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Tetra-*n*-butylammonium phenyltrifluoroborate

Tan D. Quach, Robert A. Batey and Alan J. Lough*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Correspondence e-mail:
alough@chem.utoronto.ca

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.051
wR factor = 0.130
Data-to-parameter ratio = 17.5

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

The title compound, $C_{16}H_{36}N^+\cdot C_6H_5BF_3^-$, crystallizes as discrete tetra-*n*-butylammoniun ions and phenyltrifluoroborate ions. There are no close contacts between anions and cations.

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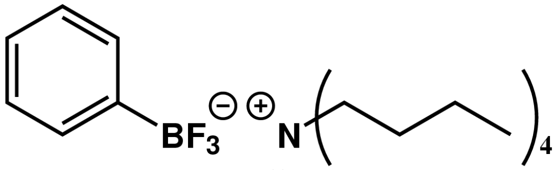
Comment

Recently, potassium organotrifluoroborate salts have gained considerable interest in organic synthesis as alternatives to boronic acids in reactions such as rhodium(I)-catalyzed 1,4-additions to α,β-unsaturated carbonyl compounds (Batey *et al.*, 1999), Lewis acid catalyzed allylation of aldehydes (Batey *et al.*, 2000), palladium catalyzed couplings with aryldiazonium compounds (Genet *et al.*, 1999), and the synthesis of oxazaborolidinones (Vedejs *et al.*, 1993). Their stability towards air and moisture also makes them ideal reagents for combinatorial synthesis. One drawback to their use, however, is their decreased solubility in non-polar organic solvents.



(I)

In an attempt to synthesize phenyldifluoroborane by treating the corresponding boronic acid with hydrofluoric acid (Kinder & Katzenellenbogen, 1985), it was discovered that the organodifluoroborane species would quickly convert to an organotrifluoroborate species (confirmed by ^{11}B NMR). It was hypothesized that the species formed was the hydronium organotrifluoroborate salt; however, all attempts to isolate this compound were unsuccessful, and the compound was only observable spectroscopically in solution *via* ^{11}B and ^{19}F NMR. Fortunately, treatment of the intermediate with the base tetra-*n*-butylammonium hydroxide affected a counterion exchange to produce the isolable title compound, (I).

The tetra-*n*-butylammonium derivative was found to have comparable reactivity to that of its potassium counterpart in the aforementioned reactions with the added advantage of having excellent solubility in nonpolar organic solvents. Compound (I) was also found to have greater reactivity than its potassium counterpart in palladium catalyzed Suzuki cross-coupling reactions with aryl- and alkenylhalides (Batey & Quach, 2001).

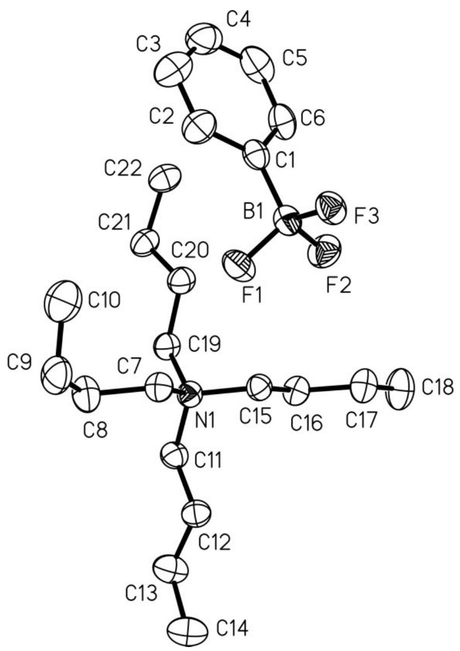


Figure 1
View of (I) showing the atom-labelling scheme. Ellipsoids are at the 50% probability level.

Compound (I) crystallizes as discrete tetra-*n*-butylammonium and phenyltrifluoroborate ions (see Fig. 1). There are no close contacts between the anions and cations in the structure. The tetra-*n*-butylammonium ion in (I) has three butyl groups which are in the staggered conformation and one group (containing the atoms C7, C8, C9 and C10) which is in a coiled conformation (see Table 1 for torsion angles) The structure of the related potassium phenyltrifluoroborate salt (Conole *et al.*, 1995) has also been determined.

Experimental

The title compound, (I), was synthesized by treatment of phenylboronic acid (0.52 g, 4.27 mmol), dissolved in a minimum amount of methanol (*ca* 1 ml), with a 5.0 *M* solution of hydrofluoric acid (2.65 ml, 13.25 mmol), added dropwise with vigorous stirring over a period of 1 min at room temperature. The reaction mixture was then cooled to 273 K, and a 1.54 *M* solution of tetra-*n*-butylammonium hydroxide (2.76 ml, 4.27 mmol) was added dropwise over a period of 5 min. The reaction mixture was then warmed to room temperature and stirred for another hour. Dichloromethane (10 ml) was added to dilute the biphasic reaction mixture, the layers were separated, and the aqueous layer was further extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford the pale yellow crystalline solid (I). Subsequent recrystallization from ethyl acetate and hexanes yielded the desired crystals.

Crystal data

$C_{16}H_{36}N^+\cdot C_6H_5BF_3^-$
$M_r = 387.37$
Orthorhombic, *Pbcn*
$a = 13.5626$ (6) Å
$b = 17.1534$ (7) Å
$c = 20.3567$ (7) Å
$V = 4735.9$ (3) Å^3
$Z = 8$
$D_x = 1.087$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 559 reflections
$\theta = 2.6$–25.4°
$\mu = 0.08$ mm^{-1}
$T = 150$ (1) K
Needle, colourless
0.40 × 0.35 × 0.34 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with φ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.970$, $T_{\max} = 0.974$
20 559 measured reflections
4341 independent reflections
2858 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 25.4°$
$h = -16 \rightarrow 16$
$k = -20 \rightarrow 20$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.130$
$S = 1.02$
4341 reflections
248 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 1.1252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—B1	1.600 (3)		
C7—C8—C9—C10	67.5 (2)	C15—C16—C17—C18	179.70 (18)
C11—C12—C13—C14	−177.23 (19)	C19—C20—C21—C22	−168.75 (17)

H atoms were included in calculated positions with C—H distances ranging from 0.95 to 0.99 Å.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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