organic papers

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

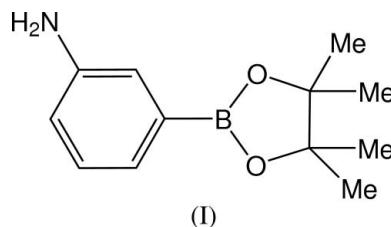For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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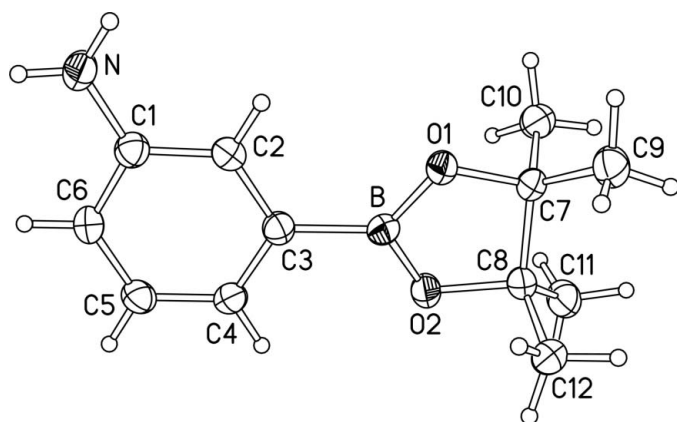
Figure 1
Molecular structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level.

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$_2$	$D_x = 1.172$ Mg m^{-3}
$M_r = 219.08$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2346
$a = 9.823$ (1) Å	reflections
$b = 10.658$ (1) Å	$\theta = 2.6$–27.0°
$c = 12.547$ (1) Å	$\mu = 0.08$ mm^{-1}
$\beta = 109.10$ (1)°	$T = 120$ (2) K
$V = 1241.3$ (2) Å^3	Block, orange
$Z = 4$	$0.3 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer	1905 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.029$
Absorption correction: none	$\theta_{max} = 27.0°$
7402 measured reflections	$h = -12 \rightarrow 12$
2697 independent reflections	$k = -13 \rightarrow 11$
	$l = -16 \rightarrow 13$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.043$	
$wR(F^2) = 0.122$	
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2]$
2697 reflections	where $P = (F_o^2 + 2F_c^2)/3$
161 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.25$ e Å^{-3}
	$\Delta\rho_{min} = -0.20$ 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^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 $U_{iso}(H) = 1.2U_{eq}(C)$. 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 $U_{iso}(H)$ 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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supporting information

