An asymmetrically substituted borazine

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The B_3N_3 ring in the title compound, 1,3,5-tri-*tert*-butyl-2,4-difluoro-6-phenylcyclotriborazane, [PhF$_2$B$_3$N$_3$^{t}Bu$_3$] or $C_{18}H_{32}B_3F_2N_3$, an asymmetrically substituted borazine, is distorted from planarity. The molecule resides on a twofold axis. The N atoms of the N—B(Ph)—N group lie on opposite sides of the least-squares plane formed by the four remaining ring atoms, due to steric accommodation of the *tert*-butyl groups, a conformation not previously observed for a borazine. The B—N bond lengths are in the range 1.4283 (14)–1.4493 (12) Å, due to the F substituents residing on two of the B atoms, which also produce a large deviation from 120° in one of the B—N—B angles [*ca* 113.6 (1)°]. The phenyl group is twisted with respect to the B_3N_3 ring, the interplanar angle being 62.87 (5)°.

Comment

Recently, we reported the first boraamidinate, $[RB(NR')_2]^{2-}$, complexes of group 13 elements. We described the syntheses, spectroscopic characterization and X-ray structures of [μ-Li(OEt$_2$){PhB(μ-N^{t}Bu)$_2$}$_2$E], (I) (E = Ga, In), in which the spirocyclic anion [{PhB(μ-N^{t}Bu)$_2$}$_2$E]$^-$ is N,N'-chelated to a monosolvated lithium cation (Chivers *et al.*, 2003), and the solvent-separated ion-pair complexes [Li(OEt$_2$)$_4$][{PhB(μ-NDipp)$_2$}$_2$E], (II) (E = Ga, In; Dipp = 2,6-diisopropylphenyl), where the spirocyclic anion [{PhB(μ-NDipp)$_2$}$_2$E]$^-$ is stabilized by the steric bulk provided by the four Dipp substituents attached to the N atoms (Chivers *et al.*, 2004). In an effort to synthesize the boron analogue of (I), E = B, the dilithiated boraamidinate {Li$_2$[PhB(N^{t}Bu)$_2$]}$_2$ (Brask *et al.*, 2002) was treated with BF$_3$·OEt$_2$ in a 2:1 molar ratio. A single-crystal X-ray diffraction experiment revealed that, rather than the expected complex, *viz.* (I) (E = B), the asymmetrically substituted borazine derivative [PhF$_2$B$_3$N$_3$^{t}Bu$_3$], (III), was isolated. Borazines serve as precursor molecules in boron nitride (BN) materials science, since they are relatively robust when compared with other boron–nitrogen compounds (Haberecht *et al.*, 2004). We present here the crystal structure of (III).

The molecule of (III) resides on a twofold axis which bisects atoms C9, N2, B1 and the phenyl group. A view of the structure of (III) is shown in Fig. 1, with selected bond distances and angles listed in Table 1. The B_3N_3 ring in (III) is distorted from an ideal planar structure, with torsion angles B2—N1—B1—N1^i = 15.16 (6)°, B2^i—N2—B2—N1 = 16.46 (7)° and B1—N1—B2—N2 = −32.66 (13)° [symmetry code (i) as in Table 1]. Atoms N1 and N1^i lie 0.3477 (14) Å above and below the least-squares plane formed by B1/B2/B2^i, while atom N2 does not deviate from this plane. In (III), steric congestion forces one *tert*-butyl substituent (α-carbon is atom C5) to reside on one side of the ring, while the symmetry-related *tert*-butyl group (α-carbon is atom C5^i) sits below the plane. As a result, distortion of the six-membered B_3N_3 ring occurs, in which atoms N1 and N1^i are on opposite sides of the B1/B2/B2^i/N2 plane.

Dipp = 2,6-^{i}Pr$_2$Ph-

(I) (II) (III)

