

## Manuscript Details

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<b>Title</b>	The effect of substituents of phosphonium-based ionic liquids evaluated by MP2 calculation
<b>Article type</b>	Short communication

### Abstract

Transport property such as conductivity and viscosity is important factor in designing ionic liquids (ILs). Depending on substituent type in ILs, the transport property is known to easily changeable. Introduction of a benzyl or a cyano group lowers the transport property, however in the case of a methoxy or an allyl group, the transport property is improved. It is important to reveal the static property with different substituents on the phosphonium-based ILs from the viewpoint of the microscopic analysis by theoretical calculation. For this purpose, we investigated the charge distribution, interaction with counter anion and torsional potential for different substituents on the phosphonium-based ILs in this study. From the MP2/6-311G\*\* calculation, the atomic charge of the phosphorus atom on the P4444+ cation was 0.57 and it was higher than that of nitrogen atom (0.14) on the corresponding ammonium cation (N4444+). The charge distributions with different substituents such as P444(3Bz), P444(3CN), P444(2Al) and P444(2O1) were also revealed in this study. According to the analysis of the torsion potential with different substituents, the methoxy substituted cations which would lead to the good transport property were stable at a torsional angle of 180 ° and the allyl substituted cations were stable at 120 ° and 240 °. On the other hand, it was found that the benzyl and the cyano substitution type cations, which were known as lower transport properties, were most stable at torsional angles of 60 ° and 300 °. Furthermore, it was revealed that the rotational barriers of the dihedral angular potential of the methoxy and the allyl group are smaller than those of the cyano and the benzyl group. Moreover, from the calculated optimized geometry and the interaction energy of the cations containing various substituents, the gain (Eint) of the energy obtained by cluster formation in the ammonium cation was larger than that in the phosphonium cation. A series of the MP2 calculation results enabled us to indicate that the phosphonium cation had a higher affinity for the anion than the corresponding ammonium cation and the effect of the substituent on ionic interaction was not so influenced on each transport property.

<b>Keywords</b>	Charge distribution, Ionic liquids, MP2 calculation, Substituents
<b>Manuscript category</b>	Ionic liquids
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Dear Prof. W. Schröer  
Editor-in-Chief of Journal of Molecular Liquids

Thank you for sending e-mail and many valuable reviewer comments.  
The comments for each reviewer about the revised manuscript were written as follows.  
We hope that the revised manuscript will be suitable for the publication.  
Sincerely yours.

-----  
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## For Reviewer 1

Thank you for sending many useful comments.

According to your comments, the revised manuscript was corrected as follows.

### -Reviewer 1-

1. The last statement in abstract i.e. “the effect of the substituent on ionic interactions was not so influenced on each transport property” seems to be vague. I do not understand which transport properties the authors are taking about. The authors have not even shown a single structure-property relationship and one cannot make such strong statement without correlating with at least one of the transport property.

According to your suggestion, the data of the transport property was added in the revised manuscript. The transport property mentioned here mainly indicated the viscosity and the conductivity. By the effect of the substituent, it contributes to improvement in conductivity and decrease in viscosity. (p.1L1-L4, p.2L10-L12)

2. There is lack of clarity in introduction section also particularly in line 21 and 22. The author should elaborate the discussion about the transport properties. How these transport properties improved with functionality should be mentioned clearly.

According to your suggestion, the explanation about the transport property was added in the revised manuscript. The transport property mentioned here mainly indicated viscosity and conductivity. (p.1L1-L4, p.2L10-L12)

3. The authors should make use of the basis set with diffuse functions being added that is, use of the 6-311++G(d,p) basis is recommended.

According to the reference about Tsuzuki. et. al, it was reported that the result by mp2/6-311G(d,p) is close to that by mp2/aug-cc-pVTZ, which is a heavy basis set. As a result, the mp2/6-311G(d,p) is satisfied to research the phenomena. In addition, selection of basis set and electron correlation method may change calculated intermolecular interaction energy of hydrogen bonding system and van der Waals clusters. However, the main attraction source in ion pair is monopole-monopole (charge-charge) interaction. Selection of basic set and electronic correlation processing does not change monopole-monopole interaction. Therefore, selection of the basic set and the electronic correlation procedure does not significantly change the calculated interaction energy of the ion pair. (p.5L14-L19)

4. Apart from the atomic charges there are several other parameters such as various non-covalent interactions which govern the cation-anion stability which need to be presented. The authors need to carry out energy decomposition analysis giving contributions from various energy components to interaction energy.

Tsuzuki. et. al analyzes the breakdown of ionic interactions. According to the results, the majority is electrostatic force. In this paper, we also focused on the electron correlation energy. Slightly, for molecules with double bonds, an increase in dispersion force due to CH /  $\pi$  interaction was suggested. (p.6L11-L14)

5. At page No. 4, line No. 9 typographic error “onium salt” is incorrect. It should read as “ammonium salt” .

According to your suggestion, “onium salt” was corrected to “phosphonium salt” in the revised manuscript, because

the phosphonium cation used in this calculation. (p.4L22)

6. Overall the presentation of the manuscript is rather poor and need significant improvements. Most of the results, in my opinion, are expected if not obvious. For example, statement on page3, lines 25-27, “The result indicated that the phosphonium cation ...strong positive charge”. Overall the MS do not present any substantial results to warrant its publication.

Based on your comment, the following points were corrected in the revised manuscript.

