A DFT Prediction Study of Dibutyl Dithiophosphate Isomers as Extractant for Rare Earth Elements

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In this work, based on the DFT approach, the electronic structural properties of dibutyl dithiophosphate (DBDTP) and its isomers (*sec*-butyl dithiophosphate and *tert*-butyl dithiophosphate) as extracants for the separation of rare earth elements at the DFT level B3LYP/6-31G(d) were predicted and also to ascertain the DBDTP ligand isomer's conformation as well as their relative stability. Using the base function 6-31G*, the chemical reactivity was computed with the help of chemical hardness descriptors, electronic chemical potential and electrophilicity. It was found that *sec*.-BDTP has biggest energy gap, while *tert*.-BDTP exhibited the smallest energy gap. Thus, *tert*.-BDTP is the most chemically reactive and stable isomer, suggesting that the rare earth metal complexes with *tert*.-BDTP ligand is more stable.

Keywords: Dibutyl-dithiophosphate, Chemical reactivity, Rare earth elements complex.

INTRODUCTION

Rare earth elements are highly crucial in a variety of fields of advancement in materials sciences due to their unique spectroscopic, magnetic properties and these elements are found together in nature, in various minerals, such as bastnasite, monazite, xenotime and others [1,2]. Due to their comparable chemical and physical characteristics, rare earth elements are still challenging to separate and isolation [3].

There are several ways to separate the rare earth elements, one of which is by utilizing the complexing ligands. The ability of rare earth elements to form complex compounds with several ligands has been proven by several studies, *e.g.* dibutyl dithiocarbamate (DBDTC) [4] and dibutyl dithiophosphate (DBDTP) [5-7]. Dialkyldithiophosphoric acid is commonly used in the solvent extraction and the chromatographic separation of transition as well as rare earth elements [8]. One of the derivatives of dialkyldithiophosphoric acids, such as di-*n*-butyl orthophosphoric acid (DBDTP), as an extractant has better properties than the shorter homologous [9]. Therefore, DBDTP or its derivatives with longer alkyl chains have several advantages when

used as extractants in solvent extraction [7]. Therefore, in order to design ligands derived from DBDTP and to improve the extraction efficiency results in the laboratory, it is required to understand the electronic structural properties of dibutyl dithiophosphate (DBDTP) isomers using DFT studies.

EXPERIMENTAL

The dibutyl dithiophosphate (DBDTP) isomers studied in this study were *viz.* diisobutyl dithiophosphate, *sec*-butyl dithiophosphate (*sec*.-BDTP) and *tert*.-butyl dithiophosphate (*tert*.-BDTP). The geometry optimization of DBDTP ligands were visulized by Gaussian 09 Revision-B.01-SMP program [10] using GaussView 5.0.8 program [11]. Geometry optimization in this study uses the B3LYP function and the basis set 6-31G* for all the studied DBDTP isomers.

Geometry optimization: The function of geometry optimization is to find the most stable molecule. With the help of initial structure of diisobutyl dithiophosphate, *sec*.-butyl dithiophosphate and *tert*.-butyl dithiophosphate isomers, basis-set was used to calculate the energy of these isomers and then

the optimized structure of three isomers. The most stable state of a molecule is obtained at the lowest energy level [12].

Detection method: Calculations were performed using the Gaussian 09 Revision-B.01-SMP program [10] and its visualization using Gauss View 5.0.8 program [13]. The computer user has a specification Intel® Xeon® CPU X5680@3.33 GHz × 12 with 8 GB RAM. The Ubuntu 16.04 LTS serves as the operating system.

RESULTS AND DISCUSSION

By displaying the configuration of electronic molecular orbitals, the transfer of electrons between molecules can be studied. The transfer of electrons between molecules is influenced by the interactions of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) orbitals [11]. The molecule can easily reach electron equilibrium and become more reactive when its electronegativity is low. The contrary results are indicated by high electronegativity values [14].

Molecular energy calculation: The geometry optimization of DBDTP isomer was carried out using the B3LYP theory level. The minimization energy and time were calculated and are shown in Table-1. It is clear from the results that the *tert.*-BDTP isomer requires the most calculation time since it has the greatest steric hindrance in comparison to *sec.*-BDTP isomer.

