A Novel Trico-ordinated Boronium Salt: 1,3-Dimethyl-2-phenanthridin-5-yl-1,3,2-diazaborolidinium Trifluoromethanesulphonate[1]

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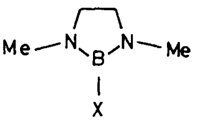
N.m.r. evidence suggests that pyridine but not phenanthridine reacts with 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (**1a**) in a 1 : 1 ratio with formation of an ionic compound; however, 1,3-dimethyl-2-trifluoromethanesulphonato-1,3,2-diazaborolidine (**1b**) produces a 1 : 1 addition product with phenanthridine which was shown to be the title compound by an *X*-ray structure determination.

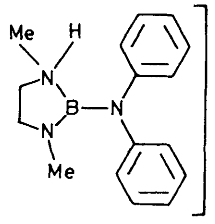
The tendency of boron to form neutral tri- and tetra-co-ordinated compounds is well established, and this is also true for anionic species. Although a boronium salt was first detected in 1906,[2] the chemistry of boron cations containing a tetraco-ordinated boron atom[3] rapidly developed after the characterisation of $H_2B(NH_3)_2^+$ by Parry and coworkers.[4]

Reports of boron salts with three ligands in the cation are scarce,[5] and the majority have been found to be incorrect.[6] However, we have recently observed that 2-halogeno-1,3-dimethyl-1,3,2-diazaborolidine (**1**, X = halogeno) adds pyridine in a 1:1 molar ratio, and ^{11}B n.m.r. data led to the conclusion that these adducts are ionic compounds.[7] Using a better leaving group we could unequivocally demonstrate that 1,3-dimethyl-2-trifluoromethanesulphonato-1,3,2-diazaborolidine, (**1b**), reacts with diphenylamine to yield the salt (**2**).[8]

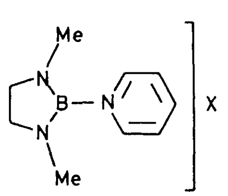
Our efforts to isolate pyridine-stabilized salts of type (**3**) have so far been unsuccessful although it was expected that pyridine might provide good charge delocalisation. Such stabilization was obtained by replacing pyridine by phenanthridine, (**4**). Compound (**1b**) reacts with (**4**) in CH_2Cl_2 solution to give the title compound (**5**), m.p. 98 °C, in 82% yield. ^{11}B N.m.r. spectroscopy [δ 27 p.p.m. (referenced to $BF_3 \cdot OEt_2$)] suggests the presence of trico-ordinated boron.‡



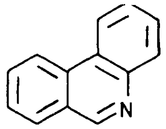
(1) a; X = Cl
b; X = SO_3CF_3



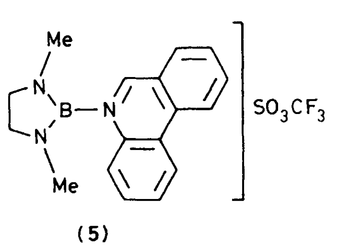
(2)



(3) X = Cl, Br, SO_3CF_3



(4)



(5)

Single crystals of (**5**) were obtained by slow diffusion of hexane into a CH_2Cl_2 solution. The *X*-ray crystal structure is shown in Figure 1.§ The diazaborolidine ring in (**5**) is almost planar. Its Me groups are twisted out of the plane [τ C(1)–N(1)–B–N(2) −166.2°, τ C(4)–N(2)–B–N(1) −168.8°], thus retaining the butterfly shape of the molecule as observed in 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine, (**1a**).[9] The two ring B–N bonds are virtually identical but 0.02 Å shorter

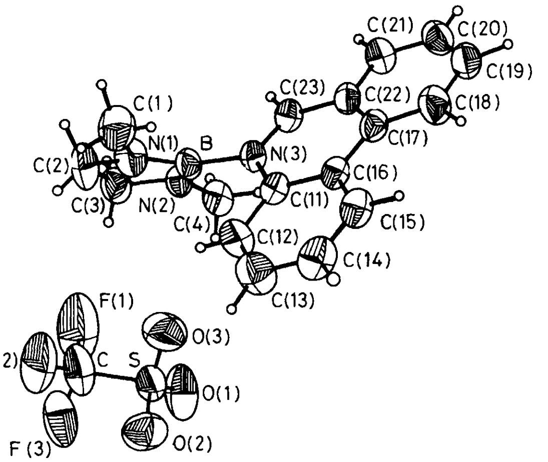


Figure 1. Molecular structure of (**5**). Selected bonding parameters: B–N(1) 1.390(5), B–N(2) 1.379(6), B–N(3) 1.530(6), N(1)–C(1) 1.436(6), N(1)–C(2) 1.457(7), C(2)–C(3) 1.509(7), N(2)–C(3) 1.472(7), N(2)–C(4) 1.440(5); C–C distances in the phenanthridine portion of the cation 1.366—1.445 Å. N(1)–B–N(2) 112.8(4), N(1)–B–N(3) 124.6(4), N(2)–B–N(3) 122.6(3) B–N(1)–C(2) 107.5(3), B–N(1)–C(1) 131.8(4), C(1)–N(1)–C(2) 118.6(3), N(1)–C(2)–C(3) 106.1(4), C(2)–C(3)–N(2) 105.1(5), C(3)–N(2)–B 107.8(3), C(3)–N(2)–C(4) 117.4(4), C(4)–N(2)–B 133.6(4)°.

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‡ The compound is fully characterized by elemental analysis, ^1H, ^{13}C and ^{19}F n.m.r., and i.r. data.

§ *Crystal data.* $C_{18}H_{19}BF_3N_3O_3S$, triclinic, $M = 425.24$, $a = 9.637(4)$, $b = 10.327(4)$, $c = 10.902(4)$ Å, $\alpha = 72.12(3)$, $\beta = 84.44(3)$, $\gamma = 75.51(3)°$, $U = 999.6$ Å^3, $Z = 2$, $D_c = 1.413$ g cm^{-3}, space group $P\bar{1}$; crystal size *ca.* 0.2 × 0.15 × 0.4 mm. 4656 Intensities were measured to $2\theta = 50°$ with Mo-K_α radiation ($\lambda = 0.71069$ Å), on a Syntex P3 diffractometer. 2605 Structure factors were available after merging the data, and 2042 [$F > 3\sigma(F)$] were used in the calculations. Nonhydrogen atoms were refined anisotropically, hydrogen atoms isotropically; $R = 0.0649$, $R_w = 0.0607$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

than in (**1a**). Also, the B–N(3) bond is 0.06 Å shorter than in Cl_3B·pyridine,[10] and we assume that this is due to the positive charge associated with (**5**).

The phenanthridine ring in (**5**) is practically planar (atoms deviate up to 0.035 Å from the best plane) except for atoms C(11) and C(12), which are located 0.11 Å out of the best plane, which is twisted by 55.0° *vs.* the B–N(1)–N(2)–N(3) plane. The N–C and C–C distances are similar to the structural features of unco-ordinated phenanthridine,[11] *e.g.* there is a short N(3)–C(23) bond and a fairly long C(16)–C(17) bond. However, C(23)–C(22) is almost normal, while long (1.486 Å) in the free ligand. The structural parameters of the trifluoromethanesulphonate group fit with known data for this anion,[12] and there is no bonding interaction between this anion and the boron atom also confirming the ionic nature of (**5**). Having established two ionic structures of amine adducts to 1,3-diazaborolidines the δ ^{11}B values (27—28 p.p.m.) are typical for diazaborolidinium cations in CH_2Cl_2 solution.

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