- The strength of the positive charge of the phosphonium cation is not inconsistent with the magnitude relation of the electronegativity. (p.4L1-L4)
- We researched the dependency of the positive charge of the central atom on the alkyl chain length and the result was added in the revised manuscript. As a result, there was a tendency that the central positive charge became lower as the cation became larger. (p.4L7-L15)
- Details of the discussion on ion-ion interaction were added in the revised manuscript. (p.5L20-p.6L2, p.6L11-L14)

Sincerely yours.

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## For Reviewer 2

Thank you for sending many useful comments.

According to your comments, the revised manuscript was corrected as follows.

### -Reviewer 2-

I have a few suggestions:

1) hartree-fock should be with a capital H & F

According to your suggestion, we corrected the capital letters of "hartree-fock" in the revised manuscript. (p.3L4)

2) in contrast, in many places Cluster with a capital C is not justified

According to your suggestion, we corrected the uppercase letters of "Cluster" to small case letter in the revised manuscript. (p.3L9, L14)

3) At least once, that is at its first appearance in the whole text, the abbreviations (MP2, MP3 for Moller Plesset perturbation), (Chelp, ChelpG CHarges from ELeCtrostatic Potentials using a Grid based method), (CCSD, CCSD (T) for coupled -cluster interaction energy contribution) be given their full form accompanied by a brief explanation to justify the literature review undertaken. For example basis set superposition error (BSSE) has been given on p6 ln 12 of pdf document

According to your suggestion, we added full form to MP2, MP3, Chelp, ChelpG, CCSD, CCSD (T) in the revised manuscript. (p.3L5, L21, L22, p.5L12, L13)

4) the counterpoise method and its need to correct BSSE

According to your suggestion, all calculation results (Table 3) were corrected BSSE in the revised manuscript. (p.3L14-L15)

5) from last line of the abstract : ....was not so influenced on each transport property. What are these transport properties being referred to ? I presume they are diffusivity, electrical conductivity and viscosity. Please clarify at least once!

According to your suggestion, the explanation about transport characteristics was added in the revised manuscript. The transport properties mentioned here mainly indicate viscosity and conductivity. (p.1L2-L5, p.2L10-L12)

6) Most of the calculations have been done with butyl substituent on P and N i.e., P444X and N444X in the paper why then is there a sudden shift to P222X and N222X in Table 2?

For your question, To discuss the torsional potential, P444X and N444X were used in this manuscript.

On the other hand, using P222X and N222X in calculation of ion-ion interaction is a problem of calculation cost. P444X and N444X have many possible local stable structures and it is difficult to calculate interaction for all structures. (p.5L20-p.6L2)

Sincerely yours.

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## Highlights

- The different substituents on the phosphonium-based ionic liquids were researched by MP2 calculation.
- The charge distribution of phosphonium-based ILs was evaluated and compared to ammonium-based ILs.
- The phosphonium cation had a stronger positive charge of the central atom than the ammonium cation.
- The degree of freedom of the conformation of the substituent was associated with the transport property.
- The gain ( $E_{\text{int}}$ ) of the energy in the ammonium cation was larger than that in the phosphonium cation.



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The effect of substituents of phosphonium-based ionic liquids evaluated by MP2 calculation

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1 **ABSTRACT**

2 Transport property such as conductivity and viscosity is important factor in designing ionic liquids (ILs).  
3 Depending on substituent type in ILs, the transport property is known to easily changeable. Introduction of a  
4 benzyl or a cyano group lowers the transport property, however in the case of a methoxy or an allyl group, the  
5 transport property is improved. It is important to reveal the static property with different substituents on the  
6 phosphonium-based ILs from the viewpoint of the microscopic analysis by theoretical calculation. For this  
7 purpose, we investigated the charge distribution, interaction with counter anion and torsional potential for  
8 different substituents on the phosphonium-based ILs in this study. From the MP2/6-311G\*\* calculation, the  
9 atomic charge of the phosphorus atom on the  $P_{4444}^+$  cation was 0.57 and it was higher than that of nitrogen atom  
10 (0.14) on the corresponding ammonium cation ( $N_{4444}^+$ ). The charge distributions with different substituents such  
11 as  $P_{444(3Bz)}$ ,  $P_{444(3CN)}$ ,  $P_{444(2Al)}$  and  $P_{444(2O1)}$  were also revealed in this study. According to the analysis of the  
12 torsion potential with different substituents, the methoxy substituted cations which would lead to the good  
13 transport property were stable at a torsional angle of  $180^\circ$  and the allyl substituted cations were stable at  $120^\circ$   
14 and  $240^\circ$ . On the other hand, it was found that the benzyl and the cyano substitution type cations, which were  
15 known as lower transport properties, were most stable at torsional angles of  $60^\circ$  and  $300^\circ$ . Furthermore, it was  
16 revealed that the rotational barriers of the dihedral angular potential of the methoxy and the allyl group are smaller  
17 than those of the cyano and the benzyl group. Moreover, from the calculated optimized geometry and the  
18 interaction energy of the cations containing various substituents, the gain ( $E_{int}$ ) of the energy obtained by cluster  
19 formation in the ammonium cation was larger than that in the phosphonium cation. A series of the MP2  
20 calculation results enabled us to indicate that the phosphonium cation had a higher affinity for the anion than the  
21 corresponding ammonium cation and the effect of the substituent on ionic interaction was not so influenced on  
22 each transport property.

