

Dimethyl(2-methylphenyl)ammonium  
hydroxotris(pentafluorophenyl)borateRobert T. Stibrany<sup>a\*</sup> and Patrick Brant<sup>b</sup><sup>a</sup>Corporate Strategic Research, ExxonMobil Research and Engineering Company, Annandale, New Jersey 08801, USA, and <sup>b</sup>Baytown Polymers Center, ExxonMobil Chemical Company, Baytown, Texas 77522, USA  
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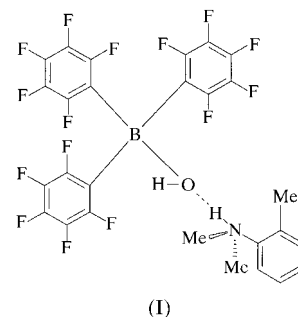
In the title compound,  $[(\text{CH}_3)_2(\text{C}_7\text{H}_7)\text{NH}][(\text{C}_6\text{F}_5)_3\text{B}(\text{OH})]$  or  $\text{C}_9\text{H}_{14}\text{N}^+\cdot\text{C}_{18}\text{HF}_{15}\text{O}^-$ , the distorted tetrahedral borate anions are strongly hydrogen bonded to the substituted ammonium cations. The  $\text{N}\cdots\text{O}$  separation in the  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond is 2.728 (3) Å.

## Comment

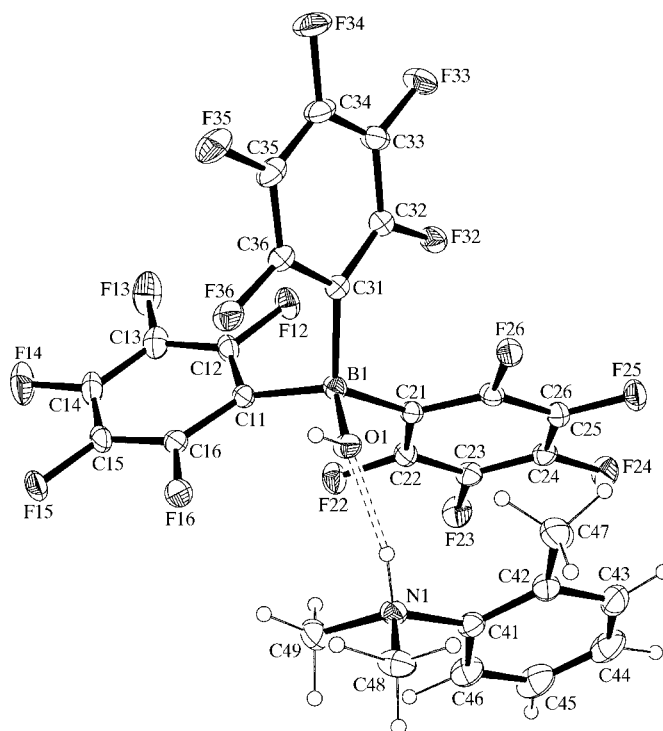
A review of the history of pentafluorophenylboranes, which have been known for over 35 years, shows that these compounds were given little attention until approximately ten years ago (Piers & Chivers, 1997). Since their discovery as highly effective activators for polymerization catalysts, a great deal of both academic and industrial research has been devoted to the understanding and improvement of these compounds (Turner & Hlatky, 1988; Hlatky *et al.*, 1989; Turner, 1997). The first reports of Lewis-acid activation of polymerization catalysts with tris(perfluorophenyl)borate also accelerated the research on these compounds (Ewen & Elder, 1995; Yang *et al.*, 1991). Recently, the nature of the ion pair found in these compounds has also become an active research topic. Such ion pairs are being examined by both experimental and theoretical techniques (Lanza *et al.*, 2000). The exact nature of the ion-pair separation has taken on added importance. Until now, many of these interactions have not been suitably characterized and they need to be in order to compare results obtained experimentally with those obtained theoretically. Ammonium hydroxyborates have also been investigated as activators (Siedle *et al.*, 1993). Specifically, the reaction of  $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$  with  $\text{Cp}_2\text{ZrMe}_2$  (Cp is cyclopentadienyl) did produce an active polymerization catalyst for 1-hexene. Ultimately, the catalyst decomposed to generate the  $(\text{C}_6\text{F}_5)_3\text{BO}^-$  anion coordinated to a metal center through the O and one of the F atoms.

No unusual bond distances or angles are observed in the perfluorophenyl moieties of the title compound, (I) (Fig. 1). The F—C bonds vary from 1.339 (3) to 1.360 (3) Å, the C—C bonds vary from 1.366 (4) to 1.393 (3) Å, and the B—C bonds vary from 1.651 (3) to 1.663 (3) Å. Similar bond lengths can be

found in compounds containing the  $(\text{C}_6\text{F}_5)_3\text{B}$  moiety (Danoopoulos *et al.*, 1998; Janiak *et al.*, 1998).