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Crystal data

$C_{12}H_{18}BNO_2$	$F(000) = 472$
$M_r = 219.08$	$D_x = 1.172$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 363 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.823$ (1) Å	Cell parameters from 2346 reflections
$b = 10.658$ (1) Å	$\theta = 2.6$–27.0°
$c = 12.547$ (1) Å	$\mu = 0.08$ mm^{-1}
$\beta = 109.10$ (1)°	$T = 120$ K
$V = 1241.3$ (2) Å^3	Block, orange
$Z = 4$	$0.3 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer	2697 independent reflections
Radiation source: fine-focus sealed tube	1905 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.029$
Detector resolution: 8 pixels mm^{-1}	$\theta_{max} = 27.0°$, $\theta_{min} = 2.2°$
ω scans	$h = -12 \rightarrow 12$
7402 measured reflections	$k = -13 \rightarrow 11$
	$l = -16 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.122$	
$S = 1.04$	H atoms treated by a mixture of independent and constrained refinement
2697 reflections	
161 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.25$ e Å^{-3}
	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Experimental. The data collection nominally covered over a hemisphere of reciprocal Space, by a combination of 3 sets of ω scans each set at different φ and/or 2θ angles and each scan (10 s exposure) covering 0.3° in ω. Crystal to detector distance 4.85 cm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.15436 (10)	0.04664 (8)	0.16868 (7)	0.0263 (3)
O2	0.22355 (11)	0.03227 (9)	0.36090 (8)	0.0316 (3)
N	0.36360 (17)	0.49698 (14)	0.11742 (11)	0.0404 (4)
H1N	0.315 (2)	0.4675 (17)	0.0457 (17)	0.059 (6)*
H2N	0.420 (2)	0.5598 (18)	0.1268 (14)	0.053 (6)*
C1	0.38192 (15)	0.41584 (13)	0.20664 (11)	0.0273 (3)
C2	0.31038 (15)	0.30068 (13)	0.19234 (11)	0.0251 (3)
H2	0.2532	0.2755	0.1186	0.030*
C3	0.32043 (15)	0.22174 (13)	0.28355 (11)	0.0245 (3)
C4	0.40955 (15)	0.25901 (13)	0.39138 (11)	0.0275 (3)
H4	0.4179	0.2071	0.4548	0.033*
C5	0.48483 (16)	0.37062 (13)	0.40580 (12)	0.0297 (3)
H5	0.5474	0.3934	0.4785	0.036*
C6	0.47049 (16)	0.44930 (13)	0.31530 (12)	0.0287 (3)
H6	0.5207	0.5270	0.3268	0.034*
C7	0.06845 (15)	−0.05605 (13)	0.19253 (11)	0.0256 (3)
C8	0.15477 (16)	−0.08840 (13)	0.31807 (12)	0.0294 (3)
C9	0.06005 (18)	−0.16155 (14)	0.11008 (13)	0.0367 (4)
H91	0.0021	−0.1346	0.0341	0.047 (3)*
H92	0.0152	−0.2350	0.1317	0.047 (3)*
H93	0.1573	−0.1833	0.1109	0.047 (3)*
C10	−0.08028 (16)	−0.00340 (14)	0.17633 (13)	0.0350 (4)
H101	−0.1204	0.0320	0.1002	0.049 (3)*
H102	−0.0735	0.0627	0.2322	0.049 (3)*
H103	−0.1436	−0.0705	0.1861	0.049 (3)*
C11	0.06293 (18)	−0.12685 (15)	0.38863 (12)	0.0396 (4)
H111	0.1246	−0.1416	0.4666	0.054 (3)*
H112	0.0103	−0.2039	0.3579	0.054 (3)*
H113	−0.0058	−0.0596	0.3871	0.054 (3)*
C12	0.27576 (17)	−0.18112 (15)	0.33107 (14)	0.0414 (4)
H121	0.3375	−0.1841	0.4103	0.051 (3)*
H122	0.3332	−0.1550	0.2840	0.051 (3)*
H123	0.2353	−0.2647	0.3074	0.051 (3)*
B	0.23205 (17)	0.09875 (15)	0.26972 (13)	0.0249 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0288 (6)	0.0239 (5)	0.0248 (5)	−0.0048 (4)	0.0070 (4)	0.0017 (4)
O2	0.0373 (6)	0.0275 (6)	0.0252 (5)	−0.0099 (5)	0.0036 (4)	0.0013 (4)
N	0.0512 (9)	0.0350 (8)	0.0296 (7)	−0.0166 (7)	0.0057 (6)	0.0049 (6)
C1	0.0271 (8)	0.0276 (8)	0.0280 (7)	−0.0006 (6)	0.0101 (6)	0.0010 (6)
C2	0.0231 (7)	0.0265 (8)	0.0245 (7)	−0.0001 (6)	0.0062 (6)	−0.0015 (5)
C3	0.0232 (7)	0.0225 (7)	0.0277 (7)	0.0007 (6)	0.0081 (6)	−0.0012 (5)
C4	0.0294 (8)	0.0240 (8)	0.0264 (7)	0.0015 (6)	0.0055 (6)	0.0025 (6)
C5	0.0296 (8)	0.0288 (8)	0.0266 (7)	−0.0013 (6)	0.0035 (6)	−0.0034 (6)
C6	0.0290 (8)	0.0241 (8)	0.0320 (8)	−0.0057 (6)	0.0087 (6)	−0.0021 (6)
C7	0.0285 (8)	0.0219 (7)	0.0247 (7)	−0.0038 (6)	0.0067 (6)	0.0027 (5)
C8	0.0301 (8)	0.0247 (8)	0.0280 (7)	−0.0066 (6)	0.0022 (6)	0.0025 (6)
C9	0.0457 (10)	0.0310 (9)	0.0311 (8)	−0.0061 (7)	0.0092 (7)	−0.0033 (6)
C10	0.0284 (8)	0.0330 (9)	0.0400 (9)	−0.0021 (7)	0.0064 (7)	0.0070 (7)
C11	0.0448 (10)	0.0404 (10)	0.0300 (8)	−0.0143 (8)	0.0073 (7)	0.0049 (7)
C12	0.0324 (9)	0.0281 (9)	0.0522 (10)	−0.0025 (7)	−0.0018 (7)	0.0095 (7)
B	0.0244 (8)	0.0221 (8)	0.0268 (8)	0.0022 (7)	0.0066 (7)	0.0024 (6)

Geometric parameters (Å, º)