23  
24 **Keywords:** Charge distribution, Ionic liquids, MP2 calculation, Substituents  
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## 1 1. Introduction

2 It is well known that inorganic salts, such as sodium chloride, have a high melting point which derived from  
3 the strong electrostatic interaction between cation and anion. However, the electrostatic interactions can be  
4 weakened by using the delocalized electrons in anions or the relatively bulky cations. A liquid state at below  
5 room temperature are referred to as room temperature ionic liquids (RTILs) and RTIL is a salt in the liquid state [1-  
6 6]. RTIL is often known as "designer solvents" [7] because of the attractive features that can synthesize RTIL of  
7 desired physicochemical properties from a wide variety of ionic species options. RTILs are also important  
8 industrial solvent for synthesis, catalysis, extraction and purification, because of its low vapor pressure and unusual  
9 catalytic properties [8-10]. In addition, it is an electrochemically stable and exhibits high transporting property,  
10 and the application to various electrochemical devices has also been studied [11-14]. **In particular, transport**  
11 **property such as conductivity and viscosity is one of the important factor in designing ILs for electrochemical**  
12 **devices and extraction media.** However, the relationship between the property of RTIL and the structure of ions  
13 has not been revealed so far. The physicochemical property of RTIL is controlled by the intermolecular  
14 interaction between cation and anion in RTIL. In recent years ab initio molecular orbital calculation was available  
15 as an effective method to estimate intermolecular interactions [15,16]. In recent calculations of small molecule  
16 clusters, ab initio calculation uses a reasonably large basis sets and correlation has been properly corrected [17-19].

17 RTILs have traditionally been handled for cations of nitrogen-containing compounds such as imidazolium and  
18 ammonium. On the other hand, the phosphonium-based ILs [20] with a phosphorus atom have higher transport  
19 and thermal stability compared to the corresponding ammonium-based ILs [21]. Further, it is reported that the  
20 catalytic activity is improved by using a phosphonium-based IL as a solvent [22]. Thus, the phosphonium-based  
21 IL has an attention in many fields [23-25]. It is very important to investigate the effect of substituents on the  
22 phosphonium-based ILs. It is known that the transport property of ILs is improved by introducing a methoxy or  
23 an allyl group [12,21,26,27]. Additionally, it is also reported that the introduction of a benzyl or a cyano group  
24 lowers the transport properties [28,29]. However, there are no investigation about the microscopic reason by  
25 theoretical calculation. Therefore, we investigated the influence of the various substituents from the viewpoint of  
26 the charge distribution, interaction with counter anion and torsional potential in this study.

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## 1 **2. Experimental**

### 2 **2.1 Calculation methods**

3 All the ab initio calculations were carried out using the software program Gaussian09 [30]. The **Hartree-**  
4 **Fock** equation [31-33] was used in geometric structure optimizations with the 6-311\*\* [34-37] basis set for cations  
5 in the gas phase. Electron correlation was accounted for at the **second-order Moller-Plesset (MP2)** level [38,39].  
6 The atomic charge distributions of various cations were calculated by electrostatic potential fitting, with the Merz-  
7 Singh-Kollman scheme [40,41] from the MP2/6-311G\*\* basis set of isolated ions. Torsional potentials are  
8 calculated from the MP2/6-311G\*\* level for the various cations. The torsional potential was defined as a  
9 difference of potential energy to the minimum energy value. The geometric structure of **clusters** was optimized  
10 from initial geometries cations and bromide anion from the HF/6-311G\*\* basis set. The MP2 level interaction  
11 energy ( $E_{MP2}$ ) was calculated by the supermolecule method. The basis set superposition error (BSSE) [42] was  
12 corrected for all calculations using the counterpoise method [43,44]. The total interaction energy ( $E_{int}$ ) was  
13 calculated as the sum of  $E_{MP2}$  and the deformation energy ( $E_{def}$ ). Deformation energy is determined as the  
14 increase of the energies of monomers by the deformation of geometries in **clusters** formation. **All energies are**  
15 **corrected by BSSE and outputted.**

## 17 **3 Results and discussion**

### 18 **3.1 Charge distribution**

19 The electrostatic potential fitting optimizes the charge of the atom to reproduce the electrostatic potential of  
20 the lattice point of the molecular surface calculated by the molecular orbital method. Several methods related with  
21 different lattice points are proposed, among which the Merz-Singh-Kollman, **Charges from electrostatic potentials**  
22 **(Chelp)** [45] and **charges from electrostatic potentials using a grid-based method (ChelpG)** [46] schemes were often  
23 used. It is known that all methods agree well with the dipole moment calculated directly from the molecular  
24 orbital method based on MP2 wave functions [47]. The result of the electrostatic potential fitting with the Merz-  
25 Singh-Kollman scheme from the MP2/6-311G\*\* wave function of  $X_{4444}^+$  (X=P or N) cation was shown in **Fig. 1**.  
26 The atomic charge of phosphorus or nitrogen in the  $X_{4444}^+$  cation (X=P or N) was 0.57 or 0.14, respectively. The  
27 result indicated that the phosphonium cation and the corresponding ammonium cation showed a different tendency  
28 of an atomic charge distribution. At the center of phosphorus atom, there was a phosphonium cation which has a

