

Gas-phase computational study of tetra-*n*-butylammonium ion conformational mobility

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Abstract. The energy profiles of various configurations of the tetra-*n*-butylammonium ion (Bu_4N^+) arising by changing the angle between a pair of butyl ligands, as well as by rotating of various alkyl fragments in gas phase, were calculated using DFT methods. A hypothesis about the most probable way of changing the conformations of tetra-*n*-butylammonium ions during the phase transitions in highly conductive solid electrolytes was proposed.

1 Introduction

Organic ionic plastic crystals (OIPC) is a special class of materials characterized by high mobility of structural fragments. Many salts which contain quaternary alkylammonium cations, in particular, tetra-*n*-butylammonium ions ($(\mu\text{-C}_4\text{H}_9)_4\text{N}^+$ (Fig. 1), belong to this class [1]. These systems were grouped by Professor J. Timmermans, who noticed that compounds with the structure built of centrosymmetric molecules or containing fragments easily rotating around symmetry axis in the crystal lattice have low melting entropy [2]. In earlier studies it was found that such compounds may have high ionic conductivity [1,3,4,5, 6] and relatively high plasticity. In particular, it has been demonstrated that the most probable charge carriers in tetrabutylammonium salts $(\mu\text{-C}_4\text{H}_9)_4\text{NX}$, where $\text{X} = \text{I}^-, \text{Br}^-$ and BF_4^- , are anions. Thus, OIPC may be regarded as promising candidates for organic solid electrolyte and a worthy alternative to polymer electrolytes. Their plasticity also helps suppressing structural deformations at the electrode/electrolyte interface which originates from morphological changes of the electrode and the electrolyte during the electrochemical processes.

The most probable mechanism of anion transfer in compounds, which contain tetra-*n*-butylammonium cations, is the cooperative movement of anions and local displacements or/and rotations of organic cation molecular fragments [7]. Thus, the activation barrier of the diffusion drops down. The energies of such deformations can be calculated using various electronic structure methods.

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The aim of the study is to identify the mechanism of the conformational changes in the structure of tetra-*n*-butylammonium ions, which lead to an increase in the conductivity of the OIPC containing this ion.

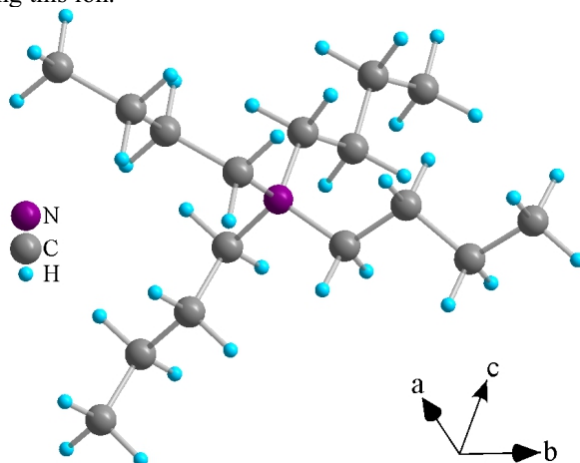


Fig. 1. The optimized structure of tetra-*n*-butylammonium ion.

2 Computational details

The geometry optimization of the ion (Bu_4N^+), as well as the calculation of the energy profiles were carried out using the Gaussian 09 software package [8]. B3LYP/6-311+G(d,p) with Grimme dispersion correction GD3BJ [9] level of theory was chosen for DFT (density functional theory) calculations. The initial geometry of the ion was taken from the structure of tetra-*n*-butylammonium iodide (Bu_4N)I (REFCODE – #RABTET01).

The energy of an organic cation was calculated as a function of the C-N-C angle (the angle between two butyl fragments) with a step of $\pm 2.5^\circ$, i.e. counterclock- and clockwise relative to the initial tetrahedral angle. Energy profiles were also calculated for the processes of rotation of $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$ and $-\text{C}_4\text{H}_9$ molecular fragments of one of the butyl ligands (relaxed scan method relative to the corresponding dihedral angles with a step of 2.5° was performed). Additionally, the values of the largest activation barriers for each profile were estimated. As a result, the geometry corresponding to the transition states was determined using transit-guided quasi-Newton (STQN) method [10] (with QST3 option) followed by the intrinsic reaction coordinate (IRC) restoration [11, 12] (with LQA option).

