

## Thermal and Transport Properties of Ionic Liquids Based on Benzyl-Substituted Phosphonium Cations

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The physicochemical properties of two novel ionic liquids based on benzyltriethylphosphonium and benzyltributylphosphonium cations are described in this report. It was found that both benzyl-substituted phosphonium cations gave low-melting salts in combination with a bis(trifluoromethylsulfonyl)amide anion. The thermogravimetric analysis suggested that the benzyl-substituted phosphonium ionic liquids showed higher thermal stability than those of not only the alkyl-substituted phosphonium ILs but also the corresponding benzyl-substituted ammonium compounds. The benzyl-substituted phosphonium ionic liquids also exhibited relatively high conductivities when compared to those of the corresponding ammonium compounds. These results indicate an improving effect of introducing a benzyl group into the phosphonium cations on both the thermal stability and the conductivity.

### Introduction

Ionic liquids (ILs), being organic molten salts with melting points below 100 °C, have been investigated for a wide variety of applications such as recyclable solvents for organic reactions and separation processes,<sup>1–4</sup> electrolytic media for various electrochemical systems,<sup>5,6</sup> lubricating fluids,<sup>7–9</sup> active pharmaceutical ingredients,<sup>10,11</sup> and so forth. This versatility is due to the fact that ILs have unique physicochemical properties including favorable solubility of organic and inorganic compounds, relatively high ionic conductivity, no measurable vapor pressure, high thermal stability, and low flammability. Another remarkable advantage of ILs is a designability of cations and anions. The purposive design of the ion structures by introducing a functional group significantly expands to obtain new ILs. For example, introduction of a benzyl group into nonaromatic onium cations should give specific physicochemical properties arising from the aromatic ring. From this point of view, Kohl and co-workers have reported a novel class of ILs based on quaternary ammonium cations containing a benzyl group together with a chloroaluminate anion, showing that the benzyl-substituted ammonium ILs have unique electrochemical properties suitable for sodium battery electrolytes.<sup>12–14</sup>

On the other hand, quaternary phosphonium based ILs have been receiving a great deal of attention as potential substitutes for the corresponding ammonium counterparts.<sup>15</sup> In the pioneering study by Bradaric and co-workers, the chemical and thermal properties of the ILs based on the trihexyl(tetradecyl)phosphonium cation ( $(C_6H_{13})_3C_{14}H_{29}P^+$ ) with various anions were reported from synthetic and industrial aspects.<sup>16</sup> Ohno and co-workers investigated that the combination of tetrabutylphosphonium cation ( $(C_4H_9)_4P^+$ ) and amino acid based anions gave thermally stable ILs showing unique miscibility and phase behavior.<sup>17,18</sup> Itoh and co-workers synthesized a variety of alkoxy-substituted

phosphonium ILs as suitable media for organic reactions such as Grignard reactions and lipase-catalyzed transesterifications.<sup>19,20</sup> We have developed a series of ILs based on relatively small phosphonium cations derived from triethylphosphine ( $(C_2H_5)_3P$ ) and tributylphosphine ( $(C_4H_9)_3P$ ) together with a bis(trifluoromethylsulfonyl)amide (TFSA) anion in order to obtain relatively low viscous phosphonium ILs as potential electrolytes for various electrochemical systems.<sup>21,22</sup> It was found that the phosphonium ILs exhibited lower viscosities and higher conductivities and thermal stabilities than those of the corresponding ammonium ILs. This characteristic feature seems to be a considerable advantage of phosphonium ILs, so that the properties of phosphonium ILs functionalized by a benzyl group are of particular interest as in the case of benzyl-substituted ammonium ILs. However, to the best of our knowledge, there has been no report on ILs containing benzyl-substituted phosphonium cations.

Here, we report the physicochemical characterization of quaternary phosphonium compounds substituted by a benzyl group. As shown in Figure 1, the cation structures investigated were derived from triethylphosphine, tributylphosphine, and the corresponding amines for the comparative examination. The TFSA anion was employed as an anionic component because it is well-known that the TFSA anion forms hydrophobic, low-melting, and thermally stable salts together with various cations. This paper describes the thermal and transport properties of the benzyl-substituted phosphonium ILs in comparison with those of the corresponding ammonium compounds, demonstrating the effects of introducing a benzyl group on the properties of the phosphonium ILs.