1 strong positive charge. So far, many electronegativity values have been proposed. Among them, it is known that  
2 the electronegativity of the nitrogen atom is larger at any value than the phosphorus atom. From this fact, the  
3 calculation result is consistent with the magnitude relationship of the electronegativity between phosphorus atom  
4 and nitrogen atom (**Table 1**). Meanwhile, there is also an ammonium cation, in which positive charge is stronger  
5 than that of phosphonium, in the alkyl chain. It is possibly because that the distance between phosphorus atom  
6 and outermost electron is shorter than that of nitrogen atom which has a tendency corresponding with  
7 electronegativity. **Fig. 2** shows the influence of the cation chain length on partial charges of phosphorus atoms or  
8 nitrogen atoms. The extension of the alkyl chain length tended to dilute the center positive charge. On the other  
9 hand, a positive charge was strengthened between the propyl and the butyl group. One of the reason for this  
10 behavior is that the electron donating property of the carbon chain is increased by the inductive effect by extending  
11 the alkyl chain. Therefore, in the butyl group, the effect of increasing the electron donating property appeared to  
12 be larger than the effect of diluting the charge, so it is considered that an increase in the positive charge was  
13 observed in the center. The charge distribution showed a tendency to decrease due to the increase in the alkyl  
14 chain length suggests that the positive charge dispersion effect strongly appeared by the increase in the cation size  
15 rather than the induction effect.

16 The result of the electrostatic potential fitting using the Merz-Singh-Kollman scheme from the MP2/6-311G\*\*  
17 wave function for the phosphonium cations containing various substituents was represented in **Fig. 3**. The charge  
18 distribution of the center phosphorus atom for various cations was tabulated in **Table 2**. Any substituent acted as  
19 an electron withdrawing group. The methoxy and the allyl groups had an effect of weakening the positive charge  
20 on the phosphorus atom. These are substituents that have an effect of good transport property, suggesting that  
21 there is a correlation between the positive charge of the central element and the transport property of the quaternary  
22 phosphonium salt.

### 24 3.2 Torsional potential

25 The result of the torsional potential (difference of potential energy to the minimum energy value) for  $X_{4444}^+$   
26 cations (X=P or N) was shown in **Fig. 4**. From this result, it was found that each cation has metastable structure in  
27 gauche conformation and the most stable structure in trans conformation. Hence, it was suggested that there was  
28 almost no effect of phosphonium cations on structure compared to the ammonium cations. The torsional potential

1 of the alkyl groups with substituents of various cations determined by ab initio molecular orbital method was  
2 shown in **Fig. 5**. The methoxy substituted cations which would lead to the good transport property were stable at  
3 a torsional angle of 180 ° and the allyl substituted cation were stable at 120 ° and 240 °. On the other hand, it was  
4 found that the benzyl and the cyano substitution type cations, which were known as lower transport properties,  
5 were most stable at torsional angles of 60 ° and 300 °. Compared to the benzyl and the cyano groups, the methoxy  
6 and the allyl groups showed less change in potential energy due to the fluctuation of the torsion angle. This result  
7 suggested that methoxy and the allyl groups of cations would be relatively mobile and enhance the transport  
8 property.

### 10 **3.3 Interaction energy**

11 According to Tsuzuki et. al., The interaction energy was evaluated using MP2 energy in this work, because it  
12 was reported that the **third-order Møller-Plesset (MP3), coupled-cluster (CCSD) [48], and coupled-cluster including**  
13 **triple excitations (CCSD(T))** interaction energy was not much different from the MP2 interaction energy in the case  
14 of estimating the ion-ion interactions. **Selection of basis set and electron correlation method may change**  
15 **calculated intermolecular interaction energy of hydrogen bonding system and van der Waals clusters [49-51].**  
16 **However, the main attraction source in ion pair is monopole-monopole (charge-charge) interaction. Selection of**  
17 **basis set and electronic correlation processing does not change monopole-monopole interaction. Therefore,**  
18 **selection of the basis set and the electronic correlation procedure does not significantly change the calculated**  
19 **interaction energy of the ion pair [18].**

20 In the case of discussing long chain alkyl chains, it is not easy to argue because it has many conformations.  
21 Therefore, as a simple model, the results of estimating the ionic interaction between phosphonium cation and  
22 ammonium cation with bromide ion are shown in **Fig. 6** and **Table 3**. In one molecule, the most stable structure  
23 was taken when the alkyl chain was in the trans conformation. On the other hand, between the two molecules, the  
24 counter anion could not approach the short distance due to the steric hindrance (1a, 2a), and the screw bent  
25 structure stably formed the aggregate (1c, 2c). The gain ( $E_{int}$ ) of the energy obtained by formation of the  
26 association body was larger in the phosphonium cation. This suggests that the phosphonium cation has a higher  
27 affinity for the anion than the corresponding ammonium cation. According to Tsunashima et. al., the  
28 phosphonium ILs are slightly more molecular than the ammonium ILs [21]. This result supports the expectation

1 that the phosphonium ILs have higher affinity for the anion than the ammonium ILs. This is because an ion pair  
2 having a high molecular character means that the ion dissociation property is low.

