# MECHANISTIC INSIGHTS RELATED TO THE DESIGN AND CONSTRUCTION OF LITHIUM SINGLE ION CONDUCTORS

By

Gregory Spahlinger

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#### ABSTRACT

## MECHANISTIC INSIGHTS RELATED TO THE DESIGN AND CONSTRUCTION OF LITHIUM SINGLE ION CONDUCTORS

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Lithium single ion conductors are a class of electrolytes, typically designed for lithium ion batteries, with the potential to improve the performance of these batteries. The benefits of single ion conductors arise out of the fact that their immobile anions are not capable of concentrating near the anode of the battery, causing an increase in resistance as the battery is discharged. Unfortunately lithium single ion conductors suffer severe drawbacks in their conductivity which have been attributed to diverse causes. Because of the low success rate of single ion conductors in the literature and previous work in the Baker group, I have chosen to investigate mechanistic questions related to the design and construction of these materials, without engineering new materials.

An attractive design strategy for the screening of immobile anion moieties for single ion conductors would be the use of the copper catalyzed alkyne azide (CUAAC) "click" reaction in order to efficiently introduce anions onto a support chemistry in a way that is efficient and tunable. A variable added by this strategy would be the presence of a 1,2,3-triazole moiety which is not commonly used in electrolyte chemistry. In order to assess the impact of the triazole on the conductivity of an electrolyte, a series of model compounds were synthesized containing a variable number of triazoles in an otherwise poly(ethylene glycol) like oligomer chain. The model compounds were subjected to differential scanning calorimetry, electrochemical impedance spectroscopy, and in one case single crystal X-ray diffraction, and solvent shells were modeled for lithium with and without triazoles using ab initio quantum chemistry calculations. It

was concluded that the affinity to Li+ of the triazole and ether oxygen are similar, however the triazole has a substantial dipole which exerts some deleterious effects on the conductivity, leading to an increase in the activation energy for the process. These effects are balanced by an increase in the pre-exponential factor which leads to "compensation behavior" due to the dependence of that quantity on the dipole density in the material. The observed effect is one of a lower conductivity for the model compounds relative to poly(ethylene glycol)dimethyl ether 500 at room temperature, which converges to roughly the same conductivity around 80 °C.

In synthetic studies, attempts were made to synthesize N-triflylpropanesultam (TPS) a five membered heterocycle whose nucleophilic ring opening would yield a desirable anion for use in single ion conductors. TPS proved to be significantly more difficult to open than expected, which prompted a computational study.

In order to study the nucleofugality of polyatomic anionic leaving groups derived from oxygen and nitrogen, a contingent of 19 methylating agents consisting of amines or alcohols activated with carbonyl or sulfonyl substituents has been examined via ab initio calculations. Activation energies for alkylation of ammonia, and gas phase methyl cation affinitys were calculated. It was found that polyatomic anionic leaving groups derived from nitrogen will have higher activation energies for Menshutkin (S<sub>N</sub>2) alkylation even when they have similar methyl cation affinities. This inherent deficit in the nucleofugality of nitrogen derived leaving groups appears to be a result of the way bond cleavage is synchronized with bond formation to the incoming ammonia nucleophile. Additionally the second sulfonyl group present in a sulfonimide appears to be less effective at activating nitrogen due to a preference for tetrahedral geometries at nitrogen in the transition states of sulfonamide groups. Optimal delocalization of electron density is therefore frustrated due to the symmetry of the leaving group.

Copyright by GREGORY SPAHLINGER 2014 To those who devote themselves to the pursuit and transmission of knowledge To those who have been my mentors and role models To science

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## **KEY TO ABBREVIATIONS**

- CUAAC Copper Catalyzed Alkyne Azide Reaction
- TPS- N-Triflylpropanesultam
- PEG- Poly(ethylene glycol)
- PEO Poly(ethylene oxide)
- DBP dynamic bond percolation model
- DDH dynamically disordered hopping model
- VTF Vogel Tamman Fulcher
- $\sigma$  conductivity
- V volts or potential
- I-Current
- R Resistance or the Gas constant (context dependant)
- G Conductance
- S Siemens
- $\Omega-Ohms$
- $\mu$  mobility or dipole moment (context dependent)
- q-charge
- D-coefficient of diffusion
- $\Lambda_m$  Molar conductivity
- F Faraday's constant
- T Temperature
- z charge count
- v stoichiometric coefficient
- $T_g$  Glass transition temperature

T<sub>m</sub> – Melting transition temperature

k or k<sub>B</sub> – Bolzmann's constant

 $\sigma_0$  – exponential prefactor for conductivity in Arrhenius or VTF formalisms

E<sub>a</sub> – activation energy

P(t) – probability of an event as a function of time

 $w_{i \rightarrow i}$  – Probability of a transition

 $\tau_{ren}$  – Renewal time

r - Displacement

<r<sup>2</sup>> - mean squared displacement of a particle (triangular braces always denote an ensemble average)

 $T_s$  – Shifted temperature

TFSI - bis(trifluoromethanesulfonyl)imide

MSD(t) - mean squared displacement of a particle as a function of time

a(T) – temperature dependent shift factor

N<sub>R</sub> - the number of Rouse segments (a bead connected to a spring) in a modeled chain

l – numerical designation of a rouse segment

a<sub>R</sub> – mean squared distance between rouse beads

 $\mathbf{R}$  – vector describing the shortest distance between the ends of a polymer chain

 $\zeta_R$  – Coefficient of friction

M<sub>1</sub> – mechanism 1 of Li+ diffusion (diffusion along polymer chains)

M<sub>2</sub> - mechanism 2 of Li+ diffusion (diffusion mediated by chain deformation)

M<sub>3</sub> – mechanism 3 of Li+ diffusion (diffusion by chain hopping)

 $\tau_1, \tau_2$ , and  $\tau_3$  – times associated with the above mechanisms (M<sub>1</sub> through M<sub>3</sub>)

 $R_0$  – initial value of R

 $R_e$  – equilibrium value of R

 $D_M$  – diffusion resulting from the three mechanisms detailed above

 $D_{c.m.}$  – diffusion resulting from movement of a lithium resulting from center of mass displacement of the polymer chain

T<sub>+</sub> - Lithium ion transference number

PEGDME – Poly(ethylene glycol) dimethyl ether

APTES – 3-aminopropyltriethoxysilane

6EO2T - A model compound, "6 ether oxygens 2 triazoles"

8EO2T - "8 ether oxygens 2 triazoles"

8EO1T – "8 ether oxygens 1 triazole"

6EO1T - "6 ether oxygens 1 triazole"

GAMESS – General Atomic and Molecular Electronic Structure System – a computational software package

HF – Hartree Fock

MP2 – Moller Plesset second order perturbation theory

MP2(full) – MP2 calculation where perturbative correction is applied to all electrons including core electrons

MP2(FC) – MP2 "frozen core" where only valence electrons receive perturbative correction. This is the default MP2 treatment, and FC need not be explicitly specified.

CCSD – Coupled Cluster Singles and Doubles

QCISD(T) – Quadratic Configuration Interaction Singles Doubles and non-iterative Triples

CCSD(T) – Coupled Cluster Singles Doubles and non-iterative Triples

B3LYP – "Becke 3 parameter Lee-Yang-Parr", B3LYP is a hybrid functional and the most common functional used in density functional theory.

G3 – Gaussian 3 theory

G3(MP2) – Gaussian 3 with reduced Moller Plesset order

cc-pVDZ or cc-pVTZ - common Dunning basis sets. DZ is double zeta TZ is triple zeta

Aug-cc-pVNZ – Dunning basis set with added diffuse functions

Aug-cc-pVNZ(Li-C) - Dunning basis set with core correlation functions on lithium

3-21G - a Pople minimal basis set

6-31G(d) – a common Pople basis set of double zeta quality. Contains a d function for polarization on first row atoms.

 $\Delta E$  – a change in energy

 $\Delta E_{ass}$  – association energy of a ligand to a metal

 $E_{complex}$  – the energy of a complex

Eligand - the energy of a ligand

 $E_{Li}$  – energy of a lithium atom or ion

THF - tetrahydrofuran

NMR - nuclear magnetic resonance spectroscopy

IR - infrared spectroscopy

Ts – Tosyl or p-toluenesulfonyl

4-MEOMET – 4-methoxymethyltriazole

1-MEOET – 1-methoxyethyltriazole

M<sub>n</sub> – number average molecular weight

Å – angstrom

T<sub>D</sub> – Disordering temperature

 $\epsilon_s - static \; dielectric \; constant$ 

N<sub>d</sub> – dipole density

D – Debye (chapter 2 only)

I – Ionization energy (chapter 3 only)

A – Electron affinity (chapter 3 only)

 $\mu$  – electronic chemical potential (chapter 3 only)

 $\eta$  – chemical hardness (chapter 3 only)

 $\omega$  – electrophilicity

 $\Delta E_{nucleofuge}$  – an energy scale to describe the ease with which a nucleofuge departs

- HPCC High Performance Computing Cluster
- MAD Mean Average Deviation
- MCA Methyl Cation Affinity
- $\Delta E_{S \rightarrow TS}$  the difference between separated species and transition states
- $\Delta E^{\ddagger}$  the difference between an association complex and a transition state
- %BE percentage bond elongation
- MSI (methylsulfonyl)imide
- FSI (fluorosulfonyl)imide
- FSA fluorosulfonamide
- MSA methylsulfonamide
- MeiprFSA methyl isopropyl fluorosulfonamide
- E<sub>c</sub> Crossing energy
- B-quantum mechanical resonance energy (chapter 3 only)
- HOMO Highest Occupied Molecular Orbital
- LUMO Lowest Unoccupied Molecular Orbital
- s singlet
- d doublet
- dd doublet of doublets
- t triplet
- q quartet
- p pentet
- m multiplet

## **1** Chapter 1: Introduction

## 1.1 General Background

In the overall scheme of fuels and energy storage technology, batteries play an important and ever increasing role. With an increasing need for a sustainable, carbon-neutral energy economy, the need for safe, energy dense batteries capable of translating electrical energy into such technologies as light duty vehicles is also increasing.<sup>1</sup> Lithium ion batteries are one of the most famous and promising technologies with the potential to fill this niche.<sup>2</sup>

The Lithium ion battery was first proposed in 1976 based on lithium intercalation into a  $TiS_2$  cathode.<sup>3</sup> Energy storage in a lithium ion battery is facilitated by the difference in electron affinity between  $Li^0$ , which is strongly electropositive, and an oxidizing transition metal center.<sup>4</sup> During the discharge process of the battery, electrons flow from the anode (lithium metal or an intercalation compound such as lithium intercalated graphite) through an outside circuit, providing energy to a device, and finally to the cathode where they reduce the cathode material, which is usually a transition metal chalcogenide.<sup>1</sup> The accompanying process within the cell consists of lithium atoms undergoing oxidation in the anode and traveling as Li+ through the electrolyte and into the cathode, where they intercalate to balance the reduction of the cathode material.<sup>1</sup>



Figure 1 - A Schematic of a lithium ion battery, featuring typical materials for the anode (graphite) and the cathode (LiCoO<sub>2</sub>). A likely choice of electrolyte would be ethylene carbonate and dimethyl carbonate 1:1.<sup>1</sup> Figure 1 is reprinted with permission from Bruce, P.; Scrosati, B.; Tarascon, J. *Angew. Chem. Int. Ed.* 2008, *47*, 2930 – 2946. Copywrite 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The electrolyte of a lithium ion battery is a solvent capable of dissociating a lithium salt, and allowing the ions to migrate under an applied potential. Such solvents must be relatively polar, and relatively unreactive toward the anode and cathode.<sup>4,5</sup> The most common choices of electrolytes are solutions of the lithium salts of strong acids such as  $LiSO_3CF_3$  or  $LiClO_4$ , in polar aprotic organic solvents such as propylene carbonate, dimethyl carbonate or tetrahydrofuran.<sup>4,6</sup> The conductivities of optimized electrolytes of this class may be as high as  $10^{-2}$  S/cm at room temperature.<sup>4,6</sup>

Most of the drawbacks of liquid electrolytes are straightforward consequences of the fact that they are organic liquids. Organic electrolytes are flammable, and may leak from a damaged battery casing.<sup>7</sup> Lithium metal anodes may not be used with most liquid electrolytes, as they are

too reactive.<sup>4,7</sup> Additionally, the application of an over potential during the charging process can cause dendrites of lithium metal to form which can lead to reduced capacity and failure of the battery.<sup>4,7</sup> These drawbacks have led to the development of solid polymer electrolytes, particularly for applications in electric vehicles.<sup>7</sup>

Solid polymer electrolytes should, in theory, be capable of resolving many of the problems associated with liquid electrolytes, and these systems have been the focus of intensive study since Wright and Armand first reported the conductivity of salt complexes of polyethylene glycol in the late 1970s.<sup>5</sup> Polyethylene glycol (PEG or PEO) is a linear polymer of the formula  $(CH_2CH_2O)_n$  which is capable of acting as a solvent for alkali metal salts. Polyethylene glycol based electrolytes run into their own problems, however, due to ionic conductivities which are dramatically lower than those of liquid electrolytes; on the order of  $10^{-5}$  S/cm or less.

#### 1.2 Physical Models of Lithium Ion Transport in Liquid and Polymer Electrolytes

The conductivity of a lithium electrolyte is the inverse of its resistance as given by Ohm's law V=IR, such that conductivity ( $\sigma$ ) can be understood as a measure of current (I) per unit potential (V).<sup>4,5</sup> Conductivity is an intensive property of the system derived from the extensive property Conductance (G) through the relation  $\sigma$ =Gl/A, where A is the cross sectional area of a sample and 1 is the thickness.<sup>8</sup> G is typically reported in Siemens (S) which are the inverse of Ohms ( $\Omega$ ) the SI unit for resistance. Conductivity is therefore typically given in S/cm.

Physics and physical chemistry have well defined tools for understanding the conductivity of dilute aqueous solutions of ions, which have been understood for decades. If full dissociation and independent motion of ions are assumed, then conductivity can be related to the mobilities of the ions by the Kohl-Rausch summation:

$$\sigma = \sum_{i} \mu_{i} n_{i} q_{i} \tag{eq. 1}$$

where  $\mu$  is the carrier mobility, n is the carrier concentration, and q is the charge of the carrier species in the electrolyte.<sup>4,5,9</sup> Additionally, molar conductivity ( $\Lambda_m$ ) can be related to the sum of the coefficients of diffusion (D) of ions in a solution by the Nernst-Einstein equation:

$$\Lambda_m = \frac{F^2}{RT} \sum_i D_i z_i^2 \nu_i \tag{eq. 2}$$

Where F is Faraday's constant, R is the gas constant; T is the temperature of the system, z is the charge of the ion and v is the count of the ion in the chemical formula (e.g. the Cl(-) in ZnCl<sub>2</sub> would have v = 2, while Zn(2+) would have z = 2).<sup>5,8,9</sup> Conceptually, these relationships still hold in liquid and solid polymeric lithium ion electrolytes, but they become less and less useful for describing the conductivity of a system, as lithium ion conductors tend to be more concentrated, non-aqueous, and have less than full dissociation.<sup>5,9,10</sup>

Polymer hosts for lithium electrolytes do exhibit local fluidity analogous to ionic solutions, provided they are amorphous rather than crystalline, and provided they are above their glass transition temperature  $(T_g)$ .<sup>5</sup> The importance of side chain flexibility can be understood by invoking the Vogel Tamman Fulcher (VTF) model of conductivity, a modified Arrhenius equation:

$$\sigma T = \sigma_0 e^{\frac{-B}{k(T-T_0)}} \tag{eq. 3}$$

wherein temperature T is normalized by subtracting the equilibrium glass transition temperature  $T_0$  which is generally considered to be a value 'close to' but not equal to  $T_g$ .<sup>5</sup> This rationalization

is made based on the fact that the polymer behaves as a frozen solid beneath its glass transition temperature, and thermal energy cannot enhance segmental motion below this point.<sup>5</sup>

Ratner, Nitzan and co-workers have attempted to derive a more satisfactory model, a Dynamic Bond Percolation theory (DBP) their model builds on static bond percolation: a microscopic theory of diffusion based on the probability of ionic movement in a disordered material whose local structure is stationary.<sup>5, 9, 11-15</sup> Ratner et al. begin by defining a static bond percolation theory in a system of 1 spatial dimension, with an immobile lattice and spaces in the lattice which may or may not contain particles.<sup>11</sup> There is said to be a "bond" between any two sites in the lattice with a traversable path between them, and the bond is "filled" if a particle is present in one of the sites and can traverse the path. The transport of ions can be described in this system by first defining P(t) the probability of a particle being at a given site *i* per unit time, t.<sup>11</sup> A related quantity is defined which describes the probability of a particle traveling from site *i* to an adjacent site *j* : this is  $w_{i\rightarrow j}$ .<sup>11</sup> From here diffusive behavior can be derived from a differential equation which relates the evolution of probability with time to a sum of probabilities across the full lattice:

$$\frac{dP}{dt}(t) = \sum_{j \neq i} \{P_j(t) w_{j \to i} - P_i(t) w_{i \to j}\}$$
(eq. 4)

A variety of individual restrictions apply to the migration probabilities which are explained in detail in the paper. However we can generalize that in cases where sites *i* and *j* are unconnected, or a lattice element or particle prevents migration, w is set to zero.<sup>11</sup> A similar, but more general model, known as the Dynamically Disordered Hopping (DDH) model was also derived in which some of the conditions for hopping are relaxed, the most notable of these being the condition that hopping only occur between a site and its nearest neighbor.<sup>12</sup> The key feature of the DBP and DDH models, is that the lattice is not static, but rather bonds  $i \rightarrow j$  may open and close via time dependent changes in the lattice configuration. Ratner et al. therefore define a renewal time  $\tau_{ren}$  after which the bonds in the lattice are randomly assigned to be open or closed.<sup>11</sup> In their seminal paper on the model, Ratner et al. devised simulations of a one dimensional system and reported that for running times greater than  $\tau_{ren}$  diffusive behavior was observed. In a one dimensional system the coefficient of diffusion, D, is related to the ensemble average of the squared distance traveled by a particle,  $\langle r^2 \rangle$  over the renewal time, such that D= $\langle r^2 \rangle / \tau_{ren}$ .<sup>11</sup>

After the initial formulation of the DBP and DDH models modifications and expansions were proposed in order to make the theories more applicable to real systems. This included developing a frequency dependent formalism, which is important because of the prevalence of electrochemical impedance spectroscopy, which utilizes an AC potential in the analysis of polymer electrolytes.<sup>12</sup> Additionally, the idea of  $\tau_{ren}$  was further developed.<sup>13,15</sup> Because dynamic movements in a polymer host are thermal in nature, it was proposed that  $\tau_{ren}$  is temperature dependant.<sup>13,15</sup>

A complementary approach to the theoretical methods of Ratner et al. for gaining mechanistic insight into diffusive phenomena in lithium electrolytes, is the use of molecular dynamics (MD) simulations. MD simulations have been used extensively in understanding the microscopic dynamic behaviors of polymers generally, and this work has been the topic of at least one review.<sup>16</sup> In the field of polymer electrolytes, Grant Smith, Oleg Borodin, and co-workers have published a series of papers which bring significant new insight.<sup>17-21</sup> The work of these authors was not the first attempt to apply molecular dynamics to the diffusive behavior of ions in a polymer matrix. They are notable, however, in their attention to detail in designing a

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polarizable force field, capable of reproducing experimental diffusion measurements in models of lithium tetrafluoroborate (LiBF<sub>4</sub>) doped PEO.<sup>17,18</sup> Further studies focused on lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) doped PEO.<sup>19-21</sup>

The PEO/LiTFSI system utilized PEO chains in the Rouse dynamic regime (which governs relatively short, unentangled polymers) with 54 repeating units (2380g/mol) at temperatures ranging from 333 K to 423 K and salt concentrations ranging from 39 – 7.5 ethylene oxide units per lithium ion.<sup>19</sup> The results were shown to be in good agreement with experimental measures, both from diffusion NMR measurements, and structural characteristics.<sup>19</sup> Lithium ions in the simulations were shown to have an average of 4.6 coordinating oxygens in their first solvent shell, which was in good agreement with the 4.9 oxygen average found using neutron diffraction.<sup>19</sup> Additionally degree of dissociation was compared to inferred dissociation from Raman data, and found to be in good agreement; degree of dissociation ranged from 0.95 (95% free ions) to 0.77, and was negatively correlated with concentration.<sup>19</sup>

Molecular dynamics simulations give detailed information about the movement of particles in a system, so coefficients of diffusion can be calculated from the Einstein equation such that

$$D = \lim_{t \to \infty} \frac{\langle MSD(t) \rangle}{6t}$$
(eq. 5)

Where MSD(t) is the mean square displacement of a particle as a function of time.<sup>19</sup> Smith and Borodin then determined temperature dependent coefficients for the polymer host by scaling the time domain obtained at 423K by a "temperature-dependent time-shift factor" such that D(T)=D(423K)/a(T).<sup>19</sup> This was done because of the excessive simulation time demands involved in observing true diffusion at lower temperatures for a host polymer of this size.<sup>19</sup> Once the simulations were shown to conform to experimental results, analyses of the transport of TFSI(-) and Li(+) were conducted based on the observed trajectories. In contrast to previous theory, two separate kinds of motion were found to contribute to the overall coefficient of diffusion for the lithium ion.<sup>19</sup> The first motion was a chain to chain transfer, which the authors considered comparable to the "hops" described in dynamic bond percolation, while a second type of diffusive motion consisted of diffusion of the lithium along the polymer chain.<sup>19</sup> Additionally it was found that lithium ions could be grouped by mobility; lithium ions which had undergone a chain to chain transfer event generally were more mobile than ions which had remained complexed with a single polymer chain, while ions in complex with two separate chains were the least mobile.<sup>19</sup> A microscopic model of lithium ion transport was formulated using the two different transport processes observed and the Monte Carlo algorithm for simulating movement.<sup>19</sup> This simplified simulation was able to reproduce results from the initial runs.<sup>19</sup>



Figure 2 - Rouse theory describes a polymer chain as a series of balls connected by springs. A hypothetical Rouse chain contains  $N_R$  segments of 1 bead and 1 spring; beads have a designation l which starts at 0 such that  $l = N_R$  at the end of the chain. The end to end distance vector of the chain is R, and the mean square length of a segment is  $a_R$ , such that a Gaussian distribution of segment lengths exist in the chain (length variability not represented above).<sup>22</sup>

The model proposed by Borodin and Smith was an improvement on standard dynamic bond percolation, but it still did not explicitly incorporate any physical theories of polymer dynamics. In order to address this omission Maitra and Heuer revisited the simulations and proposed a microscopic theory of lithium transport using the formalisms of Rouse theory.<sup>22,23</sup>

Rouse theory is a model of polymer chain dynamics, in which molecular details of the chain are absent, and the chain is instead modeled as a series of beads connected by springs.<sup>22</sup> Each bead and the spring connected to it make a Rouse segment, such that N<sub>R</sub> Rouse segments exist in the chain.<sup>22</sup> When a polymer of know composition is modeled using this formalism, N<sub>R</sub> will generally be less than the number of monomer units in the chain, and as such, Rouse theory is not useful for describing movements at the level of conformational changes, and can only be applied in order to model large scale coiling behavior.<sup>22</sup> At any point there will exist a vector **R** representing the distance from one end of the chain to another, and a mean square distance, a<sub>R</sub>, defines the length of a Rouse segment (see figure 2). The velocity (d**r**<sub>l</sub>/dt) of each bead (designated *l*) can then be written as a differential equation with a term for friction,  $\zeta_R$ , and forces originating from the nearest neighbor beads being given by a term deriving from spring mechanics  $3k_bT/a_R^2$ , and the displacement vectors of the beads, such that the form of the equation is

$$\zeta_{\rm R} \frac{dr_l}{dt} = \frac{3k_B T}{a_{\rm R}^2} \left( \boldsymbol{r}_{l+1} - \boldsymbol{r}_l \right) + \frac{3k_B T}{a_{\rm R}^2} \left( \boldsymbol{r}_{l-1} - \boldsymbol{r}_l \right)$$
(eq. 6)

As such this is a description of velocity that derives from a restoring force that a bead feels when the displacements **r-r** between the bead and its neighbor differ from the equilibrium distance  $a_R^{2,22}$ .



Figure 3 – Three mechanisms (M) and times (τ) are associated with lithium ion transport Rouse model adapted theory of Maitra and Heuer. Lithium diffusion parallel to a chain, chain relaxation, and chain to chain transfer.<sup>23</sup>

There will be one such equation for each segment in the model, and solving the set of equations leads to a set of eigenvalues known as the rouse modes, which describe the motions of the polymer chain. The lowest order mode designated mode 0 describes translational motion of the polymer, and as the mode number increases the motions described become increasingly more localized, such that most of the motion occurs in the lower order modes.<sup>22</sup>

Maitra et al. approached the problem by first defining three mechanisms for transport in polymer hosts. Mechanism 1 (M1) is defined as the motion of lithium ions along polymer chains, mechanism 2 (M2) is Rouse mediated diffusion, not including displacement of the lithium ion as a result of translational motion of the polymer, and M3 is transfer of a lithium ion from one chain to another (see figure 3).<sup>23</sup> Each mechanism has an associated time  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  so lithium diffusion  $D_{Li}$  can be written as a function  $D_{Li} = D_{c.m.} + D_M(\tau_1, \tau_2, \tau_3)$  where  $D_{c.m.}$  is lithium ion transport mediated by diffusion of the ion in concert with the polymer chain such that the center of mass of the chain is displaced (i.e. movement arising from Rouse mode 0).<sup>23</sup> The times  $\tau_1$  and
$\tau_3$  are relatively straightforward to understand, but  $\tau_2$  is related to a quantity  $\tau_R$  which is the Rouse time or relaxation time of the polymer chain. This is the time associated with relaxation; the process where the initial end to end distance of the polymer,  $\mathbf{R}_0$ , approaches its equilibrium value  $\mathbf{R}_e$ . Rouse time  $\tau_R$  is a property of a neat polymer medium, but the presence of complexing ions slows down relaxation, creating a need for a separate value  $\tau_2$  to describe the equivalent time in a chain with an associated ion.<sup>23</sup>

The authors then derived approximate analytical expressions for the dependence of  $D_M$  on the various times associated with each mechanism. The reader is referred to the paper for the full derivation, but it is necessary to clarify that the authors have used  $1/\tau_{12}=1/\tau_1+1/\tau_2$  for convenience in the result. It was shown that the result depends on the relative magnitude of the times involved such that

$$D_M = \frac{R_e^2}{6\pi} \left(\frac{1}{\tau_3 \tau_{12}}\right)^{\frac{1}{2}} \qquad \text{when } \tau_3 << \tau_{12} \tag{eq. 7}$$

$$D_M = \frac{R_e^2}{18\tau_3}$$
 when  $\tau_3 >> \tau_{12}$  (eq. 8)

In order to make sense of this model and connect it to DBP theory, it should be noted that as the size of the polymer chains of increases (increasing  $N_R$ )  $\tau_{12}$  should increase.<sup>23</sup> Furthermore the authors felt that  $\tau_3$  should be proportional to the  $\tau_{ren}$  described in DBP, as they describe a similar process. It is therefore shown that in systems of large polymers DBP can systematically err due to the increasing contribution of diffusion along polymer chains and with the chains as they relax.<sup>23</sup>

Finally, the authors compared their model with data from simulations similar to those of Borodin et al. and experimental diffusion data from <sup>7</sup>Li pulse gradient spin echo experiments,

and estimated the dependence of diffusivity on Rouse number  $N_R$ , which for this study was defined as the number of monomer units. Results are shown in figure 4.<sup>23</sup>



Figure 4 – The Maitra and Hueur model as compared to experimental data. N denotes the number of rouse segments in the model, while D is the coefficient of diffusion. Experimental data comes from the work of Shi et al.<sup>42</sup> D<sub>M</sub> is the coefficient of diffusion from the three mechanisms discussed above and D<sub>c.m.</sub> arises from diffusion of the polymer chain with associated lithium ions. Figure 4 has been reprinted with permission from Maitra, A.; Hueur, A. *Phys. Rev. Lett.* 2007, *98*, 227802. <u>http://journals.aps.org/prl/abstract/10.1103/PhysRevLett.98.227802</u>

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Using this data we can come up with a few generalizations about the low conductivity of dry polymers. Most importantly Maitra et al. show that as  $N_R$  increases  $D_M$  stays relatively constant but  $D_{c.m.}$  approaches zero.<sup>23</sup> This implies that most of the loss in conductivity between liquids and dry polymers is from  $D_{c.m.}$ . It follows that a liquid component is probably important for all or most electrolyte design. An important limitation to note about this model is that it does not take phenomena such as polymer crystallization or entanglement into account, which could additionally diminish both modes of conductivity, and cause departure from predicted behavior.

# **1.3** Electrolyte Polarization in Lithium Ion Batteries

Aside from low conductivity, the next problematic behavior exhibited by polymer electrolytes is anion mediated polarization. As the cations percolate through the polymer matrix, the anions are also free to move, and migrate in the direction of the anode. This movement results in a high concentration of anions near the anode which experience a coulombic attraction to cations moving toward the cathode; hindering their mobility, and leading to a reduction of current density in the outside circuit. Anions are often 5 to 10 times more mobile than the lithium cations in common electrolyte materials.<sup>4</sup>

The figure of merit used to describe polarization in an electrolyte is the lithium transference number,  $T_+$ , which is defined by two values of DC current.<sup>132</sup> The initial value of DC current,  $I^0$ , will be high, because it accounts for both anionic and cationic diffusion. The current drops as the electrolyte polarizes, until it reaches an equilibrium value  $I^s$ , which is considered to be an approximate value of the portion of current due to cation diffusion. Lithium ion transference  $T_+$  is computed simply as  $T_+ = I^s/I^0$  and is interpreted to be related to the relative mobilities of the cation relative to the anion.<sup>132</sup> When transference is measured experimentally though, these values are not measured directly, but rather calculated from DC conductivity values.<sup>132</sup> The reader is referred to the work of Bruce et al. for the details of this experimental setup and calculation.<sup>132</sup> Figure 5 illustrates the concept of polarization and its relationship to  $T_+$ .

Literature strategies for improving solid or solid like lithium ion electrolytes typically focus on one or both of these problems, with optimization of the overall carrier mobility being emphasized over selective lithium ion transference. Electrolytes that have value of  $T_+$  which approach unity are termed single ion conductors and resist polarization because the only mobile ions in the system are lithium ions, and therefore  $I^0 = I^s$  for these systems.