### Experimental Section

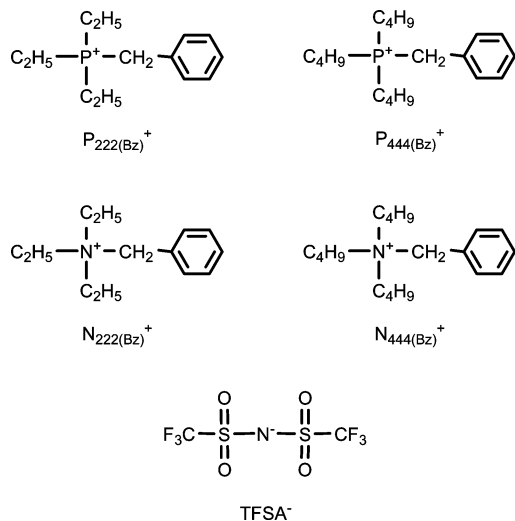
**Preparation.** The benzyl-substituted phosphonium and the corresponding ammonium compounds were prepared according to the procedure described elsewhere.<sup>21,22</sup> Benzyltriethylphosphonium and benzyltributylphosphonium chlorides were supplied by Nippon Chemical Industrial Co., Ltd. (trade names Hishicolin PX-2BZC and Hishicolin PX-4BZC, respectively).

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**Figure 1.** Structural illustration of ionic components of ILs investigated in this work.

The corresponding ammonium chlorides (benzyltriethylammonium and benzyltributylammonium chlorides) were used as purchased from Tokyo Chemical Industry Co., Ltd. The aqueous ion exchange reactions of the chlorides with Li-TFSA (Kanto Chemical Co., Inc.) were carried out at ambient temperature to obtain the corresponding TFSA salts. The resulting crude compounds were extracted by dichloromethane and then purified by washing with pure water several times until no residual chloride anion was detected with the use of  $\text{AgNO}_3$ . All of the compounds were dried under high vacuum for at least 8 h at 120 °C and were stored in an argon atmosphere glovebox. The water content in each compound, which was measured by using a Karl Fischer moisture titrator (Kyoto Electronics Manufacturing Co., Ltd., MKC-610), was in the range between 50 and 100 ppm. The products obtained were confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMRs. The residual contents of the chloride anion (<50 ppm) and lithium cation (<5 ppm) were checked by an ion chromatography and an inductively coupled plasma spectrometer (Varian, ICP-AES Liberty LR Sequential), respectively.

**NMR Characterization Data.** Benzyltriethylphosphonium bis(trifluoromethylsulfonyl)amide ( $\text{P}_{222}(\text{Bz})\text{-TFSA}$ ),  $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_2\text{H}_5)_3\text{P-N}(\text{SO}_2\text{CF}_3)_2$ :  $^1\text{H}$  NMR (300.40 MHz in  $\text{CDCl}_3$ )  $\delta$  1.13–1.33 (m, 9H,  $\text{CH}_3$ ); 2.07–2.19 (m, 6H,  $\text{CH}_2$ ); 3.59–3.67 (d, 2H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ); 7.26–7.42 (m, 5H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ) ppm.  $^{13}\text{C}$  NMR (75.45 MHz in  $\text{CDCl}_3$ )  $\delta$  4.69, 10.88, 25.03 (various d,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_2$ ); 119.54 (q,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ); 127.05–129.39 (various s,  $\text{C}_6\text{H}_5$ ) ppm.  $^{19}\text{F}$  NMR (282.65 MHz in  $\text{CDCl}_3$ )  $\delta$  -80.15 (d,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ) ppm.  $^{31}\text{P}$  NMR (121.55 MHz in  $\text{CDCl}_3$ )  $\delta$  37.77 (s,  $\text{P}^+$ ) ppm.