3 The optimized geometry and the interaction energy of the cations containing various substituents with Br<sup>-</sup> was  
4 shown in Fig. 7. The detailed information was summarized in Table 4. The gain ( $E_{int}$ ) of the energy obtained by  
5 cluster formation was larger in the ammonium cation than in the phosphonium cation. This suggests that the  
6 phosphonium cation has a higher affinity for the anion than the corresponding ammonium cation. The effect of  
7 the substituent on ionic interaction was not so large, and there was no correlation with the transport properties.  
8 Exceptionally, the cation with a cyano group showed somewhat higher interaction energy. Interaction between  
9 the cyano group and the halogen was recognized inside the crystal [52]. Thus, it was conjectured that the cyano-  
10 halogen interaction would not be neglected also in the gas phase. The high viscosity of the cyano group might be  
11 due to the high ionic interaction. During the interaction between ions, there was no significant difference in  
12 electron correlation energy in any cluster. However, P<sub>222Bz</sub><sup>+</sup> and P<sub>222(2Al)</sub><sup>+</sup> having a double bond have slightly large  
13 electron correlation energy. One of the reasons for this might be the increase in dispersion force due to the  $\pi$   
14 electrons possessed by the CH bond.

#### 16 4. Conclusion

17 From the standpoint of the microscopic analysis using theoretical calculation, it is very important to evaluate  
18 the effect of the substituents on the phosphonium-based ionic liquids (ILs). In this study, we investigated the  
19 charge distribution, interaction with counter anion and torsional potential for different substituents on the  
20 phosphonium-based ILs compared to the ammonium-based ILs. Based on the theoretical calculation using a  
21 basis-set with MP2/6-311G\*\*, the atomic charge of the phosphorus or the nitrogen atom on the P<sub>4444</sub><sup>+</sup> or N<sub>4444</sub><sup>+</sup>  
22 cation was 0.57 or 0.14, respectively. On the other hand, the charge distributions with different substituents such  
23 as P<sub>444(3Bz)</sub>, P<sub>444(3CN)</sub>, P<sub>444(2Al)</sub> and P<sub>444(2O1)</sub> were also researched and the torsion potential with different substituents,  
24 the methoxy substituted cations were stable at a torsional angle of 180 ° and the allyl substituted cations were stable  
25 at 120 ° and 240 °. It was also revealed that the benzyl and the cyano substitution type cations were most stable at  
26 torsional angles of 60 ° and 300 °. Moreover, according to the optimized geometry and the interaction energy of  
27 the cations containing various substituents, the gain ( $E_{int}$ ) of the energy obtained by cluster formation in the  
28 phosphonium cation was larger than that in the ammonium cation. A series of results suggested that

1 intermolecular interactions can not account for transport property, however ionisity of ILs can be predicted from  
2 affinity with anions. In addition, it was suggested that the evaluation of freedom of conformation by torsional  
3 potential is important for transport property.

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## Caption of Figures

**Fig. 1** Atomic charges obtained by electrostatic potential fitting using Kollman's scheme from the MP2/6-311G\*\* wave functions.

●: hydrogen atom, ●: carbon atom, ●: nitrogen atom, ●: phosphorus atom

**Fig. 2** Effect of electrostatic potential of phosphorus atom using Kollman scheme from MP2/6-311G\*\* wave function by alkyl chain length.

○: nitrogen atom, ●: phosphorus atom

**Fig. 3** Atomic charges obtained by electrostatic potential fitting for the cations containing various substituents using Kollman's scheme from the MP2/6-311G\*\* wave functions.

●: hydrogen atom, ●: carbon atom, ●: nitrogen atom, ●: oxygen anion, ●: phosphorus atom

**Fig. 4** Torsional potentials calculated at MP2/6-311G\*\*//HF/6-311G\*\* level for the various cations. The torsional potential was defined as a difference of potential energy to the minimum energy value. blue line: N<sub>4444</sub><sup>+</sup>, and red line: P<sub>4444</sub><sup>+</sup>.

**Fig. 5** Torsional potential calculated at MP2/6-311G\*\*//HF/6-311G\*\* levels for the cations containing various substituents.

blue line: P<sub>4442(AI)</sub><sup>+</sup>, red line: P<sub>444(2O1)</sub><sup>+</sup>, green line: P<sub>4443(CN)</sub><sup>+</sup>, and black line: P<sub>4443(Bz)</sub><sup>+</sup>

**Fig. 6** HF/6-311G\*\* level optimized geometries and interaction energies of various structure clusters with Br-. Total interaction energies ( $E_{\text{int}}=E_{\text{MP2}}+E_{\text{def}}$ ) are shown. BSSE corrected interaction energies at the MP2/6-311G\* level ( $E_{\text{MP2}}$ ) are shown in parentheses.  $E_{\text{def}}$  is the increase of the energies of monomers by deformation of geometries in complex formation.

●: hydrogen atom, ●: carbon atom, ●: nitrogen atom, ●: phosphorus atom, ●: bromide atom.

**Fig. 7** HF/6-311G\*\* level optimized geometries and interaction energies of five phosphonium clusters with Br-. Total interaction energies ( $E_{\text{int}}=E_{\text{MP2}}+E_{\text{def}}$ ) are shown. BSSE corrected interaction energies at the MP2/6-311G\* level ( $E_{\text{MP2}}$ ) are shown in parentheses.  $E_{\text{def}}$  is the increase of the energies of monomers by deformation of geometries in complex formation.

●: hydrogen atom, ●: carbon atom, ●: nitrogen atom, ●: oxygen anion, ●: phosphorus atom, ●: bromide atom.