Lithium Transferrence,  $T_+ = I^s/I^0$ 

 Figure 5 – Lithium ion transference, T<sub>+</sub>, is a figure of merit describing the relative mobility of the cation and anion. It is defined as the ratio of the initial current which passes through an electrolyte (which drops during discharge) and the current flowing once an equilibrium has been

established.4, 132

# 1.4 Design Strategies for the Improvement of Lithium Ion Electrolyte Performance

In attempts to make dry polymer electrolytes which are more conductive than high molecular weight PEG, many polymers have been synthesized and characterized for conductivity.<sup>7</sup> These schemes included linear polymers aimed at preventing crystallization, and at improving segmental mobility, and "comb like" polymers with low molecular weight side chains. However dry systems have invariably shown suboptimal conductivity.<sup>4,7</sup> Conductivity can be improved through the use of "gel" electrolytes, which are comprised of a porous solid polymer membrane which has been swelled by an organic solvent.<sup>7</sup> Gel like systems can be as conductive as liquids, as the conductivity is mediated by the solvent, rather than the motion of the polymer chains. However they may lose of mechanical stability, as well as electrochemical stability, due to the reactivity of the solvent toward the anode.<sup>6,7</sup>

A third class of materials has been assembled in an attempt to improve the conductive properties of polymer electrolytes by blending them with inorganic filler materials. In the late 1990s Scrosati and coworkers reported a composite of PEG with TiO<sub>2</sub> nanoparticles, which they showed to enhance the mechanical strength of the material, as well as the interfacial stability with a lithium electrode.<sup>26</sup> These materials were later shown to have the effect of reducing crystallinity in the electrolyte, by providing so many nucleation centers for the formation of crystals that the formation of a lattice is actually impeded by the competing affects.<sup>1,4,7,26</sup>

A similar approach was employed by the Baker group during this time period. A low molecular weight PEG dimethyl ether, which is a highly conductive liquid, was used as a conductive media.<sup>27,28</sup> Mechanical support was provided by a variety of surface functionalized fumed silica particles (fig.4), which could be dispersed in the PEG and cured using a UV crosslinking reaction. These electrolyte systems showed improved mechanical strength, and conductivities in the range of  $10^{-4} - 10^{-3}$  S/cm.<sup>27,28</sup>

A more recent approach involves the direct functionalization of silica or zirconia nanoparticles with a conductive medium, of either PEG or ionic liquid derivation.<sup>8,29,30</sup> PEG derivatives were bound directly to the nanoparticles, using either a covalent silicate linkage, or acid base chemistry between amine functionalized particles, and sulfonic acid functionalized PEG chains.<sup>24</sup> PEG functionalized particles were doped with 1M lithium Bis(trifluoromethane)sulfonimide (TFSI), and showed molecular weight dependant conductivity, which was above 10<sup>-4</sup> S/cm for some materials.<sup>24</sup> Additionally, silicate functionalized particles with a corona of 400 molecular weight PEG (fig.4) were blended with poly(ethylene glycol) dimethyl ether 250 (PEGDME250) a short polyethylene glycol chain terminated with a methyl ether at each end. This improved the conductivity of the system over that of the solvent free particles.<sup>30</sup> It was shown that the onset of solid like behavior occurs in the PEGDME at a composition of roughly 38% particles (v/v), at which point the system has a conductivity of

nearly  $10^{-3}$  S/cm.<sup>30</sup> While the ionic liquid functionalized particle is an intriguing idea, this system had lower performance at room temperature; on the order of  $10^{-5}$  to  $10^{-6}$  S/cm.<sup>29</sup>





The problem of lithium transference in polymer electrolytes has also been an area of prolific research, with many of the proposed schemes involving synthetic modifications of PEG derived macromolecules. Published polymeric single ion conductors chiefly employ one of two common strategies to suppress anion movement; Lewis acidic anion receptors can be installed in the polymer, to bind anions after the introduction of a lithium salt,<sup>31</sup> or a polyelectrolyte can be synthesized, consisting of polymer bound anions with lithium counter ions.<sup>32,33</sup>

Mehta, Inoue and colleagues offer a representative example of the anion receptor approach.<sup>31</sup> Their material is composed of a blend of PEG mono methyl ether and triethylene glycol which is condensed in the presence of boroxine, to yield a solid material composed of

branched PEG chains with Lewis acidic boroxine rings at the branch points. This material is compatible with a variety of common lithium salts, including LiTFSI, LiClO<sub>4</sub> and lithium triflate. Transference numbers measured for lithium were in the range of 0.62-0.88 (where a value of unity indicates that all current is a result of lithium transport) which is a significant improvement over the typical values given for PEG of 0.15 - 0.45.<sup>31</sup> Single ion conductive systems unfortunately are also subject to problems of low conductivity; values for this system were on the order of  $10^{-5} - 10^{-7}$  S/cm.<sup>31</sup>



Figure 7 – Monomers produced by Kerr et al. (left) produced a crosslinked single ion conducting solid in the presence of a platinum catalyst. Endo et al. produced monomers (right) which could produce the same effect when heated.<sup>32,33</sup>

A common approach for the production of single ion conductors based on covalently bound anions is the synthesis of alkylated lithium salts, which can then be used to chemically crosslink the conductive material *in situ*.<sup>32,33</sup> The groups of Kerr and Endo have described materials based on schemes such as these, relying on PEG derivatives and hydrosilation, or epoxide ring opening chemistry respectively for crosslinking (fig 5).<sup>32,33</sup>

Ionic liquids have likewise been considered as candidates for high transference electrolytes. Unlike most of the electrolytes previously discussed, ionic liquids are true liquids, but their resistance to flammability, inherent conductivity, and low vapor pressure make them good candidates for electrolyte materials.<sup>91</sup> On the other hand, there is no obvious reason that a conventional binary ionic liquid would offer an advantage with respect to Lithium transference.

Ohno and coworkers have made several attempts at designing selective lithium conductors based on ionic liquids.<sup>123-125</sup> One such attempt involved the use of linked zwitterions blended with lithium TFSI.<sup>123</sup> A set of zwitterions were synthesized, each of which contained a cation and anion linked by an alkyl spacer group.<sup>123</sup> The cation and anion chemistries were varied in the study, and so was the length of the spacer group. While most of the zwitterions themselves had melting points over 100 °C, it was discovered that some of them could be blended with LiTFSI to make liquids. Unfortunately these liquids suffered from low conductivity and low transference.<sup>123</sup>

A similar class of materials engineered by this group was composed of triple ions containing two anions and one cation.<sup>124,125</sup> The first of these was obtained by reacting imidazoles with two equivalents of 1,3-propanesultone under basic conditions, which led to the formation of imidazolium salts with twin sulfonate groups and an alkali metal counter ion.<sup>124</sup> A second class of similar materials was later developed, containing one borate and one sulfonate group on an imidazolium scaffold.<sup>125</sup> These classes of materials had lithium transference numbers as high as 0.76. However the general tendency of these materials was to have a high melting (T<sub>m</sub>) and glass transition temperature (T<sub>g</sub>).<sup>124,125</sup> The materials with dual sulfonates were the worst in this regard; they melted above 200 °C and had glass transitions around room temperatures.<sup>124</sup> The borate materials improved significantly; they were liquids with T<sub>g</sub> as low as -25 °C.<sup>125</sup> The highest room temperature conductivity for any of these materials was below  $10^{-7}$  S/cm, well below what would be useful in application.<sup>125</sup>

At least one novel approach has sought to avoid the limitations of dynamic percolation altogether. In noting that PEG forms helical structures when crystalline<sup>34</sup> Bruce and co-workers authored several remarkable papers in which they sought to tune ionic mobility of lithium ions in crystalline PEG lithium salt complexes.<sup>35-37</sup> By crystallizing PEG with several different anions including antimony hexafluoride or tetrafluoroborate it was possible to generate regular structures, in which lithium ions were mobile, and could percolate down the helical channels in the crystal structure of the polymer, with the counter ions trapped in the lattice. Successive attempts were made to raise the room temperature conductivity of this system, which started on the order of  $10^{-7}$  to  $10^{-8}$  S/cm, by using doping with different monovalent ions,<sup>35</sup> doping with divalent Li<sub>2</sub>SiF<sub>6</sub> in order to increase the number of mobile lithium ions in the channels,<sup>36</sup> and using low molecular weight glymes as a host.<sup>37</sup> Unfortunately, none of these strategies resulted in a conductivity above  $10^{-5}$  S/cm at room temperature.

## 1.5 Strategies of Single Ion Conductor Design from the Baker Research Group

Attempts to improve the lithium transference in polymer nanocomposites have been made in the Baker Group starting with the work of Fadi Asfour in the early 2000s.<sup>26</sup> This scheme entailed grafting a single layer of trifluorosulfonamide terminated alkyl chains (Fig. 6) which would be deprotonated using butyl lithium to yield nanoparticle localized negative charges, which would then be combined with PEGDME 500 for analyses of conductivity. The particles tested by Fadi had low loadings of lithium, limited by the grafting density of the particles. The lithium to ether oxygen ratios tested were in the range of 1:250 to 1:710, depending on the

loading of nanoparticles, which increased to 40% w/w.<sup>26</sup> Conductivities observed for this system were on the order of  $10^{-6}$  S/cm at 30°C.



Figure 8 – Nanoparticle designed of Asfour (top), and the most conductive design of Zhao (middle) and an attempt to improve the interfacial properties of synthesized polyelectrolytes (bottom). Polyelectrolytes allow for higher ratios of lithium to oxygen, but have not improved conductive performance to date.<sup>4, 26</sup>

This work was continued by Hui Zhao, who designed a variety of nanocomposites with many layers of ions, in an attempt to improve on earlier work by increasing the concentration of lithium ions in the electrolye.<sup>4</sup> These polymers are comb-like polyelectrolytes based on hydrophobic alkyl chains constructed through radical polymerizations of functionalized styrenes and methacrylates (Fig. 6). Oxygen to Lithium ratio in these experiments was in the range of 1:250 to 1:30, with optimal loading typically occurring in the neighborhood of 1:60. The best system of Zhao's devising has a measured room temperature conductivity of roughly 10<sup>-6</sup> S/cm.<sup>4</sup>

of the system significantly relative to Asfour's materials, but the performance he observed was no better.

Several hypotheses were considered for why the higher lithium density polymers of Zhao have not outperformed the monolayer particles of Asfour. In considering equation 1, it can be reasoned that if carrier concentration has been increased, while new sets of carrier species have not been introduced by experimental design; a comparable ionic conductivity should therefore reflect an overall loss in the mobility of lithium. The most apparent potential problem of the polyelectrolyte particles that our lab has so far produced is related to solubility. The significantly lipophilic polymethacrylates and polystyrene backbones are being expected to interface with water soluble PEGDME 500. Zhao has attempted to improve the interfacial properties between the PEGDME500 and polyelectrolyte particles in the synthesis of a random copolymer of styrene sulfonate and PEG methacrylate monomers (fig.6). This approach did not significantly improve conductivity in composites.<sup>4</sup>

An additional consideration for the ionic mobility of a polyelectrolyte is the flexibility of the particle bound chains. While differential scanning calorimetry data have not been published on the polyelectrolyte particles to date, literature values put the  $T_g$  of 1 – 4 carbon n-alkyl polymethacrylates in the range of 20 to  $100^{\circ}C^{43}$  indicating that a high glass transition may be a problem for these materials.

Finally, we considered a problem which might reasonably be described as "micropolarization"; in effect, when the concentration of charge carriers is increased in the composite the new charges are all bound to particles. The particles are then introduced into PEGDME 500 which has no charge carriers. As the lithium cations move under an applied

potential, the lithium cation becomes isolated in the PEGDME 500 and a coulombic attraction builds between the negative charge left on the particle and the cation in the PEGDME. Mobile cations must therefore pass from particle to particle, and the conductivity will be inversely proportional to the distance between particles. A suggested fix for this would be the use of an ionic liquid conductive media rather than PEGDME 500. Alternatively, at high concentrations of particles this should become a negligible problem.

A solution I proposed for oral exam is shown below; it is composed of a silica nanoparticle functionalized with a brush of alkyne terminated PEG chains (fig. 7). The alkyne termination is intended to make use of the copper catalyzed alkyne azide cycloaddition (CUAAC) "click" reaction, which exhibits excellent yield and conversion, with easily removable side products.<sup>44</sup> This allows rapid assembly of a nanoparticulate electrolyte system which was designed to be tunable in lithium content and interfacial properties by "clicking" with alkylated lithium salts of various derivations, chain lengths and lithium contents. Systems like this have been reported previously in the literature,<sup>40,41</sup> but, to the best of my knowledge such a scheme has not been previously proposed for use as a lithium electrolyte material.



Figure 9 – Proposed fillers for nanocomposite conductors. Clickable Particle 9 can be used to access designs 10 and 23 among others.

At the time of my oral however we were unaware of a helpful physical study into the nature of the underlying problems with single ion conductors. This study will be described in the next section.

# **1.6** Problems with Single Ion Conductors Demonstrated in Experiment and Simulation

Problems with single ion conductors have attracted interest from others, and in 2006 a seminal paper was published exploring the fundamental problem with these materials. The paper was a collaboration between the theorists Borodin and Smith, and the research group of Darryl DesMarteau, an experienced fluorine chemist.<sup>20</sup> In order to isolate the tethered anion as a variable, the experimentalists compared a system of methyl capped PEO with 12 repeating units  $(EO_{12}/LiTFSI)$  with a synthetic analogue composed of a PEO system with a tethered bis(sulfonimide) group closely resembling the TFSI(-) moiety (figure 10).<sup>20</sup>



Figure 10 – Tethering anions to a host material has a dramatic deleterious effect on the conductivity of single ion conductors.<sup>20</sup> Image reprinted with permission from Borodin, O.;
Smith, G. D.; Geiculescu, O.; Creager, S. E.; Hallac, B.; DesMarteau, D. J. Phys. Chem. B 2006, 110, 24266 – 24274. Copywrite 2006, American Chemical Society.

Measurements done by the experimental part of the group provide a powerful demonstration of the problems inherent in polymer single ion conductors. The data shown in fig. 10 indicates that at 294 K (21 °C) conductivity drops from roughly 10<sup>-3</sup> S/cm (binary) to roughly 10<sup>-6</sup> S/cm (tethered) or three orders of magnitude.<sup>20</sup> This data puts the work of Zhao and Asfour in a new light, as it demonstrates that the concerns about phase separation and Tg of particle

grafted polymers are probably not necessary to explain the low conductivity observed, because neither would have been a factor in the work of DesMarteu et al.

Borodin et al. used this data as a benchmark for their MD simulations.<sup>20</sup> The close agreement between the experimental and simulated results lends credibility to insights drawn from the simulated systems.

The authors looked at mechanisms similar to those described in the Rouse based model of lithium ion transport detailed above. The authors mainly discussed conductivity resulting from diffusion of a lithium ion with an associated chain, and conductivity resulting from migration of a lithium between chains; to use the formalism developed later by Maitra et al., the first of these would be  $D_{c.m.}$ <sup>20,23</sup> When considering the contribution of  $D_M$ , Borodin et al. explicitly consider the effect of  $M_3$  (interchain transfer) and neglect  $M_1$ , and  $M_2$ .<sup>20,23</sup> This is a defensible omission, as the contribution of these mechanisms should be negligible for systems composed of short chains which should be governed by the dependence described by equation 8.<sup>23</sup>

The most important difference between a tethered system and a binary system relates to the nature of  $D_{c.m.}$  in these systems.<sup>20,23</sup> Classical conductivity described by the Nernst/Einstein equation (eq. 2) either assumes full dissociation (i. e. independent movement) of cations and anions in the system, or explicitly includes a term,  $\alpha$ , to describe the ratio of ions which are diffusing independently of a counter ion.<sup>20</sup> In a binary system this term is independent of  $D_{c.m.}$  as a lithium ion may diffuse with a chain whether or not an anion is also associated.<sup>20</sup> When the anion is connected to the chain however,  $D_{c.m.}$  describes the diffusion of an associated ion pair by definition, and does not contribute to the conductivity of an electrolyte unless multiple cations are bound to the chain.<sup>20</sup> This problem was evident in the  $\alpha$  values reported for the two

electrolytes at 294 K, whereas the value in the binary electrolyte was 0.9, the tethered electrolyte had an  $\alpha$  value of 0.5.<sup>20</sup>

This change causes the conductivity to be more dependant on the rate of interchain transfer events in the electrolyte with a tethered anion.<sup>20</sup> Unfortunately, chain to chain transfer is also retarded by the presence of an anionic head group on the chain.<sup>20</sup> The reported Li(+)-chain residence time ( analogous to the  $\tau_3$  of Maitra et al.) was over twice as long for the tethered system as it was for the binary system (~40 ns to ~90 ns) at ~90 °C.<sup>20</sup>

# **1.7** On the Construction of Lithium Single Ion Conductors and the Making of Lemonade

A critical reading of the literature on single ion conductors might seem like a hopeless litany of failure, but this is not necessarily the case. While there is unlikely to be an organically based lithium single ion conductor which is itself useful as an electrolyte, single ion conductors such as the ones produced by DesMarteau or Ohno might be a useful additive to binary electrolytes in order to reduce polarization without completely sacrificing conductivity.

On the other hand, research strategies that require difficult synthesis of elaborate materials are probably a misguided way to approach the single ion conductor problem. Many papers in the materials literature describe complicated materials designed to be applicable, rather than simple materials designed to test a hypothesis. If no clear hypothesis is being tested, disappointing results equate to wasted time, as it becomes difficult to draw conclusions from the data. In this regard the work of DesMarteau and Borodin et al. is inspiring; regardless of whether the single ion conductor they report is useful for application, the results are clearly interpretable because of good study design, adequate controls, and the attention paid to rigorous mechanistic interpretation of the results.

This change in thinking is the main reason why the synthesis and characterization of the materials in figure 9 will not be reported in this work. Too many variables exist in such systems to be adequately controlled for, and the synthesis of particle **9** is a difficult six step process with two steps related to nanoparticle functionalization that are difficult to do reproducibly. Further, functionalized nanoparticles produced from orthosilicate materials such as 3-aminopropyltriethoxysilane (APTES) and its derivatives are chemically ill-defined due to variables in functionalization density and oligomer formation. Finally, the work of DesMarteau and Borodin et al. make the success of ionomer grafted nanoparticle designs of the sort that we were considering seem unlikely.

While work in the style of Zhao and Asfour has been abandoned, the use of the CUAAC reaction to construct lithium ion electrolytes is still an intriguing and untested idea. The CUAAC reaction accomplishes a coupling by forming a triazole from alkyne and azide precursors. However triazoles are not a common feature of lithium ion elecrolytes. Professor Baker was interested in potential effects of triazoles on conductivity as an unintended consequence of introducing them into the electrolytes, and encouraged Zhao to investigate this problem.<sup>126</sup> Zhao synthesized a series of polymer containing triazoles with molecular weights of roughly 10<sup>4</sup> g/mol and showed that at 90 °C their salt composites had conductivity similar to that of PEG of a similar molecular weight.<sup>126</sup> A study which controls for dispersity, and analyzes this finding can be found in chapter 2 of this document.

A second focus was the pursuit of a single ion conductor material to improve the chain to chain transfer time of lithium ions. A class of triple ions similar to those of Ohno et al. was initially proposed for this, partially owing to the fact that we were not aware of their work, and did not expect the high  $T_m$  and  $T_g$  and low conductivity that they observed.<sup>124,125</sup>



Figure 11 – Ohno-like triple ions proposed as novel single ion conductors.

Synthesis of the triple ions shown in figure 11 proved to be a significant challenge and several different routes were attempted in the process (figure 12). In one of the routes attempted, an analogue of 1,3-propanesultone which we called N-triflylpropanesultam (TPS) was used as a precursor to the triple ion. A synthesis of TPS was devised and successfully executed, but the difficulties of obtaining pure samples of triple ions, and the discovery of Ohno's work led to the abandonment of the triple ion project. Instead attempts were made to map the reactivity of TPS and establish whether it could be a useful material for producing alkylated TFSI-like anions.

Initial expectations were that TPS would be a highly reactive material given that it contained a nitrogen leaving group which had two sulfonyl groups and ring strain activating it. Preliminary exploration in the beginning of the triple ion project had suggested that alkylated TFSI materials were very powerful alkylating agents. Several experiments were done in which amines were quaternized with these materials in good yield with modest reaction times. However TPS had to be boiled with an amine for days in order to react, and it often gave significant amounts of side products resulting from nucleophilic attack at sulfur.



Figure 12 – Three attempts to synthesize triple ions. The last of these featured TPS, a previously unknown molecule whose reactivity was much less pronounced than expected, sparked interest

in the nucleofugality of polyatomic anionic nitrogen nucleofuges.

While the reactivity of TPS did not appear to be promising, the surprise of its relative inertness seemed worth investigating. Computational studies were initiated which analyzed Menshutkin reactions of polyatomic anionic leaving groups of nitrogen and oxygen in order to better understand why TPS had been less reactive than expected. While the proceedings of this study are probably of limited use to the materials chemistry community, there is ongoing discussion in the physical chemistry literature about the precise nature of nucleofugalty (leaving group ability) which would benefit from this research. This research appears in its entirety in chapter 3 of this document.

# 2 Chapter 2: 1,2,3-Triazoles as Pseudo-Ether Moieties in Oligo (Ethylene Glycol) Based Lithium Ion Electrolytes

### 2.1 Introduction

As the average global temperature continues to rise, the importance of finding novel, clean strategies for generating and storing energy continues to be an imperative for scientists and engineers. Lithium ion batteries were first demonstrated in the 1976,<sup>42</sup> and research into cathode, anode and electrolyte materials for lithium ion batteries continues to be avidly pursued today. Polymer electrolytes were developed contemporaneously with lithium battery technologies, however the conductivity of polymer electrolytes are often too low for use in lithium batteries.

In the interest of raising the conductivity of dry polymer electrolytes, many different host polymers including polyethers, polysiloxanes, polyphosphazines, and architectures including comb polymers and nanoparticle composites have been tried.<sup>7</sup> Additionally, physical studies have been performed and models proposed in order to rationalize lithium ion transport dynamics in a polymer host.<sup>5,9</sup> Among these models, one of the most prominent is the dynamic bond percolation theory (DBP) of Ratner et al.<sup>11-15</sup> DBP is formulated in terms of a renewal time  $\tau$  in which one path between coordination sites has opened and closed to each lithium ion in a system. The conductivity of a system depends on the renewal time and therefore has been found to depend on polymer segmental dynamics generally and the glass transition temperature (T<sub>g</sub>) specifically.<sup>15</sup> Additional studies have utilized ab-initio calculations to show that glyme-derived complexes with divergent geometries have similar energies within the same coordination number, at coordination numbers of 4, 5 and 6 ether oxygens around lithium.<sup>43</sup>

A recently developing trend in polymer chemistry has been the application of click chemistry; a set of reliably working, high efficiency reactions originally promoted for rapid

construction of complexity in drug discovery,<sup>39</sup> which have been adopted by materials chemists for such tasks as post synthetic modifications of polymers and surface functionalization of nanoparticles, and the construction of dentrimers.<sup>44,45</sup> One of the most common of these socalled "click" reactions is the copper catalyzed alkyne azide cycloaddition reaction (CuAAC) or Huisgen reaction used to couple materials through the formation of a distinctive 1,2,3- triazole motif.<sup>39</sup> The 1,2,3-triazole species has been used in the manipulation of ionic species previously in the design of anion receptors<sup>46</sup> and occasionally proton conductors,<sup>47-49</sup> however these heterocycles have been use in only one lithium conductor that we are aware of.<sup>50</sup>

The decision by the materials community to eschew the use of the CuAAC reaction in the development of lithium ion conductors may have its roots in concerns about the effect of the 1,2,3-triazole moiety formed in the reaction on the conductivity of the electrolyte. Deleterious effects of on conductivity might reasonably include a net stiffening of the polymer material and associated increase in the  $T_g$ ,<sup>15</sup> a decrease in lithium ion mobility due to a higher energy association between the lithium cation and the triazole ring, or a loss of solubility of lithium due to unfavorable association.<sup>43</sup> Lithium ion affinities of various nitrogen heterocycles including 2-H-1,2,3-triazole, 1-H-1,2,4-triazole and various other azoles and azines have been measured using collision induced dissociation mass spectrometry, and calculated at various levels of theory, by Rodgers and co-workers.<sup>51-54</sup> These affinities typically exceed those measured and calculated for dimethyl ether using the same methods (Fig. 14), making loss of solubility of lithium salts seem unrealistic, but strong complex formation with lithium potentially problematic.<sup>43</sup>



Scheme 1 – Model compounds with whole number triazole to ether oxygen ratios. Each has a name derived from the number of ether oxygens and triazoles in the compound, hence "8 ether oxygens, 2 triazoles" becomes "8EO2T".

In order to investigate the effect of 1,2,3-triazole moieties on the conductivity of lithium ion transporting polymers, we report a study on a series of monodisperse oligomer model compounds (Scheme 1) with increasing 1,2,3-triazole to ether oxygen ratios. In order to build on the work of Rodgers et al. we model hypothetical solvation shells for lithium ions using high level ab initio calculations. Additionally we have synthesized the model compounds and measured the conductivity of oligomer salt complexes using AC impedance spectroscopy.

Calculations and empirical modeling of the conductivity enable us to pinpoint dynamic effects brought on by introduction of the stiff triazole moieties into the chain as the chief reason for depressed conductivity in the model compounds.

# 2.2 Experimental

#### 2.2.1 Computational methods

All calculations were initiated on the Cambridge Software Chem3D interface for General Atomic and Molecular Electronic Structure System<sup>55</sup> (GAMESS) in order to find coordinates for the model compounds. Our main calculation for smaller models was the MP2(full)/Aug-cc-pVTZ(Li-C)//MP2(full)/cc-pVDZ(Li-C) composite method previously reported by Rodgers et al.<sup>51</sup> This calculation was one of the best performers in a study conducted by these authors which included high quality methods such as coupled cluster methods, complete basis set extrapolation, and the Gaussian theory methods of Pople et al.<sup>51</sup>

Our models were typically run at the HF/3-21G level of theory prior to the application of higher levels of theory, and in the case of 2, 3 and 4 coordinate models the complexes were manipulated manually in the Chem3D interface to get the highest number of ligations possible and minimized using the MM2 force field prior to minimization at HF/3-21G. Pre-optimization calculations were run on a laptop. Starting points from HF/3-21G, were then optimized using three composite methods: MP2(full)/Aug-cc-pVTZ(Li-C)//MP2(full)/cc-pVDZ(Li-C),<sup>51</sup> Gaussian 3 (G3),<sup>56</sup> or G3(MP2)<sup>57</sup> using the Gaussian 03 computational package.<sup>58</sup> The Aug-cc-pVTZ(Li-C) and cc-pVDZ(Li-C) basis sets reported by Rodgers et al. were generated by obtaining cc-pCVDZ and Aug-cc-pCVTZ basis sets<sup>59</sup> for lithium from EMSL Basis Set

Exchange,<sup>60, 61</sup> and applying them to the Li ion, while the other atoms received the parent ccpVDZ or Aug-cc-pVTZ basis set. This allocation was accomplished in Gaussian 03 through use of the Gen keyword. Association energies ( $\Delta E_{ass}$ ) were calculated by comparison of the minimized ligand to the complex and lithium ion such that

$$\Delta E_{ass} = E_{complex} - E_{ligand} - E_{Li}$$
 (eq. 9)

Zero point energy corrections were applied from the MP2(full)/cc-pVDZ(Li-C) level of theory and scaled by a factor of 0.9646.<sup>51</sup> The reader is referred to the original paper for additional details on the MP2(full)/Aug-cc-pVTZ(Li-C)//MP2(full)/cc-pVDZ(Li-C) calculation.<sup>51</sup> G3 and G3(MP2) were used as implemented in Gaussian 03. All Gaussian 03 calculations were run on the MSU Chemistry Department hydra cluster.

#### 2.2.2 Electrochemical Impedance Spectroscopy

All impedance spectroscopy was done on an HP4192A LF impedance analyzer setup which has been fed into a Vacuum Atmospheres Dri-Train M040-1 model glove box with a nitrogen atmosphere. Model compounds were rigorously dried in preparation for conductivity measurements by stirring on a mass equivalent of 4 Å molecular sieves in dry ethyl ether or dichloromethane. Following this the compounds were filtered and solvent was removed on a standard rotovap connected to a vacuum aspirator. Finally, model compounds were placed on a Schlenk line and heated to 70°C. The line was allowed to equilibrate to a pressure of < 100mTorr which was sustained for at least 24 hours. Inhibitors were removed from PEG500 DME prior to drying, by elution through a flash column with a dry ethyl ether mobile phase. All samples were then inserted and stored in the glove box. Samples were prepared by addition of LiTFSI or LiClO<sub>4</sub> to the electrolyte media, followed by stirring until the salt composite became

homogenous. The amount of salt added was normalized to the number of ligand atoms in the PEG 500 DME or model compound, such that a triazole was considered to have two ligand atoms, and PEG 500 DME was considered to contain 12 ligand atoms on average. Samples were loaded into a homemade coin cell with stainless steel blocking electrodes, and clamped together with leads from the impedance analyzer in a homemade temperature controlled bell jar. Measurements were taken from 30°C - 85°C, using a virtual instrument code written for Labview 5. Temperature control was adjusted manually, and is estimated to have a precision of +/- 1°C.

#### 2.2.3 Single Crystal X-Ray Diffraction

Single crystals of 6EO2T (C<sub>9</sub>H<sub>16</sub>N<sub>3</sub>O<sub>3</sub>) were crystallized from toluene. A suitable crystal was selected and mounted on a nylon loop using Paratone Oil. The crystal was kept at 173.01 K during data collection. Data were collected using a Bruker APEX-II CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO,<sup>74</sup> where redundancy was expected to be 4.0 and completeness to 0.83 Å to 100%. Cell parameters were retrieved using APEX II software<sup>75</sup> and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software<sup>76</sup> which corrects for Lp. Scaling and absorption corrections were applied using SADABS<sup>77</sup> multi-scan technique, supplied by George Sheldrick. Using Olex2,<sup>77</sup> the structure was solved with the XS <sup>78</sup> structure solution program using Direct Methods and refined with the XL <sup>79</sup> refinement package using Least Squares minimisation.

The structure was solved in the space group C2/c (no. 15). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model.

# 2.2.4 Synthesis of Model Compounds



Scheme 2 - Synthesis of triazole containing poly(ethylene glycol) based model oligomers

# 2.2.4.1 Materials and Instrumentation

Starting materials were procured and used as obtained from commercial suppliers including Sigma-Aldrich, Alfa Aesir and Jade Scientific. NMR spectra were obtained using Varian 500 MHz and 300 MHz instruments in the MSU NMR facility, all NMR specra were run in CDCl<sub>3</sub>. IR Spectra were obtained using a Mattson Galaxy FTIR spectrometer. High resolution mass spectrometry was performed by the MSU Mass Spectrometry Core using a Micromass Q-TOF Ultima instrument. Phase and glass transitions of the model compounds were measured using the TA Q2000 Differential Scanning Calorimeter in the Composite Materials and Structures Center at MSU College of Engineering.

