Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*Z*)-1-Phenyl-3-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylamino]but-2-en-1-one

Andreas Decken,[a]* Diane A. Dickie,[b] Paul A. Chapman,[b] Christopher M. Vogels[b] and Stephen A. Westcott[b]

[a]Department of Chemistry, University of New Brunswick, Fredericton, NB, Canada E3B 6E2, and [b]Department of Chemistry, Mount Allison University, 63C York Street, Sackville, NB, Canada E4L 1G8

Correspondence e-mail: adecken@unb.ca

Received 10 August 2005
Accepted 1 September 2005
Online 7 September 2005

Key indicators

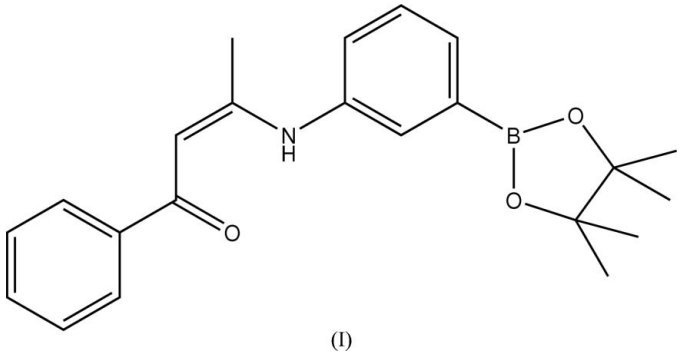
Single-crystal X-ray study
T = 208 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.103
Data-to-parameter ratio = 12.6

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

The title compound, $C_{22}H_{26}BNO_3$, is the first example of a boron-containing enaminone to be characterized by X-ray diffraction. The B atom lies in a three-coordinate environment and shows no additional intra- or intermolecular interactions. The 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl group is roughly coplanar with the adjacent aromatic ring, as expected if considerable dative bonding is occurring between the aromatic p-π electrons and the empty p-orbital on the B atom.

Comment

The synthesis of amines containing boronate esters is of considerable interest owing to their potential use in Suzuki–Miyaura cross-coupling reactions (Miyaura & Suzuki, 1995) and their potent biological activities (Yang *et al.*, 2003). For instance, boronic amino acid derivatives are strong inhibitors of human arginase II, whose primary function appears to be in L-arginase homeostasis. Related α-aminoboronic acid derivatives are well known for their ability to act as serine protease inhibitors. Serine proteases are a diverse group of proteolytic enzymes whose numerous physiological functions include digestion, growth, differentiation and apoptosis. Proteases are also vital in the generation of most disease processes. Some of the biological properties of these molecules have been attributed to the ability of the three-coordinate B atom to form covalent bonds with biomolecules, as well as the potential to form hydrogen bonds with adjacent O atoms. As part of our ongoing investigation into generating novel aminoboron compounds, we have prepared a novel enaminone derivative. Enaminones themselves are important synthetic intermediates (Stanovnik & Svete, 2004) and many have potent biological properties (Kombian, *et al.*, 2005).



(I)

The title compound, (I), is shown in Fig. 1, from which it can be seen that the aryl-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) ring system is essentially planar, as is the phenylbut-2-en-1-one fragment. However, rotation about the N10—C11 bond

results in dihedral angles of 41.05 (2)° for C9—N10—C11—C12 and 35.74 (13)° for C9—N10—C11—C16. Dimers are formed through C—H···O hydrogen bonds in the range 2.56 (2) Å (H22*B*···O17′) to 2.58 (2) Å (H21*B*···O7′), and intramolecular hydrogen bonding is observed for the enaminone group (Table 1). Bond distances and angles, including intramolecular hydrogen bonding and dihedral angles, are similar to those reported for related (*Z*)-3-[2-(hydroxyphenylamino)]-1-phenylbut-2-en-1-one (Glowiac & Sobczak, 1992).

The 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl, *i.e.* Bpin, skeleton displays bond lengths and angles as found in related aryl–Bpin compounds (Norman *et al.*, 2002). Optimization of orbital overlap between the boron p_z and the aryl π-electron system is achieved through the coplanar orientation of the two rings. While steric crowding at the B center is not present, the molecule shows no intra- or intermolecular Lewis acid–base interactions.