Fig. 1

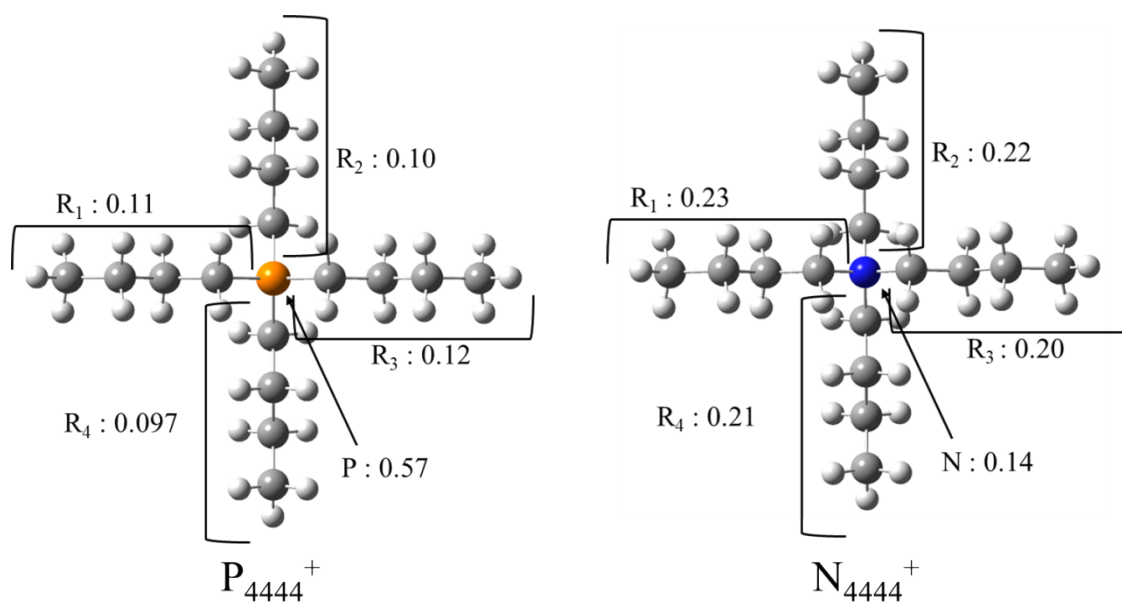


Fig. 2

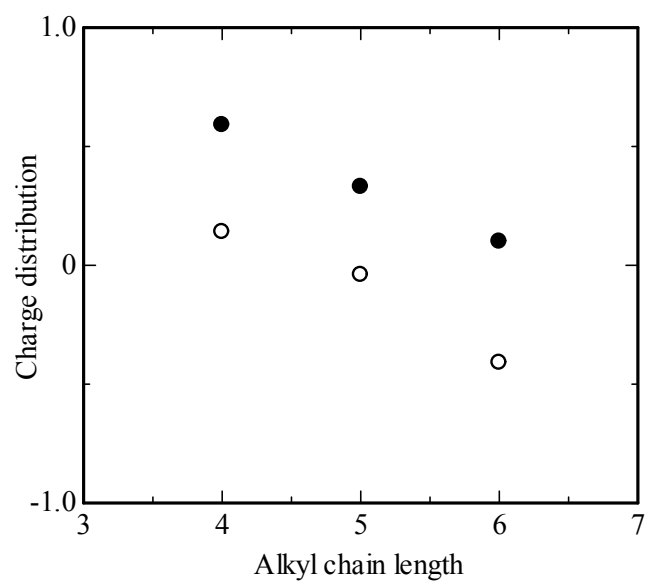


Fig. 3

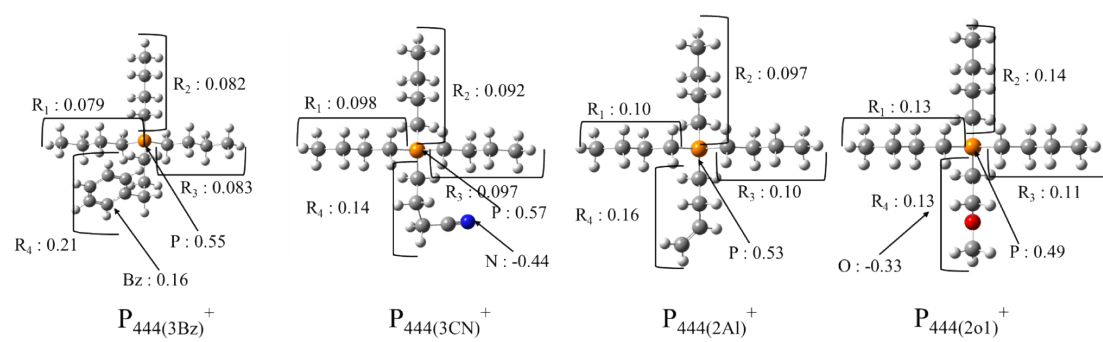


Fig. 4

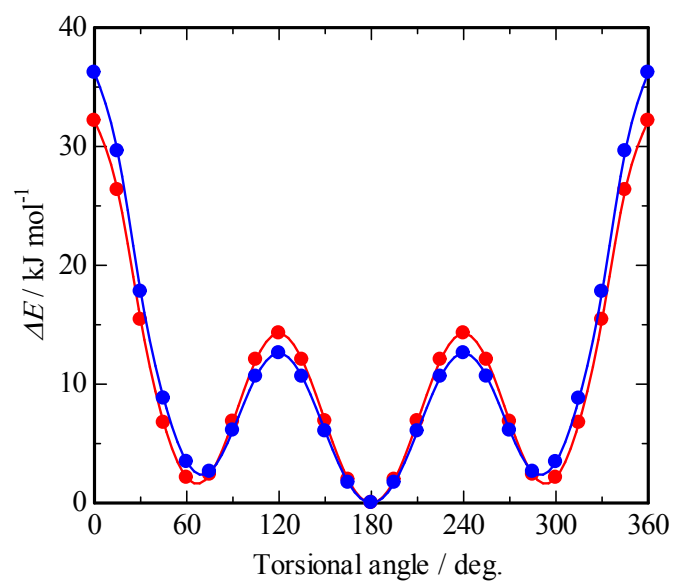


Fig. 5

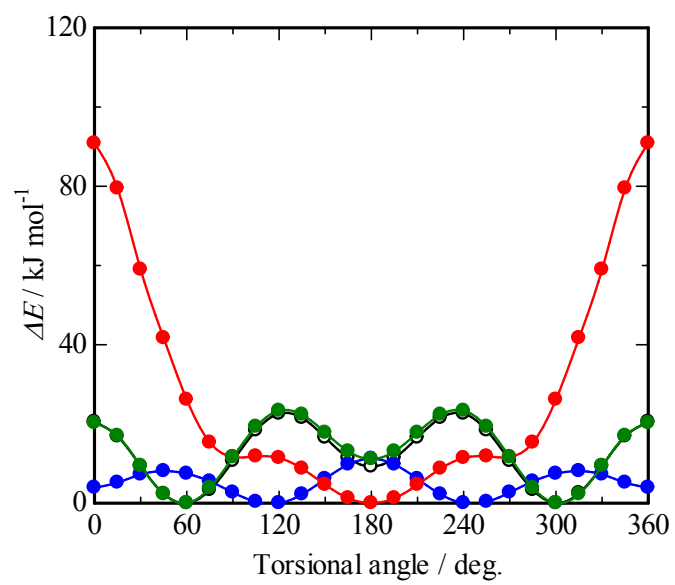
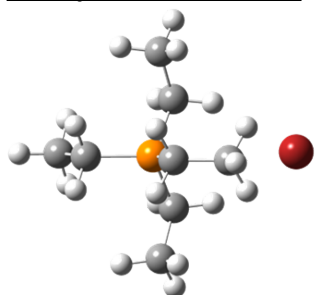


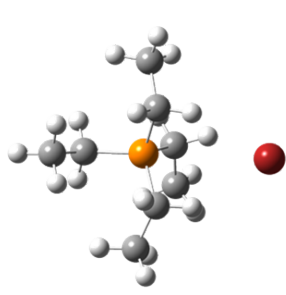


Fig. 6

