Three chiral vinyldioxazaborocanes

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The structures of three chiral vinyldioxazaborocanes are reported, namely (2E)- and (2Z)-6-benzyl-2-buten-2-yl-1,3,6,2-dioxazaborocane, $C_{27}H_{30}BNO_2$, (II) and (III), respectively, and (2Z)-2-buten-2-yl-6-isobutyl-1,3,6,2-dioxazaborocane, $C_{24}H_{32}BNO_2$, (IV). These compounds may be useful in asymmetric reactions. In the structures reported here, the N—B donor–acceptor bond is longer than in any previously reported analogous compounds.

Comment

Enantiomerically pure organoboron compounds are versatile synthetic intermediates that can be transformed into numerous functionalities without loss of optical purity (Brown & Singaram, 1987, 1988). Different methods for their synthesis therefore continue to be developed. Vinyl boronates containing a chiral auxiliary *via* attachment to the boron group are potentially useful starting materials for the production of these compounds. Such vinyl boronates have been used to control the absolute stereochemistry of cyclopropanations (Imai *et al.*, 1990; Pietruszka & Widenmayer, 1997), Diels–Alder reactions (Bonk & Avery, 1997) and dipolar cyclo-additions (Marsden *et al.*, 1998, 2000). We recently reported a novel method for the synthesis of chiral organoboron compounds *via* asymmetric hydrogenation of vinyloxazaborolidines under ambient conditions (Gamsey *et al.*, 2005). However, although relatively easy to prepare, these chiral vinyloxazaborolidines have a few drawbacks in terms of their utility in asymmetric reactions. For example, apart from being hydrolytically unstable, the prochiral olefin is somewhat distal from the chiral ligand, due to the planarity of the boronate group. We anticipated that both these problems could be ameliorated through the use of vinyldioxazaborocanes. Since dioxazaborocanes are stable to air and water, their preparation, isolation, storage and handling are straightforward. Most importantly, the tetrahedral geometry of the B atom should exert more sterochemical influence in asymmetric reactions (Seebach *et al.*, 1996). Marsden *et al.* (2000) have synthesized

vinyldioxazaborocanes from *trans*-disubstituted alkenyl-boronic acids. We report here the syntheses and X-ray structures of three new vinyldioxazaborocanes, (II)–(IV), derived from α-substituted alkenylboronic acids. Diolamines (Ia) and (Ib) were synthesized from either benzylamine or isobutyl-amine and two equivalents of (R)-(+)-styrene oxide, according to previously published procedures (Trost *et al.*, 1992; Sundararajan & Manickam, 1997).
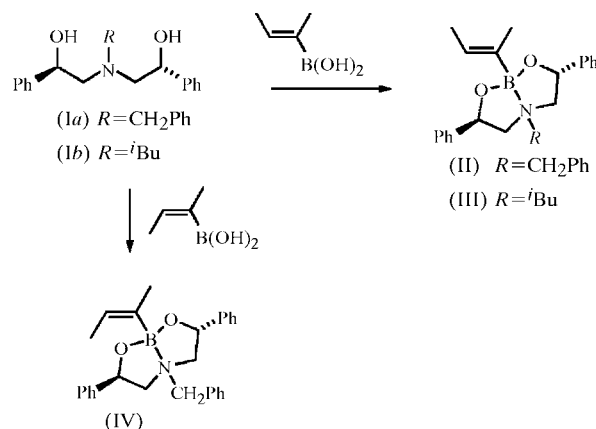
The compounds in this report were synthesized as shown in the scheme. The structural results confirm that they are chiral. Compounds (II), (III) and (IV) all crystallize with no molecules of solvation and no unusual intermolecular contacts. Compound (IV) has two molecules in the asymmetric unit which differ slightly in the dihedral angles of the phenyl rings. In addition, the two N—B distances differ by five s.u.'s for no apparent reason.

In all three compounds, each of the dioxazaborocane rings is in a chair-like conformation. The most surprising structural feature is the length of the N—B donor–acceptor bonds, which
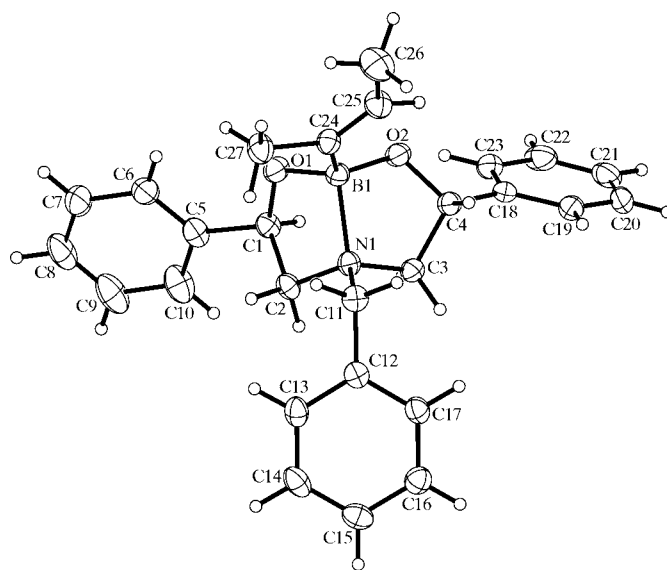

