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A 1,3,2-oxazaborolidine dimer derived from (*S*)-*α*,*α*-diphenylprolinol

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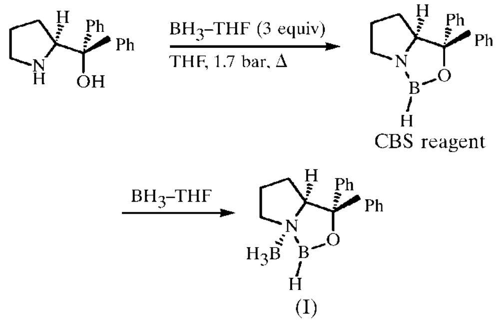
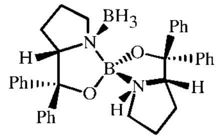
The reaction of (*S*)-α,α-diphenylprolinol with an excess of borane–tetrahydrofuran complex yields a stable crystalline material with the composition $C_{34}H_{38}B_2N_2O_2$, which features a borane adduct of a spirocyclic structure with two oxazaborolidine rings joined by a central tetrahedral B atom. This dimeric oxazaborolidine complex, *viz.* 3,3,3′,3′-tetraphenyl-1,1′-spirobi(3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*c*][1,3,2]oxazaborole)–7-borane, is the dominant product under various reaction conditions; its crystal structure is consistent with ^{11}B, ^{1}H and ^{13}C NMR and IR analyses.

Comment

Oxazaborolidines derived from chiral β-amino alcohols are regarded as important catalysts for the enantioselective reduction of C═O and C═N bonds (Corey & Helal, 1998; Deloux & Srebnik, 1993; Singh, 1992; Quallich *et al.*, 1996; Puigjaner *et al.*, 1999), and for other enantioselective organic transformations (Wallbaum & Martens, 1992; Joshi *et al.*, 1989). The 1,3,2-oxazaborolidine, (I), derived from the (*S*)-α,α-diphenyl prolinol known as the Corey, Bakshi and Shibata (CBS) catalyst is the most efficient for the reduction of aromatic ketones (Corey *et al.*, 1987; Mathre *et al.*, 1991). The CBS reagent is reported to be extremely sensitive to air and moisture and difficult to purify. Therefore, it is usually prepared *in situ*, without characterization, and used as a reagent or catalyst in many enantioselective transformations (Corey & Helal, 1998; Deloux & Srebnik, 1993; Singh, 1992; Yadav *et al.*, 2000; Garrett *et al.*, 2002). Pure CBS oxazaborolidine was isolated and characterized by Corey and co-workers (Corey *et al.*, 1987), who prepared the reagent by refluxing the corresponding chiral amino alcohol with an excess of borane–tetrahydrofuran (THF) complex under a closed argon–borane atmosphere system. However, ^{11}B NMR and FT–IR spectroscopic analyses indicated the presence of an additional unidentified dimeric species [$\delta_{\rm THF(0.17\,\it M)}$ = 7.6 p.p.m., *d*, $J_{\rm BH}$ = 130 Hz, $\nu_{\rm BH,THF(0.1\,\it M)}$ = 2413 cm^{-1}]. On the other hand, Mathre and co-workers (Mathre *et al.*, 1993) have attempted to prepare the CBS reagent by the same method without success. Moreover, they did not observe the dimer reported by Corey and co-workers, but instead proposed a different dimeric complex, (II). In addition, further dimeric forms or aggregates for different oxazaborolidines have been obtained (Lang *et al.*, 1997) and studied by quantum molecular modelling calculations (Nevalainen, 1994). Thus, further experimental study is needed to corroborate the structure of the possible dimeric forms of the CBS reagent to establish the true nature of the catalyst. In an effort to prepare the CBS reagent for a subsequent reaction, we isolated a remarkably stable crystalline sample (m.p. 477–483 K), which was identified by ^{11}B NMR (δ, CDCl$_3$, 10.5 and −14.4 p.p.m) and FT–IR ($\nu_{\rm BH}$ = 2321 cm^{-1}) as complex (II) (Mathre *et al.*, 1993). The structure of this complex has now been confirmed by single-crystal X-ray diffraction analysis. The structure shows very interesting features and is presented in this paper.



