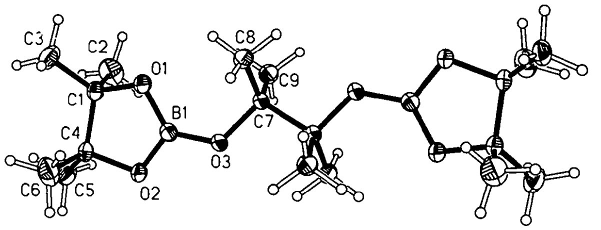


Fig. 1. The molecular structure with atom labels and 50% probability ellipsoids for non-H atoms.

Experimental

Crystals of B_2pin_3 were first obtained from treatment of B_2pin_2 with a large excess of 4-picoline, and a preliminary room-temperature structure was determined from this sample. The crystals used in the present low-temperature study were obtained as a by-product from a preparation of B_2pin_2, and were grown by slow evaporation of solvent from a solution in diethyl ether/hexanes. The compound was characterized by ^1H (δ 1.36, *s*, 12H; 1.23, *s*, 24H), $^{13}C\{^1H\}$ (δ 81.85, 4C; 79.40, 2C; 24.07, 8C; 22.65, 4C) and $^{11}B\{^1H\}$ (δ 21.4) NMR spectroscopy in $CDCl_3$ solution at room temperature on a Bruker AM200 spectrometer.

Crystal data

$C_{18}H_{36}B_2O_6$
$M_r = 370.09$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/c$
$a = 10.6038\,(11)$ Å
$b = 10.4252\,(11)$ Å
$c = 10.8255\,(12)$ Å
$\beta = 118.675\,(2)°$
$V = 1050.0\,(2)$ Å^3
$Z = 2$
$D_x = 1.171$ Mg m^{-3}
D_m not measured

Cell parameters from 3946 reflections
$\theta = 2.19–28.37°$
$\mu = 0.083$ mm^{-1}
$T = 160\,(2)$ K
Block
0.24 × 0.18 × 0.12 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: none
6359 measured reflections
2417 independent reflections

2048 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0429$
$\theta_{\rm max} = 28.60°$
$h = -14 \rightarrow 10$
$k = -11 \rightarrow 14$
$l = -11 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0471$
$wR(F^2) = 0.1064$
$S = 1.133$
2414 reflections
125 parameters
H atoms riding (see text)
$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 0.5007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.304$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.178$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.0124 (15)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
B1	0.2305 (2)	0.29306 (15)	0.1218 (2)	0.0222 (3)
O1	0.16843 (10)	0.17695 (9)	0.11710 (11)	0.0269 (2)
O2	0.37523 (10)	0.28542 (9)	0.16571 (11)	0.0282 (3)
C1	0.27523 (14)	0.07899 (13)	0.13726 (15)	0.0250 (3)
C2	0.2402 (2)	0.0331 (2)	−0.0090 (2)	0.0442 (4)
C3	0.2606 (2)	−0.0302 (2)	0.2216 (2)	0.0442 (4)
C4	0.41931 (14)	0.15429 (13)	0.21466 (15)	0.0245 (3)
C5	0.5331 (2)	0.1133 (2)	0.1762 (2)	0.0368 (4)
C6	0.4824 (2)	0.1558 (2)	0.3736 (2)	0.0429 (4)
O3	0.16445 (9)	0.40863 (9)	0.08914 (10)	0.0236 (2)
C7	0.01009 (13)	0.42569 (12)	0.00416 (14)	0.0199 (3)
C8	−0.06864 (15)	0.36220 (14)	0.0744 (2)	0.0260 (3)
C9	−0.03698 (15)	0.36709 (14)	−0.14068 (14)	0.0259 (3)

Table 2. *Selected geometric parameters (Å, °)*

B1—O3	1.353 (2)	O2—C4	1.460 (2)
B1—O1	1.367 (2)	C1—C4	1.557 (2)
B1—O2	1.373 (2)	O3—C7	1.4532 (15)
O1—C1	1.461 (2)	C7—C7$^{\rm i}$	1.561 (3)
O3—B1—O1	126.79 (12)	O1—C1—C4	102.59 (10)
O3—B1—O2	119.65 (13)	O2—C4—C1	102.49 (10)
O1—B1—O2	113.56 (12)	B1—O3—C7	124.01 (10)
B1—O1—C1	106.75 (10)	O3—C7—C7$^{\rm i}$	103.86 (12)
B1—O2—C4	106.85 (11)		

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

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. The crystal-to-detector distance was 4.941 cm. Coverage of the unique set is virtually complete to at least 26.4° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections.

H atoms were placed geometrically and refined with a riding model including free rotation about C—C bonds, and with $U_{\rm iso}$ constrained to be 1.5 times $U_{\rm eq}$ of the carrier C atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). 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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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1397). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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