The images of the tetra-*n*-butylammonium conformations were created by using the Diamond 3 program [13].

3 Results and discussion

3.1 Changing C-N-C angle

As the value of the initially tetrahedral ($\approx 108.5^\circ$) C-N-C angle changes (the rest of geometric parameters are optimized), a rapid increase of the ion energy up to several hundreds of kJ/mol was observed (Fig. 2). When the angle between butyl fragments reaches $\approx 75^\circ$ (what is similar to $\approx 285^\circ$), butyl fragment splits off from the ion, i.e. the covalent bond breaks and the system loses its integrity. When butyl fragments come closer or move apart at C-N-C angle values of less than 15° , the change in energy remains comparable to the

energy of thermal vibrations. As one can see from Figs. 3a, 3b, in this case no significant changes in the overall geometry of organic cations are observed compared to the initial state, in both the cases the cation has nearly tetrahedral shape.

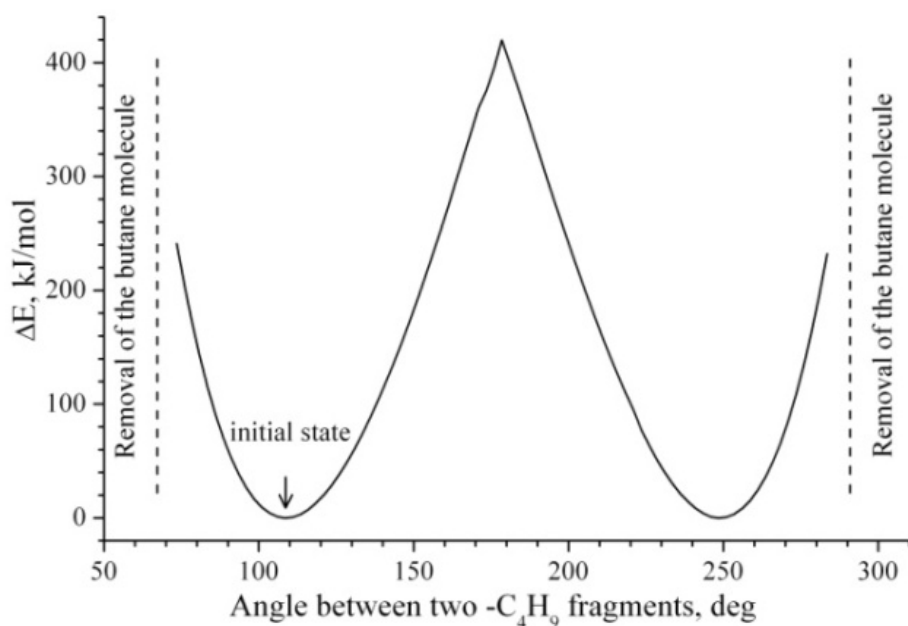


Fig. 2. Angular (C-N-C angle) dependence of the tetra-n-butylammonium ion energy.

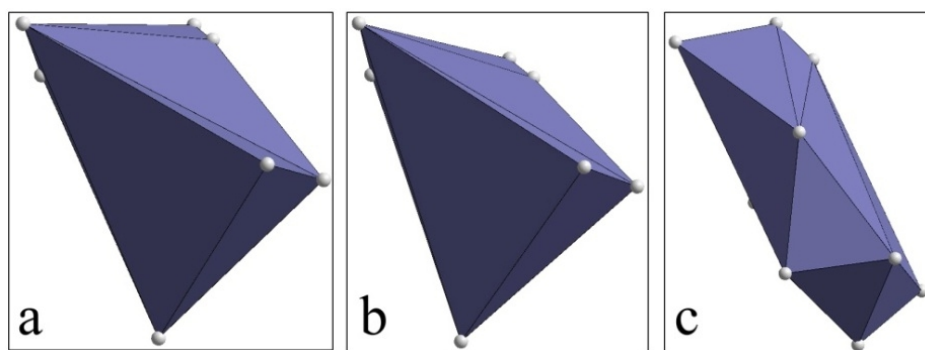


Fig. 3. Coordination polyhedra constructed for different conformations of the tetra-n-butylammonium ion: a) free cation optimized structure, b) after decreasing the C-N-C angle value by -15° (the rest of the parameters are optimized), c) the structure of the cation in $[(C_4H_9)_4N]_3[Pb(NO_3)_5]$.