(I)



(II)

The bond lengths in the oxazaborolidine rings of (II) (Table 1) are mostly in accord with interatomic distances in similar compounds. However, the B—N distances are shorter than expected. The B1—N1 distance [1.590 (4) Å] is the second shortest reported B—N distance in structurally characterized oxazaborolidines. The only shorter distance [1.486 or 1.489 Å] was reported for (*S*)-diphenylprolinolmethylborolidine–borane (Corey *et al.*, 1992; Mathre *et al.*, 1993). This is also the only oxazaborolidine-containing *N*-boryl group, and thus it is suitable for comparison with the title compound, (II). Oxazaborolidines with H instead of a boryl group have significantly longer B—N distances (1.626–1.660 Å) (Rettig & Trotter, 1977; Mathre *et al.*, 1991). The B1—N2 distance in (II) [1.636 (4) Å] fits into this range well.

On the other hand, B—NH distances from all three known structures are shorter than the B—N distances for compounds with monosubstituted N in non-conjugated oxazaborolidine rings, which span the range 1.643–1.693 Å (Trujillo *et al.*, 1998; Hopfl *et al.*, 1997, 1998; Rico *et al.*, 1999). If no substituent is

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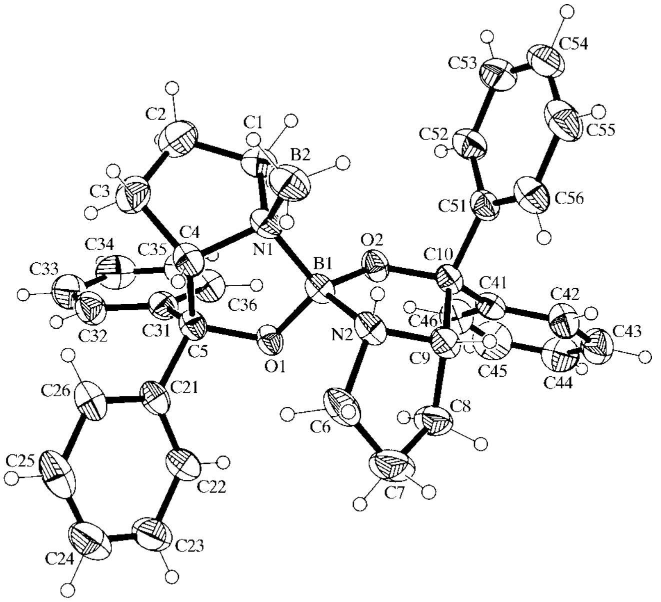

Figure 1
A view of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

located on the N atom, typical B—N distances are longer (1.607–1.658 Å) (Low *et al.*, 2000; Trujillo *et al.*, 1998; Rettig & Trotter, 1973, 1974, 1976; Hopfl *et al.*, 1997; Cynkier & Hope, 1978; Gravelle & Bott, 1995; Cox & Wardell, 2002). If two substituents are present, the range is 1.670–1.744 Å (Rettig & Trotter, 1983; Huskens *et al.*, 1998; Hopfl *et al.*, 1997, 1998; Ebeling *et al.*, 1989; Short & Masamune, 1989).

The B—O distance in oxazaborolidine seems to be less sensitive to the character of the N or B atom in the ring. Typical B—O distances span the range of 1.450–1.547 Å, with the exception of (*S*)-diphenylprolinolmethylborilidine–borane (1.349 or 1.335 Å) (Corey *et al.*, 1992; Mathre *et al.*, 1993). Both B—O distances in (II) are identical to within experimental error [1.433 (3) and 1.436 (3) Å] and apparently not affected by the different N-atom environment. The N—B—O angles seem to be sensitive to the oxazaborolidine substituents. While compounds with a non-conjugated oxazaborilidine ring have N—B—O angles in the range 95.9–100.7° and do not show dependence on N or B substituents, pyrrolooxazaboroles with H on N show smaller N—B—O angles (98.5–99.8°) than (*S*)-diphenylprolinolmethylborilidine–borane (110.3 or 111.3°). Values for the N—B—O angles of (II) are not sensitive towards N-atom substituents [102.41 (19) and 104.25 (19)°] and are similar to those found in other oxazaborolidine dimers (Lang *et al.*, 1997; Kim *et al.*, 1999; Chi *et al.*, 1999, 2001). The observed B2—N1 distance of 1.618 (3) Å falls into the range of typical B—N distances (1.591–1.649 Å).

