

The molecular structures and the relationships between the calculated molecular and observed bulk phase properties of phosphonium-based ionic liquids

Ryan P. Morco, Ahmed Y. Musa, J. Clara Wren*

Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada



ARTICLE INFO

Article history:

Received 4 September 2013

Received in revised form 9 January 2014

Accepted 3 February 2014

Available online 22 February 2014

Keywords:

Quantum chemical calculations

Phosphonium ionic liquids

Electrostatic potential

Vibrational frequencies

Electronic transitions

ABSTRACT

The molecular and electronic structures of six ionic liquids (ILs) having the same cation (tetradecyl(trihexyl) phosphonium [P₆₆₆₁₄]), but with different anions, were obtained by quantum chemical calculations using density functional theory (DFT). Various molecular parameters were computed, including the inter-ionic H-bond length and angle, the energies of various molecular orbitals including HOMO and LUMO, the dipole moment (μ), the cation–anion interaction energy (ΔE) and the electrostatic potential. The wavelengths and oscillator strengths of vibrational and electronic transition lines were also calculated and found to be in good agreement with measured IR and UV–vis absorption spectra. We have found strong correlations between the calculated quantum chemical parameters and the measured physical and chemical properties of the phosphonium ILs. In general, molar conductivity (Λ) increases, whereas viscosity decreases, exponentially with μ , and the melting point increases linearly with $-\Delta E$.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids (ILs) are composed of distinct ion pairs that remain in the liquid state below 100 °C. They usually contain a bulky, long-chain, organic cation that is weakly coordinated to a smaller organic or inorganic anion. Recently, interest in ILs has grown due to their many desirable physical and chemical properties. These include: good conductivity, negligible vapour pressure at room temperature, high chemical and thermal stability, and wide electrochemical windows. Ionic liquids are often termed ‘designer solvents’ because their properties (such as density, viscosity, Lewis acidity, hydrophobicity, and hydrogen-bonding) can be easily tuned by varying the structure of the component ions [1–10]. There is an enormous number of possible ILs; Rogers and Seddon [10] estimated the number to exceed 1 trillion. Given this large choice, we need an efficient methodology for pre-determining the physico-chemical properties of any particular ion pair. A versatile method for predicting the fundamental properties of a molecule is the use of quantum chemical calculations. Such computations allow us to simultaneously predict the values of multiple parameters (such as dipole moment, bond lengths, and atomic charges) that are related to a molecule’s kinetic, thermodynamic and physico-chemical properties.

Computational quantum chemical calculations using density functional theory have been used extensively to obtain molecular properties

of ILs, such as hydrogen (H-) bond strengths [11–16], cation–anion interaction energies [16,17], electron affinities and ionization energies [18]. The results have been used to elucidate relationships between molecular properties and macroscopic, bulk-phase properties of ILs [11–29]. Due to their high conductivity (ca. 10 mS/cm) and wide window of electrochemical stability (ca. 4 V), imidazolium-based ILs are excellent candidates for a range of applications including, but not limited to, catalysis, super-capacitors, and photovoltaics [30]. Thus, imidazolium-based ILs have been most extensively investigated by using quantum chemical calculations [11–19,22–28]. Phosphonium-based ILs have been less well studied. These ILs have shown higher thermal stability and lower toxicity, compared to imidazolium-based ILs, and there are exciting prospects for their use in industrial applications [7–9,29].

In this work, we performed quantum chemical calculations using density functional theory (DFT) on the six tetradecyl(trihexyl)phosphonium [P₆₆₆₁₄] cation-based ILs that had different anions, chloride [Cl], bromide [Br], dicyanamide [DCA], tetrafluoroborate [BF₄], hexafluorophosphate [PF₆], and bis(trifluoromethylsulfonyl) imide [NTf₂], Fig. 1. Quantum chemical parameters of the ILs that were obtained include the inter-ionic H-bond lengths and angles, the energies of various molecular orbitals including those of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), the dipole moment (μ), the cation–anion interaction energy, and the electrostatic potential. The calculated dipole moment (μ) and interaction energy (ΔE) were compared to some of the observed bulk properties of the ILs (conductivity, melting point and viscosity).

* Corresponding author.

E-mail address: jcwren@uwo.ca (J.C. Wren).

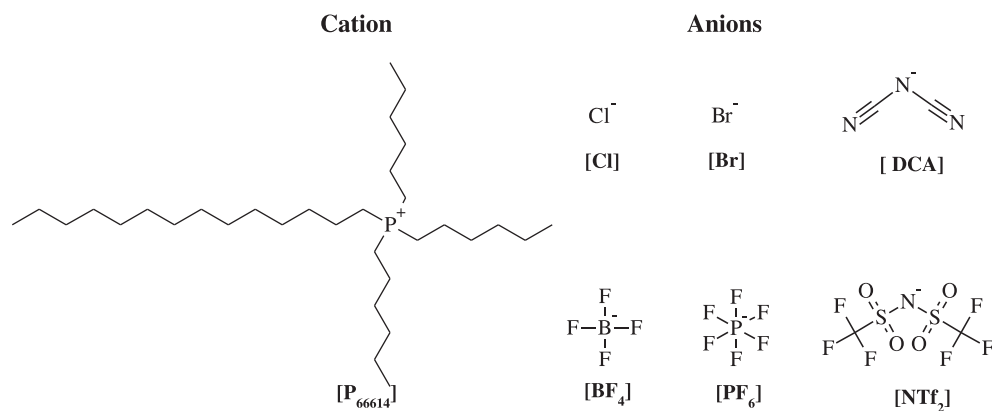


Fig. 1. Chemical formula of the phosphonium cation and the anions of the ILs used in this study.