# **2.2.4.2** Synthesis of Tosylates 1 – 5.

Method 162

Methoxy oligo(ethylene glycol) precursors and p-toluenesulfonylchloride (1.02 equiv. per hydroxyl) were added to flask equipped with a mechanical stirring apparatus, and charged with  $CH_2Cl_2$  on ice, such that the concentration of the oligo(ethylene glycol) species was approximately 0.95 M. Potassium hydroxide was then measured (4 equiv. per hydroxyl) and added without crushing in portions over a one hour period. After the addition of the potassium hydroxide pellets was complete, the ice bath was allowed to melt and warm to room temperature. Stirring was allowed to continue for 24 hours. Reaction was quenched by the slow addition of water until water soluble salts were dissolved. The layers were then separated, and the aqueous layer extracted with two additional portions of  $CH_2Cl_2$ . The combined organic layer was dried over sodium sulfate and solvent was removed on a Rotovap, followed by a hard vacuum. The products were used without further purification.

Method 2<sup>63</sup>

A tetrahydrofuran solution of the methoxy oligo(ethylene glycol) solution of roughly 0.75 M concentration was prepared in a round bottom flask with magnetic stirring. To this solution 1.5 equiv. of p-toluenesulfonyl chloride were added, and the flask was chilled on ice. To the cooled flask a 16 M solution of potassium hydroxide (6.5 equiv. per hydroxyl group) in water were added in parts over roughly 1 hour. Following addition of the potassium hydroxide, the ice bath was removed. The reaction was then allowed to stir roughly 12 hours at room temperature. The reaction was subsequently quenched by addition of the reaction mixture to 5 mL ice per mL of the mixture and extracted with 3 portions of  $CH_2Cl_2$ . Drying and solvent removal proceeded as in method 1. Product was used without further purification. This method was used for compound **4** only and was discontinued due to poor yield.

2-methoxyethyl 4-methylbenzenesulfonate (**1**) 92% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 2.42 (s, 3H, C**H**<sub>3</sub>O) 3.28 (s, 3H, Tosyl-C**H**<sub>3</sub>) 3.55 (dd, 2H, CH<sub>3</sub>OC**H**<sub>2</sub>, J= 5 Hz, J= 5 Hz) 4.13 (dd, 2H, TsOC**H**<sub>2</sub>, J= 5 Hz, J= 5 Hz) 7.31 (d, 2H, CH<sub>3</sub>CC**H**CHCSO<sub>3</sub>, J = 8 Hz) 7.77 (d, 2H, CH<sub>3</sub>CCHCHCSO<sub>3</sub>, J = 8 Hz) <sup>13</sup>C NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 21.82, 59.17, 69.25, 70.13, 128.16, 129.99, 133.25, 144.96

2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (**2**) 93% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>) δ: 2.41 (s, 3H, C**H**<sub>3</sub>O) 3.31 (s, 3H, Tosyl-C**H**<sub>3</sub>) 3.45 (m, 2H, CH<sub>3</sub>OC**H**<sub>2</sub>) 3.53 (m, 2H, CH<sub>3</sub>OCH<sub>2</sub>C**H**<sub>2</sub>) 3.65 (m, 2H, TsOCH<sub>2</sub>C**H**<sub>2</sub>) 4.13 (m, 2H, TsOC**H**<sub>2</sub>) 7.30 (d, 2H, CH<sub>3</sub>CC**H**CHCSO<sub>3</sub>, J = 8 Hz) 7.76 (d, 2H, CH<sub>3</sub>CCHC**H**CSO<sub>3</sub>, J = 8 Hz) <sup>13</sup>C NMR (600 MHz) (CDCl<sub>3</sub>) δ: 21.79, 59.20, 68.88, 69.40, 70.85, 71.99, 128.16, 129.98, 133.19, 144.97 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**3**) 91% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>) δ: 2.41 (s, 3H, C**H**<sub>3</sub>O) 3.31 (s, 3H, Tosyl-C**H**<sub>3</sub>) 3.49 (m, 2H, CH<sub>3</sub>OC**H**<sub>2</sub>) 3.57 (m, 6H, OC**H**<sub>2</sub>C**H**<sub>2</sub>O) 3.64 (t, 2H, TsOCH<sub>2</sub>C**H**<sub>2</sub>, J= 5 Hz ) 4.12 (t, 2H, TsOC**H**<sub>2</sub>, J= 5 Hz ) 7.30 (d, 2H, CH<sub>3</sub>CC**H**CHCSO<sub>3</sub>, J = 8 Hz) 7.75 (d, 2H, CH<sub>3</sub>CCHC**H**CSO<sub>3</sub>, J = 8 Hz) <sup>13</sup>C NMR (500 MHz) (CDCl<sub>3</sub>) δ: 21.76, 59.15, 68.82, 69.39, 70.69, 70.71, 70.89, 72.06, 128.11, 129.96, 133.23, 144.92

2,5,8,11-tetraoxatridecan-13-yl 4-methylbenzenesulfonate (**4**) 66% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>) δ: 2.41, (s, 3H, C**H**<sub>3</sub>O) 3.33 (m, 3H, Tosyl-C**H**<sub>3</sub>) 3.50 (m, 2H, CH<sub>3</sub>OC**H**<sub>2</sub>) 3.54 (m, 4H, OC**H**<sub>2</sub>C**H**<sub>2</sub>O) 3.60 (m, 6H, OC**H**<sub>2</sub>C**H**<sub>2</sub>O) 3.65 (m, 2H, TsOCH<sub>2</sub>C**H**<sub>2</sub>) 4.13 (m, 2H, TsOC**H**<sub>2</sub>) 7.30 (d, 2H, CH<sub>3</sub>CC**H**CHCSO<sub>3</sub>) 7.75 (m, 2H, CH<sub>3</sub>CCHC**H**CSO<sub>3</sub>) <sup>13</sup>C NMR (500 MHz) (CDCl<sub>3</sub>) δ: 21.79, 59.17, 68.81, 69.40, 70.67, 70.73, 70.74, 70.88, 72.07, 128.12, 129.97, 133.14, 144.95

(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) (**5**) 81% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 2.43 (s, 6H, Tosyl-C**H**<sub>3</sub>) 3.50 (s, 4H, OC**H**<sub>2</sub>C**H**<sub>2</sub>O) 3.63 (dd, 4H, TsOCH<sub>2</sub>C**H**<sub>2</sub>O, J = 5 Hz J = 5 Hz ) 4.12 (dd, 4H, TsOC**H**<sub>2</sub>CH<sub>2</sub>O, J= 5 Hz J=5 Hz ) 7.33 (d, 4H, CH<sub>3</sub>CC**H**CHCSO<sub>3</sub>, J = 8 Hz) 7.77 (d, 4H, CH<sub>3</sub>CCHC**H**CSO<sub>3</sub>, J = 8 Hz) <sup>13</sup>C NMR (500Hz) (CDCl<sub>3</sub>)  $\delta$ : 21.27, 68.79, 69.37, 70.73, 128.026, 129.97, 132.97, 145.01

# 2.2.4.3 Synthesis of Azides 6 – 8

A flask was set up with a condenser magnetic stir bar, and charged with DMF, and a tosylate precursor (3 - 5). Two equiv. sodium azide were then added such that 0.44 mol of sodium azide were added per liter of DMF (note: sodium azide did not fully dissolve, and some amount of precipitate persisted throughout reaction, intensifying as TsONa is produced). DMF solution was heated to 70°C and allowed to react overnight or roughly 12 hours. DMF was

removed directly by distillation under reduced pressure. Concentrated reaction mixture and solids were dissolved into 1 portion water and 1 portion diethyl ether. The layers were separated and the water was washed with two additional portions of diethyl ether. The ether layer was combined and dried over sodium sulfate and concentrated on a rotovap and a vacuum line. Azides (especially **8**) may be volatile enough that extended use of a vacuum pump will reduce yield considerably. Residual DMF was removed by flash chromatography on a silica mobile phase with diethyl ether eluent, followed by reconcentration.

WARNING: The synthesis and concentration of organic azides is an especially hazardous procedure. Concentrated azides may detonate in contact with heat, reactive chemical species or mechanical stimulation. Sodium azide can react to form extremely unstable compounds if exposed to chlorinated solvents (including but not limited to dichloromethane and chloroform) or transition metals. None of the azides described in this paper have caused the authors problems, but scaling these procedures should not be done by anyone not experienced in the synthesis of azides or related compounds. The authors, furthermore, make no representation that synthesis on the scale done by the authors is safe for other chemists to attempt. Azides must be diluted in solvent before catalyst is introduced in the CuAAC reaction, or potentially fatal explosions can result. Azides were stored under nitrogen gas, and protected from light in a -20°C freezer.

1-azido-2-(2-(2-methoxyethoxy)ethoxy)ethane (**6**) 65% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>) δ: 3.34 (m, 5H) 3.51 (m, 2H, CH<sub>3</sub>OC**H**<sub>2</sub>) 3.63 (m, 8H) <sup>13</sup>C NMR (500Hz) (CDCl<sub>3</sub>) δ: 50.85, 59.15, 70.17, 70.76, 70.82, 70.86, 72.09

13-azido-2,5,8,11-tetraoxatridecane (**7**) 93% (500 MHz) (CDCl<sub>3</sub>) δ: 3.33 (m, 5H) 3.50 (m, 2H, CH<sub>3</sub>OC**H**<sub>2</sub>) 3.63 (m, 12H) <sup>13</sup>C NMR (500Hz) (CDCl<sub>3</sub>) δ: 50.79, 59.15, 70.14, 70.63, 70.73, 70.75, 70.77, 70.80, 72.05

1,2-bis(2-azidoethoxy)ethane (8) 91% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 3.36 (t, 4H, N<sub>3</sub>CH<sub>2</sub>, J = 5 Hz) 3.65 (m, 8H) <sup>13</sup>C NMR (500Hz) (CDCl<sub>3</sub>)  $\delta$ : 50.87, 70.31, 70.9

# 2.2.4.4 Synthesis of Alkynes 9 – 11

To sylate precursor (1 - 3) was diluted in THF to a concentration of 0.5 M and chilled on ice in a flask with magnetic stirring. In a separate flask a 1.2 M solution of propargyl alcohol (5 equiv. per tosyl ester) was made in THF and chilled on an ice bath. NaH (60% dispersion in mineral oil, 2 equiv. per tosyl ester) was measured, and washed twice with hexane in order to remove the mineral oil. After two washes, the NaH hexane slurry was added to the propargyl alcohol, and the deprotonation was monitored visually by the release of hydrogen. NaH was added at a slow enough rate that the bubbling was steady but not overly rapid. Bubbling was allowed to subside completely, and solution was observed to clear. The partially deprotonated propargyl alcohol solution was then carefully but rapidly poured into the tosylate solution, which was kept on ice until the addition was complete. The reaction flask was allowed to stir on ice roughly 20 min longer, after which time the ice was removed and the flask was stirred for 16 - 24 hours longer. All portions of this reaction were carried out under nitrogen. Reaction was quenched by addition of water until all solids are dissolved, followed by rotary evaporation to remove most of the THF. The resulting aqueous layer was extracted three times with dichloromethane. The combined organic layer was then dried over sodium sulfate and evaporated. Alkyne products were purified by distillation under reduced pressure. (Note: this reaction should not be run more concentrated than specified – concentration has been optimized against eliminative biproducts)

3-(2-methoxyethoxy)prop-1-yne (9) 45% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 2.40 (t, 1H, CH<sub>2</sub>CCH, J = 2.4 Hz) 3.35 (s, 3H) 3.54 (m, 2H, CH<sub>2</sub>OCH<sub>3</sub>) 3.65 (m, 2H, CH<sub>2</sub>OCH<sub>2</sub>CC) 4.17 (d, 4.17, J = 2.4 Hz) <sup>13</sup>C NMR (500Hz) (CDCl<sub>3</sub>)  $\delta$ : 58.58, 59.20, 69.09, 71.83, 74.76, 79.70

3-(2-(2-methoxy)ethoxy)prop-1-yne (**10**) 71% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 2.39 (t, 1H, CH<sub>2</sub>CCH, J = 2.5 Hz) 3.33 (s, 3H, OCH<sub>3</sub>) 3.51 (m, 2H) 3.61 (m, 2H) 3.65 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>O) 4.16 (d, 2H, CH<sub>2</sub>CCH, J = 2.4 Hz) <sup>13</sup>C NMR (500Hz) (CDCl<sub>3</sub>)  $\delta$ : 58.55, 59.19, 69.25, 70.58, 70.70, 72.06, 74.67, 79.79

2,5,8,11-tetraoxatetradec-13-yne (**11**) 80% <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 2.38 (t, 1H, CH<sub>2</sub>CCH, J = 2.4 Hz) 3.32 (s, 3H, OCH<sub>3</sub>) 3.49 (m, 2H, CH<sub>2</sub>OCH<sub>3</sub>) 3.61 (m, 10H, OCH<sub>2</sub>CH<sub>2</sub>O) 4.14 (d, 2H, CH<sub>2</sub>CCH, J = 2.5 Hz) <sup>13</sup>C NMR (500Hz) (CDCl<sub>3</sub>)  $\delta$ : 58.50, 59.14, 69.20, 70.52, 70.63, 70.71, 72.04, 74.64, 79.77

# 2.2.4.5 Synthesis of Model Compounds 12 – 15<sup>127</sup>

A magnetic stirrer, Azide (6 - 8) and chloroform (such that the concentration of alkyne+azide in chloroform = 0.6M) were added to a Schlenk flask followed by the alkyne (9 - 11, 2.1 equiv. for azide 8, 1.2 equiv. otherwise). IMPORTANT: this order must be used; under NO CIRCUMSTANCES should catalyst be added to neat precursor materials. Catalytic Tris(triphenylphosphine)copper(I)bromide was then added at a rate of 2% mol relative to the molar amount of the azide. Three freeze-pump-thaw cycles were carried out in order to de-gas the reaction (synthesis of Tris(triphenylphosphine)copper(I)bromide is described elsewhere). Following this the reaction was placed on an oil bath and heated to 60°C for 24h with stirring. Nitrogen was not reintroduced into the reaction after the last freeze-pump-thaw, so the atmosphere in the reaction should be mostly chloroform. Some refluxing off the side was

observed. Following the reaction, the chloroform was extracted with three washes of 0.1 disodium EDTA pH 8. In all cases the final EDTA wash was colorless. Aqueous layer was back extracted once with  $CH_2Cl_2$ ; the combined organic layer was then dried over sodium sulfate and concentrated using a rotovap. Material was purified using silica gel chromatography with  $CH_2Cl_2$  eluent containing 8 – 10% methanol v/v%. Materials were pale yellow to colorless oils. 6EO2T was observed to crystalize spontaneously below room temperature.

# 12 6EO1T 3.9g, 70%

HR-ESI-MS Calculated  $C_{15}H_{30}N_3O_6$  (M+H)+: 348.2135, Observed: 348.2138 <sup>1</sup>H NMR (500MHz) (CDCl<sub>3</sub>)  $\delta$ : 3.32 (s, 6H, OCH<sub>3</sub>) 3.50 (m, 4H, CH<sub>2</sub>OCH<sub>3</sub>) 3.57 (m, 12H, OCH<sub>2</sub>) 3.81 (t, 2H, N-CH<sub>2</sub>CH<sub>2</sub>O, J = ) 4.48 (t, 2H, N-CH<sub>2</sub>CH<sub>2</sub>-O, J=) 4.63 (s, 2H, OCH<sub>2</sub>-triazole) 7.70 (s, 1H, triazole H) <sup>13</sup>C NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 50.33, 59.15, 64.73, 69.59, 69.74, 70.61, 70.64, 70.66, 72.03, 123.93, 145.06 IR (neat): 3569 (water), 3136, 2873, 1956, 1641, 1547, 1460, 1353, 1247, 1199, 1102, 932, 850, 776

#### 13 8EO1T 74%

HR-ESI-MS Calculated  $C_{19}H_{38}N_3O_8$  (M+H)<sup>+</sup>: 436.2659, Observed: 436.2670 <sup>1</sup>H NMR (500MHz) (CDCl<sub>3</sub>)  $\delta$ : 3.32 (s, 6H, OCH<sub>3</sub>) 3.50 (m, 4H, CH<sub>2</sub>OCH<sub>3</sub>) 3.59 (m, 20H, OCH<sub>2</sub>) 3.82 (t, 2H, N-CH<sub>2</sub>CH<sub>2</sub>O, J = 5 Hz) 4.48 (t, 2H, N-CH<sub>2</sub>CH<sub>2</sub>-O, J = 5Hz ) 4.63 (s, 2H, OCH<sub>2</sub>-triazole) 7.69 (s, 1H, triazole H) <sup>13</sup>C NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 50.35, 59.15, 64.74, 69.61, 69.76, 70.62, 70.65, 70.70, 70.73, 72.06, 123.92, 145.07 IR(neat): 3566 (water), 3137, 2873, 1957, 1645, 1545, 1457, 1351, 1297, 1247, 1199, 1105, 1048, 984, 850, 776 HR-ESI-MS Calculated  $C_{18}H_{33}N_6O_6$  (M+H)<sup>+</sup>: 429.2462, Observed: 429.2457 <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta = 3.31$  (s, 6H, OCH<sub>3</sub>) 3.51 (m, 8H, OCH<sub>2</sub>) 3.64 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>-triazole) 3.78 (t, 4H, N-CH<sub>2</sub>CH<sub>2</sub>O, J = 5Hz ) 4.47 (t, 4H, N-CH<sub>2</sub>CH<sub>2</sub>-O J= 5 Hz) 4.64 (s, 4H, OCH<sub>2</sub>-triazole) 7.66 (s, 2H, triazole H) <sup>13</sup>C NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta = 50.33$ , 59.13, 64.86, 69.60, 69.79, 70.56, 71.97, 76.97, 77.23, 77.48, 123.83, 145.12 IR(neat): 3537 (water), 3137, 2875, 1944, 1652, 1549, 1459, 1361, 1292, 1223, 1198, 1094, 1049, 982, 924, 892, 848, 776 **15** 8EO2T 77%

HR-ESI-MS Calculated  $C_{22}H_{41}N_6O_8 (M+H)^+$ : 517.2986, Observed: 517.2992 <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ : 3.33 (s, 6H, OCH<sub>3</sub>) 3.51 (m, 8H, OCH<sub>2</sub>) 3.59 (m, 4H) 3.62 (m, 4H) 3.79 (t, 4H, N-CH<sub>2</sub>CH<sub>2</sub>O, J=5 Hz) 4.47 (t, 4H, N-CH<sub>2</sub>CH<sub>2</sub>-O, J=5 Hz) 4.64 (s, 4H, OCH<sub>2</sub>-triazole) 7.67 (s, 2H, triazole H) <sup>13</sup>C NMR (600 MHz) (CDCl<sub>3</sub>)  $\delta$  = 50.30, 59.10, 64.77, 69.56, 69.85, 70.52, 70.58, 70.62, 72.01, 123.86, 145.07 IR (neat): 3557 (water), 3137, 2892, 1955, 1646, 1549, 1459, 1354, 1294, 1245, 1223, 1199, 1100, 982, 928, 892, 848
### 2.3 Results and Discussion

### 2.3.1 Ab Initio Calculations

Lithium ion affinities with various nitrogen heterocycles are calculated using the MP2(full)/Aug-cc-pVTZ(Li-C)//MP2(full)/cc-pVDZ(Li-C) calculation recommended for this kind of estimate by Rodgers et al. which we show to be in good agreement with the G3 and G3(MP2) calculations of Pople and co-workers. G3(MP2) was found to be the most amenable to larger species, so we use this level of theory to model a hypothetical solvation shell for the lithium ion with and without triazole participation.

The absolute ligand – lithium association energies of heterocyclic and other ligands have been extensively studied by Rodgers and co-workers, but computational estimates accompanying the measurements have been carried out using calculations with varying levels of sophistication.<sup>52-54</sup> Additionally, Rodgers et al. have benchmarked the MP2(full)/Aug-ccpVTZ//MP2(full)/cc-pVDZ calculation against a test set which included few nitrogen heterocycles.<sup>51</sup> In order to test the applicability of this calculation to nitrogen heterocycles we have extended these calculations to azines and azoles, and found similar agreement to experiment as the initial test set (fig. 14). Additionally we have two bidentate lithium complexes at this level of theory on models designed to resemble complexation geometries expected in the model compounds. As the number of dative bonds between lithium and its coordination sphere increases, the strength of each additional dative bond has been seen to decrease in previous studies.<sup>43</sup> It is notable however that while 1-H-1,2,3-triazole shows an association energy 51.5 kJ/mol greater than dimethyl ether, the difference between the binding energy of stronger of the two bidentate complexes and glyme is only 15.1 kJ/mol. This result is attributable to the geometries of the two complexes; the 1-H-1,2,3-triazole minimum is a scalene triangular

complex, which features bonds from the two adjacent aprotic nitrogen atoms to the lithium ion, whereas the minimum observed in the 4-methoxymethyl-1H-1,2,3-triazole (4MeOMeT) complex features only one lithium nitrogen bond.

Attempts to calculate the energies of larger complexes became impractical due to the prohibitive expense of the MP2(full)/Aug-cc-pVTZ(Li-C) single point calculation on complexes featuring coordination numbers of three and four. A small comparison of G3 and G3(MP2) energies to experiment and theory for only the most relevant glyme and triazole species was conducted to evaluate the appropriateness of these methods (fig. 14). The agreement of G3 theory with mass spectrometry experiments was tested for lithium association calculations, and found to have a mean average deviation of 8.6 kJ/mol compared to 8.1 kJ/mol for MP2(full)/Aug-cc-pVTZ(Li-C)//MP2(full)/cc-pVDZ(Li-C) in the test set of Rodgers et al.<sup>51</sup> Additionally both G3 and G3(MP2) are extensively benchmarked for general thermochemical accuracy in a variety of applications.<sup>56,57</sup>

Larger coordination spheres were modeled using two distinct "chains" up to a coordination sphere of four. Justification for this treatment can be found in molecular dynamics simulations which show that lithium cations complexed between two chains are the most important for lithium ion transport, and that the average occupancy of the first coordination shell around lithium contains four.<sup>19</sup> oxygens, meaning that four and five coordinate complexes should be most important in transport behavior, with lithium rarely containing less than four ligands.<sup>19</sup>



Figure 13 – As more solvent moieties are added to the lithium coordination sphere the average bond strength decreases, effecting both triazole and ether ligands. Triazoles can interact with the

2p orbitals of the lithium ion leading to net stabilization in the two and three coordinate complexes which are planar. Lithium becomes sp3 hybridized in the tetracoordinate complex, and this effect is seen to diminish. Simulations and experimental data have shown four and five

membered complexes to be most common in polyether ion conductors.<sup>19</sup>



Figure 14 – Gas phase lithium ion to ligand affinities in experiment and theory. Typical agreement between the experiments of Rodgers et al.<sup>51-54</sup> and the MP2(full)/Aug-cc-pVTZ(Li-C)//MP2(full)/cc-pVDZ(Li-C) calculations recommended by the same group for quantitatively accurate lithium ion affinities are shown in (a).<sup>51</sup> Calculations typically over estimate affinities relative to experiment but are usually within 10 kJ/mol, which is comparable to the uncertainty of the experiment. In (b) G3 methods were compared to the methods of Rodgers et al. due to unfavorable scaling of the latter to larger ligand systems.<sup>51</sup> The computational expense of G3 is similar to that of the Rodgers method, with G3(MP2) being somewhat cheaper. G3(MP2) was found to be in better agreement with experiment due to being consistently lower in its energy

estimates.

Figure 14 (cont'd)

b)



c)



The behavior seen in our three and four coordinate complexes (fig. 13) shows that as the coordination number increases, the lithium triazole bond becomes roughly indistinguishable from a lithium ether bond on the basis of energy. The difference in energies between the four coordinate complex with and without a triazole is approximately 3 kJ/mol.

### 2.3.2 Experimental Measurement of Conductivity and Thermal Behavior

Model compounds 8EO1T, 6EO1T, 8EO2T, and 6EO2T were first synthesized using the methodologies described by scheme 2. Model compounds were designed such that their molecular weights cluster around 500 g/mol so that they can be fairly compared to poly (ethylene glycol) dimethyl ether  $M_n$ =500 ( henceforth PEGDME 500), and such that each model gives a whole number ratio of ether oxygen atoms and triazole rings; 8:1, 6:1, 4:1, and 3:1 respectively. The model compound 6EO2T was also devised intentionally to make five and six coordinate complexes containing only ether oxygens uncommon, so that triazole containing complexes resembling the one shown in fig. 13 would be relevant to the transport behavior.

Synthesized materials were purified and dried as described in the experimental section. Dry materials were then analyzed by differential scanning calorimetry without additives, and by AC impedance spectroscopy as neat materials with dissolved LiTFSI. The thermal behavior of PEGDME500 was not characterized, because our equipment cannot access temperatures less than -80°C. 6EO1T was found to lack thermal behavior in the available temperature window, and was therefore not used in conductivity measurements; the observed lack of thermal behavior was probably due to the fact that 6EO1T has the lowest molecular weight of the model compounds.

Compound	Melting Temperature, T <sub>m</sub> (°C)	Glass Transition Temperature, T <sub>g</sub> (°C)	Activation Energy, E <sub>a</sub> (kJ/mol)	Pre-exponential factor, $\sigma_0$ (S/cm)	Arrhenius fit R <sup>2</sup>
8EO1T, <b>13</b>	-	-74.9	29.7	$1.19 \cdot 10^3$	0.9707
6EO1T, <b>12</b>	-	-	n/a	n/a	n/a
8EO2T, <b>15</b>	-	-59.6	40.4	3.13·10 <sup>5</sup>	0.9872
6EO2T, <b>14</b>	22.6	-59.1	41.8	5.21·10 <sup>5</sup>	0.9807
PEG 500 DME	-	-	17.5	17.8	0.9583

Table 1 – Physical Data Pertaining to Thermal and Conductive Properties of Materials

It was found that the model compounds 6EO2T, 8EO2T, and 8EO1T all had measurable glass transition temperatures  $(T_g)$  and that the measured glass transition was weakly dependent on the ether oxygen to triazole ratio, and more strongly dependent on the number of ether oxygens in the chain (Table 1.). 6EO2T and 8EO2T had  $T_g$  that were almost identical, and 8EO1T had a  $T_g$  roughly 6 degrees lower. 6EO2T was shown to have a melting temperature near room temperature. Crystallization behavior was noticeable in 6EO2T at reduced temperatures (including low temperature storage), however room temperature crystallization of samples was only observed in one occasion, whereas the material usually maintained fluidity at room temperature. Because of this and the fact that the lowest conductivity measurements taken occurred at 30°C, crystallization behavior was not observed to affect the conductivity of the material directly.



b)



Figure 15 – Conductivity of oligomer salt complexes. In (a) model oligomer salt complexes were run at a concentration of 1 Li : 64 ligand atoms, where two of the triazole nitrogens were considered ligands (but not the pyrrole-like nitrogen) run with PEG 500 dimethyl ether controls. Model oligomers and the PEG control were run with LiTFSI, while a variable concentration standards curve was run with LiClO<sub>4</sub>. In (b) the same data shown without standards.



b)



Figure 16 – Descriptions of trends in the conductivity of oligomer salt complexes. In part (a) a strong correlation between conductivity at 30°C and the glass transition temperature is found within the model series. In part (b) a linear relation is shown between the pre-exponential factor and activation derived from Arrhenius plotting in PEG and the triazole containing model

compounds.

A crystal of 6EO2T was obtained for single crystal X-ray diffraction analysis by slow evaporation of a toluene solution in a -20°C freezer. While cases of triazole C-H to heteroatom hydrogen bonding have been reported in the literature,<sup>46</sup> hydrogen bonding was not present in the crystal structure as the closest intermolecular N-H distance was 2.75Å and the shortest O-H distance was 2.79Å. Triazoles were not observed to pi stack in the crystal. While compound was observed to crystalize in layers (fig 17b) the faces of the triazole rings seem to avoid one another (fig 17c). The triazole ring does carry a dipole along which the rings in the model compound seem to align (fig 17d). We conclude that the most important factors that lead to ordering and crystallization in the most triazole rich model are loss of conformational freedom and dipole dipole interactions.

The 30°C conductivity of 6EO2T and 8EO2T salt composites was nearly identical, with 8EO1T being half an order of magnitude and PEGDME 500 being a full order of magnitude higher (Fig 1.). Room temperature conductivity was shown to correlate nearly perfectly with the  $T_g$  of the material. It was observed that as the temperature was increased, the conductivity of the materials approached convergence at a single value. This behavior is known as compensation law, or Meyer-Neldel behavior (Fig 2.).<sup>66-68</sup>

Meyer-Neldel or entropy-enthaply compensation behavior is a behavior of a set of processes or reactions that occur in families of materials with similar compositions which are well described by the Arrhenius equation

$$\sigma(T) = \sigma_0 e^{\frac{-L_a}{RT}}$$
(eq. 10)

where  $\sigma(T)$  is temperature dependent conductivity,  $E_a$  is the activation energy of the process,  $\sigma_0$  is an empirical exponential prefactor, and R is the gas constant.<sup>66-68</sup>



Figure 17 – Single crystal X-ray diffraction of 6EO2T. In part (a) the Single Crystal XRD structure of 6EO2T is shown with thermal elipsoids set at 50% probability. Packing as viewed from the b axis of the 6EO2T crystal is shown in (b) and the c axis in (c). While a layered structure is evident in the crystal, pi-pi stacking interactions and hydrogen bonding appear to be absent. The angle shown in (c) reveals that triazole moieties align roughly along the dipole of the ring within the layers.

Figure 17 (cont'd)

c)



d)



Table 2 – Crystal Data and Structure Refinement for 6E
--

Identification code	6EO2T			
Empirical formula	$C_9H_{16}N_3O_3$			
Formula weight	214.25			
Temperature/K	173.01			
Crystal system	monoclinic			
Space group	C2/c			
a/Å	47.5520(19)			
b/Å	5.5312(2)			
c/Å	8.1912(3)			
α/°	90.00			
β/°	97.576(3)			
γ/°	90.00			
Volume/Å <sup>3</sup>	2135.64(14)			
Z	8			
$\rho_{calc} mg/mm^3$	1.333			
m/mm <sup>-1</sup>	0.843			
F(000)	920.0			
Crystal size/mm <sup>3</sup>	$0.189 \times 0.066 \times 0.059$			
$2\Theta$ range for data collection	3.74 to 140.76°			
Index ranges	$-57 \le h \le 57, -6 \le k \le 6, -9 \le l \le 9$			
Reflections collected	14377			
exptl absorpt T max, min	0.7533, 0.6448			
Independent reflections	1987[R(int) = 0.2141]			
Data/restraints/parameters	1987/0/138			
20 70.38 fraction collected	0.979			
Goodness-of-fit on F <sup>2</sup>	1.007			
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0620, wR_2 = 0.1222$			
Final R indexes [all data]	$R_1 = 0.1497, wR_2 = 0.1585$			
Largest diff. peak/hole / e Å <sup>-3</sup> 0.28/-0.26				

Compensation behavior is an apparently exponential dependence observed between the pre-exponential term and the activation energy appear exponential related such that

$$E_a = \alpha + \beta \ln(\sigma_0) \tag{Eq. 11}$$

where  $\alpha$  and  $\beta$  are arbitrary constants,  $\sigma_0$  is the pre-exponential term, and  $E_a$  is the activation energy.<sup>67,68</sup> Controversy exists over what gives rise to this sort of behavior and what (if anything) it signifies.<sup>68</sup>

This behavior is rarely discussed in the context of polymer electrolytes, however one example of compensation behavior was identified by Wieczorek in an investigation of a series of polymer composite materials.<sup>67</sup> These materials included various polyethylene glycols (PEG) and blends of PEG with poly methylmethacrylate (PMMA), which were paired with NaI or LiClO<sub>4</sub> carriers and a variety of inorganic nanoparticle fillers.<sup>67</sup> Wieczorek cited earlier work from studies of diffusion in metals in which activation energy was related to the entropy of migration ( $\Delta S_m$ ) by a characteristic temperature ( $T_D$  or disordering temperature) such that  $E_a/T_D = \Delta S_m$ .<sup>66,67</sup> In earlier study  $T_D$  was considered to be the melting point of the class of alloys showing compensation behavior.<sup>66,67</sup> Wieczorek calculated  $T_D$  for his materials (1 distinct  $T_D$  for each set of materials showing compensation behavior) and found that it was close to the  $T_m$  of the crystalline PEG domains in his materials.<sup>67</sup> Reference to the effects of inorganic fillers was used to explain the discrepancy.<sup>67</sup>

While the work of Wieczorek is an interesting precedent, it does not provide an explanation for why the compensation behavior is present in these materials. Furthermore, references to a  $T_D$  in our materials could not be related to melting, as only one of our materials shows a  $T_m$ . In order to explain and interpret our results we will look to physical theories of polymer dynamics, as well as Arrhenius based models.

