Unusual, Thermally Stable, Sublimable Aminoboranes B(NHAr)X$_2$ (X = Cl, F, or NH$_2$); X-Ray Crystal Structure of Bis(amino)(2,4,6-tri-t-butylphenylamino)borane, B(NH$_2$)$_2$(NHAr)†

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The sterically demanding 2,4,6-tri-t-butylamido ligand ($\overline{\text{N}}$HAr) confers unexpected thermal stability on the title boranes B(NHAr)X$_2$ [X = Cl, (**2**); F, (**3**); or NH$_2$, (**4**)], each of which is sublimable without elimination of HX; the difluoroborane (**3**) has significant BN double-bond character as is evident from magnetically distinct F$^-$ ligands, only one of which (presumably the *trans*) is coupled to the NHAr proton; compound (**4**) has trigonal planar boron with one of the B–NH$_2$ bonds significantly longer than the other, 1.470(4) and 1.437(4) Å, and each longer than B–NHAr, 1.412(4) Å.

We report on the synthesis [from 2,4,6-tri-t-butylanilidolithium, (**1**)] and characterisation of three sublimable 2,4,6-tri-t-butylanilinoboranes B(NHAr)X$_2$ [X = Cl, (**2**); F, (**3**); or NH$_2$, (**4**)], Scheme 1, each of which has considerable thermal stability.

The most remarkable compound is B(NH$_2$)$_2$(NHAr), (**4**), the first stable borane having a pair of geminal $\overline{\text{N}}$H$_2$ ligands. Facile ammonia elimination would have been anticipated, but was not observed even under severe conditions [see vi(a) in Scheme 1]. By contrast, BH(NH$_2$)$_2$ is only stable in solution in

liquid ammonia.[1] Even boranes having a single $\overline{\text{N}}$H$_2$ ligand are rare,[2] and the nearest compounds to (**4**) to have been reported are the mono-amides B(NH$_2$)(NMe$_2$)(NHSiMe$_2$Bu^i) (but even at 25 °C this eliminates NHMe$_2$ with concomitant formation of a borazine),[3] and B(NH$_2$)(NHPh)$_2$, characterised merely by analysis and methanolysis to yield B(OMe)$_3$(NH$_3$).[4] It is evident that B(NH$_2$)$_2$(NHAr), (**4**), shows little acidity [see vi(c), Scheme 1] and is a hindered base, being reactive towards the proton (v in Scheme 1) but not BF$_3$(OEt$_2$) [vi(b), Scheme 1].