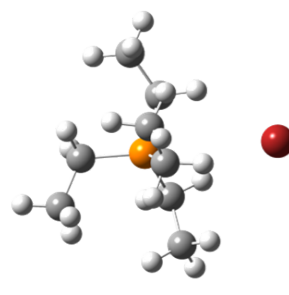
**Phosponium cation**



1a -81.94 (-82.17)

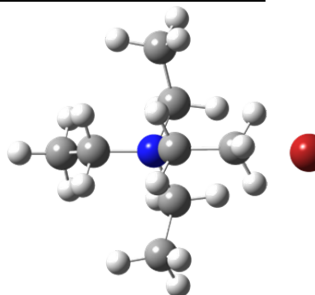


1b -86.54(-86.66)

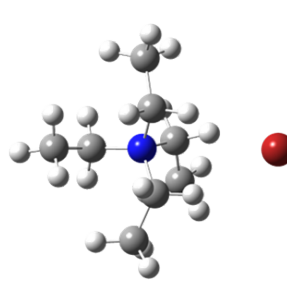


1c -87.02(-87.18)

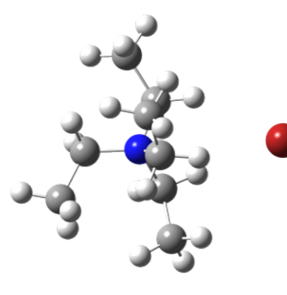
**Ammonium cation**



2a -80.15 (-80.80)

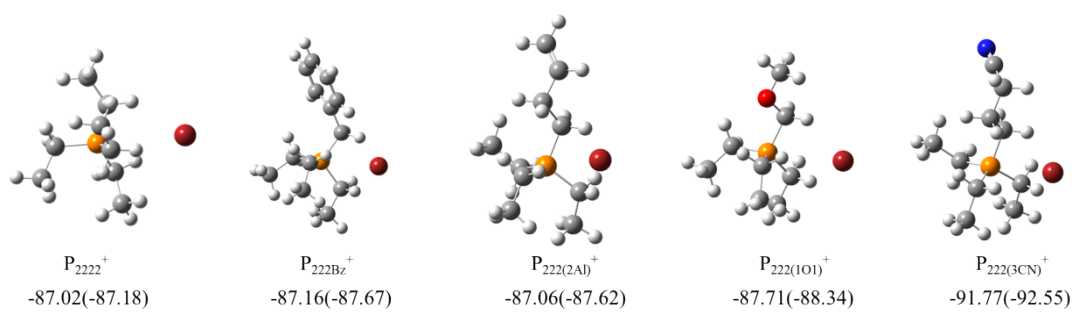


2b -84.21(-84.70)