## 2.3.3 The Explanation for and Significance of Compensation Behavior

It is generally understood that segmental dynamics of polymer electrolytes are dependent on the mobility of the individual segments of the polymer chain.<sup>5,9,14,15</sup> The connection is

conveniently rationalized using the dynamic bond percolation theory (DBP) of Ratner and coworkers.<sup>11-15</sup> A bond in the sense of DBP, is a pathway between a void in the polymer host occupied by an ion, and an unoccupied void. When one bond has opened and closed for each ionic species in the system it can be said that one renewal time has occurred. Diffusion of an ionic species can then be written as<sup>14</sup>

$$D = \frac{\langle r^2 \rangle}{2d\tau_R}$$
 (eq. 12)

Where  $\tau_R$  is the renewal time  $\langle r^2 \rangle$  is the mean square displacement of a randomly diffusing ion in the system, and d is the spatial dimensionality of the system.<sup>11</sup>

The connection between the  $T_g$  and  $\tau_R$  is somewhat foggy. A general definition of the glass transition temperature can be found in Anslyn and Doughrty's *Modern Physical Organic Chemistry*; "[a] transit from an essentially rigid glass to a more flexible rubbery material".<sup>131</sup> Based on this definition it would be intuitive to assume that renewal time becomes essentially infinite at the glass transition temperature, and would therefore be inversely proportional to T-T<sub>g</sub> as the temperature of a material rises above its T<sub>g</sub>. This logic also underlies the VTF equation (eq. 3) which makes temperature dependent conductivity  $\sigma(T)$  inversely proportional to T-T<sub>0</sub>, where T<sub>0</sub> is a fitting parameter related to T<sub>g</sub> by a constant (usually less than 45°C).<sup>15</sup> However as the replacement of T<sub>g</sub> with T<sub>0</sub> suggests there is some amount of ambiguity in this idea.<sup>15</sup> The ambiguity is generally related to the fact that T<sub>g</sub> is an empirical kinetic quantity related to molecular motion in a bulk system, and that different types of motion are exhibited by polymers.<sup>15</sup> Thus different experimental techniques may find different values of T<sub>g</sub>.<sup>15</sup> Further complexity is introduced by the fact that the addition of a salt to a polymer system increases it's

 $T_g$  by introducing dative bonds between and within chains.<sup>15</sup> These problems mean that a formal functional relationship between  $\tau_R$  and  $T_g$  has not been established.

This complexity makes interpreting the correlation we found between room temperature conductivity and  $T_g$  somewhat difficult. While we cannot use DBP quantitatively to explain this result, the conceptual connection between  $T_g$  and molecular motion is still the best way to understand it. Materials with a higher  $T_g$  are behaving as though they are at a lower temperature than those with a low  $T_g$  because molecular motion (and hence renewal behavior) doesn't vary strongly with temperature below the  $T_g$  (and in fact stops for all intents and purposes).

A physical theory of cation transport based on the Rouse model was derived by Maitra et al.<sup>23</sup> This model breaks transport down into a component mediated by diffusion of the ion with a chain ( $D_{c.m.}$ ) and three types of independent diffusion ( $D_M$ ) with three independent time scales ( $\tau_1, \tau_2, \tau_3$ ).<sup>23</sup> These consist of diffusion along a chain ( $\tau_1$ ) relaxation mediated diffusion ( $\tau_2$ ) and interchain hopping ( $\tau_3$ ) which can be considered analogous to the  $\tau_R$  of Ratner et al.<sup>23</sup> It was shown that for short chains such as those in our study that an approximate functional form can be written for  $D_M(\tau_1, \tau_2, \tau_3)$  such that

$$D_{\rm M} = \frac{R_e^2}{18\tau_3}$$
 (eq. 13)

Where  $\mathbf{R}_{e}$  is the equilibrium end to end distance of the polymer.<sup>23</sup> Because parameters of chain flexibility mostly effect  $\tau_{2}$ , we can reason that the stiffening effect of introducing triazoles into a chain are only going to be felt if they effect the diffusion behavior of the polymer for some reason, or the diffusion of lithium ions between chains.

Additionally we considered possible effects of the differing number of Rouse segments  $(N_R)$  which would affect the available Rouse modes; a set of modes that describe polymer motion. We might expect that decreasing  $N_R$  would lead to less thermal energy being lost to coiling movements which might lead to an increase in  $D_{c.m.}$ . This trend is in fact shown by Maitra et al for polymers ranging from  $N_R=1$  to ~400 where  $D_{c.m.}$  goes to zero.<sup>23</sup> The authors used PEG models and defined a rouse segment to be one monomer. We estimated  $N_R$  in our models by using the number of EO monomers and considering a triazole and the ether oxygen after it to be one segment. Using this system we found  $N_R=11$  for PEGDME 500, 8 for 8EO2T and 8EO1T, and 6 for 6EO2T. Based on the relatively small differences, and the fact that  $N_R$  doesn't appear to track with differences in the conductivity, we are disinclined to pursue this line of reasoning further.

The differences in exponential prefactor observed in the model compounds is difficult to explain, however recent work by Frech et al has focused on understanding the origins of the exponential prefactor in the conductivity of organic liquids, and using this insight to improve the Arrhenius formalism.<sup>69-72</sup> Citing deficiencies in both phenomenological approaches (such as Arrhenius, and Vogel Tamman Fulcher or VTF) which tend to yield little physical insight into a system, but fit data well, and hydrodynamic theory (Nernst-Einstein, DBP) which are theoretically rigorous, but often fail to adequately describe experimental results, Frech et al. have developed the compensated Arrhenius formalism (CAF).<sup>69-72</sup> The compensated Arrhenius Formalism starts with the insight that the exponential prefactor in the Arrhenius equation is actually a function of the static dielectric constant of the material, which is itself a temperature dependent quantity. The Arrhenius equation that results from this insight can be written

$$\sigma(\varepsilon_s, T) = \sigma_0 \left(\varepsilon_s(T)\right) e^{\frac{-E_a}{RT}}$$
(eq. 14)

where  $\varepsilon_s$  is the static dielectric constant of the material. The authors then devised a fitting method whereby the pre-exponential factor could be cancelled, and calculated separately from the activation energy.<sup>69-72</sup> They accomplished by normalizing to a conductivity measurement at a reference temperature (T<sub>r</sub>) and fitting the data using the compensated Arrhenius equation, which they give as.

$$ln\left(\frac{\sigma(T,\varepsilon_s)}{\sigma_r(T_r,\varepsilon_s)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r}$$
(eq. 15)

The activation energy  $(E_a)$  can then be obtained as a slope or intercept of the fit.<sup>69</sup> The preexponential factor is calculated separately, and must be obtained from a set of related materials that vary regularly by dielectric constant.<sup>69</sup> The pre-exponential factor is given by transforming the conductivity data so that

$$\sigma_0 = \frac{\sigma}{e^{\frac{-\overline{E}a}{RT}}}$$
(eq. 16)

Where  $\bar{E}_a$  is the average activation energy for the entire set of materials analyzed.

While this procedure would be impractical for our own data, due to the need for the materials analyzed to be sets that vary by a single parameter (e.g. primary alcohols of varying chain length from ethanol to octanol) the insights gained from the development of this formalism are quite useful.<sup>69-72</sup> When this method was used to analyze the ionic conductivity of various ions in families of polar organic liquids conductivity of each liquid in a class (i.e. 1-alcohols or methyl ketones of varying chain length) varied roughly linearly by temperature dependent dielectric constant  $\varepsilon(T)$  and gave rise to separate curves when plotted. On the other hand, the pre-exponential factors of each class of liquids overlapped in a single curve when plotted against

 $\varepsilon$ (T). This is a good indication that their assumptions about the dependence of pre-exponential factor on dielectric constant are likely justified.

Dielectric constant isn't a useful metric for thinking about molecular details, and structure activity relationships, as it is a macroscopic property of a system.<sup>71</sup> In order to make their model more useful the authors used Onsager's model to relate dielectric constant to permanent dipole, and dipole density of sets of thiols, methyl ketones, nitriles and acetates of various chain lengths.<sup>71</sup> They used a version of the CAF adapted to diffusion, and showed that the pre-exponential factor D<sub>0</sub> varied by N<sub>d</sub>/T (where N<sub>d</sub> is the dipole density of the material) and that it varied by solvent class.<sup>71</sup> The dipole density used in this study was a number density, which was easily obtained because the authors used liquids with only one polar functional group per molecule.<sup>71</sup> Thus the were able to calculate the quantity from the molar volume.<sup>71</sup> This was true because very strong correlations were present between  $\varepsilon(T)$  and N<sub>d</sub>(T).<sup>71</sup> Finally, it was shown that alcohols had higher activation energies than the polar aprotic liquids studied.<sup>69,70</sup> This was attributed to the hydrogen bonding capabilities of alcohols, which required additional energy to dissociate relative to polar aprotics.<sup>72</sup>

The molecules used in the present study are more complicated than those examined by Frech et al. in that they are large and contain many polar groups per molecule. One comparison that is easy to make however is the strength of the permanent dipole moment in a 1,2,3- triazole ring, relative to that of dimethyl ether, the basic dipole creating moiety in a chain of polyethylene glycol. The dipole moment of dimethyl ether has been experimentally measured to be 1.310 D, additionally, ethyl methyl ether has a dipole moment of 1.174 D.<sup>73</sup> The dipole for 1,3-dimethyl-1,2,3-Triazole has not been measured experimentally, however we have calculated the dipole at the MP2(full)/6-31G(d) level of theory and found a value of 1.4 D for dimethyl ether, and a

value of 4.7 D for the triazole. Additionally and in contrast to standard PEG chains, the triazole is known to be a hydrogen bond donor with roughly the same affinity for an acceptor as pyrrole.<sup>44</sup>

Based on the factors considered up to this point an explanation for the observed compensation behavior can be proposed. It seems likely that the introduction of the triazole moiety into the PEG chain provides a ligand for the lithium ion similar to that of an ether oxygen. However the triazole differs significantly in the magnitude of its dipole which produces effects that both enhance and impede conductivity. Triazoles stiffen the chains and (probably more importantly) enhance chain to chain dipole-dipole interactions, which lead to an increase in  $T_g$  and lead to crystallization in the extreme case of 6EO2T. The greater attraction between chains leads to a higher activation energy for transport as triazoles become a greater fraction of the ligands in the material. However, conductivity can also be enhanced by the presence of triazoles. This occurs because the greater polarity of the triazole moiety enhances the Arrhenius pre-exponential factor which enhances the global conductivity of the material at all temperatures. A mechanism proposed by Frech et al. for the enhancement of the pre-exponential factor cites transition state theory of transport processes and ties the polarity of the environment to the  $\Delta G^{\dagger}$ of a moving particle.<sup>72</sup> This proposal was favored in part because the authors have observed similar dependencies on the pre-exponential for self-diffusion of polar liquids.<sup>70,72</sup> A similar effect on self-diffusion of our systems would be unexpected based on the observed thermal behavior, however the polarity likely is affecting the environments of the mobile ions. We propose that the presence of strong dipoles is stabilizing to individual ions in the system, and helps them overcome coulombic correlation to their counter ion. This leads to a higher effective concentration of ions mediating transport.

# 2.4 Conclusions

As a potential architectural feature of lithium ion elecrolytes, triazoles have some degree of potential. Triazoles do have a negative effect on conductivity of polymer salt composites, but it is relatively modest, and the concentrations of triazoles studied were quite high; exceeding most plausible concentrations of the moieties one would expect to find in functional materials.

Triazoles seem to exert most of their effects on conductivity through their dipole moment which is significantly stronger than that of dimethyl ether or polyethylene glycol. This has the effect of attracting the chains together, inducing crystallization and increasing the glass transition of the material. The stiffness of the triazole may also contribute to these effects.

The deleterious effects of the triazole moiety on conductivity manifest themselves in the increase in activation energy observed for conductivity seen in the Arrhenius model of the process. However increases in dipole density have also been shown to enhance the pre-exponential factor of these processes, which leads to compensation behavior.

Frech et al. who first observed effects of this kind proposed that increasing the dipole density of conductive materials might be a novel way to increase conductivity in polymer electrolytes. While it has been shown in this work that triazoles have undesirable effects that counter the pre-exponential boost in the particular systems studied, it is possible to envision strategic uses of such moieties in electrolyte design, such as placing strong dipoles (triazoles or otherwise) near stationary anions found in single ion conductors in order to activate charge separation. Strategies such as this warrant future study and may be the subject of future work.

# 3 Chapter 3: Nucleofugality in Nitrogen and Oxygen derived leaving groups<sup>\*</sup>

### 3.1 Introduction

Nucleofugality, or leaving group ability, is a fundamental concept of organic chemistry, and plays a key role in a broad array of chemical reactions. Despite its centrality to reactions such as E1, E2,  $S_N1$  and  $S_N2$ , that feature a leaving group (nucleofuge) departure in the rate limiting step, nucleofugality was sparsely studied until fairly recently.<sup>80</sup> The last decade, however, has seen several attempts to develop an absolute scale of nucleofugality.<sup>81-84</sup> These began with the work of Ayers et al. who attempted to use a truncated Taylor series to model the electronic energy of a leaving group as a function of increasing charge. In that expression the first order term is  $\mu$ , the electronic chemical potential (which can be expressed as -[I+A]/2) and the second order term is  $\eta$ , or chemical hardness (expressed as [I-A]).<sup>81</sup> Using this construction they argued that electrophilicity  $\omega$ , could be defined as

$$\omega = \frac{\mu^2}{2\eta} = \frac{(l+A)^2}{8(l-A)}$$
(eq. 17)

Where *I* is the ionization potential and *A* is electron affinity; thus this formulation approximates continuous derivatives of energy with respect to charge based on quantities that represent a change in energy with the gain or loss of a full electron.<sup>82</sup> Electrophilicity in this sense is described as "the energy [of] stabilization resulting from the presence of a perfect electron donor".<sup>81</sup> In an attempt to correct for partial charge already present in a leaving group prior to leaving, they derived a related quantity  $\Delta E_{nucleofuge}$  which is defined such that

<sup>&</sup>lt;sup>\*</sup>This chapter is an adapted republication of Spahlinger, G.; Jackson J. E. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24559 – 24569. It has been republished with permission from the PCCP Owner Societies. The original article may be found online at the following link: <u>http://pubs.rsc.org/en/content/articlelanding/2014/cp/c4cp03741c#!divAbstract</u>

$$\Delta E_{\text{nucleofuge}} = \frac{(\mu + \eta)^2}{2\eta} = \frac{(I - 3A)^2}{8(I - A)}$$
(eq. 18)

Because  $\Delta E_{nucleofuge}$  is derived solely from the ionization potential and electron affinity, this quantity is relatively easy to calculate, and several groups have followed up by conducting DFT studies wherein attempts were made to apply or refine this scale.<sup>82,83</sup> Most notably, Geerlings et al. modified the theory to include solvent effects, and applied the resulting formalism to an extended set of leaving groups.<sup>82</sup>

Mayr et al., have taken a different approach, utilizing an empirical scale parameterized with rate constants for the solvolysis of benzhydryl derivatives.<sup>84</sup> The benzhydryl group has the advantage of being tunable via addition of electron donating and withdrawing groups on the aryl rings, such that leaving groups whose solvolysis rate constant is too fast or slow for study on one scaffold can be measured on another.<sup>84</sup> The group focused on sulfonate, carboxylate and halide leaving groups in this analysis, and claims to have found a scale that is useful for rates spanning 12 orders of magnitude.<sup>84</sup>

A noticeable omission from the recent literature on nucleofugality is the amine-derived anionic leaving group.<sup>81-84</sup> While sulfonates and carboxylic acid esters are relatively common, amides, sulfonamides, imides and sulfonimides have to the best of our knowledge been absent from any study of nucleofugality to date.

Attempts to activate amines for substitution and elimination do exist in the literature however, and date back to the 1960s. Based on its low  $pK_a$  of 1.6,<sup>85</sup> initial work explored derivatives of saccharine.<sup>86</sup> Unfortunately these were found to undergo preferential attack at the carbonyl carbon; however, the authors discovered that bis(sulfonyl)imides (e.g. ditosylamines) could undergo substitution and elimination.<sup>86</sup> The most common activation in this vein appears to be through the addition of dual triflyl groups to form bis(trifluoromethanesulfonyl)imide derivatives.<sup>87-89</sup> This strategy for activation is becoming more common in part because the bis(trifluoromethanesulfonyl)imide (TFSI) anion is an attractive component in certain types of ionic liquids.<sup>90</sup> Metal salts and ionic liquids derived from TFSI have attracted a great deal of attention from scientists researching transport materials for lithium ion batteries. TFSI is generally considered to be a poorly associating ion; it is also thought to plasticize polymeric lithium ion conductors, leading to a lower glass transition temperature in the polymer, and hence better conductivity than other anions of similar lithium ion affinities.<sup>90,91</sup>

Despite this trend, the activation of nitrogen as a nucleofuge remains a rare strategy. While various researchers have pointed out the viability of alkyl TFSI derivatives for the synthesis of ionic liquids,<sup>88,89</sup> TFSI containing liquids are more commonly accessed by the general synthetic method used for ionic liquids:<sup>92</sup> an onium halide salt is first formed by reaction of an alkyl halide with an amine; it is then subjected to ion exchange metathesis by treatment with silver TFSI.<sup>92</sup>

We elected to study the nucleofugality of polyatomic anionic oxygen and nitrogen derived leaving groups by modeling the Menshukin reaction, in which ammonia displaces a leaving group by an  $S_N2$  mechanism. The  $S_N2$  reaction is itself much better studied than nucleofugality as a general concept; theoretical studies exist for both ionic and Menshutkin-type  $S_N2$  reactions, including solvent effects,<sup>93,94</sup>  $S_N2$  reactions at neutral nitrogen,<sup>95,96</sup> comparisons of front side vs. back side  $S_N2$ ,<sup>97,98</sup> studies employing valence bond methods,<sup>99</sup> analyses of  $S_N2$ based on Marcus theory,<sup>100</sup> and analyses of the influences of periodicity on the anionic  $S_N2$ reaction.<sup>118,119</sup> Additionally, the formation of quaternary amine mesylates via the Menshutkin reaction has been modeled using DFT methods.<sup>101</sup> Although we are unaware of any recent

reviews of theoretical work on the  $S_N^2$  reaction, a contribution from Laerdahl and Uggerud provides a good perspective on the state of the field as of twelve years ago, including discussion on experimental mechanistic work, and reaction dynamics.<sup>102</sup> Surprisingly there seem to be no studies that systematically analyze and compare the reactivities of nitrogen and oxygen derived polyatomic anionic leaving groups as a class.

Reservations have previously been expressed about using  $S_N 2$  reactions as a probe of nucleofugality.<sup>80</sup> In particular Stirling argues in his 1978 account that  $S_N 2$  and E2 reactions are tainted by the involvement of a nucleophile or base in the rate limiting step of the reaction.<sup>80</sup> While it is true that the nucleophile is an integral part of an  $S_N 2$  reaction, the present work controls for this issue by using the same nucleophile throughout the study. Moreover, studies of bimolecular reactions are necessary to understand the role of nucleofugality in mechanisms that feature electronic reorganization concurrent with leaving group departure.

## **3.2** Computational Methods

All calculations were performed using GAMESS versions 12 R3 (2009) and 1 R1 (2012).<sup>55</sup> Calculations were run on a personal laptop, the MSU chemistry department hydra cluster, or the MSU High Performance Computing Cluster (HPCC) depending on the demands of the job.

Activation energies were calculated by finding minima for Van der Waals complexes of ammonia and each respective alkylating agent shown in scheme 1, then by locating transition states for the  $S_N 2$  reaction.  $\Delta E^{\dagger}$  was considered to be the difference in these two energies.  $\Delta E_{complex}$  is the difference in energy between the Van der Waals complex and the sum of ammonia and the alkylating agent being studied. Van der Waals complexes and transition state

structures were first located at the HF/3-21G level of theory, and in cases where the conformational space allowed multiple minima or transition state structures, the lowest energy of these were selected. Additional geometric optimizations were run at HF/6-31G(d), and MP2(full)/6-31G(d). In all cases vibrational analyses were run at HF/6-31G(d) on the HF/6-31G(d) geometries in order to confirm that minima and transition states had zero and one imaginary vibrations respectively. All calculations were initially run with  $C_1$  symmetry. After optimization, structures were found which converged to  $C_1$ ,  $C_s$ ,  $C_2$ ,  $C_{2v}$  and  $C_{3v}$  symmetries. Structures which appeared to converge out of  $C_1$  symmetry were rerun at MP2(full)/6-31G(d) using the new point group. Coordinates for stationary points and their corresponding Abelian point groups are listed for all structures in the supporting information.

In order to get relatively accurate energies economically, we have chosen to simplify the G3(MP2) method of Pople et al.<sup>57</sup> The G3(MP2, CCSD(T)), or G3(MP2, CCSD) as it is also known, is the variant of G3(MP2) implemented in GAMESS.<sup>103</sup> The difference between the two is that QCISD(T) calculations are not available in GAMESS, and therefore have been replaced by CCSD(T) calculations as shown in equation 3.

 $E_{0}[G3(MP2, CCSD(T))] = E[CCSD(T)/6-31G(d)//MP2(full)/6-31G(d)] + E[MP2(FC)/G3large//MP2(full)/6-31G(d)] - E[MP2(FC)/6-31G(d)//MP2(full)/6-31G(d)] + ZPE + HLC$ (eq. 19)

Where HLC is a higher level correction and ZPE is the zero point energy at the HF/6-31G(d) level of theory scaled by an empirical factor of 0.8929.<sup>57,103</sup> We have modified this method by omitting the CCSD(T)/6-31G(d) calculation and the higher level correction. For brevity we will refer to this as an "MP2/G3large" calculation, however it is defined below in equation 4.

The quantities described as " $\Delta E$ " in this paper are  $\Delta E_0$ [MP2/G3large] energies unless otherwise indicated.  $\Delta H^{\dagger}$  was also calculated for all activation energies by applying thermal corrections from the HF/6-31G(d) vibrational analyses which were calculated at 298K.

MP2/G3large calculations of activation showed good agreement with the G3(MP2, CCSD(T)) in sulfonates (Supporting information). A second set of calculations at the CCSD(T)/6-31+G(2d,p)//MP2(full)/6-31G(d) level suggested that MP2/G3large might systematically overestimate barriers, however this level of theory not a feasible basis for the study at large. MP2/G3large calculations had mean average deviations (MAD) from experimental methyl cation affinity data similar to G3 and W1 calculations performed by Zipse et al. (Table 2).<sup>104</sup> It is often considered important to include diffuse functions in quantum chemical descriptions of ions, and structures with partial bonding. This concern has been studied in the case of  $S_N2$  reactions with ionic nucleophiles.<sup>105</sup> Boyd et al. found that  $S_N2$  transition states had different geometries when calculations were done with and without diffuse functions, but that the differences in energy between these geometries were negligible in single point calculations including diffuse functions.<sup>105</sup> Taken together these data lead us to conclude that the MP2/G3large calculation is adequate for our analysis in this paper.

All graphical representations of wavefunctions or geometries shown in this paper were generated using MacMolplot V 7.4.3.<sup>106</sup>

### 3.3 Results and Discussion

### 3.3.1 Energies Associated with Nucleofugality, and their Trends

Gas phase activation energies ( $\Delta E^{\dagger}$  and  $\Delta H^{\dagger}_{298K}$ ) have been calculated at the MP2/G3large level of theory for all alkylating agents found in Scheme 3. These energies are defined in Scheme 2. The alkylating agents studied consisted of 20 methylating agents, including a contingent of sulfonamides, sulfonimides, sulfonates, carboxylate esters, carboxamides, and one carboximide. Additionally, two of the alkylating agents studied were five membered rings which would be opened by the attack of nitrogen, these were 1,3-propanesultone, and N-triflyl-1,3-propanesultam (TPS). Methyl Chloride was run as a convenient reference point with a single atom leaving group. The results of these calculations are displayed in order of  $\Delta E^{\dagger}$  magnitude in figure 18. It was found that most methylating agents had comparable  $\Delta E_{complex}$  energies, which were on the order of 4 - 6 kcal/mol. Carboxamides proved to be an outlier, as they contained a hydrogen bond from the ammonia lone pair to the amide proton, instead of an ammonia proton to oxygen bond. However, the  $\Delta E_{complex}$  should not be relevant to analyses of nucleofugality, and therefore was subtracted out of the activation energy, so that the "activation energy" presented,  $\Delta E_{S \to TS}$ , represents the energy difference between the separated species and the transition state of interest. Geometrical parameters of interest from the transition states were tabulated, and can be found in table 3.





Scheme 3 – Relevant energies are derived from electronic structures calculated along the reaction coordinate of an  $S_N$ 2 reaction (A) The difference in energy between a methylating agent in its bound state, and the sum of the separated ions after heterolytic cleavage is defined as the

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methyl cation affinity (MCA) (B)
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Methyl cation affinity is defined as the sum of the energies of a leaving group anion and a methyl cation, less the energy of the parent methylating agent (scheme 3).<sup>104</sup> Methyl cation affinities appear in table 4, along with a set of experimental and calculated values which appear in the work of Zipse et al. for comparison.<sup>104</sup>

Because the energy of a methyl cation is invariant between methylating species, the methyl cation affinity should depend straightforwardly on the energy of the leaving group anion relative to its methylated counterpart. Methyl cation affinity should therefore give the contribution to  $\Delta H_{rxn}$  arising directly from anion stability, where methylating agents with lower methyl cation affinities arise from more stable anions. This quantity should also give a trend analogous to  $\Delta E_{nucleofuge}$ , of Ayers et al. as it shows the change in energy resulting from the leaving event, and can be thought of as the activation energy for the corresponding gas phase  $S_N1$  reaction.

The  $\Delta E_{S \rightarrow TS}$  for nitrogen and oxygen derived leaving groups follow an intuitive pattern. Sulfonates have the lowest average  $\Delta E_{S \rightarrow TS}$  (25.8 kcal/mol), followed by sulfonimides (30.3 kcal/mol) followed by esters (38.7 kcal/mol), followed by sulfonamides (50.3 kcal/mol) followed by amides (58.4 kcal/mol). Nothing in this series challenges conventional thinking, but a few interesting observations can be made. The first of these is simply that while excellent leaving groups can be obtained by adding sulfonyl groups to alcohols, those obtained from the less electronegative amines are significantly and uniformly less reactive, even though a second sulfonyl group may be added to the amine. On average the difference in  $\Delta E^{\dagger}$  between a sulfonate and its sulfonimide analogue (for instance methyl mesylate and methyl MSI) was 4.5 kcal/mol.

Scheme 4 – Alkylating agents and the names they are referred to by in this study.



Figure 18 - Computed Barrier Heights from the MP2/G3large level of theory. Thermal

corrections for the  $\Delta H$  values were computed at 298K.

	$r_{TS}(N-C)$	$r_{TS}(C-X)$	$r_0(C-X)$	$\Delta E_{S \rightarrow TS}$	% C-X
	Å	Å	Å	kcal/mol	elongation
0					
R-S=0					
	1.007	2 000	1 451	21.0	29
$R = CH_3$	1.907	2.000	1.451	31.9	38
$R = OCH_3$	1.926	1.963	1.454	25.7	35
$R = CF_3$	1.962	1.940	1.459	22.0	33
R=F	1.951	1.944	1.457	23.4	33
R O CH <sub>3</sub>					
$R = CH_3$	1.798	2.088	1.439	45.3	45
$R = CF_3$	1.858	2.028	1.446	35.5	40
R=OCH <sub>3</sub>	1.836	2.040	1.440	40.1	42
R=CN	1.873	2.016	1.448	33.8	39
O H=O R'∽S=O N−CH <sub>3</sub> R					
$R'=CF_3$ $R=SO_2CF_3$	1.960	2.004	1.484	26.7	35
$R'=CH_3$ $R=SO_2CH_3$	1.899	2.050	1.475	36.8	39
$R'=F$ $R=SO_2F$	1.964	1.995	1.480	27.3	35
$R'=CH_3$ $R=H$	1.805	2.178	1.459	53.5	49
R'=F $R=H$	1.840	2.121	1.467	47.8	45
$R'=F$ $R=CH(CH_3)_2$	1.818	2.135	1.471	49.6	45
R <sup>-CH<sub>3</sub></sup>					
R=CH <sub>3</sub>	1.771	2.199	1.448	65.1	52
R=CF <sub>3</sub>	1.809	2.154	1.475	57.2	46
R=OCH <sub>3</sub>	1.771	2.185	1.448	64.5	51
R=CN	1.816	2.146	1.453	55.5	48
O N-CH <sub>3</sub> O	1.770	2 159	1.440	57.0	40
Methylsuccinimide	1.//9	2.158	1.449	57.0	49

Table 3 – Calculated  $\Delta E_{S \rightarrow TS}$  values and Relevant Transition State Geometries

Methyl Cation affinity	MP2/G3large	Experiment <sup>104</sup>	G3 <sup>104</sup>	W1 <sup>104</sup>
(Kcal/mol)		-		
Cl (-)	225.3	228	226.6	227.0
Br (-)	218.0			
CH <sub>3</sub> SO <sub>3</sub> (-)	209.1			
CH <sub>3</sub> OSO <sub>3</sub> (-)	201.2			
FSO <sub>3</sub> (-)	193.2			
CF <sub>3</sub> SO <sub>3</sub> (-)	190.5			
CH <sub>3</sub> CO <sub>2</sub> (-)	238.2			
CF <sub>3</sub> CO <sub>2</sub> (-)	215.8			
CH <sub>3</sub> OCO <sub>2</sub> (-)	227.7			
NCCO <sub>2</sub> (-)	210.1			
CH <sub>3</sub> C(O)NH(-)	262.4			
CF <sub>3</sub> C(O)NH(-)	234.8			
CH <sub>3</sub> OC(O)NH(-)	258.5			
NCC(O)NH(-)	238.1			
(CH <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N(-)	218.2			
$(CF_3SO_2)_2N(-)$	192.8			
(FSO <sub>2</sub> ) <sub>2</sub> N(-)	191.6			
CH <sub>3</sub> SO <sub>2</sub> NH(-)	240.3			
FSO <sub>2</sub> NH(-)	227.0			
CH <sub>3</sub> SO <sub>2</sub> NCH(CH <sub>3</sub> ) <sub>2</sub> (-)	230.6			
	243.7			
U O				
F(-)	258.1	258.1	258.0	258.8
OH (-)	276.0	277	276.9	276.8
SH (-)	246.3	246.9	246.6	247.8
PH <sub>2</sub> (-)	268.6	266.7	268.0	269.5
NH <sub>3</sub>	104.6	105	104.8	105.4
H <sub>2</sub> O	65.4	66.7	66.0	66.5
Mean Absolute Deviation	1.13		0.66	0.89

Table 4 – Methyl Cation Affinity in Experiment and Theory. All values are in kcal/mol.