O1—B	1.3657 (18)	C7—C9	1.5118 (19)
O1—C7	1.4714 (16)	C7—C10	1.515 (2)
O2—B	1.3712 (18)	C7—C8	1.5636 (18)
O2—C8	1.4703 (16)	C8—C12	1.513 (2)
N—C1	1.3790 (18)	C8—C11	1.513 (2)
N—H1N	0.92 (2)	C9—H91	0.9800
N—H2N	0.85 (2)	C9—H92	0.9800
C1—C2	1.3964 (19)	C9—H93	0.9800
C1—C6	1.4024 (19)	C10—H101	0.9811
C2—C3	1.3976 (19)	C10—H102	0.9811
C2—H2	0.9500	C10—H103	0.9810
C3—C4	1.4070 (19)	C11—H111	0.9800
C3—B	1.550 (2)	C11—H112	0.9800
C4—C5	1.3810 (19)	C11—H113	0.9800
C4—H4	0.9500	C12—H121	0.9809
C5—C6	1.3812 (19)	C12—H122	0.9809
C5—H5	0.9501	C12—H123	0.9808
C6—H6	0.9500		
B—O1—C7	107.29 (10)	C12—C8—C11	110.97 (12)
B—O2—C8	107.05 (11)	O2—C8—C7	102.01 (10)
C1—N—H1N	117.7 (12)	C12—C8—C7	113.62 (12)
C1—N—H2N	118.3 (12)	C11—C8—C7	114.74 (12)
H1N—N—H2N	120.4 (17)	C7—C9—H91	109.4
N—C1—C2	121.36 (13)	C7—C9—H92	109.5
N—C1—C6	120.29 (14)	H91—C9—H92	109.5

C2—C1—C6	118.32 (13)	C7—C9—H93	109.5
C1—C2—C3	121.75 (13)	H91—C9—H93	109.5
C1—C2—H2	119.0	H92—C9—H93	109.5
C3—C2—H2	119.2	C7—C10—H101	109.6
C2—C3—C4	118.19 (13)	C7—C10—H102	109.5
C2—C3—B	122.04 (12)	H101—C10—H102	109.4
C4—C3—B	119.72 (12)	C7—C10—H103	109.6
C5—C4—C3	120.48 (13)	H101—C10—H103	109.4
C5—C4—H4	119.7	H102—C10—H103	109.4
C3—C4—H4	119.8	C8—C11—H111	109.6
C4—C5—C6	120.60 (13)	C8—C11—H112	109.6
C4—C5—H5	119.8	H111—C11—H112	109.5
C6—C5—H5	119.6	C8—C11—H113	109.3
C5—C6—C1	120.58 (13)	H111—C11—H113	109.5
C5—C6—H6	119.7	H112—C11—H113	109.5
C1—C6—H6	119.7	C8—C12—H121	109.5
O1—C7—C9	108.69 (11)	C8—C12—H122	109.6
O1—C7—C10	106.81 (11)	H121—C12—H122	109.4
C9—C7—C10	110.44 (13)	C8—C12—H123	109.5
O1—C7—C8	102.17 (10)	H121—C12—H123	109.4
C9—C7—C8	114.55 (12)	H122—C12—H123	109.4
C10—C7—C8	113.46 (12)	O1—B—O2	113.35 (13)
O2—C8—C12	106.33 (11)	O1—B—C3	124.76 (13)
O2—C8—C11	108.28 (12)	O2—B—C3	121.89 (13)

N—C1—C2—C3	−175.49 (14)	C9—C7—C8—O2	145.12 (12)
C6—C1—C2—C3	2.7 (2)	C10—C7—C8—O2	−86.79 (13)
C1—C2—C3—C4	−2.2 (2)	O1—C7—C8—C12	−86.21 (13)
C1—C2—C3—B	175.13 (13)	C9—C7—C8—C12	31.12 (17)
C2—C3—C4—C5	−0.1 (2)	C10—C7—C8—C12	159.20 (12)
B—C3—C4—C5	−177.57 (13)	O1—C7—C8—C11	144.62 (12)
C3—C4—C5—C6	2.0 (2)	C9—C7—C8—C11	−98.05 (16)
C4—C5—C6—C1	−1.6 (2)	C10—C7—C8—C11	30.03 (18)
N—C1—C6—C5	177.44 (15)	C7—O1—B—O2	8.34 (16)
C2—C1—C6—C5	−0.8 (2)	C7—O1—B—C3	−170.73 (13)
B—O1—C7—C9	−143.96 (13)	C8—O2—B—O1	11.01 (16)
B—O1—C7—C10	96.87 (13)	C8—O2—B—C3	−169.88 (13)
B—O1—C7—C8	−22.51 (14)	C2—C3—B—O1	9.9 (2)
B—O2—C8—C12	95.31 (13)	C4—C3—B—O1	−172.73 (13)
B—O2—C8—C11	−145.38 (13)	C2—C3—B—O2	−169.06 (13)
B—O2—C8—C7	−23.98 (14)	C4—C3—B—O2	8.3 (2)
O1—C7—C8—O2	27.80 (13)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O2[i]	0.92 (2)	2.20 (2)	3.0743 (17)	158.4 (16)

Symmetry code: (i) x, $-y+1/2$, $z-1/2$.