Both oxazaborolidine rings in (II) are distorted from planarity, as expected, and form a dihedral angle of 87.81 (12)°. Molecules of (II) do not show any intra- or intermolecular hydrogen bonds. The closest intermolecular contacts were found between H atoms (2.23–2.47 Å). The closest contacts between H and non-H atoms were found in the range 2.84–2.99 Å.

Experimental

For the preparation of (II), a solution of (*S*)-(−)-α,α-diphenyl-2-pyrrolidinemethanol (3.95 mmol, 1.00 g) in dry tetrahydrofuran (THF; 10 ml) was added slowly (20 min) to a stirred solution of BH_3–THF (10.3 ml, 1.0 *M*, 10.3 mmol) at ambient temperature. The colourless mixture was stirred overnight at 298 K and concentrated under vacuum leaving a white powder, which was then heated gradually from 313 to 403–408 K in an oil bath for 45 min. After dissolving the white solid residue in dry THF (15 ml) and cooling the mixture to 195 K, a solution of *n*-BuLi (1.56 ml, 2.85 *M* in hexane, 4.46 mmol) was added dropwise. The blue mixture was stirred overnight at 298 K. After a mild acid hydrolysis with solid ammonium chloride at 273 K for 3 h, the solid was removed using a Schlenk filter and the filtered solution was concentrated under vacuum. The white solid was heated in an oven at 453 K and 0.8 mmHg (1 mmHg = 133.322 Pa) and then the solid in the distillation flask was partially dissolved in dry CH_2Cl_2. After evaporation of the solvent, a colourless powder containing a hard crystalline material appropriate for X-ray diffraction study was obtained.

Crystal data

$C_{34}H_{38}B_2N_2O_2$
$M_r = 528.28$
Monoclinic, $P2_1$
$a = 11.455$ (2) Å
$b = 9.1008$ (17) Å
$c = 14.779$ (3) Å
$\beta = 106.993$ (3)°
$V = 1473.4$ (5) Å^3
$Z = 2$
$D_x = 1.191$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 911 reflections
$\theta = 2.7$–27.9°
$\mu = 0.07$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.40 × 0.31 × 0.12 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*XPREP*; Sheldrick, 1990)
$T_{\min} = 0.974$, $T_{\max} = 0.991$
10 262 measured reflections
3774 independent reflections

2974 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 28.1°$
$h = -15 \rightarrow 12$
$k = -12 \rightarrow 10$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.126$
$S = 1.10$
3774 reflections
362 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.1498P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

B1—O2	1.433 (3)	O2—C10	1.420 (3)
B1—O1	1.436 (3)	N1—C4	1.501 (3)
B1—N1	1.590 (4)	N2—C9	1.499 (3)
B1—N2	1.636 (4)	C4—C5	1.571 (3)
B2—N1	1.618 (3)	C9—C10	1.543 (4)
O1—C5	1.426 (3)		
O2—B1—O1	111.84 (19)	O1—B1—N2	111.8 (2)
O2—B1—N1	116.4 (2)	N1—B1—N2	110.32 (18)
O1—B1—N1	104.25 (19)	C4—N1—B1	104.39 (19)
O2—B1—N2	102.41 (19)	C9—N2—B1	103.60 (18)

Compound (II) is chiral, but its absolute configuration could not be determined because of a lack of heavier atoms in the molecule. Friedel pairs were merged before the final refinement. However, the absolute configurations of atoms C4 and C9 can be assigned as *S*, based on the (*S*)-α,α-diphenylprolinol used as a starting material. The H atom on nitrogen was located from a difference map, fixed at an N—H distance of 0.89 Å, refined and then fixed. Other H atoms were positioned geometrically and treated as riding, with C—H distances in the range 0.93–0.98 Å and B—H distances of 0.96 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}({\rm B})$.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1998); software used to prepare material for publication: *SHELXTL-NT*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1462). Services for accessing these data are described at the back of the journal.

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