It is well known that alkylating agents can be activated by factors such as ring strain and inductive effects, and our series was designed to assess these effects on the barrier height to alkylation. The most familiar activated sulfonates are activated with fluorine, and this is for good reason; the replacement of a methyl group with a trifluoromethyl lowers the barrier by 10. kcal/mol between methyl mesylate and methyl triflate, and 10. kcal/mol between methyl MSI and methyl TFSI. Perhaps the most interesting illustration of the activating power of fluorine is seen in the amides, where trifluoroacetamide has a barrier 7.9 kcal/mol lower than acetamide, while succinimide with an extra carboxyl group is a roughly equivalent 8.1 kcal/mol lower. Halogens are often considered to be  $\pi$  electron donating, however the differences we find on barrier height between a fluorine and a trifluormethane group are modest. Oxygen can also act as an electron withdrawing group by way of the inductive effect so it is unsurprising that we find the barrier for dimethylsulfate 5.9 kcal/mol lower than the barrier for methyl mesylate. The effect of ring strain on alkylation is more difficult to assess in our series, as changing the substitution from methyl to primary alkyl is known to increase the barrier to alkylation for S<sub>N</sub>2 reactions. It has been recently proposed that this effect is due to weakening of the electrostatic interactions between the alkyl chain and the incoming nucleophile, although steric repulsion remains a popular explanation among organic chemists.<sup>107</sup> Calculations done at the B3LYP/6-31G(d) level of theory estimate the ring strain in 1,3-propanesultone to be 10. kcal/mol, and 9.0 kcal/mol in TPS (see supporting information for more details). While these species are not used for further analysis, we can conclude that the activation of a 5 membered ring for sulfonates and sulfonimides is not enough to counteract the transition from methyl to primary alkyl.

Conformations in the Sulfonates are degenerate with regard to an S-C bond rotation, however N-S bond rotations of sulfonimides are capable of producing anti, gauche and syn

rotamers with bond rotation. Methyl TFSI and Methyl MSI were found to have minima in the anti and gauche geometries, and transition states were found corresponding to these minima. Methyl FSI did not appear to have a gauche minima, but instead converged toward an eclipsed relationship between the two fluorine substituents this geometry was discarded, and only the anti geometry was used for FSI in this study. Gauche MSI, and TFSI were found to have  $\Delta E^{\dagger}$  values very close in energy to their corresponding anti geometries, but the anti-conformers (lowest minima) were found to lie ~2 kcal/mol and ~6 kcal/mol lower in energy in TFSI and MSI respectively.

In order to assess the degree to which the Hammond postulate is obeyed by these Menshutkin reactions we have taken an approach similar to that used by Schlegel et al. for ionic  $S_N 2$ .<sup>108-110</sup> These authors defined a % bond elongation (%BE) formula for a similar analysis of the geometries of  $S_N 2$  transition states.<sup>110</sup> We use this formula in our analysis as it is given in equation 21.

$$\%BE = 100[r_{TS}(C-X)-r_0(C-X)]/r_0(C-X)$$
(eq. 21)

Where %BE is percent bond elongation,  $r_{TS}(C-X)$  is the transition state C-X bond length, and  $r_0(C-X)$  is the C-X bond length in the isolated species.

We found the correlation between %BE of the transition state and the methyl cation affinity to be strong ( $R^2$ =0.9646, fig. 3B). Schlegel et al. reported that barriers correlate strongly with transition state geometry in the ionic S<sub>N</sub>2 reaction with simple leaving groups derived from a variety of elements including H, N, C and O.<sup>108,109</sup> The dependence of  $\Delta E_{S \to TS}$  on %BE in our own work is even stronger than the correlation with methyl cation affinity ( $R^2$ =0.9813, fig. 3A).
With respect to these dependencies, the full set of nitrogen and oxygen derived leaving groups behave as a single set.

## 3.3.2 On the Fitness of MCA to Describe Inherent Nucleofugality

Perhaps the most unexpected and important finding presented here is the quantitatively different relationship between the  $\Delta E_{S \rightarrow TS}$  and methyl cation affinity between oxygen and nitrogen derived leaving groups. As shown in figure 19, These quantities are strongly correlated within each class of leaving group, but they resolve into distinct groups; with two lines appearing when these energies share the same plot. This discrepancy suggests that there are differences in  $\Delta E_{S \rightarrow TS}$  that derive solely from the electronic structure of the transition states, which are not captured simply by the differences in energy between methyl bonded and ionized leaving groups. In order to better understand this, analysis was extended to the transition state geometry.



Figure 19 – Barrier heights are very well predicted by methyl cation affinities within subsets derived from oxygen and nitrogen, but less so in the full set. Nitrogen leaving groups universally have higher barriers at a given value of MCA.



b)

a)



Figure 20 – Correlations between  $\Delta ES \rightarrow Ts$ , MCA and bond length.  $\Delta E_{S \rightarrow Ts}$  correlates very strongly to methyl leaving group bond length, as a percentage of its value in the parent methylating agent at its ground state (a) This is also true for the MCA (b) which shows that our simulated reactions obey the Hammond postulate.

While MCA and  $\Delta E_{S \to TS}$  both correlate well with %BE (fig. 20), in the transition states of nitrogen derived leaving groups the elongation of the C-X bond is more pronounced relative to shortening of the nascent C-N bond than it was in the oxygen derived leaving groups (fig. 22). This effect is especially noticeable when the bond lengths are compared directly (fig. 22A) but, it remains significant even when the C-N and C-O bonds are normalized via %BE to the lengths of those found in their parent electrophiles (fig. 22B). In nitrogen derived leaving groups the dissociation process of the S<sub>N</sub>2 is ahead of the displacement process, relative to oxygen.



Figure 21 – Dependence of activation energy on theoretical method. At HF/6-31G(d) Methyl FSI and Methylfluorosulfonate have the same activation energy. When the wave function is correlated FSI is found to have a higher activation energy by several kcal/mol. Additional MP2 and CCSD(T) calculations at the MP2(full)/6-31G(d) geometry confirm this trend. Of the leaving groups calculated, only the sulfonimides show a higher activation energy at MP2(full)/6-31G(d) than HF/6-31G(d).



b)



Figure 22 – Nitrogen leaving groups exhibit more extensive C-X bond elongation in their transition states than do oxygen groups. This is very apparent when raw bond lengths are compared (a) But this trend holds up even when %C-X elongation is used to correct for the longer C-N bonds present in the parent alkylating agents (b).

According to the principle of nonperfect synchronization proposed by Bernasconi, a reaction containing two or more fundamental processes will have a higher inherent barrier if

these processes are poorly synchronized than if they are concurrent.<sup>111,112</sup> This clearly describes the difference between the transition states of nitrogen and oxygen leaving groups seen in this work; however, why this difference would lead to systematically higher  $\Delta E_{S \rightarrow TS}$  is difficult to understand. A strong correlation was not observed between the  $\Delta E_{S \rightarrow TS}$  and the order of either of the partial bonds found at the transition state. A classic case of nonperfect synchronization cited by Bernasconi is the late development of resonance stabilization in the deprotonation of carbon acids.<sup>111</sup> An analogy could be drawn between that and the stabilization of the charge on the leaving group. However, we found no indication that the charge is distributed significantly differently between the transition states and the corresponding anions of our methylating agents.

A reasonably strong correlation does exist between the natural charge on the leaving group atom at the transition state, and the  $\Delta E_{S \rightarrow Ts}$  (supporting information). The effect of the nonperfect synchronization in the nitrogen cases could be explained based on this fact, as the nitrogen groups tended to have stronger charges which were more localized on the nitrogen atom. It seems likely that the gap in barriers is explained generally by the fact that the C-N bond had to move further, ionizing almost completely, with less involvement of the nucleophile. Distortions from linearity were observed in the transition states of the nitrogen derived groups which could be explained by this notion. Whereas oxygen derived groups were nearly linear, nitrogen derived groups exhibited N-C-X angles which ranged down to ~173° and correlated moderately well with %BE (supporting information). Additionally, carboxamides and imides formed hydrogen bonds between the carbonyl oxygen and the in-plane hydrogen of the departing methyl fragment. These hydrogen bonds, which appeared to oppose the forward path of the reaction, were not observed in the transition states of esters.





Figure 23 – A correlation is evident between the transition state HOMO energy and the

magnitude of  $\Delta E_{S \rightarrow TS}$ .



Figure 24 – Natural charge on the leaving group atom correlates with  $\Delta E_{S \rightarrow TS}$ .

Additional support for rationalizing these results can be found in the work of Shaik et al. who have developed models for understanding kinetic barriers using concepts from valence bond (VB) theory.<sup>113,114</sup> The central theme of their work is the view of a transition state as an avoided crossing between the ground states and high energy vertically excited states.<sup>113</sup> Ionic character may play a role in one or both of these representations.<sup>113</sup> A correlation diagram can be constructed including the reactant and product complexes in which lines are drawn from the high energy VB states to the product ground states (and vice versa) and the center point is defined as the crossing.<sup>113</sup> The activation energy can then be given as  $\Delta E^{\ddagger} = \Delta E_c$ -B where  $\Delta E_c$  is the energy at the crossing, and B is "quantum mechanical resonance energy" which results from mixing between different valence bond representations of the transition state.<sup>113,114</sup> Factors influencing B were studied for  $S_N 2$  transition states including H<sub>3</sub>(-) and CH<sub>5</sub>(-) and in both cases it was found that B was at its highest (i.e. lowest activation energy) when the angle corresponding to the reaction coordinate was 180°, and decreased with as the angle became more accute.<sup>114</sup> Additionally B decreases when the bond lengths of the forming and breaking bond increase.<sup>114</sup> Both effects were attributed to a destabilizing increase in the amount of ionic character present in the transition state.<sup>114</sup> These findings seem consistent with our own observations, and might imply a causal relationship between the relatively loose and bent transition states of nitrogen centered nucleofuges, and their higher barriers.



Figure 25 – The transition states of nitrogen leaving groups become progressively more bent as C-X bond gets longer. No such trend occurs in oxygen leaving groups.

A separate phenomenon is evident in the difference between sulfonates and sulfonimides. Two of the three sulfonimides (methyl TFSI and methyl FSI) had comparable

barriers to their sulfonate analogues at the HF/6-31G(d) level of theory; the  $\Delta E^{\dagger}$  values of methylfluorosulfonate and methylFSI differed by only 0.03 kcal/mol. When the geometries are reoptimized using MP2(full)/6-31G(d) we find that the difference has expanded to 4.3 kcal/mol. In order to exclude the possibility of an artifact in the MP2 calculation, the barriers to alkylation in methylfluorosulfonate and methylFSI were calculated using two coupled cluster calculations,<sup>115-117</sup> CCSD(T)/6-31G(d) and CCSD(T)/6-31+G(2d,p) at the MP2(full)/6-31G(d) geometry. These calculations affirm the difference, with the CCSD(T)/6-31+G(2d,p) showing a  $\Delta\Delta E^{\dagger}$  of 5.1 kcal/mol, whereas the  $\Delta\Delta E^{\dagger}$  for the MP2/G3large (the single point calculation without vibrational correction) was 5.4 kcal/mol. (fig. 21) We also note that while differences are present in the methyl cation affinities of sulfonates and sulfonimides, they are not systematic. The change in activation energy in sulfonimides that we observe occurs concurrently with a geometric perturbation. The nitrogen atoms of sulfonimide groups are nearly planar at HF/6-31G(d), whereas they become mildly pyramidal at MP2(full)/6-31G(d). A similar, but more dramatic effect is noticeable in sulfonamides, where FSA and MSA are basically tetrahedral at MP2(full)/6-31G(d), and MSA is significantly pyramidal at HF/6-31G(d) (see table 5). When an isopropyl group is introduced onto the sulfonamide in the case of MeiprFSA, the pyramidalization effect is somewhat retarded, but not as much as in the case of Methyl FSI with two sulfonyl groups.



Figure 26 – Some origins in the gap between the nucleofugality of sulfonimide and sulfonate leaving groups can be linked to differences in the electronic structure. Imide spanning orbitals such as HOMO-5 in FSI (Top Left) have better overlap in the planar HF/6-31G(d) geometry ( left) In the MP2(full)/6-31G(d) geometry (Right) HOMO-5 and HOMO-6 mix. Presumably these bonding interactions are opposed by  $n \rightarrow \sigma^*$  interactions localized to one sulfonyl group or the other.

The above observations suggest that orbital interaction between the nitrogen atom and the two sulfonyl groups are preventing a pyramidalization analogous to that which occurs when only one is present. Sulfonyl groups have been well studied, and it is commonly been concluded that hyperconjugative  $n_N \rightarrow \sigma^*$  interactions with the S-O bond, delocalize electrons in the sulfonyl group.<sup>118,119</sup> Additionally, it has been shown that sulfamidates, which have a negatively charged sulfonamide bound to a nitrogen cation, have sulfonyl oxygens that form significantly stronger

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hydrogen bonds than do sulfonamides, or even the usually more basic sulfones and sulfoxides.<sup>120</sup> This suggests an explanation for the drive to pyramidalization as sulfonamide derived species ionize: a pyramidal geometry at nitrogen facilitates better overlap in the  $n\rightarrow\sigma^*$  conjugation, but when two sulfonyl groups are present, ideal interaction with each is not possible. While the size of the sulfonimide wave functions and the relative ambiguity of their frontier orbitals make a full accounting of this phenomenon difficult, a convincing example of this is illustrated in figure 23, in the HOMO-5 and HOMO-6 energy levels of the FSI transition state. In the HF/6-31G(d) structure, HOMO-5 contains a bonding orbital that spans the length of the imide moiety, whereas at MP2(full)/6-31G(d), mixing occurs between HOMO-5 and HOMO-6, destabilizing both orbitals.

	HF/6-31G(d)	MP2(full)/6-31G(d)	
	Dihedral (S-N-R-C)	Dihedral (S-N-R-C)	Angle(S-N-R)
Methyl FSI	178.86	161.00	121.39
Methyl FSA	174.97	126.36	109.31
Methyl MSI	178.83	169.65	121.89
Methyl MSA	132.05	121.27	107.27
Meipr FSA	177.83	134.43	119.9

Table 5 – Transition State Pyramidalization in Sulfonamide Species at HF and MP2 geometries (all values are given in degrees).

A literature precedent does exist for the dependence of intrinsic the barrier of  $S_N 2$ reactions on the leaving group atom. Hoz et al. used G2 derived calculations to study symmetrical anionic  $S_N 2$  reactions and concluded that the intrinsic barrier changes between groups of the periodic table, and stays relatively constant within them, up until the border between metals and non-metals.<sup>121</sup> Nitrogen and oxygen had intrinsic barriers of 29.3 and 19.5 kcal/mol respectively, whereas the halogens clustered near 10 kcal/mol.<sup>121</sup> This inherent difference was then shown to extend to similar  $S_N2$  displacements occurring at nitrogen.<sup>122</sup> In this work we have shown that these findings generalize beyond symmetric, charged variants of the  $S_N2$ , and rationalize them within the context of our systems of interest.

### 3.4 Conclusion

The  $\Delta E_{S \rightarrow TS}$  of nitrogen and oxygen derived leaving groups in the Menshutkin reaction correlate well with the thermodynamic stability of the ions, as determined by MCA, differences exist between the two classes. These differences are rooted in the synchronization of the events inherent in the  $S_N 2$  process, as well as geometric limitations on the efficiency of activating groups on nitrogen. This finding is relevant to recent work on indices of nucleofugality, because it shows that complicating factors may exist which are relevant to the dissociation of a nucleofuge, but are not directly related to the stability of the fully dissociated group.

### 4 Chapter 4: Summary and Future Study

### 4.1 Summary

In summary, two significant findings have come from my research and have been described in this work. The first concerns the effect of triazoles on the conductivity of lithium ion electrolytes.

Model compounds were synthesized which contained increasing numbers of triazoles per ether oxygen. It was found that increasing the number of triazoles in the material increased the glass transition temperature, which was inversely proportional to room temperature conductivity. Increasing the proportion of triazoles also lead to crystallization behavior which enable us to obtain a single crystal X-ray structure of one of our model compounds, 6EO2T. Ab initio calculations showed that tetra coordinate solvent shells containing a triazole have roughly the same energy as those which do not contain triazoles, which led implies another explanation for the effect of triazoles on conductivity.

A second effect triazoles were observed to have on temperature dependant conductivity was the induction of compensation behavior, whereby the Arrhenius pre-exponential factor has an approximately exponential dependence on the activation energy. We rationalize our data by invoking the polarity of the traizole which has been shown in other studies to affect the Arrhenius pre-exponential factor of transport processes in polar liquids. Additionally, our crystal structure showed dipole-dipole interactions between triazole moieties which shows how dipoles are most likely enhancing the glass transition temperature and the activation energy of conductivity. A second study probed the nuclefugality of polyatomic oxygen and nitrogen derived leaving groups. By optimizing the transition states of Menshutkin reactions, and calculating the methyl cation affinities of the same species, we have been able to pinpoint a difference in the nucleofugality between these sets of leaving groups that relies on transition state organization rather than anion stability.

The inherent differences between polyatomic oxygen and nitrogen leaving groups seem to stem from a few different factors. The first factor is the non-linearity of the nitrogen nucleofuge transition states relative to those of oxygen nucleofuges. This distortion has been attributed to a less effective delocalization of electron density, and thus a higher energy in other work. A second difference arises from the preferred geometry of sulfonamides during the leaving process. Sulfonamides show a tendancy to pyramidalize during the leaving process which can most likely be attributed to stabilization via  $n \rightarrow \sigma^*$  interactions from the nitrogen to the sulfur. When a second sulfonyl group is added, pyramidalization becomes less favorable due to the presence of orbitals whose lowest energy results from a planar geometry at nitrogen. The effect of this is that a second sulfonyl group becomes less effective at activating nitrogen as a nucleofuge than the first sulfonyl.

These findings raise additional questions, which might be addressed by other researchers, or myself at a later time in my career. These will be expounded in the two sections that follow.

## 4.2 Future Directions for CUAAC Derived Lithium Single Ion Conductors

The effects exerted by the triazole on the conductivity of lithium ion salt complexes are interesting from a mechanistic standpoint, however the study described here did not demonstrate any useful consequences of this behavior. Frech et al. actually proposed that the synthesis of highly polar electrolyte materials aimed at increasing the Arrhenius pre-exponential term might be a productive way to increase the conductivity of electrolytes for batteries;<sup>72</sup> however, my work has inadvertently shown a limitation of this approach.

However if my explanation for compensation behavior is correct, then the triazoles are activating and impeding the conductivity of electrolyte materials through different mechanisms, and this fact could be manipulated to improve single ion conductor materials. Des Marteau and Borodin et al. showed earlier that ionic correlation is a problem for lithium single ion conductors, affecting the chain to chain transfer time of the lithium ion in these materials as well as the ability of the materials to transport charge through co-diffusion of the lithium with the chain.<sup>20</sup>

A possible mechanism for enhancing the conductivity of lithium electrolytes might be the enhancement of local dipole density in the region of the anion moiety. In order to keep the overall concentration of triazoles in the material relatively low this would mean the introduction of one triazole near an anion moiety (**19**). Materials of nearly identical composition (**22**) but lacking triazoles would be used as controls (Scheme 5).



Scheme 5 – Proposed materials and synthesis for the investigation of triazoles as an activating moiety in lithium single ion conductors.

The PEG starting materials used for materials **19** and **22** could be in the range of  $M_n$ = 300 – 1000, and the study would probably benefit from the synthesis and testing of several chain lengths. Shorter PEG materials are technically easier due to the fact that PEG becomes waxy around  $M_n$ = 600 and its solubility in organic solvents diminishes as molecular weight increases. Additionally blends of **19** and **22** with PEGDME 500 might be worth testing as neat materials would have high concentrations of ions. Internal data to the Baker group has shown that PEGDME 500 complexes with LiTFSI show the highest conductivity when they contain roughly 1 lithium per 32 ether oxygens.<sup>4</sup> The proposed single ion conductors could have several times that concentration of lithium depending on the chain length.

In the event that useful data comes from this project, these systems should be modeled using molecular dynamics simulations in order to better understand the nature of the activation. Modeling lithium ion transport is tricky and requires a specialized polarizable force field. Rather than modeling ourselves, I believe it would be advantageous to approach Oleg Borodin about a collaboration.<sup>17</sup>

#### 4.3 Future Directions for Studies of Nucleofugality in Activated Leaving Groups

In chapter 3 we showed that inherent differences exist between the Nucleofugality of polyatomic oxygen and nitrogen derived leaving groups using computational methods. The obvious next step for this work would be to continue exploring different classes of leaving groups using similar computational methods. The first group that might be fruitful would be polyatomic carbon leaving groups. Polyatomic carbon leaving groups are interesting, because carbon acids are known with pK<sub>a</sub> values of less than 10, however carbon nucleofuges are extremely rare in any other context. Polyatomic carbon leaving groups might prove more viable than expected, or similar problems might be observed to those seen in nitrogen nucleofuges.

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An additional set of leaving groups which might be interesting to look at would be positively charged ammonium leaving groups in comparison with negatively charged borates and borohydrides. These compounds might be an interesting comparision, as the initial electronic structures should be quite similar, however they lead to quite different outcomes. **APPENDICES** 

## 4.4 Appendix 1 – Additional Study of TPS

# Introduction

The Synthesis of TPS was a part of an effort to make stable triple ion type ionic liquids, similar to those of Ohno et al.<sup>124-126</sup> Synthesis of TPS was accomplished in four steps from 1,3 propanesultone, and proceeded mostly through known materials. TPS itself was not a known material and has been fully characterized, including single crystal X-Ray Diffraction. While most of the synthetic work shown is derived from literature protocols,<sup>127-129</sup> the final step required extensive independent optimization and is not a trivial procedure. A variety of bases and running times were tried, however Hünig's base worked best, under the conditions described below. This choice was partially informed by the literature synthesis of similar compounds.<sup>130</sup> X-Ray section is courtesy of Dr. Richard Staples. Single crystal geometric data was compared with a geometric optimization of the TPS structure at MP2(full)/6-31G(d) and the two were found to be in good agreement.

### Synthesis of TPS



Scheme 6 – Synthetic Route from 1,3 Propane sultone to TPS.

# 3-Chloropropane-1-sulfonyl chloride 1<sup>127</sup>

To an oven dried round bottom flask were added 50g (0.41 mol) 1,3-propanesultone, 100g (0.84 mol) thionyl chloride, and 0.25 g dimethylformamide (3.4 mmol). A jacketed condenser and drying tube containing anhydrous calcium chloride pellets were affixed to the round bottomed flask, which was then heated to reflux at 75°C (oil bath temperature). The flask was allowed to reflux over night after which point it was cooled, and a short path distillation apparatus replaced the condenser. Excess thionyl chloride and byproducts were removed by distillation (Vapor T = 73°C). Product **1** was purified by distillation under reduced pressure. Two fractions were collected, the first of which had a  $T_{vap}$ = 60°C at P = 9.7 Torr. This fraction reacted vigorously with water and contained very little hydrogen when analyzed by NMR, this was believed to be mostly a mixture of chlorosulfinic acid, and chlorosulfinic anhydride. A second fraction had a  $T_{vap}$ =105°C at P = 898 mTorr; this proved to be product **1**, which was obtained as a tan liquid in 98% yield (69.5g) and stored under nitrogen. Compound was confirmed by comparison to data in

(1) and publicly available spectra from Sigma Aldrich. <sup>1</sup>H NMR (600MHz) (CDCl<sub>3</sub>) δ= 2.49 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) 3.70 (dd, 2H, CH<sub>2</sub>CH<sub>2</sub>S(O)<sub>2</sub>, J=6.2, 6.2 Hz) 3.84 (dd, 2H, ClCH<sub>2</sub>CH<sub>2</sub>, J=7.5, 7.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ= 30.01, 44.18, 65.06.

### 3-Chloropropane-1-sulfonamide $2^{127}$

To an oven dried three neck round bottom flask were added 10g (0.056 mol) **1** and 250 mL dichloromethane, which had been freshly distilled off of calcium hydride to insure dryness. The flask was cooled on an ice salt bath which was kept at a temperature at or below -5°C for the duration of the reaction. The flask was initially shielded from water through use of a nitrogen line. An aspirator and bubbler were affixed to the flask to facilitate the introduction of ammonia gas. Anhydrous ammonia gas was then bubbled through the reaction for one hour with continuous stirring using a Teflon coated stirbar. White precipitate developed in the flask. After the ammonia cylinder was disconnected, the reaction was allowed to stir for an additional forty five minutes to insure completion. Ammonium chloride was removed by gravity filtration, and rinsed with acetonitrile. Crude product was concentrated on a rotovap. Pure 3-chloropropane-1-sulfonamide was obtained by recrystallization from chloroform in 91% yield (8.2g). The product was a colorless solid. mp= 62 - 65°C <sup>1</sup>H NMR (600 MHz) (CD<sub>3</sub>CN)  $\delta$ = 2.22 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) 3.20 (dd, 2H, CH<sub>2</sub>CH<sub>2</sub>S(O)<sub>2</sub>, J=7.6, 7.6 Hz) 3.72(t, 2H, ClCH<sub>2</sub>CH<sub>2</sub>, J=6.4 Hz) 5.35 (broad singlet, 2H, S(O)<sub>2</sub>NH<sub>2</sub>) <sup>13</sup>C NMR (CD<sub>3</sub>CN)  $\delta$ = 29.82, 45.79, 54.61.

## 1,3-Propanesultam 3<sup>127</sup>

Absolute ethanol (150 mL) was added to a rigorously dried round bottom flask and sparged with dry nitrogen for 5 - 10 min to remove oxygen. The solvent was cooled on an ice bath, and then 5.08g NaH in 60% dispersion with mineral oil (0.127 mol NaH) were added to the ethanol in pieces. Once alkoxide generation was complete 20g (0.127 mol) 2 were added as a solution in 625 mL absolute ethanol. The reaction mixture was protected with a condenser and a calcium chloride drying tube, and refluxed overnight until high conversion was evident in NMR. Ethanol was removed by rotovap, and reaction mixture was dissolved in chloroform and filtered, then dried over sodium sulfate. Sodium chloride produced in the reaction was washed with additional chloroform. Product was purified by distillation under reduced pressure (T<sub>vap</sub>= 179 °C, P=629 mTorr) however mineral oil codistilled. Mineral oil was removed by washing the product with hexanes. Product was then dissolved in dichloromethane and dried over Sodium Sulfate to remove excess water. Product was obtained in 79% yield (12.1g) as a light yellow oil. Method used is similar to that of King et al. (127). Product confirmed by comparison to data of Askin et al. (128) <sup>1</sup>H NMR (500 MHz) (CDCl<sub>3</sub>)  $\delta$ = 2.39 (p, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, J=7.2 Hz) 3.03 (t, 2H, NHCH<sub>2</sub>CH<sub>2</sub>, J=7.6 Hz) 3.36 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>, J= 6.9 Hz) 4.55 (broad singlet, 1H,  $SO_2NHCH_2$ ) <sup>13</sup>C NMR  $\delta$ = 24.10, 42.36, 46.73.

## N-triflylpropanesultam (TPS) 4

0.5 g (4.1 mmol) **3** where added to a rigorously dry round bottom flask equipped with a teflon coated stir bar. A 10 mL addition funnel was added and placed on a nitrogen line to shield the reaction from water. The round bottom flask was cooled on a dry ice acetone bath. Following

cooling, 1.5 mL (8.9 mmol) of trifluoromethanesulfonyl anhydride were added to 8 mL of freshly distilled rigorously dried dichloromethane, which were added to the flask and allowed to cool. An aliquot of 0.71 mL (4.1 mmol) diisopropylethylamine was then added to an additional 8 mL of dichloromethane in the addition funnel. The resulting solution was added dropwise over a period of roughly five minutes. After the reagents were combined, the bath was removed, and the flask allowed to equilibrate to room temperature. The color of the solution gradually darkened until it was an opaque jet black. The reaction was allowed to stir for roughly 48 hours, after which, 10 mL distilled water were added. The biphasic mixture was transferred to a separatory funnel, and after separation the aqueous phase was extracted with 2 aliquots of 15 mL dichloromethane. The organic phase was dried of sodium sulfate, and concentrated with a rotovap to yield darkly colored and tarry crude solids. The crude product was sublimed (p = 668mTorr, Bath  $T = 100^{\circ}$ C) to yield a white crystalline solid in 65% yield (0.67g). Crystals were grown for single crystal X-Ray study by slow evaporation from Toluene. Compound is previously unknown. mp=111-115°C HRMS [M-H]<sup>-</sup> Calculated: 251.9612 Measured: 251.9604 ppm: -3.2. <sup>1</sup>H NMR (CD<sub>3</sub>OD) (600 MHz)  $\delta$ = 2.50 (p, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, J= 6.6 Hz) 3.66 (t, 2H, SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, J=7.3) 4.00 (t, 2H, (SO<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, J=6.8 Hz) <sup>13</sup>C NMR, (600 MHz) (CD<sub>3</sub>CN)  $\delta = 19.10, 48.88, 50.15, 119.47$  (q, CF<sub>3</sub>, J= 323 Hz) IR (KCl Pellet) cm<sup>-1</sup> = 3022, 2965, 1478, 1403, 1387, 1347, 1325, 1283, 1237, 1204, 1177, 1149, 1133, 1070, 1045, 1014, 980, 851, 727, 661, 600, 575, 552, 499, 449, 427, 403.

## **Crystallography of TPS**

### **Experimental Section**

A colorless plate crystal with dimensions  $0.30 \ge 0.27 \ge 0.03$  mm was mounted on a Nylon loop using very small amount of paratone oil.

