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3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline

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Key indicators

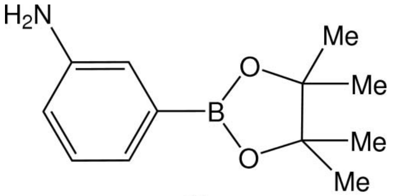
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.122
Data-to-parameter ratio = 16.8

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

In the title compound, $C_{12}H_{18}BNO_2$, the amino group is less pyramidal than in aniline, only one of its H atoms forming a strong hydrogen bond.

Comment

In the course of our studies (Giles *et al.*, 2003; Coghlan *et al.*, 2005) into the potential catalytic utility of bifunctional compounds (Rowlands, 2001) containing both a nitrogen-based Lewis base and a boron-based Lewis acid, we turned to the title compound, (I), as a protected precursor for the synthesis of phenylguanidine-2-boronic acid derivatives, which we were interested in as bifunctional catalysts. Unfortunately, synthesis of such compounds proved unsuccessful, producing a complex mixture of products.



(I)

Compound (I) was prepared by a modified version of the procedure reported by Vogels *et al.* (1999), who synthesized it *en route* to various platinum complexes and imines (Vogels *et al.*, 2001; King *et al.*, 2002).

The asymmetric unit contains one molecule. The B atom has planar-trigonal coordination; the coordination plane is inclined by 10.4 (2)° to the benzene ring plane. The borolane ring adopts a twist conformation, the C7 and C8 atoms deviating from the BO_2 plane by 0.20 (2) and 0.27 (2) Å in opposite directions, with two equatorial (C9 and C11) and two axial (C10 and C12) methyl substituents. The amino group forms one strong intermolecular hydrogen bond (Table 2). The remaining amino hydrogen atom, H2N, points towards the $p\pi$ orbital of the benzene C4 atom of another molecule. The H2N$\cdots$C4^{ii} distance [2.61 (2) Å, corrected for the idealized N—H bond length of 1.01 Å; symmetry code: (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$], which is considerably shorter than the sum of van der Waals radii of 2.88 Å (Rowland & Taylor, 1996) and the N—H$\cdots$C angle of 167 (2)° suggest that this contact is a weak hydrogen bond.

The N atom in (I) has a less pyramidal geometry than in unsubstituted aniline. The dihedral angle between the benzene ring and the NH_2 group (so-called 'inversion angle'), which equals 37–38° in both solid (Fukuyo *et al.*, 1982) and gaseous (Lister *et al.*, 1974) aniline, is reduced to 16 (2)° in (I). The

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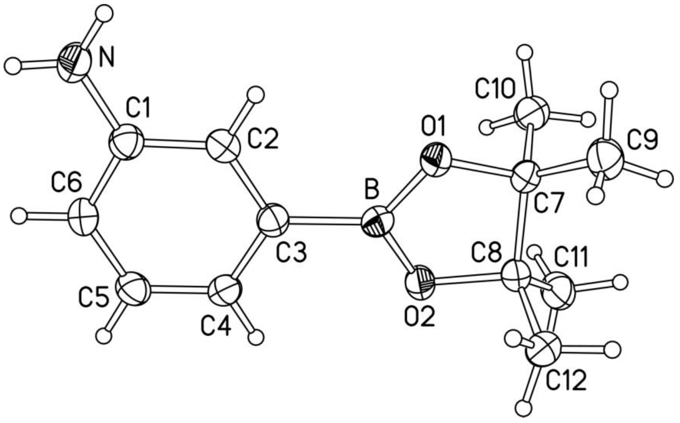

Figure 1
Molecular structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level.

C1—N bond in (I) [1.3790 (18) Å] is shorter than in aniline [solid: 1.392 (6) Å; gas: 1.402 (2) Å]. Both differences indicate that the boryl substituent enhances the interaction of the electron lone pair of N with the aromatic ring and hence sp^2 hybridization of the N atom. It is noteworthy that, in the two complexes of Pd and Pt where molecule (I) acts as an N-ligand (Vogels *et al.*, 1999), the C—N bond is lengthened to 1.438 (4) and 1.45 (1) Å, respectively, as the π-conjugation is disrupted, the lone pair being donated to the metal atom instead.

In (I), the N atom deviates by 0.081 (2) Å from the benzene ring plane, but its H atoms are situated on the other side of this plane, 0.04 (2) Å from it. A similar, but stronger, distortion is shown by the aniline molecule in its crystal structure, where the amino group both donates and accepts a hydrogen bond.

Experimental

3-Aminophenylboronic acid (1.00 g, 6.45 mmol) and pinacol (0.763 g, 6.45 mmol) were added to ethyl acetate (150 ml). After stirring for 20 h, the solution was dried ($MgSO_4$), filtered and evaporated to yield a brown solid, which was dissolved in a minimal amount of ethyl acetate and absorbed on to silica gel. Purification was by silica gel chromatography (hexane/ethyl acetate, 1:1 as eluant), which gave an orange oil which crystallized on standing for 48 h to give large orange crystals of (I) [yield 1.31 g, 93%; m.p. 363 K, *cf.* 366 K according to Vogels *et al.* (1999)]. UV ε, mol dm^{-3} cm^{-1} (MeCN) 215 (ε 27410), 246 (ε 7100), 311 (ε 2560); MS (ES+) 220.1 (M^+ + H). Found: C 65.77, H 8.31, N 6.31%; $C_{12}H_{19}BNO_2$ requires: C 65.70, H 8.28, N 6.39%. All other spectroscopic and analytical details were identical to those reported by Vogels *et al.* (1999).

Crystal data

$C_{12}H_{18}BNO_2$
M_r = 219.08
Monoclinic, $P2_1/c$
a = 9.823 (1) Å
b = 10.658 (1) Å
c = 12.547 (1) Å
β = 109.10 (1)°
V = 1241.3 (2) Å^3
Z = 4

D_x = 1.172 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2346 reflections
θ = 2.6–27.0°
μ = 0.08 mm^{-1}
T = 120 (2) K
Block, orange
0.3 × 0.3 × 0.2 mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer
ω scans
Absorption correction: none
7402 measured reflections
2697 independent reflections

1905 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.029
$\theta_{\rm max}$ = 27.0°
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 11$
$l = -16 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.122
S = 1.04
2697 reflections
161 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.20 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—B	1.3657 (18)	O2—C8	1.4703 (16)
O1—C7	1.4714 (16)	N—C1	1.3790 (18)
O2—B	1.3712 (18)	C3—B	1.550 (2)
C2—C1—C6	118.32 (13)	O1—B—C3	124.76 (13)
C2—C3—C4	118.19 (13)	O2—B—C3	121.89 (13)
O1—B—O2	113.35 (13)		
B—O1—C7—C8	−22.51 (14)	C8—O2—B—O1	11.01 (16)
B—O2—C8—C7	−23.98 (14)	C2—C3—B—O1	9.9 (2)
O1—C7—C8—O2	27.80 (13)	C4—C3—B—O2	8.3 (2)
C7—O1—B—O2	8.34 (16)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O2$^{\rm i}$	0.92 (2)	2.20 (2)	3.0743 (17)	158.4 (16)

Symmetry code: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Amino H atoms were refined in an isotropic approximation, giving N—H distances of 0.92 (2) and 0.85 (2) Å. Phenyl H atoms were treated as riding in idealized positions with C—H bond lengths of 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Methyl groups were refined as rigid bodies rotating around the C—C bonds, with C—H bond lengths of 0.98 Å and a common refined $U_{\rm iso}$(H) for all three H atoms of each methyl group.

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

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