Benzyltributylphosphonium bis(trifluoromethylsulfonyl)amide ( $\text{P}_{444}(\text{Bz})\text{-TFSA}$ ),  $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_4\text{H}_9)_3\text{P-N}(\text{SO}_2\text{CF}_3)_2$ :  $^1\text{H}$  NMR (300.40 MHz in  $\text{CDCl}_3$ )  $\delta$  0.90–0.94 (t, 9H,  $\text{CH}_3$ ); 1.42–1.48 (m, 12H,  $\text{CH}_2$ ); 2.03–2.13 (m, 6H,  $\text{CH}_2$ ); 3.57–3.62 (d, 2H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ); 7.21–7.25 (m, 2H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ); 7.33–7.42 (m, 3H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ) ppm.  $^{13}\text{C}$  NMR (75.45 MHz in  $\text{CDCl}_3$ )  $\delta$  13.06–26.29 (various s,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_2$ ); 119.54 (q,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ); 127.50–129.68 (various s,  $\text{C}_6\text{H}_5$ ) ppm.  $^{19}\text{F}$  NMR (282.65 MHz in  $\text{CDCl}_3$ )  $\delta$  -80.12 (d,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ) ppm.  $^{31}\text{P}$  NMR (121.55 MHz in  $\text{CDCl}_3$ )  $\delta$  29.51 (s,  $\text{P}^+$ ) ppm.

Benzyltriethylammonium bis(trifluoromethylsulfonyl)amide ( $\text{N}_{222}(\text{Bz})\text{-TFSA}$ ),  $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_2\text{H}_5)_3\text{N-N}(\text{SO}_2\text{CF}_3)_2$ :  $^1\text{H}$  NMR (300.40 MHz in  $\text{CDCl}_3$ )  $\delta$  1.37–1.42 (m, 9H,  $\text{CH}_3$ ); 3.15–3.23 (q, 6H,  $\text{CH}_2$ ); 4.30 (s, 2H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ); 7.38–7.51 (m, 5H,

**TABLE 1: Thermal Properties of Benzylphosphonium and the Corresponding Ammonium Compounds**

compound	FW <sup>a</sup>	$T_m$ <sup>b</sup> /°C	$T_g$ <sup>c</sup> /°C	$T_{\text{dec}}$ <sup>d</sup> /°C
$\text{P}_{222}(\text{Bz})\text{-TFSA}$	489.43		-67	430
$\text{P}_{444}(\text{Bz})\text{-TFSA}$	573.59	43		389
$\text{N}_{222}(\text{Bz})\text{-TFSA}$	472.47	41		353
$\text{N}_{444}(\text{Bz})\text{-TFSA}$	556.63	58		341

<sup>a</sup> Formula weight. <sup>b</sup> Melting point. <sup>c</sup> Glass transition temperature. <sup>d</sup> Thermal decomposition temperature (10% weight loss).

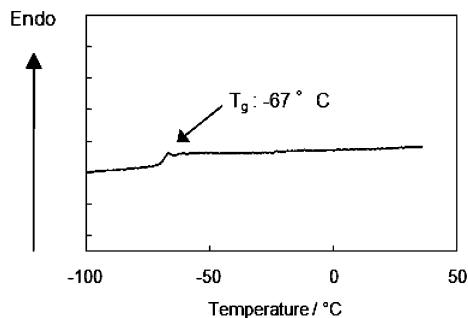
$\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ) ppm.  $^{13}\text{C}$  NMR (75.45 MHz in  $\text{CDCl}_3$ )  $\delta$  7.60, 52.58, 60.73 (various s,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_2$ ); 119.54 (q,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ); 126.27–132.05 (various s,  $\text{C}_6\text{H}_5$ ) ppm.  $^{19}\text{F}$  NMR (282.65 MHz in  $\text{CDCl}_3$ )  $\delta$  -80.19 (d,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ) ppm.