Figure 1
A drawing of the structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

are significantly longer than those in the previously reported structures with the same dioxazaborocane ring size and similar derivatization (Rettig & Trotter, 1975; Caron & Hawkins, 1998; Doidge-Harrison *et al.*, 1998; Thadani *et al.*, 2001*a*,*b*, 2002; Sopková-de Oliveira Santos *et al.*, 2004). In this set of eight related molecules, the average N—B bond length is 1.667 [11] Å, whereas it is 1.778 [8] Å in the four independent molecules in this study (the average deviations from the mean are given in square brackets).

In seven of the previous structures, the N atom is bonded to H, and in the eighth it is bonded to methyl. It has already been noted (Sopková-de Oliveira Santos *et al.*, 2004) that the N—B bond is lengthened [1.696 (7) Å] in the methyl derivative.
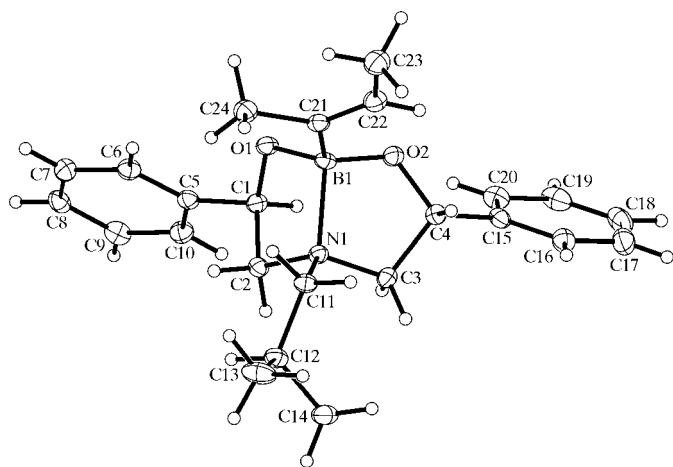
However, the lengthening is far greater in (II), (III) and (IV), in which the N atom is bonded to either benzyl or isobutyl groups. Thus, the bulkier substituent appears to have an impact on the basicity of the N atom. In fact, an examination of the degree of pyramidalization of both the N and B atoms in this study shows that they are flattened relative to the other eight similar molecules. Using the program *POAV1* (Haddon, 1999), the pyramidalization angles at the N and B atoms in this study have averages of 16.4 and 13.6°, respectively (the angle for sp^2 is 0° and for sp^3 is 19.5°). Average values for the other eight structures are 17.4 and 15.6° for N and B, respectively. These results suggest a loss of p character in the lone-pair orbital used by nitrogen and a weaker dative bond, in agreement with the increased nitrogen bond length.

Figure 2
A drawing of the structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
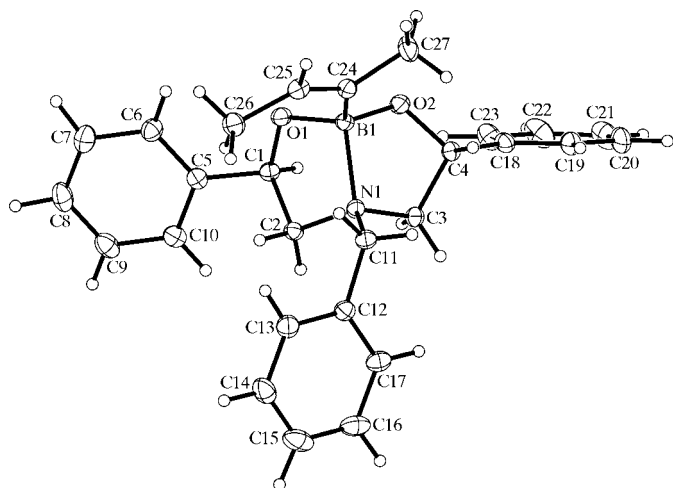

Figure 3
A drawing of the structure of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only one of the two molecules is shown; the second molecule shows no distinctive differences in overall geometry.

Experimental

For the preparation of each of compounds (II)–(IV), the appropriate boronic acid (2.7 mmol) was added to a solution of either diolamine (I*a*) or (I*b*) (2.8 mmol) in dry diethyl ether (10 ml). CaH$_2$ (6 mmol) was added and the reaction was refluxed for 12 h. The CaH$_2$ was filtered off and the ether was removed under reduced pressure, affording the dioxazaborocane as a white foam. Single crystals of compounds (II) and (IV) suitable for X-ray analysis were obtained by dissolving the compounds in a minimal amount of warm diethyl ether and allowing the flask to stand at room temperature overnight. Single crystals of compound (III) suitable for X-ray analysis were obtained similarly, but CDCl$_3$–diethyl ether (1:1) was used as the recrystallization solvent.