2. Methodology

2.1. Computational details

Quantum chemical calculations were performed by using a quantum mechanics computer program, Materials Studio version 5.5 software

(Accelrys Inc., San Diego, CA) [31]. The geometrical structures of the ILs were sketched by using tools available in the Materials Visualizer module of the Materials Studio program. The DMol³ module was then used to optimize the geometries of the IL molecules and to obtain quantum chemical parameters. The DMol³ module performs DFT calculations by using ab initio, generalized gradient approximations (GGA) with a

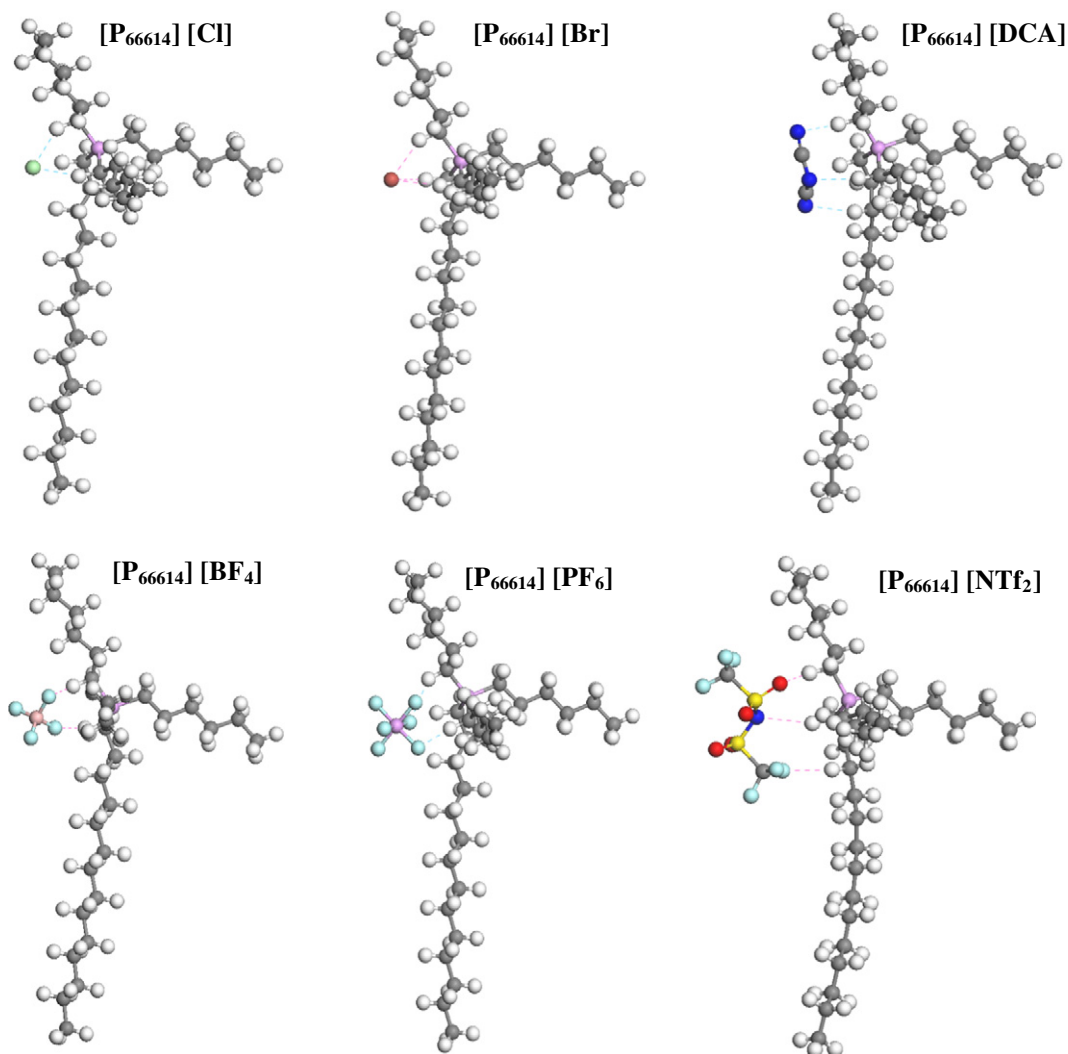


Fig. 2. The equilibrium geometries of phosphonium ILs. Dashed lines represent the hydrogen bonds between the atoms. The colour assignments for the atoms are: purple – P, maroon – Br, blue – N, red – O, yellow – S, light-blue – F, peach – B, dark-grey – C atoms, and light-grey – H.

Download English Version:

<https://daneshyari.com/en/article/1295642>

Download Persian Version:

<https://daneshyari.com/article/1295642>

[Daneshyari.com](https://daneshyari.com)