Experimental

3-(4,4,5,5-Tetramethyl[1,3,2]-dioxaborolan-2-yl)phenylamine (151 mg, 0.69 mmol) was added to benzoylacetone (116 mg, 0.72 mmol) in toluene (5 ml) with molecular sieves (5 g). The reaction mixture was allowed to stand for 7 d, after which the sieves were filtered off and the solvent removed under vacuum to give an orange oil. The oil was dissolved in a minimum of hot hexane and crystals of the title compound precipitated upon cooling. Yield 254 mg (70%). ^{1}H NMR ($CDCl_3$): δ 13.12 (*br s*, 1H), 7.90 (*m*, 2H), 7.66 (*s*, 1H), 7.45 (*m*, 2H), 7.20 (*m*, 1H), 6.79 (*d*, J = 8 Hz, 1H), 6.17 (*s*, 1H), 5.88 (*s*, 1H), 4.08 (*s*, 1H), 2.18 (*s*, 3H), 1.34 (*s*, 12H); ^{11}B ($CDCl_3$): δ 31; ^{13}C ($CDCl_3$): δ 188.6, 162.4, 140.0, 138.5, 132.1, 131.1, 130.9, 129 (*br*, BC), 128.7 (2C), 128.3, 127.6 (2C), 127.1, 94.2, 84.1 (2C), 24.9 (4C), 20.6. FT–IR (nujol): 2914 (*br*), 2858 (*s*), 1606 (*m*), 1460 (*s*), 1362 (*s*), 1319 (*m*), 1145 (*m*), 706 (*m*) cm^{-1}.

Crystal data

$C_{22}H_{26}BNO_3$
M_r = 363.25
Triclinic, $P\overline{1}$
a = 5.9593 (5) Å
b = 13.4318 (12) Å
c = 14.4116 (13) Å
α = 117.219 (1)°
β = 92.646 (2)°
γ = 98.159 (2)°
V = 1007.32 (15) Å^3
Z = 2
D_x = 1.198 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3688 reflections
θ = 2.8–28.3°
μ = 0.08 mm^{-1}
T = 208 (1) K
Irregular fragment, colorless
0.35 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*a*)
T_{min} = 0.825, T_{max} = 0.992
7066 measured reflections
4397 independent reflections
3200 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 27.5°
$h = -7 \rightarrow 7$
$k = -17 \rightarrow 16$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.103
S = 1.05
4397 reflections
348 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

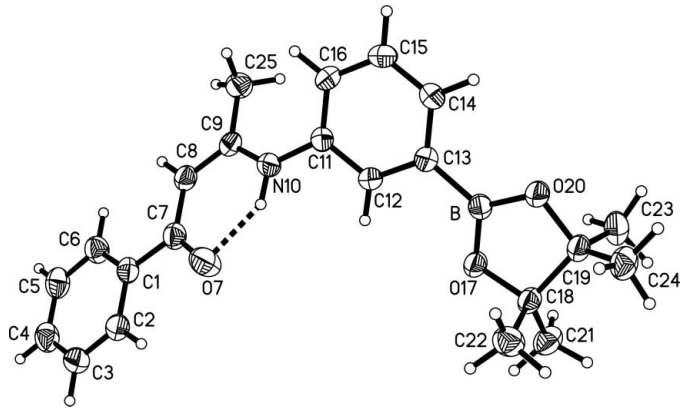


Figure 1
View of (I), with displacement ellipsoids at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C21—H21*B*···O7^{i}	0.99 (2)	2.58 (2)	3.5400 (19)	164 (1)
C22—H22*B*···O17^{i}	1.03 (2)	2.56 (2)	3.5719 (19)	170 (1)
N10—H10···O7	0.93 (2)	1.82 (2)	2.6113 (15)	142 (1)

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

H atoms were located in Fourier difference maps and refined freely using isotropic displacement parameters: C—H distances were in the range 0.950 (14)–1.033 (17) Å and the N—H distance was 0.925 (17) Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

Thanks are extended to the University of New Brunswick and Mount Allison University, the Natural Science and Engineering Research Council (Canada), the Canada Research Chairs Program, and the Canadian Foundation for Innovation/Atlantic Innovation Fund for financial support.

References

Bruker (1999). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SAINT*. Version 6.45. Bruker AXS Inc., Madison, Wisconsin, USA.
Glowiac, T. & Sobczak, J. M. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 673–678.
Kombian, S. B., Edafiogho, I. O. & Ananthalakshmi, K. V. V. (2005). *Br. J. Pharmacol*, **145**, 945–953.
Miyaura, N. & Suzuki, A. (1995). *Chem. Rev.* **95**, 2457–2483.
Norman, D. W., Edwards, J. P., Vogels, C. M., Decken, A. & Westcott, S. A. (2002). *Can. J. Chem.* **80**, 31–40.
Sheldrick, G. M. (1997*a*). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*b*). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
Stanovnik, B. & Svete, J. (2004). *Chem. Rev.* **104**, 2433–2480.
Yang, W., Gao, X. & Wang, B. (2003). *Med. Res. Rev.* **23**, 346-368.