(IV)
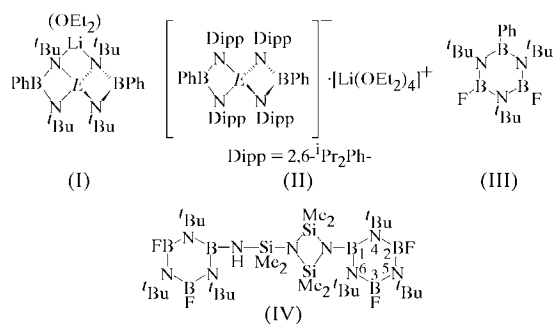
Most structurally characterized borazine compounds are symmetrically substituted (*i.e.* the three B atoms have the same substituent and identical atoms or groups are attached to the three N atoms) and tend to have planar B_3N_3 rings, as in the compound [HB—NPh]$_3$ (Jaska *et al.*, 2003). Very few
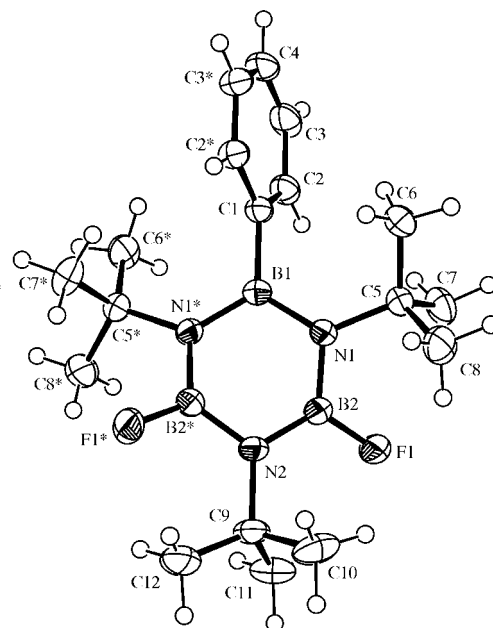

Figure 1
A view of (III), with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. The methyl groups at C9 are disordered because of the imposed twofold symmetry and atoms C10*, C11* and C12* have been omitted. [Symmetry code: (*) $-x, y, \frac{3}{2} - z$.]

asymmetrically substituted borazines have been characterized to date by single-crystal X-ray analyses (Jaschke *et al.*, 2002; Nöth & Habereder, 2001; Srivastova *et al.*, 1998; Welker *et al.*, 1989). One such example is compound (IV) (Jaschke *et al.*, 2002), in which five of the B_3N_3 ring substituents are identical to those in (III). The B_3N_3 rings in (IV) adopt boat conformations. For example, atoms B1 and N5 (in one ring) are 0.598 and 0.355 Å, respectively, out of the plane formed by the other four ring atoms, N4/B2/B3/N6. Perusal of borazine compounds, whether symmetrically or asymmetrically substituted, characterized in the solid state (Cambridge Structural Database, Version 5.25, 2003 release; Allen, 2002), reveals that the conformation of the central B_3N_3 ring in (III) has not previously been observed. To date, planar (or very slightly deviating from planar), chair (ideal and puckered) and boat (ideal and twisted) conformations of the B_3N_3 ring have been reported.

Although the B_3N_3 ring in $[Ph_3GeMe_2B_3N_3{}^iPr_3]$ adopts a twisted-boat conformation, resulting from steric repulsion between the Ph_3Ge group and the isopropyl groups attached to the N atoms, the B—N bond lengths [1.439 (4)–1.451 (4) Å] remain almost unaffected by this twisting (Nöth & Habereder, 2001). In contrast, the B—N distances in the title compound range from 1.428 (1) to 1.449 (1) Å. The longest B—N bond lengths are B1—N1 and B2—N1, which are similar within experimental error [1.4433 (15) and 1.4493 (12) Å], despite the up–down distortion at N1 and N1^i. The shortest B—N bond length is B2—N2 [1.4283 (14) Å], due to the F substituents that reside on these B atoms and the resulting π-interaction. This variability in bond lengths within the B_3N_3 ring is also observed in (IV) [1.408 (3)–1.491 (3) Å], on account of the F substituents on two of the three B atoms and the boat conformation, which lengthens the B1—N4 and B1—N6 [average 1.488 (3) Å], and B3—N5 and B2—N5 [average 1.441 (3) Å] distances. In the symmetrically substituted borazine $[HB-NPh]_3$, the B—N—B [120.6 (2)–121.1 (2)°] and N—B—N angles [118.7 (2)–119.4 (2)°] are all close to 120° (Jaska *et al.*, 2003), while those in (III) deviate from 120°. The B2^i—N1—B1, B2—N1—B1 and N1—B1—N1^i angles are 117.1°, while the largest deviation occurs at N2, with a B2^i—N2—B2 angle of 113.6 (1)°. This deviation is also observed in (IV), with a range of 110.2 (2)–120.1 (2)°. The phenyl group in (III) is twisted with respect to the B_3N_3 ring, with an angle of 62.87 (5)° between the two planes. This angle is larger than those observed in the borazine $[HB-NPh]_3$ (48.8, 43.7 and 42.3°; Jaska *et al.*, 2003), but is similar to those in the structure of hexaphenylborazine $[PhB-NPh]_3$, which has angles between the ring planes in the range 62.5–71.4° (Lux *et al.*, 1979). The structure is devoid of any C—H···F-type intermolecular interactions, due to the disposition of the *tert*-butyl groups preventing such interactions.