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 1.0° per frame for 30 s. The total number of images was based on results from the program COSMO<sup>74</sup> where redundancy was expected to be 4.0 and completeness to 0.83 Å to 100%. Cell parameters were retrieved using APEX II software<sup>75</sup> and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software<sup>76</sup> which corrects for Lp. Scaling and absorption corrections were applied using SADABS<sup>77</sup> multiscan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F2, SHELXL-975, which are incorporated in OLEX2.<sup>77</sup>

The structure was solved in the space group P21/c(no. 14). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. All drawings are done at 50% ellipsoids.

Acknowledgement. The CCD based x-ray diffractometer at Michigan State University were upgraded and/or replaced by departmental funds.

Table 6 -	Crystal	Data and	Structure	Refinement for	TPS
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Identification code	nej413		
Empirical formula	$C_4H_6F_3NO_4S_2$		
Formula weight	253.22		
Temperature/K	173.0		
Crystal system	monoclinic		
Space group	$P2_1/c$		
a/Å	13.9496(7)		
b/Å	5.9882(3)		
c/Å	10.5155(5)		
α/°	90		
β/°	92.202(3)		
$\gamma/^{\circ}$	90		
Volume/Å <sup>3</sup>	877.74(7)		
Z	4		
$\rho_{calc} mg/mm^3$	1.916		
m/mm <sup>-1</sup>	6.009		
F(000)	512.0		
Crystal size/mm <sup>3</sup>	$0.296 \times 0.269 \times 0.034$		
$2\Theta$ range for data collection	6.34 to 144.042°		
Index ranges	$\textbf{-16} \leq h \leq 16,  \textbf{-7} \leq k \leq 7,  \textbf{-11} \leq \textbf{l} \leq 12$		
Reflections collected	6768		
Independent reflections	1675[R(int) = 0.0742]		
Data/restraints/parameters	1675/0/127		
Goodness-of-fit on F <sup>2</sup>	1.140		
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0681, wR_2 = 0.1893$		
Final R indexes [all data]	$R_1 = 0.0812, wR_2 = 0.1993$		
Largest diff. peak/hole / e Å <sup>-3</sup> 0.85/-0.45			



b)

a)



Figure 27 – The crystal structure of TPS. A view of a single molecule is shown in part a with thermal elipsoids shown at 50% probability. The packing along the b axis of the crystal is also shown (b).

Table 7 – Comparison Between the Crystal Geometry of TPS and Geometry at MP2(full)/6-

31G(d) (Bond Lengths)

Dona Lenguis for 115.				
Atom	Atom	Experiment/Å	Calculated/Å	Deviation/Å
<b>S</b> 1	03	1.410(4)	1.450	0.040
<b>S</b> 1	O4	1.412(5)	1.455	0.043
<b>S</b> 1	N1	1.621(5)	1.653	0.032
S1	C4	1.843(6)	1.840	-0.003
S2	<b>O</b> 1	1.426(5)	1.454	0.028
S2	O2	1.428(5)	1.459	0.031
S2	N1	1.715(4)	1.754	0.039
S2	C1	1.757(5)	1.789	0.032
F1	C4	1.303(8)	1.330	0.027
F2	C4	1.297(8)	1.334	0.037
F3	C4	1.310(8)	1.345	0.035
N1	C3	1.483(7)	1.475	-0.008
C1	C2	1.524(8)	1.519	-0.005
C2	C3	1.517(8)	1.528	0.011

# Bond Lengths for TPS.

Table 8 - Comparison Between the Crystal Geometry of TPS and Geometry at MP2(full)/6-

31G(d) (Bond Angles)

Bond Angles for TPS.				
Atom	Atom	Experiment/°	Calculated/°	<b>Deviation</b> /°
<b>S</b> 1	O4	121.8(3)	124.8	3.0
<b>S</b> 1	N1	108.3(2)	109.0	0.7
<b>S</b> 1	C4	107.0(3)	106.1	-0.9
<b>S</b> 1	N1	109.9(3)	107.4	-2.5
<b>S</b> 1	C4	105.1(3)	105.6	0.5
<b>S</b> 1	C4	103.1(3)	101.6	-1.5
S2	O2	118.0(3)	121.4	3.4
S2	N1	108.0(3)	110.3	2.3
S2	C1	111.4(3)	112.0	0.6
S2	N1	110.0(3)	108.6	-1.4
S2	C1	113.8(3)	109.7	-4.1
S2	C1	92.6(2)	90.4	-2.2
N1	S2	122.0(3)	123.8	1.8
N1	<b>S</b> 1	124.0(4)	121.7	-2.3
N1	S2	113.9(4)	114.5	0.6
C1	S2	103.9(4)	104.4	0.5
C2	C1	107.4(4)	106.0	-1.4
C3	C2	104.7(4)	104.4	-0.3
C4	<b>S</b> 1	110.4(4)	110.2	-0.2
C4	F3	107.4(6)	109.1	1.7
C4	<b>S</b> 1	108.9(5)	109.1	0.2
C4	F1	110.5(6)	109.8	-0.7
C4	F3	110.2(6)	109.1	-1.1
C4	<b>S</b> 1	109.3(4)	109.4	0.1
	ngles for '   Atom   S1   S2   S2 <td>AtomAtomS1O4S1N1S1C4S1N1S1C4S1C4S1C4S1C4S2O2S2N1S2C1S2C1S2C1S1S2N1S2N1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C2C1C3C2C4S1C4F3C4S1</td> <td>hybrid stor TPS.AtomExperiment/°S1O4<math>121.8(3)</math>S1N1<math>108.3(2)</math>S1C4<math>107.0(3)</math>S1C4<math>107.0(3)</math>S1C4<math>105.1(3)</math>S1C4<math>103.1(3)</math>S2O2<math>118.0(3)</math>S2O2<math>118.0(3)</math>S2C1<math>111.4(3)</math>S2C1<math>111.4(3)</math>S2C1<math>113.8(3)</math>S2C1<math>113.8(3)</math>S2C1<math>92.6(2)</math>N1S2<math>122.0(3)</math>N1S1<math>124.0(4)</math>N1S2<math>103.9(4)</math>C1S2<math>103.9(4)</math>C2C1<math>107.4(4)</math>C3C2<math>104.7(4)</math>C4S1<math>110.4(4)</math>C4F3<math>107.4(6)</math>C4F3<math>107.4(6)</math>C4F3<math>107.4(6)</math>C4F3<math>107.4(6)</math>C4S1<math>108.9(5)</math>C4F3<math>102.6(6)</math>C4S1<math>109.3(4)</math></td> <td>Atom Atom Experiment/° Calculated/°S1O4<math>121.8(3)</math><math>124.8</math>S1N1<math>108.3(2)</math><math>109.0</math>S1C4<math>107.0(3)</math><math>106.1</math>S1N1<math>109.9(3)</math><math>107.4</math>S1C4<math>105.1(3)</math><math>105.6</math>S1C4<math>103.1(3)</math><math>101.6</math>S2O2<math>118.0(3)</math><math>121.4</math>S2N1<math>108.0(3)</math><math>110.3</math>S2C1<math>111.4(3)</math><math>112.0</math>S2C1<math>113.8(3)</math><math>109.7</math>S2C1<math>92.6(2)</math><math>90.4</math>N1S2<math>122.0(3)</math><math>123.8</math>N1S1<math>124.0(4)</math><math>121.7</math>N1S2<math>103.9(4)</math><math>104.4</math>C2C1<math>107.4(4)</math><math>106.0</math>C3C2<math>104.7(4)</math><math>104.4</math>C4S1<math>107.4(6)</math><math>109.1</math>C4S1<math>107.4(6)</math><math>109.1</math>C4S1<math>108.9(5)</math><math>109.1</math>C4S1<math>100.3(4)</math><math>109.4</math></td>	AtomAtomS1O4S1N1S1C4S1N1S1C4S1C4S1C4S1C4S2O2S2N1S2C1S2C1S2C1S1S2N1S2N1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C1S2C2C1C3C2C4S1C4F3C4S1	hybrid stor TPS.AtomExperiment/°S1O4 $121.8(3)$ S1N1 $108.3(2)$ S1C4 $107.0(3)$ S1C4 $107.0(3)$ S1C4 $105.1(3)$ S1C4 $103.1(3)$ S2O2 $118.0(3)$ S2O2 $118.0(3)$ S2C1 $111.4(3)$ S2C1 $111.4(3)$ S2C1 $113.8(3)$ S2C1 $113.8(3)$ S2C1 $92.6(2)$ N1S2 $122.0(3)$ N1S1 $124.0(4)$ N1S2 $103.9(4)$ C1S2 $103.9(4)$ C2C1 $107.4(4)$ C3C2 $104.7(4)$ C4S1 $110.4(4)$ C4F3 $107.4(6)$ C4F3 $107.4(6)$ C4F3 $107.4(6)$ C4F3 $107.4(6)$ C4S1 $108.9(5)$ C4F3 $102.6(6)$ C4S1 $109.3(4)$	Atom Atom Experiment/° Calculated/°S1O4 $121.8(3)$ $124.8$ S1N1 $108.3(2)$ $109.0$ S1C4 $107.0(3)$ $106.1$ S1N1 $109.9(3)$ $107.4$ S1C4 $105.1(3)$ $105.6$ S1C4 $103.1(3)$ $101.6$ S2O2 $118.0(3)$ $121.4$ S2N1 $108.0(3)$ $110.3$ S2C1 $111.4(3)$ $112.0$ S2C1 $113.8(3)$ $109.7$ S2C1 $92.6(2)$ $90.4$ N1S2 $122.0(3)$ $123.8$ N1S1 $124.0(4)$ $121.7$ N1S2 $103.9(4)$ $104.4$ C2C1 $107.4(4)$ $106.0$ C3C2 $104.7(4)$ $104.4$ C4S1 $107.4(6)$ $109.1$ C4S1 $107.4(6)$ $109.1$ C4S1 $108.9(5)$ $109.1$ C4S1 $100.3(4)$ $109.4$

# Estimation of Ring Strain in $TPS^{\dagger}$

Ring strain was calculated for 1,3-Propanesultone and N-Triflylpropanesultam using the following homeodesmotic reactions seen in figure 25.



Figure 28 – Homeodesmotic reactions used to calculate the strain energy of sulfonyl herterocycles.

Structures were minimized at the B3LYP/6-31G(d) level of theory in GAMESS using the DFT=B3LYP keyword (as opposed to the slightly different DFT=B3LYP1 version). Ring strain was estimated to be 10.2 kcal/mol in 1,3-Propanesultone, and 9.0 kcal/mol in N-triflylpropanesultam.

<sup>&</sup>lt;sup>†</sup> This page is a republication of data from the supporting information of Spahlinger, G.; Jackson J. E. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24559 – 24569. It has been republished with permission from the PCCP Owner Societies. The original article may be found online at the following link: <u>http://pubs.rsc.org/en/content/articlelanding/2014/cp/c4cp03741c#!divAbstract</u>

### 4.5 Appendix 2 – Spectal Data and Geometric Results from Computations

This section contains annotated proton and carbon 13 NMR spectra from the compounds appearing in this work which had not previously been synthesized. Labels have been added to the spectra to show how the <sup>1</sup>H and <sup>13</sup>C atoms in the proposed structure correspond to the lines in the specra. Additionally, output geometries have been provided for geometric optimizations of compounds whose electronic structures or energies were analyzed in chapters 2 and 3 at the relevant levels of theory. All structures described were first optimized in C<sub>1</sub> symmetry. The structures described in Chapter 3 were scrutinized carefully for possible symmetry, and rerun in the highest Abelian point group they seemed to be capable of converging to. Point groups given for this set should be considered the highest symmetry in the converged structures. Structures in chapter 2 were not rerun to confirm symmetry. Although some structures appeared to be converging to higher symmetries, the point group in these calculations is assumed to be C<sub>1</sub>.



 ${}^{1}\mathrm{H}$ 

















 $^{1}\mathrm{H}$ 



<sup>13</sup>C

1H



Figure 31 - 6EO1T









Figure 32 - 8EO1T

<sup>1</sup>H (Methanol d<sub>4</sub>)





Figure 33 - N-Triflylpropanesultam (TPS)
MP2(full)/6-31G(d) Geometries and Energies of Simulated Solvent Shells from G3MP2 Calculations with and without a Bound Lithium Cation.

Table	9 -	Glyme, Energy	<b>:</b> -307.87678	
С	6	0.641616	0.399513	0.00000
С	6	-0.641616	-0.399513	0.00000
0	8	1.708579	-0.531639	0.00000
0	8	-1.708579	0.531639	0.00000
С	6	2.965284	0.120394	0.00000
С	6	-2.965284	-0.120394	0.00000
Н	1	0.677787	1.045847	-0.889262
H	1	0.677787	1.045847	0.889261
H	1	-0.677787	-1.045847	-0.889262
H	1	-0.677787	-1.045847	0.889262
Н	1	3.090045	0.749078	0.891947
Н	1	3.726478	-0.660232	0.00000
H	1	3.090045	0.749080	-0.891945
H	1	-3.726478	0.660232	-0.000001
Н	1	-3.090045	-0.749080	-0.891946
Н	1	-3.090046	-0.749078	0.891947

Table 10 - Glyme-(Li+), Complex Energy: -315.22669

С	6	-0.714327	-0.912652	0.242036
С	6	0.714326	-0.912652	-0.242036
0	8	-1.313495	0.329428	-0.182073
0	8	1.313495	0.329428	0.182072
С	6	-2.748016	0.336643	-0.002444
С	6	2.748017	0.336643	0.002445
Li	3	0.00000	1.676941	0.00000
Н	1	-1.258219	-1.755075	-0.198903
Н	1	-0.765347	-0.984161	1.334828
Η	1	1.258219	-1.755075	0.198903
Н	1	0.765346	-0.984162	-1.334828
Н	1	-3.101517	1.313806	-0.326419
Н	1	-3.196376	-0.442621	-0.621636
Н	1	-2.996115	0.173268	1.049427
Н	1	3.101517	1.313806	0.326419
Н	1	3.196376	-0.442621	0.621638
Η	1	2.996116	0.173267	-1.049426

Table 11 - Glyme + DME, Energy: -462.40188

С	6	-2 749443	-1 340694	-0 536394
C	6	-1 845247	0 557657	0 498539
$\circ$	8	-1 561499	-0 671012	-0 151179
C	6		1 2697/1	0.700503
	0	-0.549944	1 766724	0.790393
0	8	-0.01991/	1./55/34	-0.42/915
С	6	1.225974	2.402627	-0.211788
С	6	1.555618	-1.936414	0.955154
0	8	2.121614	-0.852544	0.236125
С	6	1.757107	-0.922555	-1.137342
Н	1	-2.445309	-2.270828	-1.016968
Н	1	-3.380290	-1.570933	0.333246
Н	1	-3.333940	-0.739570	-1.245194
Н	1	-2.473329	1.195884	-0.140051
Н	1	-2.388798	0.373054	1.439571
Н	1	-0.747625	2.102893	1.485212
Н	1	0.158084	0.580776	1.269913
Н	1	1.575174	2.741666	-1.187951
Н	1	1.110864	3.273207	0.449661
Н	1	1.954637	1.710349	0.223281
Н	1	1.851353	-1.813572	1.998419
Н	1	0.462493	-1.933950	0.875308
Н	1	1.939401	-2.898355	0.586107
Н	1	2.253954	-0.090417	-1.636383
Н	1	2.102877	-1.866106	-1.583124
Н	1	0.674491	-0.827695	-1.259858

Table 12 - Glyme-(Li+)-DME, Energy: -469.796041

0	8	1.066685	-1.317252	0.133927
Н	1	3.150957	-1.263785	0.121744
С	6	2.299057	-0.700824	-0.276792
С	6	1.017221	-2.716841	-0.205224
С	6	2.299057	0.700822	0.276794
0	8	1.066687	1.317252	-0.133929
С	6	1.017225	2.716841	0.205221
Li	3	-0.327147	0.000001	-0.000004
0	8	-2.199003	-0.000005	-0.000004
С	6	-3.007060	-0.604703	1.026706
С	6	-3.007069	0.604707	-1.026700
С	1	2.356559	-0.692824	-1.372322
С	1	2.356555	0.692822	1.372325
С	1	3.150959	1.263782	-0.121739
С	1	0.044734	3.083454	-0.118649
С	1	1.129833	2.850156	1.285009
С	1	1.809283	3.253161	-0.322316
С	1	-2.326282	-1.034589	1.760995
С	1	-3.634586	0.153422	1.502159
С	1	-3.632522	-1.389995	0.594504
С	1	-2.326297	1.034583	-1.761001
С	1	-3.634614	-0.153408	-1.502142
С	1	-3.632511	1.390008	-0.594486
С	1	0.044727	-3.083452	0.118643
С	1	1.809276	-3.253163	0.322315
С	1	1.129831	-2.850155	-1.285011

Table	13	-	Glyme	+	Glyme,	H	Energy:	-615.	75824
~	C		4 2	11,	0.0.1	1	00000	0	

С	6	-4.341091	1.058400	-0.559869
0	8	-3.010677	0.628004	-0.331164
С	6	-2.943020	-0.775380	-0.130095
С	6	-1.485976	-1.103986	0.095384
0	8	-1.373980	-2.501374	0.279006
С	6	-0.036362	-2.860332	0.593603
С	6	0.046079	2.870331	0.614345
0	8	1.356048	2.502812	0.207230
С	6	1.506729	1.096719	0.214243
С	6	2.925895	0.777455	-0.193210
0	8	3.028982	-0.637976	-0.215615
С	6	4.327327	-1.058707	-0.595780
Н	1	-4.303736	2.138367	-0.704640
Н	1	-4.764751	0.586363	-1.456178
Н	1	-4.988097	0.828745	0.297166
Н	1	-3.539637	-1.079653	0.742065
Н	1	-3.320992	-1.319710	-1.007591
Н	1	-0.899511	-0.775052	-0.773864
Н	1	-1.119520	-0.556357	0.976275
Н	1	-0.004200	-3.949457	0.634485
Н	1	0.668541	-2.496106	-0.164540
Н	1	0.264864	-2.450036	1.566771
Н	1	-0.023711	3.953379	0.508708
Н	1	-0.720045	2.387047	-0.005489
Н	1	-0.133035	2.596278	1.663031
Н	1	1.306699	0.679006	1.212786
Н	1	0.812237	0.625964	-0.493121
Н	1	3.135992	1.205549	-1.184065
Н	1	3.636004	1.214618	0.523637
Н	1	4.322004	-2.148990	-0.587054
Н	1	4.582947	-0.704949	-1.603428
Н	1	5.087476	-0.693743	0.107663

Table 14 - Glyme-(Li+)-Glyme, Energy: -623.18874

0	8	1.435719	1.094065	0.743055
Н	1	3.519662	1.027054	0.741968
С	6	2.659720	0.350627	0.666653
С	6	1.342860	1.869429	1.950054
С	6	2.659693	-0.350662	-0.666707
Н	1	-3.519644	0.742019	-1.027058
0	8	1.435677	-1.094080	-0.743068
Н	1	-2.703904	1.489831	0.374338
С	6	1.342759	-1.869436	-1.950066
Li	3	0.00000	0.000010	0.00009
0	8	-1.435694	-0.743058	1.094081
С	6	-2.659703	-0.666676	0.350655
С	6	-1.342800	-1.950062	1.869432
Н	1	2.703921	-0.374332	1.489800
Н	1	2.703877	0.374296	-1.489855
Н	1	3.519622	-1.027102	-0.742051
Н	1	0.379570	-2.376120	-1.921319
Н	1	1.397517	-1.218377	-2.828058
Н	1	2.148514	-2.607238	-1.983832
Н	1	-2.703894	-1.489819	-0.374309
С	6	-2.659708	0.666688	-0.350626
Η	1	-3.519638	-0.742012	1.027088
Н	1	-0.379614	-1.921332	2.376123
Н	1	-2.148562	-1.983819	2.607227
Η	1	-1.397566	-2.828049	1.218368
Н	1	0.379678	2.376129	1.921341
Н	1	2.148630	2.607217	1.983784
Η	1	1.397641	1.218373	2.828046
0	8	-1.435700	0.743080	-1.094054
С	6	-1.342821	1.950082	-1.869409
Н	1	-0.379635	1.921361	-2.376102
Н	1	-1.397595	2.828071	-1.218349
Н	1	-2.148584	1.983827	-2.607203

Table 15 - 4-Methoxymethyl-1,2,3-Triazole, Energy: -394.90167

Ν	7	-1.400475	-1.159229	-0.000539
С	6	-0.370011	-0.272576	0.000493
С	6	-0.870993	1.014156	0.000896
Ν	7	-2.211938	0.822928	0.000018
N	7	-2.547851	-0.485243	-0.000823
Н	1	-2.954152	1.513956	-0.000173
С	6	1.054389	-0.709306	0.001325
0	8	1.855637	0.460258	-0.001432
С	6	3.236678	0.138116	-0.000326
Н	1	-0.398586	1.983562	0.001496
Н	1	1.263739	-1.326018	0.889093
Н	1	1.263351	-1.330141	-0.883638
Н	1	3.778956	1.083722	-0.002585
Н	1	3.511352	-0.437107	0.893653
Н	1	3.511718	-0.441570	-0.891301

Table 16 - 4-Methoxymethyl-1,2,3-Triazole-(Li+), Energy: -402.25682

Ν	7	-0.748360	0.891048	0.000537
С	6	-0.438595	-0.433561	0.000293
С	6	-1.624808	-1.145612	-0.000347
Ν	7	-2.572931	-0.181222	-0.000413
Ν	7	-2.069208	1.059394	0.000087
Н	1	-3.585893	-0.288401	-0.000820
С	6	0.989591	-0.878671	0.000805
0	8	1.813108	0.300586	-0.000487
С	6	3.219080	-0.035633	-0.000383
Li	3	0.889872	1.977293	-0.000023
Н	1	-1.857168	-2.200787	-0.000718
Н	1	1.218020	-1.477338	0.891258
Н	1	1.218006	-1.479360	-0.888279
Н	1	3.767261	0.904859	-0.001684
Н	1	3.463803	-0.608513	0.897069
Н	1	3.463385	-0.610704	-0.896543

Table	17 -	- 4-MeOMe-1,2,3	-Triazole +	DME, Energy:	-549.42683
N	7	-1.429055	-2.334785	-0.213231	
Ν	7	-2.513129	-1.686233	0.262130	
С	6	-2.353225	-0.341364	0.267825	
С	6	-1.079933	-0.169356	-0.238747	
Ν	7	-0.544086	-1.387436	-0.522410	
С	6	-0.345684	1.104280	-0.480087	
0	8	-1.042440	2.126430	0.218988	
С	6	-0.395996	3.378770	0.061215	
Н	1	-3.310039	-2.234331	0.567173	
С	6	2.948523	-0.675802	-0.997105	
0	8	2.794781	0.041361	0.220960	
С	6	2.523161	-0.850849	1.292064	
Н	1	-3.098676	0.353758	0.620231	
Н	1	0.692176	1.009627	-0.133128	
Н	1	-0.317370	1.331146	-1.558621	
Н	1	-0.976701	4.105607	0.629767	
Н	1	0.630667	3.347288	0.447406	
Н	1	-0.366387	3.682953	-0.993782	
Н	1	3.150771	0.064293	-1.772844	
Н	1	3.796195	-1.372543	-0.937548	
Н	1	2.037363	-1.233289	-1.241116	
Н	1	2.388063	-0.238898	2.185001	
Н	1	1.614469	-1.432251	1.099155	
Н	1	3.363555	-1.540582	1.452310	

Table 18 - 4-MeOMe-1,2,3-Triazole-(Li+)-DME, Energy: -556.82511

Ν	7	-2.539124	-1.949097	-0.000040
С	6	-3.019176	-0.684398	0.000349
С	6	-1.876720	0.095925	0.000135
Ν	7	-0.801333	-0.734624	-0.000250
Ν	7	-1.199674	-2.005040	-0.000456
Н	1	-3.059282	-2.824051	-0.000077
С	6	-1.682903	1.578916	0.000047
0	8	-0.270987	1.827292	0.000068
С	6	0.018535	3.238513	-0.00003
Li	3	0.909566	0.284648	-0.000422
0	8	2.623103	-0.446236	-0.000385
С	6	3.919960	0.170810	0.00008
С	6	2.713420	-1.884791	0.000483
Н	1	-4.075021	-0.455724	0.000654
Н	1	-2.134743	2.036726	-0.889266
Н	1	-2.134755	2.036726	0.889354
Н	1	1.102886	3.334805	-0.000099
Н	1	-0.396201	3.707122	-0.896251
Н	1	-0.396049	3.707166	0.896291
Н	1	3.764095	1.248972	-0.000711
Н	1	4.473732	-0.123227	0.895538
Н	1	4.474708	-0.124252	-0.894577
Н	1	1.694002	-2.269694	0.000043
Н	1	3.242174	-2.223238	-0.894524
Н	1	3.241042	-2.222245	0.896534

Table	19 -	4-MeOMe-1,2,3-	-Triazole +	Glyme, Energy:	-702.78713
С	6	-2.478803	0.196905	0.000124	
Ν	7	-2.675589	-1.148750	0.000155	
Ν	7	-3.984193	-1.397440	-0.000791	
Ν	7	-4.589200	-0.190870	-0.001408	
С	6	-3.703818	0.834167	-0.000883	
С	6	-1.120907	0.810048	0.001080	
0	8	-1.300824	2.218779	0.000641	
С	6	-0.052026	2.888165	0.001377	
Н	1	-5.602680	-0.157436	-0.002181	
С	6	5.178466	1.082167	-0.001527	
0	8	4.557816	-0.190072	-0.000020	
С	6	3.146629	-0.079314	-0.000972	
С	6	2.586424	-1.483697	0.000728	
0	8	1.176231	-1.363264	-0.000139	
С	6	0.534779	-2.634239	0.001279	
Н	1	-3.984840	1.875212	-0.001233	
Н	1	-0.549808	0.483306	0.881383	
Н	1	-0.548367	0.482880	-0.878110	
Н	1	-0.267295	3.957131	0.000951	
Н	1	0.535852	2.634824	0.893783	
Н	1	0.537148	2.634363	-0.890041	
Н	1	6.254884	0.909111	-0.000673	
Н	1	4.904722	1.660143	-0.894656	
Н	1	4.903727	1.662741	0.889610	
Н	1	2.790691	0.463721	0.887762	
Н	1	2.791692	0.461177	-0.891654	
Н	1	2.940179	-2.027253	-0.887519	
Н	1	2.939294	-2.024740	0.890859	
Н	1	-0.537682	-2.441753	0.000655	
Н	1	0.812900	-3.212544	-0.889785	
Н	1	0.812215	-3.210216	0.894064	

Table 20 - 4-MeOMe-1,2,3-Triazole-(Li+)-Glyme, Energy: -710.21590

Ν	7	3.299133	-1.391946	-0.956158
С	6	3.591498	-0.208090	-0.370007
С	6	2.358265	0.260171	0.045327
Ν	7	1.416276	-0.653765	-0.310829
Ν	7	1.988611	-1.679782	-0.936820
Н	1	3.932742	-2.054501	-1.397485
С	6	1.955881	1.489216	0.793761
0	8	0.539626	1.618758	0.644349
С	6	0.018763	2.733839	1.385323
Li	3	-0.458915	0.035883	0.005440
С	6	-2.808212	-1.373665	0.162244
С	6	-3.177147	-0.098152	-0.549501
0	8	-1.977638	0.392572	-1.160896
0	8	-1.715303	-1.058415	1.034457
С	6	-1.273437	-2.203077	1.783635
С	6	-2.208439	1.547679	-1.979974
Н	1	4.596253	0.182418	-0.300227
Н	1	2.206739	1.401335	1.859884
Н	1	2.459727	2.379743	0.396824
Н	1	-1.055442	2.744697	1.208254
Н	1	0.218827	2.609596	2.453753
Н	1	0.464224	3.666621	1.028300
Н	1	-3.660560	-1.749429	0.741491
Н	1	-2.497670	-2.142975	-0.556713
Н	1	-3.939135	-0.295526	-1.313337
Н	1	-3.565006	0.647846	0.156383
Н	1	-0.442063	-1.867561	2.401161
Н	1	-2.083851	-2.568302	2.420152
Н	1	-0.940878	-2.996768	1.107638
Н	1	-1.238828	1.850570	-2.371514
Н	1	-2.878488	1.294219	-2.805819
Н	1	-2.644500	2.357974	-1.386545

# MP2(full)/cc-pVDZ and MP2(full)/cc-pVDZ(Li-C) Geometries and Energies of Heterocycle Ligands With and Without a Bound Lithium Cation

0.000000	0 121440	
0.749274 -0.749274	-0.485761 -0.485761	0.000000 0.000000 0.000000
er-Li, Energ	gy: -83.5630	7
0.000031 0.764905 -0.765251 0.000031	-0.336917 -0.933476 -0.932955 1.520589	0.000000 0.000000 0.000000 0.000000
,2,3-Triazo	ole, Energy:	-241.56224
1.044324 -0.193485 -1.068095 -0.442347 0.860325 -2.083561 2.037764 -0.508419	0.501034 1.133670 0.091906 -1.103068 -0.851509 0.114839 0.942418 2.173217	-0.000241 -0.000047 0.000259 -0.000554 0.000522 0.000445 -0.000272 -0.000039
,2,3-Triazo	ole-(Li+), Er	ergy: -248.91584
0.440542 1.352631 0.577164 -0.719560 -0.810911 0.869483 -2.670590 0.616999	1.154937 0.102820 -1.012504 -0.714571 0.624864 -1.990796 -0.043960 2.227966	-0.000143 0.003212 0.000923 -0.005628 -0.004825 0.001092 0.013027 0.000868
	0.749274 -0.749274 r-Li, Energe 0.000031 0.764905 -0.765251 0.000031 ,2,3-Triaze 1.044324 -0.193485 -1.068095 -0.442347 0.860325 -2.083561 2.037764 -0.508419 ,2,3-Triaze 0.440542 1.352631 0.577164 -0.719560 -0.810911 0.869483 -2.670590 0.616999 2.439403	0.749274 -0.485761 -0.749274 -0.485761 r-Li, Energy: -83.5630 0.000031 -0.336917 0.764905 -0.933476 -0.765251 -0.932955 0.000031 1.520589 ,2,3-Triazole, Energy: 1.044324 0.501034 -0.193485 1.133670 -1.068095 0.091906 -0.442347 -1.103068 0.860325 -0.851509 -2.083561 0.114839 2.037764 0.942418 -0.508419 2.173217 ,2,3-Triazole-(Li+), Er 0.440542 1.154937 1.352631 0.102820 0.577164 -1.012504 -0.719560 -0.714571 -0.810911 0.624864 0.869483 -1.990796 -2.670590 -0.043960 0.616999 2.227966 2.439403 0.063643