Secondary amino(difluoro)boranes B(NHR)F$_2$ are unusual,[2] and indeed have only been observed in solution[5] for R =
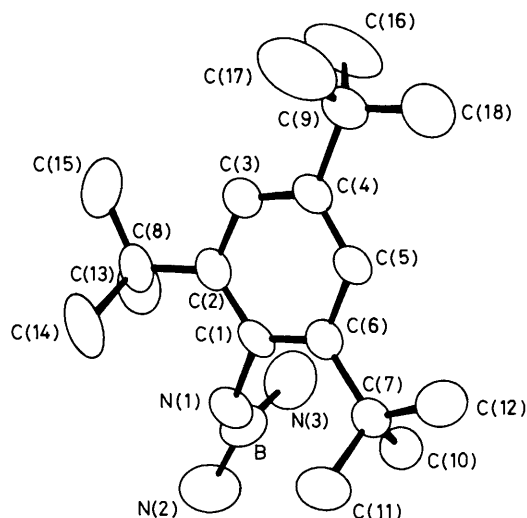
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† No reprints available.
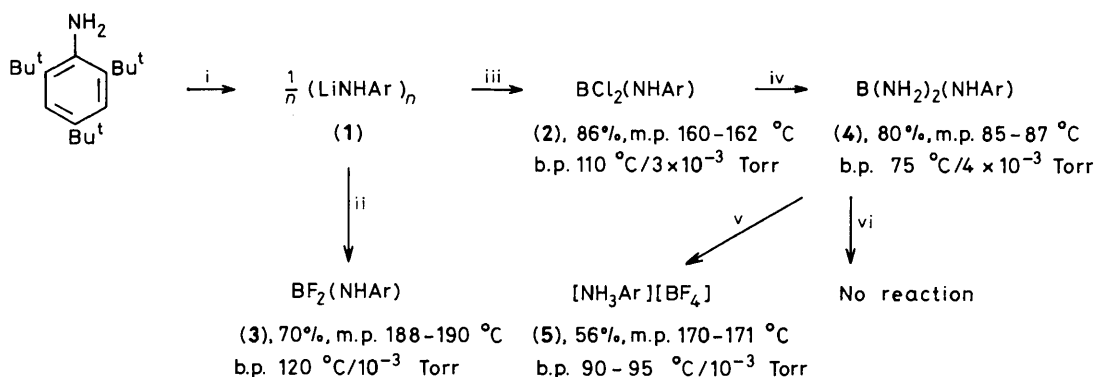
Scheme 1. *Abbreviation:* Ar = $C_6H_2Bu^t_3$-2,4,6. *Reagents and conditions:* i, $^1/_m(LiBu^n)_m$, n-C_6H_{14}, 25 °C; ii, BF_3-(OEt_2), OEt_2, 25 °C, 12 h; iii, excess of BCl_3, n-C_6H_{14}, −78 °C, then −4 °C for 12 h; iv, excess of $NH_3(g)$, n-C_6H_{14}, 25 °C, 3 h; v, 10-fold excess of $H[BF_4]$, OEt_2, 25 °C, 12 h; vi, (a) 200 °C, 5 h, or (b) $BF_3(OEt_2)$, 50 °C, 48 h, or (c) $LiBu^n$, reflux, 12 h. *Isolation procedures:* (1), removal of solvent *in vacuo*; (2)—(5), filtration and crystallisation at −30 °C from concentrated filtrate followed by sublimation. *Characterisation:* satisfactory microanalyses for each of the colourless crystalline compounds [(1)—(5)]; mass spectra [(2)—(4) gave M^+; (5) showed $(NH_2Ar)^+$]; i.r., and ^1H, ^{13}C, and ^{11}B [δ = 32.8 (2), 16.8 (3), 24.6 (4), or −0.2 (5), relative to $BF_3(OEt_2)$ = 0 p.p.m.] [also ^{19}F for (3) and (5)], n.m.r. spectra; and X-ray diffraction [for (4), see Figure 2]; the cited b.p.'s represent sublimations.
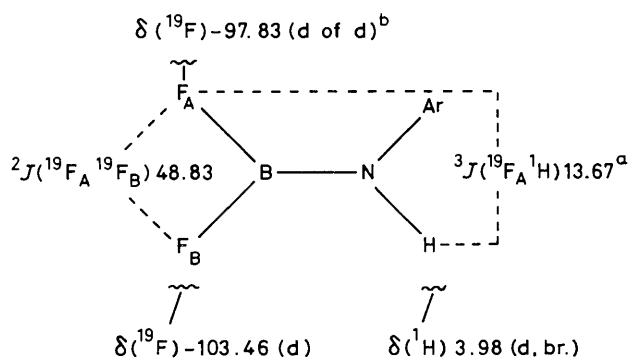
Figure 1. N.m.r. chemical shifts [centre of multiplet, δ in p.p.m., ^1H relative to $Si(CH_3)_4$ = 0, ^{19}F relative to $CFCl_3$ = 0; d = doublet, br = broad] and coupling constants, J in Hz, for $BF_2NHC_6H_2Bu^t_3$-2,4,6, (3), in C_6D_6 at 32 °C [protons of Ar (= $C_6H_2Bu^t_3$-2,4,6) omitted]. [a] From F_A signal (*ca.* 14 Hz from ^1H signal). [b] This collapsed to a doublet upon selectively decoupling the N*H*Ar proton, while δ($^{19}F_B$) was unaffected.

Figure 2. The molecular structure and atom numbering scheme for bis(amino)(2,4,6-tri-t-butylphenylamino)borane, (4). Some relevant dimensions are: B–N(1) 1.412(4), B–N(2) 1.437(4), B–N(3) 1.470(4), N(1)–C(1) 1.439(3) Å; C(1)–N(1)–B 126.8(2), N(1)–B–N(2) 119.2(3), N(1)–B–N(3) 119.3(3), and N(2)–B–N(3) 121.5(3)°.

Pr^i or Bu^t (and are isolable as the crystalline dimers),[5b] readily decomposing to afford $½BF_3(NH_2R)$ + $⅙(BFNR)_3$;[5a] while gaseous $BF_2(NH_2)$ has been identified by microwave spectroscopy.[6] The anilino(difluoro)borane (3) is noteworthy not merely for its stability, but also because it appears to be the first difluoro(amino)borane for which there is clear evidence for stereochemical rigidity due to substantial BN multiple-bond character. This is demonstrated by the ambient temperature ^{19}F spectrum, Figure 1, which shows that the two F^- ligands are magnetically inequivalent (and coupled) and only one is coupled to the N*H*Ar proton. That exclusively one of the F_A and F_B nuclei is observed to be coupled to the N*H*Ar proton is further evidence for BN double-bond character since *cis* are much smaller than *trans* couplings about isoelectronic C=C bonds. Unsymmetrical trimethylsilylamino(difluoro)-boranes $BF_2\{N(SiMe_3)R\}$ (R = Me or Pr^i) did not show similar F_A/F_B inequivalence.[5a] The ^{19}F spectrum of (3) was unchanged up to 80 °C and hence $ΔG^‡$ for BN rotation must be >100 kJ mol⁻¹.