3.2 Rotation of molecular fragments

The energy profiles obtained by rotation of the $-CH_3$, $-C_2H_5$, $-C_3H_7$ and $-C_4H_9$ (Fig. 4) molecular fragments indicate that such rotations can occur freely, since the energies of these configurations are less than 40 kJ/mol, relative to the basic structure, which is comparable to the energy of thermal vibrations. Besides, the energy barriers separating stable conformations do not exceed 26 kJ/mol. Despite the fact that the activation barriers

are quite low, the shape of the cation can change drastically due to the rotation of molecular fragments.

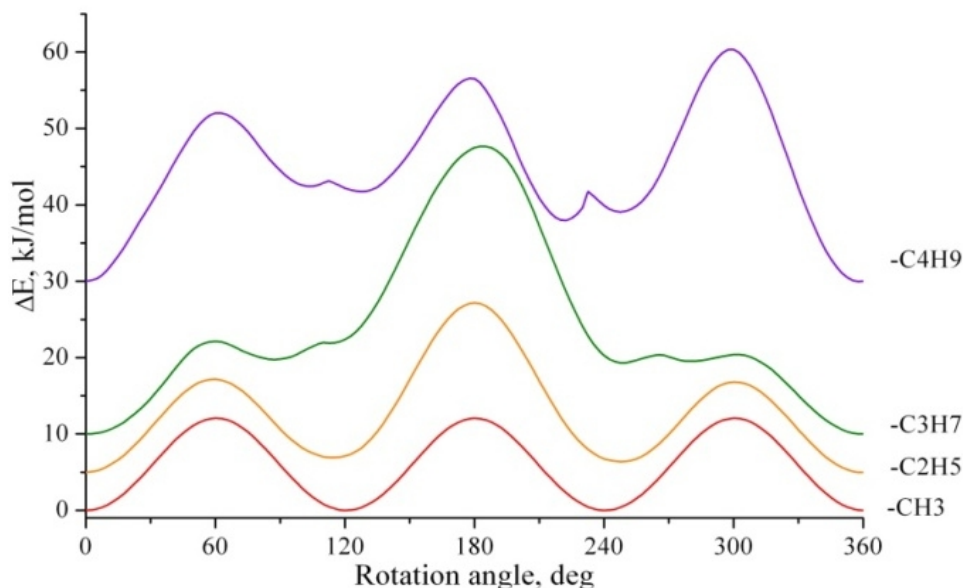


Fig. 4. The energy profiles obtained for molecular fragments rotations. Profiles are shifted along the energy axis by 0, 5, 10, 30 kJ/mol (-CH₃, -C₂H₅, -C₃H₇, -C₄H₉, respectively) for greater clarity.

The Fig. 3c illustrates the geometry of the Bu₄N⁺ cation in the compound [(C₄H₉)₄N]₃[Pb(NO₃)₅]. The structure of this compound was recently published by us [14]. Tetra-*n*-butylammonium ions in this compound seem to have a planar shape, while the C-N-C angles differ very slightly (by about 3.5°) from the ones observed in the optimized structure of the free cation.

Although, both mechanisms considered above, C-N-C angle change and molecular fragmental rotations, take place, the rotations of molecular fragments appear to be dominant. Such rotations of alkyl chains in tetra-*n*-butylammonium ions noticeably affect the shape of the organic cations. It leads to the formation of extra free volume in the crystal lattice which act as open conduction pathways for anionic transport and facilitate conductivity of tetra-*n*-butylammonium salts.

4 Conclusion

It was shown that the real shape of the tetra-*n*-butylammonium ion is primarily determined by the rotations of its molecular fragments. The energy barriers separating stable conformations (minima on energy profiles) are comparable to the energy of thermal vibrations. The optimized structures of a free tetra-*n*-butylammonium ion obtained by slight variation of the C-N-C angle (up to ±15°) does not lead to a significant change in shape of organic cation, because the remaining C-N-C angles adjust, trying to preserve the ion shape according to sp³-hybridization. Further increasing of this angle is not energetically beneficial.

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