TABLE-1
MINIMIZED ENERGY AND CALCULATION TIME

Compound	Energy (a.u.)	Solvation (kJ/mol)	Time (J:M:D)
BDTP	-1604.05924239	-1604.10552090	0:41:51.5
sec.-BDTP	-1604.06207094	-1604.10737677	0:41:6.0
tert.-BDTP	-1604.05428242	-1604.09808008	1:12:29.3

The HOMO-LUMO calculation results were displayed as an energy diagram (Fig. 1) with the orbitals associated with these energy states. As observed, the *sec.*-BDTP isomer exhibit the largest energy difference value of 4.08252 eV, indicating that *sec.*-BDTP is the most stable ligand since the energy required to move larger is less. While the *tert.*-BDTP ligand is the most reactive compound due to its small HOMO-LUMO energy difference value of 3.89776 eV, which makes it easy for the electrons to travel and makes the compound more reactive (Table-2).
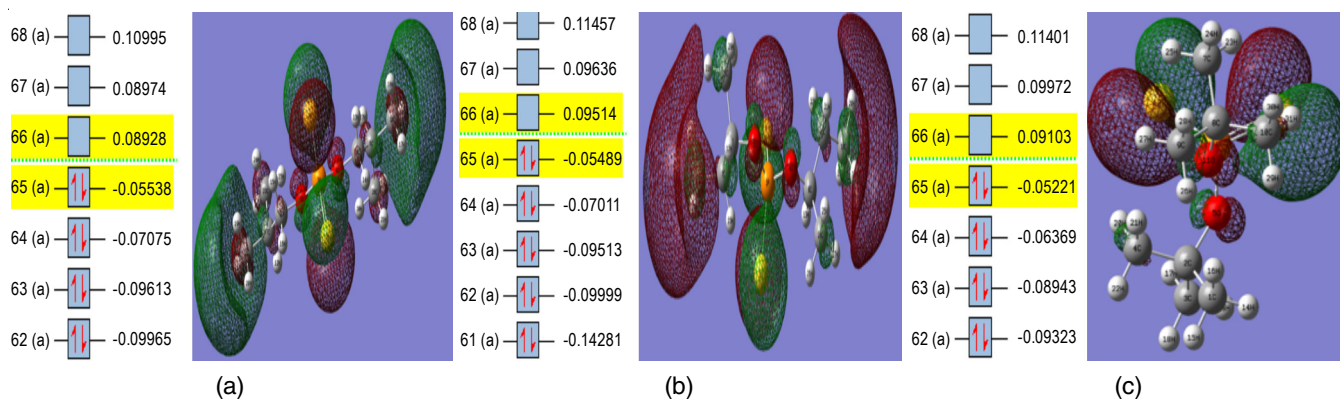
TABLE-2
ENERGY DIFFERENCE HOMO-LUMO

LIGAND	εLUMO (eV)	εHOMO (eV)	ΔεLUMO– εHOMO (eV)
BDTP	2.42943	-1.50697	3.93640
sec.-BDTP	2.58889	-1.49363	4.08252
tert.-BDTP	2.47705	-1.42071	3.89776

Calculation of chemical reactivity: The calculation of chemical reactivity was carried out using chemical reactivity descriptors, namely chemical hardness (η), electronic chemical potential (μ), electrophilicity (ω) and values for each isomer as shown in Table-3. It was found that *sec.*-BDTP was the most stable compound with the largest value of 2.0413 eV and *tert.*-BDTP compound was the most reactive compound with the lowest value of 1.9489 eV. The tendency for electrons to be released from their equilibrium state is described by the electronic chemical potential (m) value, however, the greater the electronic chemical potential, the more reactive the ligand, which, implies that *sec.*-BDTP compound is the most reactive while *tert.*-BDTP ligand is the most stable compound. Electrophilicity (ω) measures the susceptibility or capacity of a species to accept electrons. This parameter index is the measurement of energy stability after a system receives an additional amount of electronic charge from the surroundings, thus, *tert.*-BDTP isomer is the strongest and most reactive nucleophilic based on these values.

TABLE-3
CHEMICAL REACTIVITY VALUE OF DBDTP LIGAND ISOMER

Ligand	η (eV)	μ (eV)	ω (eV)
BDTP	1.9682	0.46123	0.05245
sec.-BDTP	2.0413	0.54763	0.05480
tert.-BDTP	1.9489	0.52817	0.05015

Conclusion

According to calculations made using the DFT 6-31G* base function, the total energy, HOMO-LUMO energy difference and chemical descriptors of dibutyl dithiophosphate (DBDTP) isomers were obtained. The *tert.*-butyl dithiophosphate (*tert.*-BDTP) isomer is the most reactive compound as compared to *sec.*-butyl dithiophosphate (*sec.*-BDTP), which are based on the calculation of small HOMO-LUMO energy difference

Fig. 1. Energy and orbital diagram of (a) BDTP, (b) *sec.*-BDTP and (c) *tert.*-BDTP

value of 3.89776 eV, which makes electron transfer easy and more reactive.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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