Table 25 - 2H-1,2,3-Triazole, Energy: -241.57086

Ν	7	-5.976577	-0.550631	0.130350
С	6	-5.111302	-0.381201	1.159728
С	6	-3.907648	0.144143	0.661051
Ν	7	-4.020073	0.303132	-0.680253
Ν	7	-5.259169	-0.126571	-0.907476
Н	1	-5.646359	-0.130723	-1.846358
Н	1	-5.402483	-0.642304	2.174118
Н	1	-2.986913	0.411958	1.173376

Table 26 - 2H-1,2,3-Triazole-(Li+), Energy: -248.89669

Ν	7	1.199898	-0.705115	0.00004
С	6	1.194157	0.647546	0.000047
С	6	-0.131225	1.099654	-0.000038
Ν	7	-0.945933	0.004518	-0.000018
Ν	7	-0.084359	-1.017186	-0.000028
Н	1	-0.382425	-1.991780	-0.000011
Li	3	-2.923887	0.071075	0.000093
H	1	2.124979	1.209522	0.000097
H	1	-0.535731	2.110316	-0.000127

Table 27 - Pyrazole, Energy: -225.55411

С	6	0.654429	0.959481	-0.000192
С	6	-0.740447	0.955062	0.000069
С	6	-1.090029	-0.415639	-0.000031
N	7	-0.001328	-1.216843	-0.000180
N	7	1.026709	-0.352978	0.000301
Н	1	1.971089	-0.721745	0.000245
Н	1	1.386806	1.764111	-0.000753
H	1	-1.398705	1.820833	0.000690
Н	1	-2.080583	-0.867880	-0.000105

Table 28 - Pyrazole-(Li+), Energy: -232.89344

С	6	-1.217051	-0.611604	0.000197
С	6	-1.158148	0.782397	0.000080
С	6	0.212738	1.085759	-0.000036
Ν	7	0.963468	-0.052213	-0.000100
Ν	7	0.066118	-1.054316	-0.000320
Н	1	0.373333	-2.022973	0.000834
Li	3	2.914486	-0.000124	0.000342
Н	1	-2.053066	-1.308393	-0.000238
Н	1	-1.994736	1.476575	0.000309
Н	1	0.698675	2.061555	-0.000436

#### Table 29 - Pyridizine, Energy: -263.52492

С	6	0.696581	1.190468	-0.000002
С	6	1.326496	-0.064773	0.000023
Ν	7	0.673061	-1.243688	-0.000030
N	7	-0.671684	-1.244414	-0.000011
С	6	-1.326431	-0.066219	0.000028
С	6	-0.697895	1.189698	-0.000009
Н	1	1.281260	2.114235	-0.000010
Н	1	2.417781	-0.151384	0.000076
Н	1	-2.417621	-0.154020	0.000083
Н	1	-1.283570	2.112838	-0.000105

#### Table 30 - Pyridazine-(Li+), Energy: -270.88587

С	6	1.382482	-0.698373	0.000895
С	6	0.139661	-1.352618	-0.000433
Ν	7	-1.021672	-0.674691	-0.001894
Ν	7	-1.021853	0.674247	-0.001973
С	6	0.139225	1.352606	-0.000421
С	6	1.382268	0.698777	0.000941
Li	3	-2.890148	0.00035	0.005989
H	1	2.311177	-1.274006	0.002050
H	1	0.046091	-2.441530	-0.000496
H	1	0.045262	2.441481	-0.000539
H	1	2.310773	1.274705	0.002194

Table 31 - Pyrimidine, Energy: -263.55995

С	6	-0.624273	1.192792	0.00048
С	6	-1.359606	0.001461	-0.000036
С	6	-0.627197	-1.191328	0.000042
Ν	7	0.719664	-1.210423	0.000049
С	6	1.311700	-0.001570	-0.000229
С	7	0.722287	1.208875	0.000044
Н	1	-1.123628	2.168175	0.000024
H	1	-2.452145	0.002845	-0.000120
Н	1	-1.128450	-2.165720	0.000023
Н	1	2.406827	-0.002597	0.000472

Table 32 - Pyrimidine-(Li+), Energy: -270.89194

С	6	-0.421013	1.190117	-0.000404
С	6	0.973287	1.133241	0.000080
С	6	1.562278	-0.139436	0.000478
Ν	7	0.829983	-1.269276	0.000146
С	6	-0.495668	-1.113893	-0.000487
Ν	7	-1.174769	0.061071	-0.000653
Li	3	-3.159188	0.046440	0.001982
Н	1	-0.950703	2.148084	-0.000676
Н	1	1.573161	2.045580	0.000190
Н	1	2.649698	-0.264078	0.001150
Н	1	-1.094388	-2.031644	-0.001061

Table 33 - 1-Methoxyethyl-1,2,3-Triazole, Energy: -434.13854

Ν	7	-2.660389	-1.028133	-0.078747
С	6	-2.946969	0.220350	-0.546344
С	6	-1.865096	1.061496	-0.304891
N	7	-0.964418	0.250844	0.318990
N	7	-1.439767	-1.007626	0.449009
С	6	0.392084	0.541698	0.754764
С	6	1.403030	-0.099487	-0.186760
0	8	2.678581	0.262705	0.288964
С	6	3.700606	-0.323394	-0.493869
Н	1	-3.899815	0.448900	-1.018944
Н	1	-1.670943	2.113062	-0.500751
Н	1	0.525358	1.632683	0.771686
Н	1	0.523186	0.150360	1.773181
H	1	1.257391	-1.197239	-0.187071
H	1	1.235656	0.266025	-1.221524
Н	1	4.661577	-0.005079	-0.068069
Н	1	3.643722	-1.428308	-0.473810
H	1	3.645302	0.008371	-1.548570

Table 34 - 1-Methoxyethyl-1,2,3-Triazole-(Li+), Energy: -441.52051

Ν	7	-2.057818	-1.335981	0.013517
С	6	-2.866208	-0.301990	0.366757
С	6	-2.162886	0.896430	0.251910
Ν	7	-0.926551	0.516189	-0.174355
Ν	7	-0.877527	-0.820097	-0.321138
С	6	0.243421	1.323340	-0.518017
С	6	1.487218	0.940146	0.268827
0	8	1.973659	-0.354630	-0.128106
С	6	3.329910	-0.554034	0.329461
Li	3	0.799762	-1.791957	-0.573712
Н	1	-3.894759	-0.466432	0.680158
Н	1	-2.428250	1.937013	0.424134
H	1	-0.007664	2.369653	-0.292033
H	1	0.425982	1.237932	-1.600883
Н	1	2.266529	1.690722	0.050081
Н	1	1.284353	0.943852	1.354829
Н	1	3.630291	-1.567554	0.032150
Н	1	3.997577	0.179810	-0.147675
Н	1	3.381930	-0.456208	1.425441

Table 35 - 4-Methoxymethyl-1,2,3-Triazole, Energy: -394.95807

Н	7	-1.405969	-1.162912	-0.002175
С	6	-0.368718	-0.277303	0.002012
С	6	-0.871700	1.018914	0.002962
Ν	7	-2.217947	0.822034	0.000423
Ν	7	-2.549332	-0.484718	-0.003212
Н	1	-2.959968	1.515442	-0.000579
С	6	1.063089	-0.706968	0.005110
0	8	1.858254	0.461184	-0.005453
С	6	3.234027	0.139878	-0.001272
H	1	-0.398628	1.995599	0.005670
Н	1	1.271713	-1.324555	0.902202
Н	1	1.270209	-1.340610	-0.880984
Н	1	3.791413	1.086312	-0.009800
H	1	3.515183	-0.436320	0.901277
Н	1	3.516596	-0.453294	-0.892292

Table	36		4–№	lethox	ymet	chyl	-1,2	2,3-	-Tri	azo	le-	(Li+	·),
Energy	7 <b>:</b> -	-402	2.3	34226									

Ν	7	0.749594	0.893723	0.001300
С	6	0.436171	-0.436000	0.000579
С	6	1.631230	-1.150827	-0.000871
Ν	7	2.578102	-0.177254	-0.000871
Ν	7	2.070335	1.059228	0.000317
С	1	3.592543	-0.285424	-0.001846
С	6	-0.998122	-0.877404	0.001926
0	8	-1.815983	0.302844	-0.001866
С	6	-3.217923	-0.034976	-0.000558
Li	3	-0.889380	1.974875	0.00007
H	1	1.870559	-2.211297	-0.001787
H	1	-1.225006	-1.484285	-0.892289
H	1	-1.225061	-1.478373	0.900141
Н	1	-3.778754	0.907854	-0.003961
Н	1	-3.466332	-0.618427	-0.900680
Н	1	-3.466300	-0.612070	0.903671

## MP2(full)/6-31G(d) Geometries and Energies of $S_{\rm N}2$ Transition States in Cartesian Coordinates $^{\ddagger}$

Table	37	-	Methyl	Mesylate,	C <sub>s</sub> ,	Energ	dA:	-758.5314	:5
S			16.0	1.15939	-0.4	5877	0	.00000	
0			8.0	0.34332	0.8	3946	0	.00000	
С			6.0	-1.56443	0.2	5102	0	.00000	
С			6.0	2.83434	0.1	3571	0	.00000	
Н			1.0	3.49926	-0.7	2871	0	.00000	
N			7.0	-3.39174	-0.2	9315	0	.00000	
Н			1.0	-1.77836	1.3	0659	0	.00000	
Н			1.0	-3.42903	-1.3	1310	0	.00000	
Н			1.0	-3.88908	0.0	3958	-0	.82614	
Н			1.0	-3.88908	0.0	3958	0	.82614	
Н			1.0	-1.34932	-0.2	4862	-0	.92968	
Н			1.0	-1.34932	-0.2	4862	0	.92968	
Н			1.0	2.99358	0.7	3491	-0	.89588	
Н			1.0	2.99358	0.7	3491	0	.89588	
0			8.0	0.95553	-1.2	1641	-1	.25308	
0			8.0	0.95553	-1.2	1641	1	.25308	

<sup>&</sup>lt;sup>\*</sup> This appendix is a republication of data from the supporting information of Spahlinger, G.; Jackson J. E. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24559 – 24569. It has been republished with permission from the PCCP Owner Societies. The original article may be found online at the following link: <u>http://pubs.rsc.org/en/content/articlelanding/2014/cp/c4cp03741c#!divAbstract</u>

Table	38	-	Dimeth	ylsulfate,	C <sub>1</sub> , Energ	gy: -833.56441
С О S О С О О N H H H H H H H H H H H H			$ \begin{array}{c} 6.0\\ 8.0\\ 16.0\\ 8.0\\ 6.0\\ 8.0\\ 7.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1$	-3.23105 -2.38762 -1.09812 -0.48480 0.29671 -0.26375 -1.64534 1.08021 -4.02379 -3.65542 -2.66470 -0.70677 0.81085 0.70385 0.74849 2.09771 0.83764	0.53029 1.60405 1.06888 2.41333 3.22502 0.29334 0.37490 4.04056 1.00238 -0.00086 -0.16271 3.34643 2.29328 3.95738 4.99383 4.06770 3.49160	$\begin{array}{c} 0.56815\\ 0.11677\\ -0.78967\\ -1.11775\\ 0.48992\\ 0.14471\\ -1.94913\\ 2.04906\\ 1.14786\\ -0.28628\\ 1.19552\\ 0.86179\\ 0.65588\\ -0.18691\\ 2.19684\\ 1.98137\\ 2.87422 \end{array}$
Table	39	_	Methyl	Triflate,	C <sub>1</sub> , Energ	gy: -1055.61053
S			16.0	2.35501	0.45850	0.38755
0			Q ()	2 11595	1 891/5	0 1/070
0			0.0	2.11000	1.07143	0.14970
$\cap$			8.0	2.82997	0.01740	1.69291
0			8.0 8.0 8.0	2.82997 3.09460	0.01740	1.69291 -0.77547
C			8.0 8.0 8.0 6.0	2.82997 3.09460 3.00518	0.01740 -0.19380 0.78181	1.69291 -0.77547 -2.45037
C C			8.0 8.0 6.0 6.0	2.82997 3.09460 3.00518 0.69775	0.01740 -0.19380 0.78181 -0.29530	1.69291 -0.77547 -2.45037 0.20277
C C F			8.0 8.0 6.0 6.0 9.0	2.82997 3.09460 3.00518 0.69775 0.20757	0.01740 -0.19380 0.78181 -0.29530 -0.03145	1.69291 -0.77547 -2.45037 0.20277 -1.03440
C C F F			8.0 8.0 6.0 6.0 9.0 9.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358	1.69291 -0.77547 -2.45037 0.20277 -1.03440 1.10085
C C F F			8.0 8.0 6.0 6.0 9.0 9.0 9.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989 0.74865	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358 -1.62525	1.69291 -0.77547 -2.45037 0.20277 -1.03440 1.10085 0.34790
C C F F F N			8.0 8.0 6.0 6.0 9.0 9.0 9.0 7.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989 0.74865 2.95037	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358 -1.62525 1.74648	1.69291 -0.77547 -2.45037 0.20277 -1.03440 1.10085 0.34790 -4.15797
C C F F F N H			8.0 8.0 6.0 6.0 9.0 9.0 9.0 7.0 1.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989 0.74865 2.95037 2.06759	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358 -1.62525 1.74648 0.29666	1.69291 -0.77547 -2.45037 0.20277 -1.03440 1.10085 0.34790 -4.15797 -2.65665
C C F F F N H H			8.0 8.0 6.0 9.0 9.0 9.0 7.0 1.0 1.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989 0.74865 2.95037 2.06759 3.01260	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358 -1.62525 1.74648 0.29666 1.70453	1.69291 -0.77547 -2.45037 0.20277 -1.03440 1.10085 0.34790 -4.15797 -2.65665 -1.89490
C C F F F N H H H			8.0 8.0 6.0 6.0 9.0 9.0 9.0 7.0 1.0 1.0 1.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989 0.74865 2.95037 2.06759 3.01260 3.92737	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358 -1.62525 1.74648 0.29666 1.70453 0.28607	1.69291 -0.77547 -2.45037 0.20277 -1.03440 1.10085 0.34790 -4.15797 -2.65665 -1.89490 -2.70168
C C F F F N H H H			8.0 8.0 6.0 9.0 9.0 9.0 7.0 1.0 1.0 1.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989 0.74865 2.95037 2.06759 3.01260 3.92737 3.77193	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358 -1.62525 1.74648 0.29666 1.70453 0.28607 2.34060	1.69291 -0.77547 -2.45037 0.20277 -1.03440 1.10085 0.34790 -4.15797 -2.65665 -1.89490 -2.70168 -4.26976
ССF FF NH H H H			8.0 8.0 6.0 9.0 9.0 9.0 7.0 1.0 1.0 1.0 1.0	2.82997 3.09460 3.00518 0.69775 0.20757 -0.15989 0.74865 2.95037 2.06759 3.01260 3.92737 3.77193 2.12777	0.01740 -0.19380 0.78181 -0.29530 -0.03145 0.20358 -1.62525 1.74648 0.29666 1.70453 0.28607 2.34060 2.34956	$\begin{array}{c} 1.69291 \\ -0.77547 \\ -2.45037 \\ 0.20277 \\ -1.03440 \\ 1.10085 \\ 0.34790 \\ -4.15797 \\ -2.65665 \\ -1.89490 \\ -2.70168 \\ -4.26976 \\ -4.18146 \end{array}$

Table	40	—	Methy	lfluorosul	fonate,	C1,	Energy:	-818.40115
S O O C F N H H H H H H			16.0 8.0 8.0 6.0 9.0 7.0 1.0 1.0 1.0 1.0 1.0	-0.45745 -0.73479 -0.66826 0.82628 1.03360 -1.54639 1.26902 0.19039 0.87039 2.01551 2.04944 0.42573 1.43614	-0.387 1.032 -0.990 -0.823 0.025 -1.118 0.868 -0.544 0.977 -0.415 1.524 1.390 0.188	51 62 18 80 95 87 01 94 87 91 87 54 37	1.66574 1.46126 2.96502 0.99410 -0.74241 0.67800 -2.48653 -1.09193 -0.26719 -0.75708 -2.48154 -2.72549 -3.22871	
Table	41	-	Methy	l TFSI (ar	nti) C <sub>1</sub> ,	Enei	rgy: -19	919.67259
C N S S O O O O C F F F C F F F N H			$ \begin{array}{c} 6.0\\ 7.0\\ 16.0\\ 8.0\\ 8.0\\ 8.0\\ 8.0\\ 9.0\\ 9.0\\ 9.0\\ 9.0\\ 9.0\\ 9.0\\ 9.0\\ 9$	-0.66116 0.76965 2.28825 0.29060 1.13996 -1.16191 2.38041 3.32762 0.53203 0.13186 1.81216 -0.21007 2.19505 3.34478 1.95190 1.19723 -2.06015 0.12249	-0.617 0.642 0.070 2.158 2.844 2.088 -1.126 1.087 3.018 4.289 2.984 2.984 2.984 2.984 2.412 -0.589 -1.194 0.384 -1.493 -1.848 -1.321	32 48 20 36 61 93 67 54 29 32 67 39 44 96 20 80 01	0.85893 0.24164 0.04048 -0.14497 -1.10654 -0.30589 0.87802 0.03777 1.46019 1.35324 1.83089 2.40979 -1.67185 -1.98500 -2.54919 -1.74320 1.46472 1.08911	
H H H			1.0 1.0 1.0	-0.94777 -1.08444 -1.93545	-1.321 0.120 -0.569 -2.097	36 37 63	1.58802 -0.12863 2.44612	
н Н			1.0 1.0	-2.05019 -2.98197	-2./11	45 49	0.92037	

Table	42	_	Methyl	TFSI	(ga	uche)	C1,	Energy:	-1919.67076
С			6.0	-3.879	907	-1.83	3954	0.392	61
Ν			7.0	-2.469	911	-0.60	5098	-0.407	28
S			16.0	-1.050	)71	-1.3	7594	-0.824	92
S			16.0	-3.052	201	0.69	9649	-1.121	57
0			8.0	-2.154	151	1.31	L547	-2.085	50
0			8.0	-4.469	939	0.4	7677	-1.414	06
0			8.0	-1.053	368	-2.60	5542	-0.129	75
0			8.0	-0.713	369	-1.28	3112	-2.237	27
С			6.0	-3.071	L61	1.81	L762	0.336	87
F			9.0	-3.584	159	2.99	9752	-0.023	00
F			9.0	-1.840	005	2.00	090	0.819	39
F			9.0	-3.841	L54	1.29	9557	1.314	48
С			6.0	0.212	236	-0.31	7542	0.061	72
F			9.0	0.298	384	0.84	1929	-0.460	56
F			9.0	1.396	577	-0.98	3774	-0.050	52
F			9.0	-0.105	592	-0.27	7843	1.359	79
Ν			7.0	-5.282	215	-3.00	0105	1.172	90
Н			1.0	-3.121	L77	-2.59	9309	0.531	90
Н			1.0	-4.038	398	-1.09	9180	1.149	24
Н			1.0	-4.423	346	-1.70	5888	-0.532	94
Н			1.0	-5.075	590	-3.24	1306	2.141	98
Н			1.0	-5.362	234	-3.8	7042	0.645	56
Η			1.0	-6.190	)44	-2.53	3716	1.150	92
Table	43	_	Methyl	FSI,	C1,	Energ	у: -	-1445.25	353
С			6.0	-1.163	332	-0.5	7013	0.766	93
Ν			7.0	0.237	789	0.55	5663	-0.097	00
S			16.0	1.791	L97	0.08	3379	-0.024	32
S			16.0	-0.163	317	2.09	9227	-0.432	70
0			8.0	0.699	968	2.72	2452	-1.403	57
0			8.0	-1.610	089	2.11	L438	-0.535	46
0			8.0	2.690	28	1.07	7449	0.525	32
0			8.0	1.760	582	-1.28	3644	0.456	71
F			9.0	0.153	377	2.82	2452	0.976	51
F			9.0	2.160	558	-0.02	2105	-1.586	60
Ν			7.0	-2.554	162	-1.69	9089	1.582	84
Н			1.0	-0.500	527	-1.41	L217	0.627	50
Н			1.0	-1.079	967	0.02	2351	1.661	79
Н			1.0	-1.830	)34	-0.24	1811	-0.013	61
Н			1.0	-2.209	974	-2.15	5762	2.421	95
Н			1.0	-2.869	906	-2.42	L160	0.932	91
H			1.0	-3.366	568	-1.13	3160	1.845	25

Table	44	_	Methyl	MSI	(anti	i) (	C1,	Ener	gy:	-1325.52993
С			6.0	-0.90	188	-0	.77	026	1.	01037
Ν			7.0	0.57	282	0	.37	880	0.	16851
S			16.0	2.13	085	0	.04	956	0.	55812
S			16.0	0.15	441	1	.72	961	-0.	65742
0			8.0	1.05	762	1	.97	950	-1.	79024
0			8.0	-1.29	032	1	.58	083	-0.	90549
0			8.0	2.83	856	1	.23	403	1.	06923
0			8.0	2.04	988	-1	.15	505	1.	40218
С			6.0	0.36	046	3	.08	876	0.	47314
Н			1.0	0.07	588	4	.00	057	-0.	05455
Н			1.0	1.40	447	3	.11	933	0.	78265
Н			1.0	-0.29	198	2	.92	828	1.	33173
С			6.0	2.92	255	-0	.41	104	-0.	96597
Н			1.0	3.96	082	-0	.65	469	-0.	73449
Н			1.0	2.85	635	0	.43	160	-1.	65300
Н			1.0	2.40	695	-1	.28	081	-1.	37289
N			7.0	-2.27	604	-1	.85	552	1.	74458
Н			1.0	-0.22	703	-1	.59	409	0.	85233
Н			1.0	-0.78	324	-0	.19	108	1.	91016
Н			1.0	-1.51	230	-0	.38	219	0.	21102
Н			1.0	-1.93	884	-2	.36	085	2.	56473
Н			1.0	-2.59	571	-2	.54	128	1.	06005
Н			1.0	-3.08	017	-1	.29	313	2.	02451

Methyl MSI	(gauche)	C <sub>1</sub> , Energ	y: -1325.52302
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	06292       0         13425       -0         16294       -1         73729       -0         53612       -1         33955       0         86008       -1         21158       -2         22517       0         22517       0         20811       0         59679       1         10811       0         59679       1         25597       -1         19857       0         36516       0         39700       1         30954       -0         53776       1         33659       0         55415       1	. 37339 .29456 .81098 .04374 .27794 .85874 .57131 .73173 .91248 .19195 .30094 .80065 .42786 .53264 .39992 .73627 .98395 .35027 .21640 .52860 .87953 .30200 .09124
Methyl MSA,	C <sub>1</sub> , Ener	gy: -738.	64549
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	56876       0         57481       -0         45781       -2         41401       -2         10748       -2         5136       -2         74138       0         37337       0         1501       1         49913       -0         07242       1         55369       0         24395       0         56209       -0         3270       -3         40051       -2	.30504 .52460 .10706 .56768 .54485 .85423 .91736 .40479 .04049 .68266 .87005 .30348 .89449 .17789 .93872 .54249
	Methyl MSI 6.0 -1.06 7.0 0.47 16.0 0.77 16.0 0.18 8.0 0.20 8.0 -0.97 8.0 1.17 8.0 -0.33 6.0 1.60 1.0 1.47 1.0 2.50 1.0 1.66 6.0 2.19 1.0 1.94 1.0 2.43 1.0 3.02 7.0 -2.50 1.0 -0.35 1.0 -1.13 1.0 -1.60 1.0 -2.29 1.0 -2.68 1.0 -3.36 Methyl MSA, 6.0 -1.30 7.0 0.19 16.0 0.23 8.0 1.34 8.0 -1.14 6.0 -1.30 7.0 -2.61 1.0 -0.49 1.0 -1.70 1.0 -2.45 1.0 -1.70 1.0 -2.45 1.0 -1.54 1.0 1.54 1.0 0.52 1.0 1.54 1.0 -0.21	Methyl MSI (gauche) 6.0 -1.06997 -1.0 7.0 0.47826 0.1 16.0 0.77880 -0.4 16.0 0.18542 1.7 8.0 0.20869 2.5 8.0 -0.97466 1.8 8.0 1.17581 -1.8 8.0 -0.33913 -0.2 6.0 1.60757 2.2 1.0 1.47421 3.2 1.0 2.50235 2.1 1.0 1.66760 1.5 6.0 2.19991 0.4 1.0 1.94467 1.4 1.0 2.43613 -0.0 1.0 3.02871 0.2 7.0 -2.50727 -2.1 1.0 -0.35207 -1.8 1.0 -1.13760 -0.3 1.0 -1.60266 -0.8 1.0 -2.29563 -2.6 1.0 -2.68341 -2.9 1.0 -3.36317 -1.6 Methyl MSA, C <sub>1</sub> , Ener 6.0 -1.30251 -0.6 7.0 0.19773 0.6 1.0 -2.68341 -2.9 1.0 -3.36317 -1.6 Methyl MSA, C <sub>1</sub> , Ener 6.0 -1.30251 -0.6 7.0 0.19773 0.6 1.0 -2.61886 -1.7 1.0 -0.49270 -1.3 1.0 -1.38337 0.1 1.0 -1.70728 -0.4 8.0 1.34285 -0.4 8.0 1.34285 -0.4 8.0 -1.14025 0.1 6.0 0.55593 2.0 7.0 -2.61886 -1.7 1.0 -1.38337 0.1 1.0 -1.70728 -0.4 1.0 -2.45959 -2.0 1.0 -2.69837 -2.5 1.0 -3.51020 -1.2 1.0 1.15436 0.5 1.0 0.52943 1.9 1.0 1.54139 2.4 1.0 -0.21478 2.4 1.0 -0.2	<pre>Methyl MSI (gauche) C<sub>1</sub>, Energy 6.0 -1.06997 -1.06292 0 7.0 0.47826 0.13425 -0 16.0 0.77880 -0.46294 -1 16.0 0.18542 1.73729 -0 8.0 0.20869 2.53612 -1 8.0 -0.97466 1.83955 0 8.0 1.17581 -1.86008 -1 8.0 -0.33913 -0.21158 -2 6.0 1.60757 2.22517 0 1.0 1.47421 3.27192 1 1.0 2.50235 2.10811 0 1.0 1.66760 1.59679 1 6.0 2.19991 0.40893 -2 1.0 1.94467 1.46254 -2 1.0 2.43613 -0.02782 -3 1.0 3.02871 0.25597 -1 7.0 -2.50727 -2.19857 0 1.0 -0.35207 -1.86516 0 1.0 -1.13760 -0.39700 1 1.0 -1.60266 -0.80954 -0 1.0 -2.29563 -2.63776 1 1.0 -2.68341 -2.93659 0 1.0 -3.36317 -1.65415 1</pre> Methyl MSA, C <sub>1</sub> , Energy: -738. 6.0 -1.30251 -0.66876 0 7.0 0.19773 0.67481 -0 16.0 0.23801 0.45781 -2 8.0 1.34285 -0.41401 -2 8.0 -1.14025 0.10748 -2 6.0 0.55593 2.05136 -2 7.0 -2.61886 -1.74138 0 1.0 -0.49270 -1.37337 0 1.0 -1.70728 -0.49913 -0 1.0 -2.69837 -2.55369 0 1.0 -3.51020 -1.24395 0 1.0 -3.51020 -

Table	47	-	Methyl	FSA,	C1,	Energy	<b>:</b> -79	8.522	40
C N S O O F N H H H H H H H H			$ \begin{array}{c} 6.0\\ 7.0\\ 16.0\\ 8.0\\ 9.0\\ 7.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1$	-1.19 0.43 -0.17 0.77 -1.32 -0.91 -2.69 -0.47 -1.35 -1.50 -2.68 -2.78 -3.51 1.27	943 162 642 783 823 158 177 170 666 325 539 620 082	-0.776 0.089 1.203 2.082 0.659 2.237 -1.514 -1.424 0.211 -0.975 -1.428 -2.502 -1.025 0.451	97 35 - 01 - 82 - 10 - 33 25 99 50 - 93 83 90 -	0.162 -0.879 -1.803 -2.471 -2.522 -0.712 0.948 0.625 0.561 -0.850 1.965 0.710 0.594 -0.421	278 21 23 23 203 29 582 29 18 54 29 18 54 273 284 21
Table	48	_	Meipr	FSA,	C1,	Energy:	-916	.0363	7
С N S O O F N H H H H H C H C C H			$ \begin{array}{c} 6.0\\ 7.0\\ 16.0\\ 8.0\\ 9.0\\ 7.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1$	-0.55 1.14 0.58 1.54 -0.56 -0.17 -2.05 0.16 -0.71 -0.82 -2.05 -2.15 -2.86 2.39 2.42 2.41 3.61 3.32	910 889 564 941 224 324 491 204 244 453 987 684 788 504 687 952 997 047	-0.577 0.042 0.938 1.659 0.271 2.192 -1.121 -1.093 0.477 -0.993 -0.830 -2.136 -0.706 0.424 -0.248 1.858 0.116 2.022	98 59 - 73 - 35 - 75 - 75 - 70 909 - 85 73 87 085 73 87 085 73 87 - 45 69 - 41	0.511 0.610 1.763 2.590 -2.380 -0.931 1.389 1.128 0.665 -0.446 2.368 1.355 0.930 0.073 0.930 0.073 0.943 0.599 -0.783 1.199	.73 .79 .48 .26 .87 .48 .55 .55 .55 .55 .55 .55 .55 .55 .55 .5
H H H H			1.0 1.0 1.0 1.0 1.0	1.54 2.42 4.53 3.64 3.58	541 414 926 292 153	2.066 2.570 0.261 0.772 -0.919	61 46 - 29 - 79 - 58 -	1.222 -0.228 -0.205 -1.655 -1.130	14 83 46 555