Benzyltributylammonium bis(trifluoromethylsulfonyl)amide ( $\text{N}_{444}(\text{Bz})\text{-TFSA}$ ),  $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_4\text{H}_9)_3\text{N-N}(\text{SO}_2\text{CF}_3)_2$ :  $^1\text{H}$  NMR (300.40 MHz in  $\text{CDCl}_3$ )  $\delta$  0.96–1.01 (t, 9H,  $\text{CH}_3$ ); 1.32–1.44 (q, 6H,  $\text{CH}_2$ ); 1.68–1.78 (m, 6H,  $\text{CH}_2$ ); 3.04–3.15 (m, 6H,  $\text{CH}_2$ ); 4.37 (s, 2H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ); 7.33–7.36 (m, 2H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ); 7.43–7.53 (m, 3H,  $\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ ) ppm.  $^{13}\text{C}$  NMR (75.45 MHz in  $\text{CDCl}_3$ )  $\delta$  13.27–62.29 (various s,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_2$ ); 119.54 (q,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ); 126.48–132.00 (various s,  $\text{C}_6\text{H}_5$ ) ppm.  $^{19}\text{F}$  NMR (282.65 MHz in  $\text{CDCl}_3$ )  $\delta$  -79.91 (d,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ) ppm.

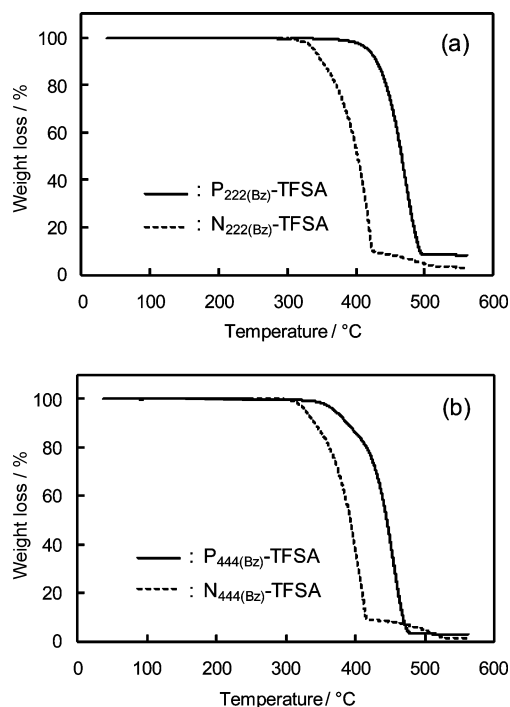
**Measurements of Physical Properties.** The melting point and glass transition temperature of each compound were analyzed by using a differential scanning calorimeter (Seiko Instruments Inc., DSC6200) with a cooling and heating rate of 1 °C  $\text{min}^{-1}$ . The density of each liquid compound was determined by gravimetric analysis using a calibrated pipet at 25 °C. The viscosity of each liquid compound was measured by using a vibration type viscometer (CBC Materials Co. Ltd., VM-10A laboratory viscometer calibrated with the Brookfield Viscosity Standard) under an argon atmosphere at 25 °C. The measurement of conductivity (Ivium Technologies, Compact-Stat, using an ac impedance mode) was carried out using a two Pt electrode conductivity cell (cell constant: 1.27  $\text{cm}^{-1}$ ) under an argon atmosphere at various temperatures. The thermogravimetric trace of each compound was recorded by using a thermogravimetric analyzer (Seiko Instruments Inc., TG/DTA6300) at a heating rate of 10 °C  $\text{min}^{-1}$  under a nitrogen atmosphere.

