

Lithium binding in fluorinated phosphazene trimers

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ABSTRACT

Density functional theory is used to model a series of cyclic phosphazenes, with and without coordinated Li^+ . Two pendant groups are used, ethoxy and 2,2,2-trifluoroethoxy, in varying combinations to generate phosphazenes with 0, 1, 2, 3, or 6 trifluoro groups. In all cases, Li^+ sits in a pocket on the ring, always bonding to a ring nitrogen, and can be three- or four-coordinate, depending on the local environment. Three-coordinate occurs when no fluorines are close enough to interact, with the lithium bonding to a ring nitrogen and the two adjacent oxygens. When Li^+ is four-coordinate, the bonding varies between the ring nitrogen, two adjacent oxygens, and one fluorine, or the ring nitrogen, one adjacent oxygen, and two fluorines. All of the possible symmetry unique structures have been calculated. The binding strength of Li^+ steadily decreases, from 74.93 kcal/mol with no trifluoro groups, to 58.01 kcal/mol when 6 trifluoro groups are present. The decrease is attributed to the electron withdrawing effect of the trifluoro groups, and also to distortions in the geometry to accommodate Li–F interactions.

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1. Introduction

Lithium ion batteries are in widespread use for a broad range of mobile power needs. However, there still remain significant challenges that must be addressed in order to move lithium ion technology into larger format applications, such as vehicle technologies and stationary power [1]. Chief among these is safety concerns of the electrolyte. Most commercial electrolytes employ a lithium salt dissolved in a mixture of organic carbonates and/or esters [2] and this mix brings several intrinsic problems. These solvents are highly volatile as well as highly flammable. This presents a serious safety problem in situations where the battery is under abuse or if the battery becomes damaged. While this concern is minimal in small cells such as those that power small electronics, the problems rapidly grow in magnitude as battery sizes grow. In order to get lithium ion power into larger power sources, this problem must be addressed.

The simplest alternative is to identify other solvents that can replace the current generation of electrolyte solvents. This subject has received much attention in recent years. Approaches under study include the use of sulfones [3] and most recently ionic liquids [4]. However it may be some time into the future before carbonates and esters may be entirely replaced. As a practical interim strategy, it has been recognized that improvements in the performance and safety record of the current generation of electrolytes may be realized through the use of additives [5]. Additives have been the subject of research since the early 1990s [6] and are

attracting growing interest, especially in the past few years. Research into additives has taken several forms to address different yet strategic challenges in lithium ion electrolytes. Some have employed additives to improve formation of the solid electrode interphase (SEI) [7], enhance overcharge protection [8], and provide flammability suppression [9]. Others have employed additives not as co-solvents but rather through the use of novel salts to achieve improved thermal stability [10]. Recent experimental work has been undertaken in our labs in the area of phosphazene additives [11,12]. One of the challenges inherent in working with these compounds as alternative solvents for electrolytes is the strong nature of lithium binding to the phosphazene cores, which would be deleterious to Li^+ transport within the cells. One approach for modifying Li^+ binding is to decorate the phosphazene core with pendant moieties that would reduce binding by either steric or electronic effects, and the trifluoromethyl group is a candidate moiety for core modification. This modeling work was initiated to study Li^+ – cyclotriphosphazene binding as the number and position of the trifluoro groups is varied, in an attempt to guide synthetic efforts and identify target molecules where this binding is minimized.

There are a large number of computational studies concerning batteries, far too numerous to list. The following examples only illustrate the usefulness of computational methods when applied to the problems discussed above. Every aspect of a battery has been investigated computationally, including the cathode material [13], the anode material [14], as well as the SEI [15,16]. The most studied aspect of a battery is the electrolyte, along with electrolyte additives. Lithium interactions with the electrolyte have been studied [17–23] and also the decomposition of the electrolyte

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[24–26]. Electrolyte additives have also been investigated computationally [27,28], with the goal of improving SEI formation, stabilizing the electrolyte to prevent decomposition, or stabilizing the LiPF_6 salt. As stated, these references are only a sampling of the computational investigations that have been performed for battery components.

Lithium binding studies are important in other applications as well. For example, addition of lithium has been found to be beneficial in materials designed for the storage of hydrogen. Lithium binding studies have been performed on a variety of materials, such as graphene, graphane, metal–organic frameworks, and covalent-organic frameworks [29–31]. The material's capacity for hydrogen storage increased upon addition of lithium. A second application for lithium binding studies is biochemistry [32,33]. Lithium is useful in the treatment of manic effects due to lithium's ability to inhibit specific enzymes. In any biological system, there are a number of functional groups available for lithium to bind with, such as amines, amides, imides, carboxylic acids, phosphates, alcohols, and thiols. Binding studies can help determine the likely lithium binding position.