Compound (II)

Crystal data

$C_{27}H_{30}BNO_2$	$Z = 4$
$M_r = 411.33$	$D_x = 1.175$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 12.0141$ (4) Å	$\mu = 0.07$ mm^{-1}
$b = 12.3388$ (5) Å	$T = 90$ (2) K
$c = 15.6913$ (6) Å	Needle, colorless
$V = 2326.07$ (15) Å^3	$0.40 \times 0.04 \times 0.03$ mm

Data collection

Bruker SMART APEX-II diffractometer	32109 measured reflections
ω scans	3885 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	3493 reflections with $I > 2\sigma(I)$
$T_{min} = 0.990$, $T_{max} = 0.998$	$R_{int} = 0.030$
	$\theta_{max} = 30.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 0.2206P]$
$wR(F^2) = 0.099$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3885 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
282 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected bond lengths (Å) for (II).

O1—B1	1.4469 (18)	N1—C11	1.5034 (18)
O2—B1	1.4490 (19)	N1—B1	1.7836 (19)
N1—C2	1.4906 (17)	C24—B1	1.600 (2)
N1—C3	1.4928 (18)		

Compound (III)

Crystal data

$C_{24}H_{32}BNO_2$	$Z = 4$
$M_r = 377.32$	$D_x = 1.173$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 10.5916 (14)$ Å	$\mu = 0.07$ mm^{-1}
$b = 11.3683 (15)$ Å	$T = 90 (2)$ K
$c = 17.747 (2)$ Å	Block, colorless
$V = 2136.8 (5)$ Å^3	$0.32 \times 0.16 \times 0.13$ mm

Data collection

Bruker SMART APEX-II diffractometer	23473 measured reflections
ω scans	2773 independent reflections
	2576 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ($SADABS$; Sheldrick, 2004)	$R_{int} = 0.028$
$T_{min} = 0.988$, $T_{max} = 0.993$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 0.4322P]$
$wR(F^2) = 0.081$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} < 0.001$
2773 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
256 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H-atom parameters constrained	

Table 2
Selected bond lengths (Å) for (III).

O1—B1	1.446 (2)	N1—C11	1.5010 (19)
O2—B1	1.450 (2)	N1—B1	1.788 (2)
N1—C2	1.4885 (19)	C21—B1	1.604 (2)
N1—C3	1.498 (2)		

Compound (IV)

Crystal data

$C_{27}H_{30}BNO_2$	$D_x = 1.224$ Mg m^{-3}
$M_r = 411.33$	$D_m = 0$ Mg m^{-3}
Monoclinic, $P2_1$	D_m measured by not measured
$a = 9.8152 (4)$ Å	Mo $K\alpha$ radiation
$b = 22.6374 (9)$ Å	$\mu = 0.08$ mm^{-1}
$c = 10.0469 (4)$ Å	$T = 90 (2)$ K
$\beta = 90.449 (2)°$	Block, colorless
$V = 2232.26 (16)$ Å^3	$0.34 \times 0.27 \times 0.17$ mm
$Z = 4$	

Data collection

Bruker SMART 1000 diffractometer	25742 measured reflections
φ and ω scans	6663 independent reflections
	6078 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ($SADABS$; Sheldrick, 2004)	$R_{int} = 0.029$
$T_{min} = 0.982$, $T_{max} = 0.990$	$\theta_{max} = 30.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 0.2168P]$
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.002$
6663 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
799 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
All H-atom parameters refined	

For (II) and (III), H atoms were treated as riding, with fixed C—H distances in the range 0.95–1.00 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$. For (IV), H atoms were refined freely with the use of isotropic displacement parameters, yielding a range of C—H distances of 0.93 (3)–

Table 3
Selected bond lengths (Å) for (IV).

B1—O1	1.441 (2)	B31—O31	1.445 (2)
B1—O2	1.460 (2)	B31—O32	1.462 (2)
B1—C24	1.610 (2)	B31—C54	1.614 (2)
B1—N1	1.775 (2)	B31—N31	1.764 (2)
N1—C2	1.493 (2)	N31—C32	1.489 (2)
N1—C3	1.498 (2)	N31—C33	1.498 (2)
N1—C11	1.508 (2)	N31—C41	1.510 (2)

1.03 (3) Å. Friedel pairs were merged for the final refinement in all three structures. The absolute configurations of all three compounds were assumed from the synthesis.

Data collection: $APEX2$ (Bruker, 2004) for (II) and (III); $SMART$ (Bruker, 2003) for (IV). Cell refinement: $SAINT$ (Bruker, 2004) for (II) and (III); $SAINT$ (Bruker, 2003) for (IV). Data reduction: $SAINT$ (Bruker, 2004) for (II) and (III); $SAINT$ (Bruker, 2003) for (IV). For all compounds, program(s) used to solve structure: $SHELXS97$ (Sheldrick, 1997); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 1997); molecular graphics: XP in $SHELXTL$ (Sheldrick, 1994); software used to prepare material for publication: $SHELXL97$.

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