



# Density functional theory study on LDFBDB and its derivatives: Electronic structures, energies, and molecular properties

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## ARTICLE INFO

### Article history:

Received 10 April 2011

Received in revised form 21 July 2011

Accepted 21 July 2011

Available online 28 July 2011

### Keywords:

DFT

Lithium salts

Lithium difluoro(1,2-benzene-diolato(2-)-o,o')borate

(LDFBDB)

Electronic structures

Molecular properties

## ABSTRACT

Theoretical studies on unsymmetrical electrolyte salts, lithium difluoro(1,2-benzene-diolato(2-)-o,o')borate (LDFBDB), and its derivatives, lithium bis[1,2-benzene-diolato(2-)-O,O']borate (LBBB) and lithium fluoroborate (LiBF<sub>4</sub>) are carried out using density functional theory (DFT) method and B3LYP theory level. Bidentate structures are preferred. Based on these conformations, a linear correlation was observed between adiabatic ionization potential  $I_p$  and the limiting oxidation potentials measured by linear sweep voltammetry, which supports experimental results that strongly electron-withdrawing substituent anions are more resistant against oxidation. The correlations were also observed between ionic conductivity and binding energy, solubility and theoretical set of parameters of anion. Wave function analyses have been performed by natural bond orbital (NBO) method to further investigate the cation–anion interactions.

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## 1. Introduction

The focus on the development of the novel lithium salts has been placed on seeking proper anions for coordination with lithium cation to obtain desired species with appropriate chemical and electrochemical property [1–4]. Barthel et al. reported a new class of wide electrochemical windows and thermally stable lithium salts [5,6] with a chelate-type boron-containing anion, such as lithium bis[1,2-benzene-diolato(2-)-O,O']borate (LBBB) [7], lithium bis[2,3-naphthalene-diolato(2-)-O,O']borate (LBNB) [8,9], lithium bis[2,2-biphenyldiolato(2-)-O,O']borate (LBBPB) [10], and lithium bis[salicylato(2-)]borate (LBSB) [10]. Xu and Angell reported advanced electrolytes of Li-ion battery, lithium bis(oxalato)borate (LBOB) [11], and lithium (malonato oxalato)borate (LMOB) [12]. Recently, a novel lithium salt, lithium oxalyldifluoroborate (LODFB) [13], has drawn intensive attention because of its significant merit such as (1) the ability to support metallic lithium cycling reversibly on the surface of copper anode current collector, (2) the ability to passivate aluminum cathode current collector at high potentials, (3) the ability to participate in formation of the SEI and support Li-ion battery operating stably at high temperatures, and (4) the ability to increase battery safety

protection and overcharge tolerance [13–16]. The common feature of these anions is an extensive charge delocalization in their anions caused by strongly electron-withdrawing substituents. Due to this particular feature, the lithium salts of these anions yield sufficiently high ionic conductivity solutions, and exhibit wide electrochemical stability windows and high thermal stability.

To save both time and resources and to provide quantitative predictions to help further focus experimental efforts, a theoretical treatment on predicting the structure and (electro) chemical characteristics is undoubtedly necessary and important for us to. Because the anion–cation interaction within the lithium salts plays an important role in determining the solubility, ionic conductivity, electrochemical windows and thermal stability [17–19], a thorough computational investigation on the electronic structures, energies, and orbitals of this B-containing lithium salts would be desirable to better our understanding their properties at a quantum chemistry level.

According to our previous theoretical researches [20–24], the pronounced charge delocalization anions, F<sup>-</sup> and C<sub>6</sub>H<sub>4</sub>O<sub>2</sub><sup>2-</sup> [dianion of 1,2-benzenediol], were chosen as the chelators to coordinate with boron to form new lithium salt, lithium difluoro(1,2-benzene-diolato(2-)-o,o')borate (LDFBDB), which yield high ionic conductivity solutions, and exhibit wide electrochemical stability windows and high thermal stability.

In this study, to further our understanding the properties of this new lithium salt at a quantum chemistry level, the density

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functional theory (DFT) B3LYP method [25,26] was chosen because it accounts better for electron correlation energies and greatly reduces the calculation expenses with rather reliable description of both geometries and energy of targeted molecules. We will address the following issues regarding the DFBDB<sup>-</sup>, the derivatives BBB<sup>-</sup> and BF<sub>4</sub><sup>-</sup>, all the three lithium salts: (a) the conformational characteristics of the three anions, (b) molecular structures and the electronic distributions of the stable L<sup>+</sup>BBB<sup>-</sup>, L<sup>+</sup>DFBDB<sup>-</sup> and Li<sup>+</sup>BF<sub>4</sub><sup>-</sup> ions pairs, (c) the nature of the bonding corresponding to each local energy minimum by estimating electrostatic and charge transfer contributions to the binding energy, and (d) the relationship between molecular structures and properties.

## 2. Calculation and experimental methods

The local minima of the complexes have been fully optimized by analytic gradient techniques. The method used was the density functional theory (DFT) with Becke's three parameters (B3) exchange functional along with the Lee–Yang–Parr (LYP) non-local correlation functional (B3LYP). All of the complexes were treated with DFT method at B3LYP/6-31++G(2df,2p) level for full geometry optimization. Nature population analysis (NPA) and natural bond orbital (NBO) [27] analysis were performed at B3LYP/6-311++G(3df,3pd) level using NBO program to obtain quantitative analysis of cation–anion interactions between NBOs of the complexes.