Amino(difluoro)boranes are known both as monomers or dimers, having $(μ$-$NRR')_2$ bridges, and are distinguished *inter alia* by their ^{11}B chemical shifts, as in[7] $BF_2(NMe_2)$ [17 p.p.m.

relative to $BF_3(OEt_2)$] and $[BF_2(μ$-$NMe_2)]_2$ (0.9 p.p.m.). For $BF_2(NHAr)$, (3), the spectroscopic data (including ^{11}B n.m.r.) (Scheme 1) are consistent with a monomeric structure, although N̄HAr as a bridging ligand is established in the crystal for $[Li(μ$-$NHAr)(OEt_2)]_2$.[8] The latter was not used for the synthesis of $BCl_2(NHAr)$, (2), because BCl_3 cleaves ethers; hence the new solvent-free anilidolithium compound (1) was employed. The ^{11}B n.m.r. chemical shift data on the borane (2) and on $B(NH_2)_2(NHAr)$, (4), leave no doubt that these compounds are also monomers in solution, *cf.* (δ in p.p.m.),[7] $BCl_2(NMePh)$ 31, $[BCl_2(μ$-$NHBu^t)]_2$ 3.7, $B(NH_2)(NHSiMe_3)\{N(SiMe_3)_2\}$ 28.5, and $B(NHMe)_3$, 24.4.

Monomeric dichloroboranes derived from primary amines, $BCl_2(NHR)$, are generally transient species, dihydrochlorinating to yield borazines, although some *o*-substituted aryl-amino compounds, including $BCl_2\{NHC_6H_3(NO_2)$-2-(CF_3)-4$\}$,[9] have been characterised.

Crystal data for (**4**): $C_{18}H_{34}BN_3$, triclinic, space group $P\bar{1}$, a = 5.948(4), b = 10.125(2), c = 17.254(3) Å, α = 99.25(2), β = 95.83(3), γ = 103.07(3)°, U = 988.7 Å^3, Z = 2, D_c = 1.019 g cm^{-1}, $F(000)$ = 336. The structure of (**4**) (Figure 2) was solved by direct methods and refined to R = 0.094, R' = 0.113,‡ for 2017 reflections measured on a CAD-4 diffractometer with Mo-K_α radiation. The hydrogen atoms could not be located.

The molecular structure is shown in Figure 2. The central carbon atoms of the *ortho*-Bu^t substituent of the Ar group of $B(NH_2)_2(NHAr)$ are raised by 0.16 Å above the mean plane of the C_6 ring as viewed in Figure 2, and N(1) is 0.16 Å below the plane. The BN_3 moiety is planar and is at an angle of 91° to the C_6 plane. The three B–N bonds are non-equivalent. The bonds B–N(1), 1.412(4) Å, and B–N(2), 1.437(4) Å, are relatively short, as seen in other molecules with a $B(NR')_3$ grouping where both B and N atoms have trigonal planar co-ordination and $(p–p)\pi$-interactions are invoked;[2] *e.g.*, for $B(NHMe)_3$, the average B–N = 1.429 Å in the gas phase.[10] The shorter of the two bonds, B–N(1), is actually closer to that seen in molecules with only one or two amino groups on the boron, *e.g.*, for gaseous $BH(NH_2)_2$ 1.414(2) Å.[1] The third bond, B–N(3), at 1.470(4) Å, is significantly longer, suggesting a reduced $(p–p)\pi$-interaction with the B atom. This may be connected with the fact that the chain of atoms C(1)–N(1)–B–N(3) curves round towards the under side of the C_6 ring. This means that if the N(3)H$_2$ group were co-planar with the BN_3 moiety, one of the H atoms would be about 2.6 Å away from

the phenyl group. It is thus possible that the N(3)H$_2$ group is twisted away from co-planarity with BN_3, reducing the π-bonding interaction between N(3) and B and increasing the B–N(3) bond length.

References

1 T. S. Briggs, W. D. Gwinn, W. L. Jolly, and L. R. Thorne, *J. Am. Chem. Soc.*, 1978, **100**, 7762.
2 *Cf.*, M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, 'Metal and Metalloid Amides,' Horwood–Wiley, Chichester, 1980, ch. 4; Gmelin Handbuch der Anorganischen Chemie, 8th edition, Springer–Verlag, Berlin–Heidelberg–New York, 2nd Supplement, vol. 1, 1983, ch. 4.2; vol. 2, 1982, chs. 5.4.1 and 6.4.1.
3 J. R. Bowser, R. H. Neilson, and R. L. Wells, *Inorg. Chem.*, 1978, **17**, 1882.
4 A. Kreutzberger and F. C. Ferris, *J. Org. Chem.*, 1965, **30**, 360.
5 (a) G. Elter, O. Glemser, and W. Herzog, *J. Organomet. Chem.*, 1972, **37**, 257; (b) N. N. Greenwood, K. A. Hooton, and J. Walker, *J. Chem. Soc. A*, 1966, 21.
6 F. J. Lovas and D. R. Johnson, *J. Chem. Phys.*, 1973, **59**, 2347.
7 *Cf.*, H. Nöth and B. Wrackmeyer, 'Nuclear Magnetic Resonance Spectroscopy of Boron Compounds,' Springer–Verlag, Berlin–Heidelberg–New York, 1978.
8 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, M. C. Misra, and A. J. Thorne, *J. Chem. Soc., Chem. Comm.*, 1984, 148.
9 J. R. Blackborow, J. E. Blackmore, and J. C. Lockhart, *J. Chem. Soc. A*, 1971, 49.
10 G. Gundersen, *Kem. Kozl.*, 1978, **49**, 261; *Chem. Abstr.*, 1978, **89**, 83257.