In this paper, a series of cyclic phosphazenes have been modeled with and without lithium to determine binding energies. The phosphazenes utilize either ethoxy or 2,2,2-trifluoroethoxy pendent groups in different amounts to generate phosphazenes with 0, 1, 2, 3, or 6 trifluoro groups. From previous studies on polymeric phosphazenes [22,23] it is known the lithium sits in a pocket, generally created by one or more nitrogens from the phosphazene backbone along with ether oxygens from the pendent groups. This pocket structure was used as a starting point for the present calculations. Given the relative positions possible for the 2,2,2-trifluoroethoxy groups to occupy, a large number of symmetry unique positions are available for lithium binding, all of which have been calculated.

2. Computational methods

All geometry optimizations and vibrational analyses were performed with the Gaussian03 program [34]. For consistency, both neutral and cationic species were calculated using density

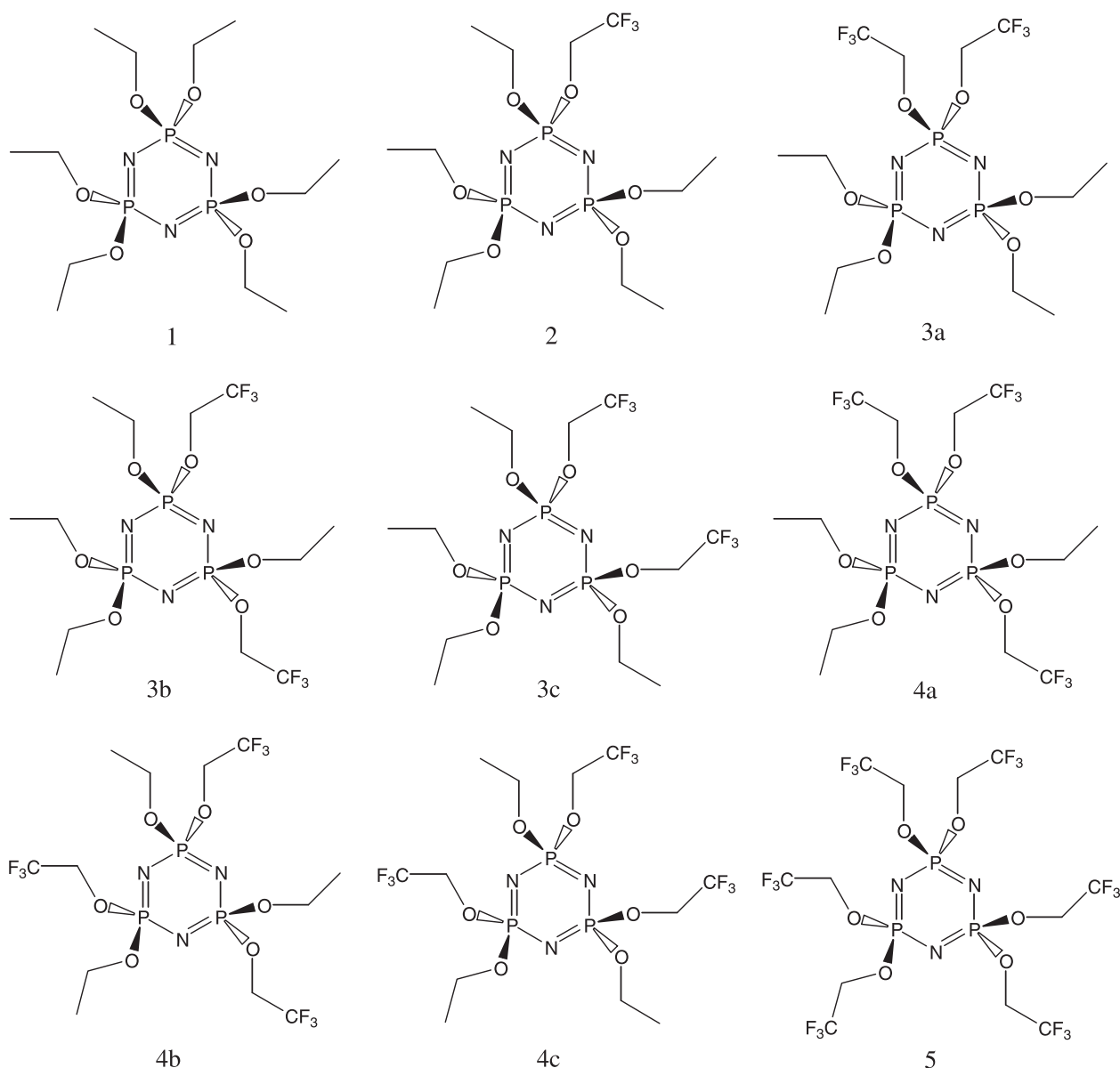


Fig. 1. (1) Hexaethoxycyclophosphazene, (2) pentaethoxy(2,2,2-trifluoroethoxy)cyclophosphazene, (3a, 3b, 3c) isomers of tetraethoxybis(2,2,2-trifluoroethoxy)cyclophosphazene, (4a, 4b, 4c) isomers of triethoxytris(2,2,2-trifluoroethoxy)cyclophosphazene, (5) hexakis(2,2,2-trifluoroethoxy)cyclophosphazene.

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