Single-point energy calculations at higher level basis set (B3LYP/6-311++G(3df,3pd)//B3LYP/6-31++G(2df,2p)) were also performed to obtain more accurate binding energies, which were defined as  $E_{\text{bind}} = E_{\text{metalcomplex}} - (E_{\text{cation-free}} + E_{\text{anion-free}})$ . All of the DFT and NBO calculations were performed using the Gaussian 03 program package [28].

The purification procedures for propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), acetonitrile (AN), and tetrahydrofuran (THF), as well as the electrochemical equipment for electrochemical studies, are given in Refs. [7,8].

Thermogravimetric (TG) analysis of the lithium organoborates was carried out with PerkinElmer Pyres-1 DMDA-V 1 model, using

a sample of about 10 mg. The decomposition voltages (*i*-*E* curves) of the electrolytes using a three-electrode system (platinum wire, surface area  $4.91 \times 10^{-4} \text{ cm}^2$ , working, Li plate counter, and Li plate reference electrodes) were measured at a scan rate of  $9 \text{ mV s}^{-1}$ . Preparation of the electrolyte solutions and the cell assembly were carried out in a glove box (Labmaster 130, MBRAUN) at low water (<1 ppm), and oxygen (<1 ppm) contents.

## 3. Results and discussion

### 3.1. Geometries

First, we shall present and discuss the results obtained for the “model” system DFBDB<sup>-</sup> and L<sup>+</sup>DFBDB<sup>-</sup>. The other two systems studied here will be discussed with reference to this first system. The lithium bis(trifluoromethylsulfonyl) imide (LTFSI) ion pair was studied by Arnaud et al. [29] using *ab initio* Hartree–Fock method up to 6-31+G\* level. Their work showed that the bidentate structures are the most stable. Francisco and Williams [30] and Spoliti et al. [31] reported that the total energy order for lithium tetrafluoroborate ion pairs is bidentate < tridentate < monodentate, and a similar energy order was reported for the lithium perchlorate ion pairs [32]. Apparently, a common feature exists for the energy of these lithium complexes, i.e. the bidentate structure has the lowest total energy calculated for these isolated ion pairs. Thus, only the most stable optimized geometries of the bidentate ion pairs (one of the three conformers of the LDFBDB, one of the two conformers of the LiBF<sub>4</sub>) are given in Table 1 and Fig. 1.

The DFBDB<sup>-</sup> belongs to the C<sub>2v</sub> point group; the equilibrium B–O2, B–O3, B–F4, B–F5 distances are 1.503, 1.503, 1.395, and 1.395 Å, respectively. The DFBDB<sup>-</sup> clearly has a symmetrical structure. Each of the moieties (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>, BF<sub>2</sub>) has a planar structure, and the two planes are perpendicular to each other. Compared with free DFBDB<sup>-</sup>, structural changes of the DFBDB<sup>-</sup> moiety in the bidentate ion pair are as follows: (1) as expected, the B–O2 in cation-unbounded moiety (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>) and B–F4 distances are shortened by 0.064 and 0.040 Å, whereas the B–O3 in cation-bounded moiety (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>) and B–F5 distances are lengthened by ca. 0.030

**Table 1**  
Optimized geometries of the free anions, their lithium ion pairs<sup>a,b</sup>.

	Anion			Ion pair		
	BBB <sup>-</sup>	DFBDB <sup>-</sup>	BF <sub>4</sub> <sup>-</sup>	LBBB	LDFBDB	LiBF <sub>4</sub>
r(B1–O2)	1.488	1.503	–	1.446	1.439	
r(B1–O3)	1.488	1.503	–	1.537	1.533	
r(B1–F5)	–	1.395	1.410		1.489	1.481
r(B1–F4)	–	1.395	1.410		1.355	1.352
r(O2–C6)	1.343	1.338	–	1.354	1.355	
r(O3–C7)	1.343	1.338	–	1.379	1.380	
r(C6–C7)	1.413	1.417	–	1.401	1.402	
r(C6–C11)	1.385	1.386	–	1.384	1.384	
r(C7–C8)	1.385	1.386	–	1.380	1.380	
r(C8–C9)	1.409	1.410	–	1.406	1.406	
r(C9–C10)	1.393	1.393	–	1.394	1.394	
r(C10–C11)	1.409	1.410	–	1.404	1.404	
r(Li–O3)	–	–	–	1.835	1.836	
r(Li–F5)	–	–	–	–	1.772	1.770
α(O2–Li–F5)	–	–	–	–	80.6	
α(O2–B1–O3)	104.0	103.5	–	103.9	105.2	
α(O2–B1–O4)	112.3	–	–	115.3		
α(O2–B1–F5)	–	110.9	–	–	101.2	
α(F4–B1–F5)	–	109.6	109.5	–	107.4	99.2
d(O2–B1–O3–C7)	0.0	0.0	–	4.0	1.1	
d(O4–B1–O3–C7)	121.6	–	–	123.1		
d(F4–B1–O3–C7)	–	119.0	–	–	127.5	
d(O2–C6–C7–C8)	180.0	180.0	–	179.4	179.3	
d(C6–C7–C8–C9)	0.0	0.0	–	0.4	0.4	

<sup>a</sup> Bond lengths in Å, bond angles and dihedral angles in degrees.

<sup>b</sup> Optimized with the DFT method at B3LYP/6-31++G(2df,2p) level.

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