## Results and Discussion

**Thermal Property.** The data of melting point, glass transition temperature, and thermal decomposition temperature of benzyl-substituted phosphonium and the corresponding ammonium compounds are listed in Table 1. In the benzyl-substituted compounds prepared in this work, only  $\text{P}_{222}(\text{Bz})\text{-TFSA}$  was a liquid at room temperature (the so-called room-temperature ionic liquid, RTIL). As shown in Figure 2,  $\text{P}_{222}(\text{Bz})\text{-TFSA}$  has no melting point even when cooled from room temperature to -100 °C, whereas a glass transition temperature was observed at -67 °C. This low-melting behavior of  $\text{P}_{222}(\text{Bz})\text{-TFSA}$  is noteworthy because the corresponding ammonium compound ( $\text{N}_{222}(\text{Bz})\text{-TFSA}$ ) was a crystalline solid at room temperature (melting point: 41 °C). Although the melting point of  $\text{P}_{444}(\text{Bz})\text{-TFSA}$  was higher than room temperature (43 °C),  $\text{P}_{444}(\text{Bz})\text{-TFSA}$  showed a lower melting point than the corresponding ammonium compound ( $\text{N}_{444}(\text{Bz})\text{-TFSA}$ ), as in the case of  $\text{P}_{222}(\text{Bz})\text{-TFSA}$ . These results indicate that benzyl-substituted phosphonium cations tend to give relatively low melting compounds when compared to the corresponding ammonium cations.



**Figure 2.** DSC thermogram of  $P_{222}(Bz)$ -TFSA.



**Figure 3.** Thermogravimetric traces of benzyl-substituted phosphonium (solid line) and the corresponding ammonium (dotted line) compounds, (a)  $P_{222}(Bz)$ -TFSA and  $N_{222}(Bz)$ -TFSA, (b)  $P_{444}(Bz)$ -TFSA and  $N_{444}(Bz)$ -TFSA.

According to the acceptable interpretation for the quaternary ammonium cations by Zhou and co-workers, the melting point significantly depends on the lattice energy controlled by following major factors: the conformational degree of freedom, intermolecular forces, and symmetry of cation structure.<sup>23,24</sup> In order to obtain low-melting compounds, the lattice energy should be reduced by increasing the conformational degree of freedom and decreasing the intermolecular forces and cation symmetry. It seems reasonable to give a similar explanation to the benzyl-substituted phosphonium compounds. When compared to the corresponding ammonium cations, the structure of phosphonium cations might be “soft” due to the relatively large radii of the phosphorus atom. This means that the phosphonium cations might contribute to a decrease of the lattice energy with an increase of the flexibility of the cation structure (that is, the conformational degree of freedom), thereby resulting in the relatively low melting points.

Thermal stability of ILs is of practical importance for various applications. As shown in Figure 3, typical thermogravimetric traces were observed for benzyl-substituted phosphonium and the corresponding ammonium compounds. Both  $P_{222}(Bz)$ -TFSA and  $P_{444}(Bz)$ -TFSA exhibited a high onset thermal decomposition temperature  $T_{dec}$  (430 and 389 °C, respectively). It was clearly