The two compounds that are most comparable to the title compound are  $[\text{Et}_3\text{NH}][(\text{C}_6\text{H}_5)_3\text{BOH}]$  and  $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$ . Unfortunately, both reports are inadequate. A B—O bond length of 1.487 (3) Å is reported for  $[\text{Et}_3\text{NH}][(\text{C}_6\text{H}_5)_3\text{BOH}]$  (Siedle *et al.*, 1993). Others have taken this report to refer to the fluorinated compound  $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$  (Hill *et al.*, 1997). Regardless, to the authors knowledge, a full crystal structure report has never been published or deposited. A structure for  $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$  has been reported recently (Duchateau *et al.*, 2000). Unfortunately, this structure was refined with an incorrect formula. While giving the correct formula in the text, the O—H atom was ignored by the authors in the refinement. No discussion of this discrepancy is offered either in the text or in the Crystallographic Information File. While this error will have little contribution to the overall refinement, it does affect the structural area of interest. The exact nature of the hydrogen



**Figure 1**  
The molecular structure of (I) showing 30% probability displacement ellipsoids.

bonding between the ion pairs is not revealed. The O—N distance in the reported compound is 2.734 (6) Å, comparable to the distance of 2.728 (3) Å in (I). The B—O—N angle of 134.6 (3)° in the above compound is also comparable to the value of 123.48 (3)° in (I). The O—N bond distances are the same within one s.u., while the B—O—N angle is compressed for (I). This compression most likely arises from cofacial accommodation of the C2 phenyl ring of the borate anion with the C4 phenyl ring of the ammonium cation.

Two structures have been reported with transition metal interactions with the [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>BOH]<sup>−</sup> anion. A [Ta(Cp\*)<sub>2</sub>(OH)-(CH<sub>3</sub>)][(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>BOH] complex (where Cp\* is pentamethylcyclopentadienyl) has a B—O distance of 1.490 (10) Å (Schaefer *et al.*, 1993). Neither the H atom of the anion nor the H atom of the OH group of the cation could be located in difference Fourier maps, but a likely hydrogen-bonding scheme is proposed. A platinum complex is reported in which the anion forms a Pt—O bond. In this complex, the B—O distance is 1.526 (3) Å (Hill *et al.*, 1997). The H atom of the anion was located in a difference Fourier map, with some imprecision, and is found to be hydrogen bonded to two F atoms on two of the phenyl rings.

## Experimental

Compound (I) was obtained as a decomposition product of a metallocene reacted with tris(pentafluorophenyl)borate in tetrahydrofuran followed by vapor diffusion of pentane at 276 K.

### Crystal data

C<sub>9</sub>H<sub>14</sub>N<sup>+</sup>·C<sub>18</sub>HBF<sub>15</sub>O<sup>−</sup>  
*M<sub>r</sub>* = 665.21  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 10.552 (5) Å  
*b* = 15.287 (2) Å  
*c* = 16.072 (9) Å  
 $\beta$  = 96.60 (5)°  
*V* = 2575.4 (19) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.716 Mg m<sup>−3</sup>  
 Cu *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 28.2–42.4°  
 $\mu$  = 1.62 mm<sup>−1</sup>  
*T* = 153 (2) K  
 Spike, yellow–brown  
 0.20 × 0.07 × 0.05 mm

### Data collection

Nonius CAD-4 diffractometer  
 $\omega$  scans  
 5131 measured reflections  
 4762 independent reflections  
 3592 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.022  
 $\theta_{\max}$  = 69.9°

*h* = −12 → 11  
*k* = 0 → 18  
*l* = 0 → 19  
 3 standard reflections every 300 reflections  
 intensity decay: 2%

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.044  
*wR* (*F*<sup>2</sup>) = 0.118  
*S* = 1.05  
 4762 reflections  
 466 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.10P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

B1—O1	1.483 (3)	N1—C41	1.490 (3)
B1—C21	1.651 (3)	N1—C49	1.497 (3)
B1—C11	1.661 (3)	N1—C48	1.509 (3)
B1—C31	1.663 (3)		
O1—B1—C21	102.67 (18)	C11—B1—C31	102.80 (18)
O1—B1—C11	114.25 (18)	C41—N1—C49	114.4 (2)
C21—B1—C11	112.80 (18)	C41—N1—C48	111.2 (2)
O1—B1—C31	111.96 (18)	C49—N1—C48	109.2 (2)
C21—B1—C31	112.75 (18)		

The refined C—H distances are in the range 0.96 (3)–1.10 (3) Å and the N—H distance is 0.95 (3) Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local programs; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97-2* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP32* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97-2*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1161). Services for accessing these data are described at the back of the journal.

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