Experimental

A solution of $Li_2[PhB(N^tBu)_2]$ (1.00 g, 4.10 mmol) in Et_2O (50 ml) was added to a stirred solution of $BF_3·OEt_2$ (0.25 ml, 2.05 mmol) in Et_2O (50 ml) at 195 K, producing a bright-pink solution. The reaction mixture was allowed to warm to room temperature, whereupon it became a clear colorless solution. After 18 h, the reaction mixture was filtered (Acrodisc syringe filter, diameter 25 mm, pore size 0.45 µm), followed by concentration of the solvent *in vacuo*. Subsequent cooling (273 K, 18 h) of the resulting violet solution yielded colorless crystals (0.30 g) of the title compound $[PhF_2B_3N_3{}^tBu_3]$, (III). Analysis calculated for $C_{18}H_{32}B_3F_2N_3$: C 59.90, H 8.94, N 11.64%; found: C 59.48, H 8.45, N 11.76%. ^{1}H NMR (D$_8$-THF, 296 K): δ 7.73–7.22 (*m*, 5H, C_6H_5), 1.40 (*s*, 9H, C_4H_9), 1.19 (*s*, 18H, C_4H_9); ^{11}B NMR (D$_8$-THF, 296 K): δ 37 [*d*, $^1J(BF) = 278$ Hz], 25 (*br s*); ^{19}F NMR (D$_8$-THF, 296 K): δ −88.9 (*s*). The diethyl ether solvent was dried with appropriate drying agents and distilled onto molecular sieves before use. The reaction and manipulation of the moisture- and air-sensitive product were carried out under an atmosphere of argon or under vacuum. All glassware was carefully dried prior to use. The compound $Li_2[PhB(N^tBu)_2]$ was prepared according to the literature procedure of Brask *et al.* (2002), while $BF_3·OEt_2$ was a commercial sample from Aldrich and was used as received.

Crystal data

$C_{18}H_{32}B_3F_2N_3$	$D_x = 1.169$ Mg m^{-3}
$M_r = 360.90$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4451
$a = 13.653$ (4) Å	reflections
$b = 13.637$ (5) Å	$\theta = 2.5$–25.5°
$c = 11.893$ (4) Å	$\mu = 0.08$ mm^{-1}
$\beta = 112.19$ (3)°	$T = 173$ (2) K
$V = 2050.3$ (13) Å^3	Block, colorless
$Z = 4$	$0.30 \times 0.25 \times 0.20$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	2327 independent reflections
	2052 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.019$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)	$\theta_{max} = 27.5°$
	$h = -17 \rightarrow 17$
$T_{min} = 0.977$, $T_{max} = 0.984$	$k = -17 \rightarrow 17$
4451 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0664P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$+ 0.77P]$
$wR(F^2) = 0.124$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
2327 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
140 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

F1—B2	1.3457 (13)	N2—B2^i	1.4283 (14)
N1—B2	1.4433 (15)	N2—C9	1.5197 (18)
N1—B1	1.4493 (12)	C1—B1	1.586 (2)
N1—C5	1.5214 (14)		
N1—B1—N1^i	117.05 (12)	B2—N1—B1	117.01 (9)
N1—B1—C1	121.48 (6)	B2—N1—C5	115.80 (8)
N1^i—B1—C1	121.48 (6)	B1—N1—C5	127.16 (9)
F1—B2—N2	119.54 (10)	B2^i—N2—B2	113.62 (12)
F1—B2—N1	118.72 (9)	B2^i—N2—C9	123.19 (6)
N2—B2—N1	121.74 (9)	B2—N2—C9	123.19 (6)
B2—N1—B1—N1^i	15.16 (6)	B2^i—N2—B2—N1	16.46 (7)
C5—N1—B1—N1^i	−167.00 (10)	C9—N2—B2—N1	−163.54 (7)
B2—N1—B1—C1	−164.84 (6)	B1—N1—B2—F1	147.38 (9)
C5—N1—B1—C1	13.00 (10)	C5—N1—B2—F1	−30.71 (14)
B2^i—N2—B2—F1	−163.58 (13)	B1—N1—B2—N2	−32.66 (13)
C9—N2—B2—F1	16.42 (13)	C5—N1—B2—N2	149.25 (9)

Symmetry codes: (i) $-x + 1, y, -z + \frac{3}{2}$.

The molecule of (III) lies on a twofold axis, with one of the *tert*-butyl groups disordered over two sites with 0.50 site-occupancy factors. The H atoms were included in the refinement at geometrically idealized positions, with C—H = 0.95 and 0.98 Å, and U_{iso}(H) = 1.5 (methyl) and 1.2 (phenyl) times U_{eq} of the atoms to which they were bonded. The final difference map was free of any chemically significant features, with the top seven peaks located in bonds.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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