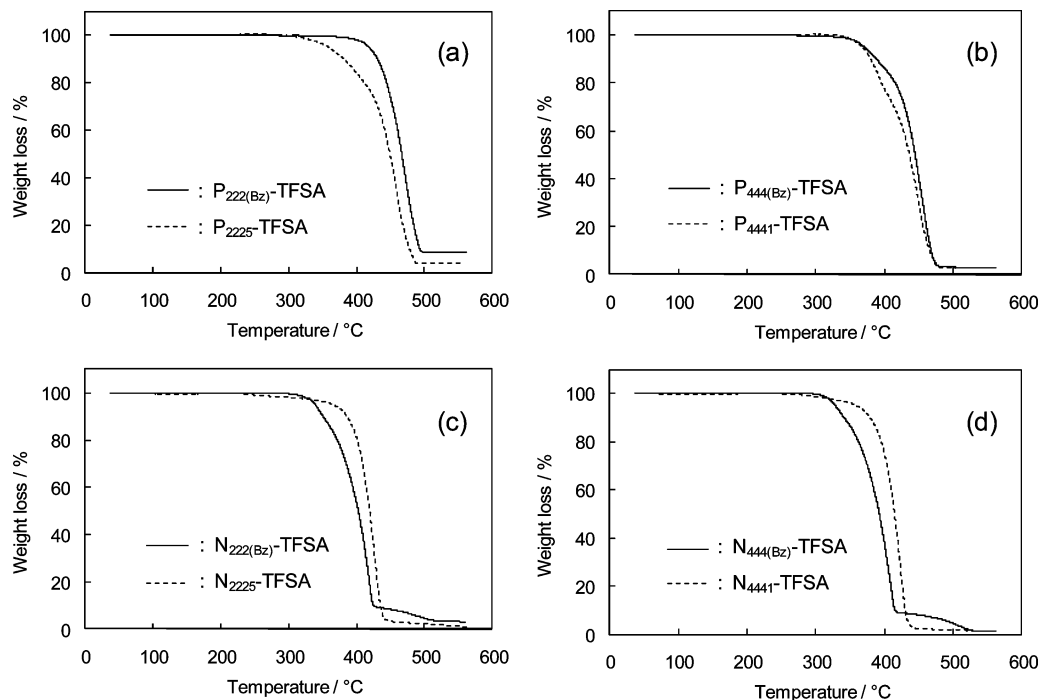
found that the thermogravimetric decreases of the benzyl-substituted phosphonium compounds took place at much higher temperatures than those of the corresponding ammonium compounds, revealing the relatively high thermal stability of the benzyl-substituted phosphonium compounds. Similar results have been reported in a previously published paper describing the thermogravimetric analysis data of alkyl-substituted phosphonium ILs not containing the benzyl group.<sup>21</sup> Additionally, the amount of residues left after the thermal decomposition of benzyl-substituted phosphonium compounds tended to be larger than those of the corresponding ammonium compounds, which seems to be attributed to the formation of less volatile phosphorus-containing species (e.g., polyphosphate derivatives). Particularly,  $P_{222}(Bz)$ -TFSA gave a relatively large amount of the residue when compared to  $P_{444}(Bz)$ -TFSA because the content of phosphorus in  $P_{222}(Bz)$ -TFSA is higher than that in  $P_{444}(Bz)$ -TFSA.

In order to discuss the influence of introducing a benzyl group on thermal stability, Figure 4 illustrates the thermogravimetric traces for the benzyl-substituted phosphonium and ammonium compounds in comparison with those for the corresponding alkyl-substituted onium compounds. As shown in Figure 4a, the onset thermal decomposition temperature ( $T_{dec}$ ) of  $P_{222}(Bz)$ -TFSA was 430 °C, indicating the higher thermal stability than that of the alkyl-substituted phosphonium IL ( $T_{dec}$  of  $P_{222}$ -TFSA: 380 °C). Slightly high thermal stability was observed in the case of  $P_{444}(Bz)$ -TFSA (Figure 4b), although the curve for the thermogravimetric decrease of  $P_{444}(Bz)$ -TFSA seems to be similar to that of the alkyl-substituted phosphonium IL ( $P_{444}$ -TFSA). This comparative result suggests an effect of introducing a benzyl group to the phosphonium cations on the improvement of the thermal stability. In contrast, Figure 4c and d clearly exhibits that the thermogravimetric decreases of  $N_{222}(Bz)$ -TFSA and  $N_{444}(Bz)$ -TFSA occurred at lower temperatures than those of the alkyl-substituted ammonium compounds, which means that the benzyl group introduced into the ammonium cations reduces the thermal stability of the ammonium compounds.