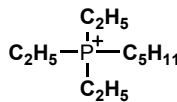
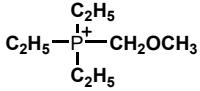
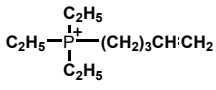
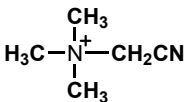
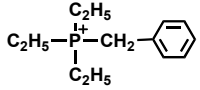


2c -84.63(-85.24)

**Fig. 7**



**Table 1** Physicochemical property of ionic liquids with different substituents.

cation	structure	$\sigma^{\text{a)}}$ / mS cm <sup>-1</sup>	$\eta^{\text{b)}}$ / mPa s	substituent	reference
P <sub>2225</sub>		1.73	88	alkyl	[12]
P <sub>222(1O1)</sub>		4.40	35	alkoxyalkyl	[12]
P <sub>222(1Pe)</sub>		2.1	71	allylalkyl	[26]
N <sub>111(1CN)</sub>		0.1 <sup>c)</sup>	-----	cyanoalkyl	[28]
P <sub>222Bz</sub>		0.74	248	benzyl	[29]

a) Conductivity at 298 K

b) Viscosity at 298 K

c) Data at 308 K

**Table 2** Charge distribution of center phosphorus atom for various cations.

cation	charge distribution of center atom
$P_{444(3BZ)}^+$	0.551
$P_{444(3CN)}^+$	0.568
$P_{444(2Al)}^+$	0.528
$P_{444(2O1)}^+$	0.490

**Table 3** Interaction energy of cations with different structures.

cation	$R_e$	$E_{\text{HF}}$	$E_{\text{MP2}}$	$E_{\text{def}}$	$E_{\text{int}}$	$E_{\text{corr}}$
$\text{P}_{2222}^+(1a)$	4.12	-77.08	-82.17	0.23	-81.94	-4.86
$\text{P}_{2222}^+(1b)$	3.82	-81.35	-86.66	0.12	-86.54	-5.19
$\text{P}_{2222}^+(1c)$	3.80	-81.73	-87.18	0.16	-87.02	-5.29
$\text{N}_{2222}^+(2a)$	4.22	-76.13	-80.80	0.65	-80.15	-4.02
$\text{N}_{2222}^+(2b)$	3.97	-79.70	-84.70	0.49	-84.21	-4.51
$\text{N}_{2222}^+(2c)$	3.95	-80.08	-85.24	0.61	-84.63	-4.55

$R_e$  : equilibrium interionic distance.

$E_{\text{HF}}$  : BSSE corrected interaction energies of complexes calculated at the HF/6-311G\*\* level.

$E_{\text{MP2}}$  : BSSE corrected interaction energies of complexes calculated at the MP2/6-311G\*\* level.

$E_{\text{def}}$  : Increase of the energies of monomers by the deformation of geometries in complex formation.

$E_{\text{int}}$  : Total interaction energy of the complex, which is the sum of  $E_{\text{MP2}}$  and  $E_{\text{def}}$ .

$E_{\text{corr}}$  : Electron correlation energy( $E_{\text{MP2}} - E_{\text{HF}}$ ).

**Table 4** Interaction energies for the various cations with bromide anion.

cation	$R_e$	$E_{\text{HF}}$	$E_{\text{MP2}}$	$E_{\text{def}}$	$E_{\text{int}}$	$E_{\text{corr}}$
$\text{P}_{222}^+$	3.80	-81.73	-87.18	0.16	-87.02	-5.29
$\text{P}_{222\text{Bz}}^+$	3.84	-81.98	-87.67	0.51	-87.16	-5.69
$\text{P}_{222(3\text{CN})}^+$	3.80	-87.77	-92.95	1.18	-91.77	-5.18
$\text{P}_{222(2\text{Al})}^+$	3.80	-82.11	-87.62	0.56	-87.06	-5.51
$\text{P}_{222(1\text{O1})}^+$	3.78	-83.32	-88.34	0.63	-87.71	-5.02
$\text{N}_{222}^+$	3.95	-80.08	-85.24	0.61	-84.63	-4.55
$\text{N}_{222\text{Bz}}^+$	3.98	-80.34	-85.77	0.12	-85.65	-5.43
$\text{N}_{222(3\text{CN})}^+$	3.96	-86.45	-91.36	0.74	-90.62	-4.91
$\text{N}_{222(2\text{Al})}^+$	3.95	-80.48	-85.72	0.15	-85.57	-5.24
$\text{N}_{222(1\text{O1})}^+$	3.95	-81.98	-86.70	0.40	-86.30	-4.72

$R_e$  : equilibrium interionic distance.

$E_{\text{HF}}$  : BSSE corrected interaction energies of complexes calculated at the HF/6-311G\*\* level.

$E_{\text{MP2}}$  : BSSE corrected interaction energies of complexes calculated at the MP2/6-311G\*\* level.

$E_{\text{def}}$  : Increase of the energies of monomers by the deformation of geometries in complex formation.

$E_{\text{int}}$  : Total interaction energy of the complex, which is the sum of  $E_{\text{MP2}}$  and  $E_{\text{def}}$ .

$E_{\text{corr}}$  : Electron correlation energy( $E_{\text{MP2}} - E_{\text{HF}}$ ).