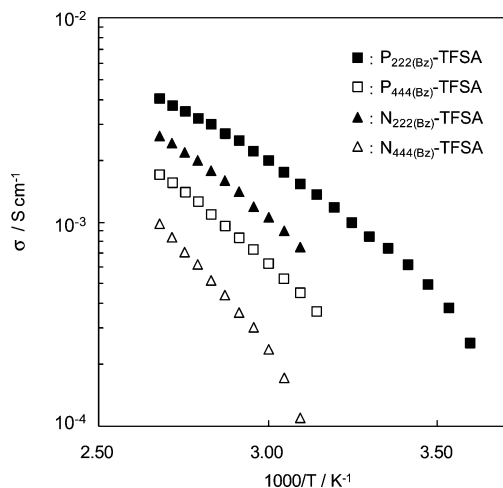
This finding suggests that the improving effect of introducing a benzyl group on the thermal stability was significantly seen only in the phosphonium cation system. At present, the reason for the effect remains unclear; however, a presence of empty d orbitals in the phosphorus atom may play an essential role in the thermal stability. It is generally accepted that quaternary phosphonium compounds are more covalent than the corresponding ammonium compounds,<sup>25</sup> which allows us to infer that the empty d orbitals in the phosphorus atom more or less interact with the counteranions to weaken the electrostatic forces between cations and anions. In the case of the benzyl-substituted phosphonium compounds, not only the TFSA anion but also  $\pi$ -electrons in the benzyl group might be associated with the d orbital interactions. These interactions seem likely to give a significant increase in the bond strength, thereby resulting in the high thermal stability. The quaternary ammonium cations have no d orbitals, so that the improving effect on the thermal stability was not observed in the benzyl-substituted ammonium compounds.

**Transport Property.** Figure 5 exhibits the Arrhenius plots for the conductivities of benzyl-substituted phosphonium and the corresponding ammonium compounds. As shown in Figure 5, the plot for each compound showed typical convex curved profiles for ionic conductivity (the so-called Vogel–Tammann–Fulcher behaviors). It should be noted that both  $P_{222}(Bz)$ -TFSA and  $P_{444}(Bz)$ -TFSA have relatively high conductivities at various temperatures when compared to the corresponding ammonium





**Figure 4.** Thermogravimetric traces of benzyl-substituted (solid line) and the alkyl-substituted (dotted line) compounds, (a)  $P_{222(Bz)}$ -TFSA and  $P_{2225}$ -TFSA, (b)  $P_{444(Bz)}$ -TFSA and  $P_{4441}$ -TFSA, (c)  $N_{222(Bz)}$ -TFSA and  $N_{2225}$ -TFSA, (d)  $N_{444(Bz)}$ -TFSA and  $N_{4441}$ -TFSA.



**Figure 5.** Arrhenius plots of the conductivity for the benzyl-substituted phosphonium and the corresponding ammonium compounds.

compounds. In our previous study, similar results have been observed in the case of the alkyl-substituted phosphonium ILs.<sup>21</sup> Although we are unable to give clear interpretation concerning such an improvement of the transport property, the decreasing effect on the negative charge of anions arising from the empty d orbitals in the phosphorus atom also seems to afford a decrease in the viscosity and the corresponding increase in the conductivity.

Particularly,  $P_{222(Bz)}$ -TFSA showed the highest conductivity in the benzyl-substituted compounds. For the evaluation of the transport property of  $P_{222(Bz)}$ -TFSA, the data of density, viscosity, and conductivity of  $P_{222(Bz)}$ -TFSA at 25 °C are listed in Table 2 in comparison with those of the alkyl-substituted phosphonium ILs. Compared to the alkyl-substituted phosphonium ILs having similar formula weights ( $P_{2225}$ -TFSA and  $P_{2228}$ -TFSA), the viscosity of  $P_{222(Bz)}$ -TFSA is considerably higher than those of the alkyl-substituted phosphonium ILs, despite the fact that the viscosity greatly depends on the van der Waals interaction of

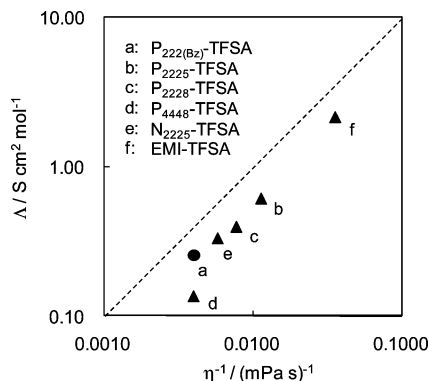
ILs. On the other hand, when compared to the alkyl-substituted phosphonium IL showing a similar viscosity ( $P_{4448}$ -TFSA),  $P_{222(Bz)}$ -TFSA exhibits relatively high conductivity.

In general, the conductivity of RTILs strongly depends on the viscosity. As shown in Table 2,  $P_{222(Bz)}$ -TFSA tends to exhibit relatively high conductivity compared to the measured viscosity. In order to discuss the correlation between conductivity and viscosity, the plots of the molar conductivity  $\Lambda$  against the inverse viscosity  $\eta^{-1}$  (the so-called Walden plot)<sup>26,27</sup> for the  $P_{222(Bz)}$ -TFSA and the alkyl-substituted phosphonium ILs are depicted in Figure 6. Each plot was positioned into a nonionic region below the ideal Walden line (dilute aqueous KCl solution) as in the case of typical RTILs (e.g., EMI-TFSA). It is noteworthy that the plot of  $P_{222(Bz)}$ -TFSA (point a) clearly approached the ideal Walden line when compared to that of  $P_{4448}$ -TFSA (point d). This result supports a relatively high degree of dissociation between the  $P_{222(Bz)}$  cation and the TFSA anion because deviation from the ideal line is thought to indicate an association of ions as suggested by the Walden rule. The plot of  $P_{4448}$ -TFSA (point d) seems to lie in a somewhat associated region, which is similar to the tendency observed in the case of large phosphonium-cation-based RTILs newly synthesized by MacFarlane and co-workers.<sup>28,29</sup> However, the plot of  $P_{4448}$ -TFSA (point d) seems likely to be exceptional since there are no clear differences in the deviation for the other plots. This also means that  $P_{222(Bz)}$ -TFSA might show the comparable degree of ion dissociation to the other ILs except  $P_{4448}$ -TFSA. On the other hand, MacFarlane and co-workers recently demonstrate that strict interpretation of the Walden plot often needs adjustment of the plots for the size of ions.<sup>29</sup> Such a viewpoint should be very significant to clarify the degree of dissociation/association in benzyl-substituted phosphonium systems. Further investigation concerning the dissociation/association behaviors of benzyl-substituted phosphonium ILs will be conducted.

**TABLE 2: Comparison of Physical Properties between P<sub>222</sub>(Bz)-TFSA and Alkyl-Substituted Phosphonium ILs**

ionic liquid	FW <sup>a</sup>	T <sub>m</sub> <sup>b</sup> /°C	d <sup>c</sup> /g cm <sup>-3</sup>	C <sup>d</sup> /mol dm <sup>-3</sup>	η <sup>e</sup> /mPa s	σ <sup>f</sup> /mS cm <sup>-1</sup>	Λ <sup>g</sup> /S cm <sup>2</sup> mol <sup>-1</sup>	reference
P <sub>222</sub> (Bz)-TFSA	489.43	< -50	1.43	2.92	248	0.74	0.25	this work
P <sub>2225</sub> -TFSA	469.44	17	1.32	2.81	88	1.73	0.61	21
P <sub>2228</sub> -TFSA	511.52	< -50	1.26	2.46	129	0.98	0.40	21
P <sub>4448</sub> -TFSA	595.68	< -50	1.18	1.99	250	0.27	0.13	22

<sup>a</sup> Formula weight. <sup>b</sup> Melting point. <sup>c</sup> Density at 25 °C. <sup>d</sup> Concentration at 25 °C. <sup>e</sup> Viscosity at 25 °C. <sup>f</sup> Conductivity at 25 °C. <sup>g</sup> Molar conductivity at 25 °C.



**Figure 6.** Plots of the molar conductivity against the inverse viscosity for various phosphonium ILs. The dotted line indicates the ideal Walden line (diluted KCl aqueous solution). EMI-TFSA shows 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.

## Conclusions

We have physicochemically characterized two novel ILs based on benzyl-substituted phosphonium cations together with a TFSA anion, revealing the effect of introducing a benzyl group into the phosphonium cations. It was found that the benzyl-substituted phosphonium ILs were lower-melting, more thermally stable, and more highly conductive than the corresponding benzyl-substituted ammonium compounds. Interestingly, the high thermal stability was significantly observed only when phosphonium cations and a benzyl group were combined. These unique features of the benzyl-substituted phosphonium ILs should be practically advantageous for various applications.

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