Table	49	-	Methyl	Acetate,	C <sub>s</sub> , Energ	y: -323.880	097
С О О С N Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н			$ \begin{array}{c} 6.0\\ 6.0\\ 8.0\\ 8.0\\ 6.0\\ 7.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1$	2.71505 1.21986 0.83498 0.46339 -1.52119 -3.22174 3.29119 -1.01488 -3.90645 -3.38394 -3.38394 -1.55695 -1.55695 2.96968 2.96968	-0.28053 0.01855 1.21455 -1.02504 -0.37468 0.20938 0.64546 0.58559 -0.54807 0.78874 0.78874 -0.93747 -0.93747 -0.87697 -0.87697	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ -0.82474\\ 0.82474\\ -0.91937\\ 0.91937\\ -0.88004\\ 0.88004 \end{array}$	
Table	50	_	Methyl	Trifluor	pacetate,	C <sub>s</sub> , Energy:	-620.97437
С			6.0	-2.74774	0.29836	0.00000	
C C			6.0 6.0	-2.74774 -1.25478	0.29836 -0.07407	0.00000 0.00000	
С С О			6.0 6.0 8.0	-2.74774 -1.25478 -0.94712	0.29836 -0.07407 -1.27898	0.00000 0.00000 0.00000	
C C O O			6.0 6.0 8.0 8.0	-2.74774 -1.25478 -0.94712 -0.50185	0.29836 -0.07407 -1.27898 0.96265	0.00000 0.00000 0.00000 0.00000	
C C O C			6.0 6.0 8.0 8.0 6.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691	0.29836 -0.07407 -1.27898 0.96265 0.36815	0.00000 0.00000 0.00000 0.00000 0.00000	
C C O C N			6.0 6.0 8.0 8.0 6.0 7.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000	
C C O C N H			6.0 6.0 8.0 8.0 6.0 7.0 1.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000	
C C O C N H H			6.0 6.0 8.0 6.0 7.0 1.0 1.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108 3.86299	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941 0.62802	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000	
C C O C N H H H			6.0 6.0 8.0 6.0 7.0 1.0 1.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108 3.86299 3.41129	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941 0.62802 -0.73166	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 -0.82442	
C C O C N H H H			6.0 6.0 8.0 6.0 7.0 1.0 1.0 1.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108 3.86299 3.41129 3.41129	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941 0.62802 -0.73166 -0.73166	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 -0.82442 0.82442	
C C O C N H H H H H			6.0 6.0 8.0 6.0 7.0 1.0 1.0 1.0 1.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108 3.86299 3.41129 3.41129 1.48885	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941 0.62802 -0.73166 -0.73166 0.91979	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ -0.82442\\ 0.82442\\ -0.92412 \end{array}$	
C C O C N H H H H H H			6.0 6.0 8.0 6.0 7.0 1.0 1.0 1.0 1.0 1.0	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108 3.86299 3.41129 3.41129 1.48885 1.48885 1.48885	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941 0.62802 -0.73166 0.91979 0.91979	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ -0.82442\\ 0.82442\\ -0.92412\\ 0.9242\\ 0.924\\ 0.9242\\ 0.924\\$	
С О О С И Н Н Н Н Н Н Н Н Н Н Е			$ \begin{array}{c} 6.0\\ 6.0\\ 8.0\\ 8.0\\ 7.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 9.0\\ 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 $	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108 3.86299 3.41129 3.41129 1.48885 1.48885 -3.55230	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941 0.62802 -0.73166 -0.73166 0.91979 0.91979 -0.77981	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.82442\\ 0.82442\\ 0.82442\\ 0.92412\\ 0.92412\\ 0.92412\\ 0.00000\\ 1.00000\\ 0.0000\\ 0.0000\\ 0.000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.000\\ 0.0$	
С С О О С N Н Н Н Н Н Н Н F F			$ \begin{array}{c} 6.0\\ 6.0\\ 8.0\\ 8.0\\ 6.0\\ 7.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 9.0\\ 9.0\\ 9.0\\ 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 $	-2.74774 -1.25478 -0.94712 -0.50185 1.43691 3.21694 1.02108 3.86299 3.41129 3.41129 1.48885 1.48885 1.48885 -3.55230 -3.05977	0.29836 -0.07407 -1.27898 0.96265 0.36815 -0.16221 -0.62941 0.62802 -0.73166 -0.73166 0.91979 0.91979 -0.77981 1.03794	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ -0.82442\\ 0.82442\\ -0.92412\\ 0.92412\\ 0.92412\\ 0.92412\\ 0.92412\\ 0.9221\\ 1.09021\\ 1.09021\\ \end{array}$	

Table	51	-	Methyl	Cyanoform	mate,	$C_{s}$ ,	Energy:	-376.72778
C O O C N H H H H H H N			6.0 6.0 8.0 6.0 7.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1	-2.69698 -1.24349 -0.93291 -0.49173 1.44202 3.24599 1.05365 3.87723 3.45214 3.45214 1.49444 1.49444 -3.85118	0.22 -0.12 -1.32 0.92 0.33 -0.14 -0.65 0.65 -0.72 0.90 0.90 0.47	2415 1266 1631 2582 5379 4958 5397 5248 1505 1505 1505 0351 0351 0351 7500	0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 -0.824 0.824 -0.925 0.925 0.000	00 00 00 00 00 00 00 00 25 25 25 10 10 00
Table	52	-	Dimeth	ylcarbona	te, C <sub>s</sub>	s, Er	nergy: -	398.92298
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0			8.0 6.0 8.0 6.0 7.0 6.0 1.0 1.0 1.0 1.0 1.0 1.0	2.03073 0.64754 0.14739 0.04691 -1.96009 -3.75966 2.59536 3.67574 -1.62111 -4.34362 -3.99559 -3.99559 -1.95109 -1.95109	0.3 0.3 1.5 -0.7 -0.4 -0.0 -0.9 -0.9 -0.8 0.62 -0.8 0.5 -0.5 -0.9 -0.9 -0.9 -0.9 -0.9 -0.9 -0.5	1305 6460 0177 7312 0610 3986 9593 4328 2333 7706 1406 6455 6455	0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000	00 00 00 00 00 00 00 00 00 00 20 20 20 2
п Н			1.0	2.29741	-1.5	6072	0.886	58

Table	53	-	Dimet	hylurethane	e, C <sub>s</sub> , 1	Energy:	-379.04927
0			8.0	2.02579	0.476	50 0.	00000
С			6.0	0.66684	0.134	93 0.	00000
0			8.0	0.34646	-1.079	29 0.	00000
Ν			7.0	-0.15741	1.168	69 0.	00000
С			6.0	-2.18990	0.368	42 0.	00000
Ν			7.0	-3.75189	-0.467	30 0.	00000
С			6.0	2.90179	-0.646	78 0.	00000
Н			1.0	3.91019	-0.229	06 0.	00000
Н			1.0	-1.53527	-0.498	58 0.	00000
Н			1.0	-4.55234	0.166	91 0.	00000
Н			1.0	0.35677	2.048	27 0.	00000
Н			1.0	-3.81515	-1.066	06 -0.	82479
Н			1.0	-3.81515	-1.066	06 0.	82479
Н			1.0	-2.29337	0.923	65 -0.	91858
Н			1.0	-2.29337	0.923	65 0.	91858
Н			1.0	2.75358	-1.269	53 -0.	88536
Н			1.0	2.75358	-1.269	53 0.	88536

Table 54 - Methyl Acetamide,  $C_{\rm s},$  Energy: -304.00329

N	7.0	0.36989	0.72035	0.00000
0	8.0	0.56626	-1.56104	0.00000
С	6.0	1.08414	-0.40181	0.00000
С	6.0	2.61143	-0.34590	0.00000
Н	1.0	0.95893	1.55229	0.00000
Н	1.0	2.98632	-0.87554	0.87987
H	1.0	2.98632	-0.87554	-0.87987
С	6.0	-1.74849	0.13165	0.00000
Н	1.0	-1.16436	-0.79005	0.00000
Н	1.0	-1.79635	0.69735	-0.91752
Н	1.0	-1.79635	0.69735	0.91752
N	7.0	-3.38196	-0.55392	0.00000
Н	1.0	-4.12634	0.14517	0.00000
Н	1.0	-3.49362	-1.14575	-0.82443
Н	1.0	-3.49362	-1.14575	0.82443
Н	1.0	3.00807	0.67358	0.00000

Table 55 - Methyl Trifluoroacetamide,  $C_s$ , Energy: -601.10242

С	6.0	2.11981	-0.52278	0.00000	
С	6.0	0.58992	-0.40223	0.00000	
0	8.0	-0.01703	-1.50505	0.00000	
Ν	7.0	0.04913	0.80354	0.00000	
С	6.0	-2.09064	0.55890	0.00000	
Ν	7.0	-3.85725	0.17215	0.00000	
F	9.0	2.76033	0.68086	0.00000	
Н	1.0	-1.71854	-0.46030	0.00000	
Н	1.0	-4.45550	0.99955	0.00000	
Н	1.0	0.74265	1.54876	0.00000	
F	9.0	2.55559	-1.19283	-1.08864	
F	9.0	2.55559	-1.19283	1.08864	
Н	1.0	-2.06198	1.11772	-0.92160	
Н	1.0	-2.06198	1.11772	0.92160	
Н	1.0	-4.08151	-0.38651	-0.82460	
Н	1.0	-4.08151	-0.38651	0.82460	

Table 56 - Methylcyanoformamide, C<sub>s</sub>, Energy: -356.85536

_				
C	6.0	-2.13211	0.05823	0.00000
С	6.0	-0.65322	-0.13475	0.00000
0	8.0	-0.22872	-1.31677	0.00000
Ν	7.0	0.08105	0.96986	0.00000
Ν	7.0	-3.30421	0.21366	0.00000
Н	1.0	-0.47753	1.82290	0.00000
С	6.0	2.15409	0.41429	0.00000
Н	1.0	1.64901	-0.54449	0.00000
Ν	7.0	3.85744	-0.21663	0.00000
Н	1.0	4.56232	0.52203	0.00000
Н	1.0	2.20896	0.96893	-0.92261
Н	1.0	2.20896	0.96893	0.92261
Н	1.0	4.00477	-0.80038	-0.82462
Н	1.0	4.00477	-0.80038	0.82462

Table 57 - Methyl Succinimide,  $C_s$ , Energy: -455.08510

N	7.0	0.05261	1.01151	0.00000
0	8.0	2.33705	0.61253	0.00000
0	8.0	-2.23756	0.72233	0.00000
С	6.0	1.17102	0.21489	0.00000
С	6.0	-1.08350	0.26114	0.00000
С	6.0	0.76545	-1.26900	0.00000
С	6.0	-0.75813	-1.23665	0.00000
Н	1.0	1.19813	-1.75517	0.87941
Н	1.0	1.19813	-1.75517	-0.87941
Н	1.0	-1.21286	-1.70250	0.87953
Н	1.0	-1.21286	-1.70250	-0.87953
С	6.0	-0.35264	3.13048	0.00000
Н	1.0	-1.34340	2.69223	0.00000
Н	1.0	0.21388	3.11421	-0.91761
Н	1.0	0.21388	3.11421	0.91761
Ν	7.0	-0.80868	4.85024	0.00000
Н	1.0	0.00960	5.46176	0.00000
Н	1.0	-1.36974	5.06521	-0.82586
Н	1.0	-1.36974	5.06521	0.82586

Table 58 - 1,3-Propanesultone, C1, Energy: -796.52517

С	6.0	-3.45351	0.75616	0.30115
С	6.0	-2.19091	0.52215	-0.52144
С	6.0	-1.79074	-0.94950	-0.57062
0	8.0	-3.45727	-1.71120	0.31553
S	16.0	-4.49739	-0.65306	-0.06605
0	8.0	-5.67323	-0.63998	0.80762
0	8.0	-4.70828	-0.59716	-1.52723
Ν	7.0	-0.11650	-0.67549	-1.48034
Н	1.0	-3.94260	1.69560	0.03500
Н	1.0	-3.25237	0.73939	1.37412
Н	1.0	-1.36522	1.11095	-0.10902
Н	1.0	-2.37547	0.85603	-1.54511
Н	1.0	-2.14297	-1.57827	-1.37184
Н	1.0	-1.32008	-1.42299	0.27731
Н	1.0	-0.27813	-0.23260	-2.38518
Н	1.0	0.32686	-1.58056	-1.64854
Н	1.0	0.54204	-0.09379	-0.96046

Table	59	-	N-Tri	flylpropan	esultam,	C1, 1	Energy:	-1660	.59152
С			6.0	-6.80903	0.6235	0 0	.94358		
С			6.0	-6.26053	1.0526	0 2	.30011		
С			6.0	-5.04418	0.24503	3 2	.73049		
Ν			7.0	-4.41467	0.07993	3 0	.77498		
S			16.0	-5.48929	0.7961	4 -0	.25481		
0			8.0	-5.20853	2.2336	1 -0	.36327		
0			8.0	-5.78052	0.01902	2 -1	.45839		
S			16.0	-3.17308	-0.88152	2 0	.43702		
0			8.0	-3.27811	-1.6592	9 -0	.79036		
0			8.0	-2.80960	-1.5185	0 1	.70950		
С			6.0	-1.83920	0.33782	2 0	.12987		
F			9.0	-2.15599	1.1096	1 -0	.91644		
F			9.0	-0.68200	-0.2892	8 -0	.11858		
F			9.0	-1.67732	1.1228	0 1	.21270		
Ν			7.0	-5.31761	0.2737	7 4	.63129		
Н			1.0	-7.12190	-0.4243	50	.93553		
Н			1.0	-7.64294	1.25823	3 0	.63005		
Н			1.0	-7.06380	0.9519	03	.03707		
Н			1.0	-5.98698	2.1106	3 2	.24992		
Н			1.0	-4.08081	0.7127	52	.84873		
Н			1.0	-5.05721	-0.8345	1 2	.70811		
Н			1.0	-5.41267	1.2230	7 4	.99570		
Н			1.0	-4.49815	-0.1527	05	.06855		
Н			1.0	-6.13924	-0.2597	54	.92010		
Table	60	_	Methy	l Chloride	e, C <sub>3v</sub> , En	ergy:	-555.0	66764	
С			6.0	0.00000	0.0000	0 0	.98077		
Н			1.0	-0.53245	0.92223	3 1	.13760		
Н			1.0	-0.53245	-0.92223	31	.13760		
Н			1.0	1.06490	0.0000	0 1	.13760		
Н			1.0	0.47750	-0.8270	6 -1	.18908		
Н			1.0	0.47750	0.8270	6 -1	.18908		
Н			1.0	-0.95501	0.0000	0 -1	.18908		
Cl			17.0	0.00000	0.0000	0 3	.41809		
Ν			7.0	0.00000	0.0000	0 — 0	.82697		

### MP2(full)/6-31G(d) Geometries and Energies of van der Waals complexes

Table	61	-	Methyl	Mesylate,	C <sub>1</sub> ,	Energ	i À.	-758.58709
S			16.0	2.07553	0.5	1573	0	.18915
0			8.0	1.98721	1.9	0663	-0	.25416
0			8.0	3.03576	0.1	5510	1	.23078
0			8.0	2.26572	-0.4	4335	-1	.10417
С			6.0	3.21452	0.0	5729	-2	.09851
С			6.0	0.47676	-0.0	7754	0	.65915
Н			1.0	-0.23040	0.1	4685	-0	.13785
Н			1.0	0.20090	0.4	4264	1	.57712
H			1.0	0.54040	-1.1	5053	0	.83612
Ν			7.0	5.32093	1.8	3568	-0	.17260
Н			1.0	3.39137	-0.7	9804	-2	.74665
Н			1.0	2.75180	0.8	7475	-2	.65164
H			1.0	4.13737	0.3	9319	-1	.62272
Н			1.0	4.61506	2.5	6859	-0	.20399
Н			1.0	6.21396	2.2	9069	0	.00351
H			1.0	5.09539	1.2	8412	0	.65259

Table 62 - Dimethylsulfate, C1, Energy: -833.61240

С	6.0	-0.53204	-2.61811	0.15498
0	8.0	0.10826	-1.31517	0.15639
S	16.0	1.70441	-1.38677	-0.06897
0	8.0	1.84848	0.16909	-0.38204
С	6.0	3.02227	0.82869	0.19709
0	8.0	2.37762	-1.72019	1.17815
0	8.0	1.96618	-2.18795	-1.25647
Ν	7.0	5.05312	-1.66836	-0.70869
Н	1.0	-1.57531	-2.40567	0.37460
Н	1.0	-0.42705	-3.08419	-0.82454
Н	1.0	-0.10311	-3.25026	0.93483
Н	1.0	2.96440	1.83652	-0.20682
Н	1.0	2.92959	0.83798	1.28227
Н	1.0	3.92979	0.31584	-0.12212
Н	1.0	5.98747	-1.86208	-1.06196
Н	1.0	4.39412	-2.11560	-1.34245
Н	1.0	4.96133	-2.16274	0.17586

Table	63	-	Methyl	Triflate,	C <sub>1</sub> ,	Energy	y:	-1055.	65367
S 0 0 0 C C F F F N H H H H H H H			16.0 8.0 8.0 6.0 6.0 9.0 9.0 7.0 1.0 1.0 1.0 1.0 1.0	2.20717 2.02832 2.91878 2.70847 3.12432 0.53321 -0.13890 -0.11248 0.61466 5.24527 3.34404 2.30471 4.00749 4.84718 6.24956 5.10327	0.6 1.9 0.3 -0.4 0.1 -0.1 -0.0 0.6 -1.3 1.7 -0.7 0.7 0.7 2.6 1.8 1.2	0708 4149 6265 2245 4170 0498 2905 0054 7976 4614 3845 1340 5565 7830 6479 9429	0. -0. -2. 0. -0. 1. 0. -0. -2. -2. -2. -0. -0. -0.	29261 25910 53519 82763 11433 51115 64295 44453 89367 13154 71390 54797 95000 04216 24715 76956	
Table	64	_	Methyl	fluorosulf	fonat	e, C <sub>1</sub> ,	Ene	ergy:	-818.44356
S			16.0	-0.61956	-0.0	1031	0.	67213	
0			8.0	-0.84288	1.3	0202	Ο.	11379	
0			8.0	0.00645	-0.2	3924	1.	95035	
0			8.0	0.00621	-1.0	0722	-0.	38821	
С			6.0	0.23617	-0.4	7692	-1.	73065	
F			9.0	-2.06612	-0.6	9736	0.	77082	
Ν			7.0	2.33568	1.1	6672	0.	26904	
H			1.0	0.60254	-1.3	3970	-2.	28119	
H			1.0	-0.698/9	-0.1	1534	-2.	15655	
H			1.0	0.98/18	0.3	0629	-1.	66285 27115	
H			1.U	∠.U0UU8	∠.⊥ 1 1	4U84 6107	0.	3/115 06705	
п II			1 0	3.3331		040/ 1101	U. 1	100E1	
н			I.U	∠.∠∠440	0./	44UI	⊥.	10034	

Table	65	_	Methyl	TFSI	(ant	i)	C1,	Ene	rgy	: -:	1919.	72254
С			6.0	-0.264	167	-1.	536	25	0.	164	84	
Ν			7.0	0.415	561	-0.	231	26	Ο.	395	25	
S			16.0	1.612	248	-0.	129	76	1.	592	17	
S			16.0	0.093	380	1.	037	33	-0.	676	79	
0			8.0	1.228	312	1.	933	40	-0.	769	02	
0			8.0	-0.555	561	0.	446	8 0	-1.	837	00	
0			8.0	1.308	338	-1.	155	64	2.	574	83	
С			6.0	3.086	527	-0.	747	37	Ο.	674	35	
С			6.0	-1.228	369	1.	928	95	Ο.	245	05	
F			9.0	-1.639	951	2.	954	37	-0.	505	40	
F			9.0	-0.765	557	2.	376	00	1.	408	24	
F			9.0	-2.254	120	1.	097	21	0.	461	51	
0			8.0	1.852	204	1.	259	43	1.	923	81	
N			7.0	-3.273	319	-1.	160	26	-1.	316	64	
Н			1.0	0.283	315	-2.	119	54	-0.	575	29	
Н			1.0	-0.283	348	-2.	057	45	1.	119	70	
Н			1.0	-1.287	730	-1.	360	89	-0.	172	66	
Н			1.0	-4.030	)26	-0.	574	55	-0.	972	46	
Н			1.0	-3.706	518	-1.	896	22	-1.	870	23	
Н			1.0	-2.732	259	-0.	586	72	-1.	960	09	
F			9.0	4.129	92	-0.	753	23	1.	503	71	
F			9.0	3.344	198	0.	029	63	-0.	374	64	
F			9.0	2.841	85	-1.	995	17	0.	252	41	

Table	66	-	Methyl	TFSI	(ga	uche)	C1,	Energy:	-1919.	71949
Table C N S S O O O O C F F F F F F F F F N H H H	66		Methyl 6.0 7.0 16.0 16.0 8.0 8.0 8.0 8.0 8.0 9.0 9.0 9.0 9.0 9.0 9.0 9.0 9.0 9.0 9	TFS1 -3.637 -2.650 -1.013 -3.145 -1.995 -4.111 -1.019 -0.142 -4.124 -4.577 -3.352 -5.159 -0.701 -0.668 0.473 -1.669 -3.311 -3.704 -4.612	(ga 764 )02 329 525 598 525 595 290 182 789 292 182 789 292 182 789 292 182 789 292 182 789 292 182 789 295 182 295 185 185 185 185 185 185 185 185 185 18	uche) -2.1 -1.0 -1.4 0.3 1.2 0.0 -2.8 -0.8 1.1 2.3 1.3 0.3 -0.5 0.8 -0.5 0.8 -0.9 -0.7 -1.5 -3.0 -2.3 -1.5	C1, 6135 6318 3548 6419 2201 5443 3780 7986 2717 0616 0963 4697 0135 0872 0339 8079 2231 4362 8431 4472	Energy: -0.088 -0.287 0.014 -1.031 -1.231 -2.073 0.395 -1.001 0.334 -0.096 1.407 0.664 1.573 1.344 2.060 2.454 -1.285 -0.635 0.976 -0.463	-1919. 45 79 36 11 36 59 23 14 68 50 60 62 48 99 28 42 63 77 18 98	. /1949
H			1.0	-7.420	86	-0.9	8022	-0.794	43	
H H			1.0	-7.214	103 133	-2.2	9124	-1.829 -1.951	37 99	
Table	67	-	Methyl	FSI,	C1,	Energ	97: -	-1445.302	276	
C			6.0	-0.835	597	-0.9	2101	0.685	70	
S			16.0	1.773	316	-0.8	3171	-0.201	20	
S			16.0	-0.000	)32	1.4	4807	-0.334	36	
0			8.0	-1.255	556	1.8	2126	0.268	70 25	
0			8.0	2.374	10	-0.2	5542	-1.374	23	
0			8.0	1.652	240	-2.2	4543	0.050	41	
F			9.0	-0.280	)41	1.3	3325	-1.911	05	
F			9.0	2.552	228	-0.2	2244	1.058	54	
N			7.0	-3.115	89	-0.0	2290	-1.569	59	
H U			1.U	-0.536	NTQ NTQ	-1.9 -0 5	00UJ 7001	U.681 1 700	0/ フク	
п u			1.0	-0.973	942 550	-0.3	8818 8818	1.700	7Z Q5	
H			1 0	-3 372	) 93 93	0.7	5147	-1 117	27	
H			1.0	-3.982	272	-0.4	7669	-1.849	60	
Н			1.0	-2.632	218	0.2	3513	-2.426	62	

Table	68	_	Methyl	MSI	(ant:	i) (	C1,	Ener	gy:	-1325.	59716
С			6.0	-0.91	580	-0.	.53	634	1.	16462	
Ν			7.0	0.32	220	0.	.17	719	0.	78978	
S			16.0	1.12	420	1.	.141	196	1.	95545	
S			16.0	0.56	593	0.	. 490	289	-0.	86013	
0			8.0	1.98	593	0.	.793	365	-1.	01966	
0			8.0	-0.04	744	-0.	643	106	-1.	55674	
0			8.0	0.47	362	0.	.83	134	3.	22596	
С			6.0	2.75	641	0.	.452	260	1.	96505	
С			6.0	-0.38	261	1.	.94	798	-1.	20549	
Н			1.0	-0.20	706	2.	.193	102	-2.	25567	
Н			1.0	-0.02	182	2.	.74	552	-0.	55717	
Н			1.0	-1.43	657	1.	.712	298	-1.	04079	
0			8.0	1.20	009	2.	.51	767	1.	46588	
N			7.0	-3.14	985	0.	.06	708	-1.	46265	
Н			1.0	-0.88	738	-1.	. 528	821	0.	71574	
Н			1.0	-0.92	754	-0.	.618	816	2.	24960	
Н			1.0	-1.80	401	0.	.002	133	0.	82537	
Н			1.0	-3.60	934	0.	41	138	-2.	30310	
Н			1.0	-3.80	087	-0.	.58	630	-1.	03252	
Н			1.0	-2.34	570	-0.	.478	849	-1.	76958	
Н			1.0	3.33	313	1.	.023	151	2.	69684	
Н			1.0	3.17	675	0.	.55	340	0.	96585	
Н			1.0	2.68	232	-0.	.593	300	2.	26269	

Table	69	_	Methyl	MSI	(gau	che)	C1,	Energ	gy:	-1325	.59135
С N S S O O O O C H H H C H H H H H H H H H H H			$\begin{array}{c} 6.0\\ 7.0\\ 16.0\\ 8.0\\ 8.0\\ 8.0\\ 8.0\\ 6.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1$	-0.60 0.45 2.05 0.15 1.39 -0.53 1.90 2.60 -1.00 -1.00 -1.05 2.92 2.92 3.96 2.45 -3.50 -0.53 -0.53 -0.53 -0.53 -3.50 -0.48 -1.57 -4.22 -3.92 -2.79	)345         )5232         )582         )5961         )997         )420         )596         )828         )596         )828         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )596         )597         )596         )597         )596         )597         )596         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597         )597	-1.0 -0.3 -0.4 -1.4 -1.4 -1.4 -1.4 -1.4 -1.4 -1.4 -1	0845 1491 7461 5476 1859 4103 4653 4106 8170 3938 4453 3580 7526 3527 4467 2710 3815 0507 2165 6363 1027 2389 6613	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.59 .13 .44 .39 .81 .27 .70 .73 .95 .18 .62 .15 .15 .02 .58 .08 .66 .37 .82 .84	308 373 523 986 604 242 841 122 342 507 812 342 507 812 107 408 314 623 440 961 625 603 982 334 392 439	
Table	70	_	Methyl	. MSA,	C <sub>1</sub> ,	Ener	dð:	-738	.74(	)12	
С N H S O O C N H H H H H H H H H H H H H H H H H H			6.0 7.0 1.0 16.0 8.0 8.0 6.0 7.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	0.29 1.38 2.29 1.11 -0.12 2.37 0.78 -2.38 0.65 -0.52 -0.06 -1.97 -3.01 -2.98 0.64 -0.12 1.64	9660         3978         9714         1500         2475         7835         3513         3816         5278         2779         5246         7799         130         3534         4067         2628         4863	-0.9 -0.9 1.0 1.1 0.2 -0.2 -1.9 -0.2 -1.9 0.0 0.0 1.0 0.0	9604 0833 5236 0846 7630 2437 2179 5506 3338 6304 63975 0776 0151 3482 3690	$\begin{array}{ccccccc} 0 & 1 \\ 9 & 1 \\ 3 & 1 \\ 4 & 0 \\ 7 & 0 \\ 3 & -0 \\ 1 & -1 \\ 7 & -0 \\ 2 & 2 \\ 6 & 1 \\ 7 & -0 \\ 2 & 2 \\ 6 & 1 \\ 7 & -0 \\ 4 & -0 \\ 6 & 0 \\ 0 & -1 \\ 8 & -2 \\ 8 & -1 \\ 6 & -1 \end{array}$	.56 .14 .00 .39 .14 .53 .59 .41 .90 .77 .20 .11 .36 .28 .42 .79	476 796 630 513 542 314 005 323 035 183 631 067 641 256 888 339 255	

Table	71	-	Methyl	FSA,	C1,	Energy:	-798.60455
C N H S O O F N H H H H H H H			$ \begin{array}{c} 6.0\\ 7.0\\ 1.0\\ 16.0\\ 8.0\\ 9.0\\ 7.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1$	0.26 1.39 2.17 1.07 -0.04 2.32 0.50 -2.33 0.69 -0.23 -0.45 -2.09 -3.34 -2.08	599 201 771 843 715 591 063 177 834 563 537 204 480 991	-1.0103 -0.2761 -0.8319 0.9599 1.7059 1.5486 0.2146 -0.4968 -1.8464 -0.3465 -1.3619 0.4350 -0.5765 -0.5079	4 1.21145 9 0.60706 7 0.27763 6 -0.39351 9 0.12390 2 -0.81861 0 -1.72081 0 -0.91025 2 1.76055 7 1.91401 8 0.47071 2 -0.57764 2 -0.85746 7 -1.89789
Table	72	_	MeiprF	SA, C	1, Er	nergy: -	916.11962
С			6.0	-0.14	543	-1.1862	1 0.75151
N			7.0	0.86	069	-0.1536	0 0.43946
С			6.0	2.25	515	-0.4828	4 0.85894
S			16.0	0.62	201	0.6579	4 -0.94614
0			8.0	-0.75	302	1.1025	8 -1.03469
0			8.0	1.74	177	1.5323	4 -1.21453
F			9.0	0.72	827	-0.5253	6 -2.06457
N			7.0	-3.39	035	-0.3966	3 -0.20120
Н			1.0	0.10	402	-2.1382	8 0.27073
Н			1.0	-0.15	009	-1.3155	0 1.83470
H			1.0	-1.14	042	-0.8681	0 0.43931
H			1.0	-2.81	037	0.3031	2 -0.65932
H			1.0	-4.06	842	0.1097	7 0.36340
H			1.0	-3.91	890	-0.8631	6 -0.93464
С			6.0	3.04	897	-1.2459	5 -0.19605
H			1.0	2.08	369	-1.1534	3 1.70724
С			6.0	2.98	864	0./41/	/ 1.38628
H 			1.0	3.91	OT 0	0.4204	3 1.88086
H			1.0	2.36	910	1.2683	8 2.115/2
H			1.U	3.24	651 000	1.4288	5 U.58146
H			1.U	3.99	002	-1.590/	δ U.24163
H 			1.0	3.28	536 001	-0.6035	7 -1.04622
Н			1.0	2.49	994	-2.1191	/ -0.55669
Table	73	-	Meth	yl Acetate	, C <sub>1</sub> , Ener	rgy: -323.95	778
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С			6.0	-4.76330	-0.87502	0.56099	
С			6.0	-3.48640	-0.13526	0.29454	
0			8.0	-2.68648	-0.36043	-0.59484	
0			8.0	-3.30869	0.86734	1.20657	
С			6.0	-2.09098	1.61402	1.02202	
Ν			7.0	-6.29875	2.16070	1.18625	
Н			1.0	-4.88517	-1.65388	-0.19018	
Н			1.0	-4.72516	-1.32253	1.55723	
Н			1.0	-5.60502	-0.17832	0.53898	
Н			1.0	-2.08778	2.35558	1.81839	
H			1.0	-1.22546	0.95574	1.10386	
H			1.0	-2.08180	2.09519	0.04315	
H			1.0	-6.74213	2.36174	2.07912	
H			1.0	-6.36621	3.01098	0.63224	
Н			1.0	-5.31062	2.00614	1.37478	
Table	74	- ]	Methy	l Trifluor	pacetate,	C <sub>1</sub> , Energy:	-621.03443
С			6.0	-1.75678	-0.01532	0.44186	
С			6.0	-0.37804	0.65146	0.42408	
0			8.0	0.54553	-0.29094	0.23608	
0			8.0	-0.20424	1.84151	0.58277	
F			9.0	-1.91152	-0.71456	1.58235	
F			9.0	-2.72629	0.89983	0.36481	
F			9.0	-1.89017	-0.87075	-0.59275	
С			6.0	1.91810	0.17812	0.20045	
Н			1.0	2.47950	-0.68333	-0.14917	
Н			1.0	2.21883	0.49004	1.20088	
Н			1.0	1.99973	1.01833	-0.48857	
Ν			7.0	1.48996	-2.76366	-1.32055	
Н			1.0	1.39698	-2.95790	-2.31484	
Н			1 0	1 16155	-3 66566	-0 85089	
			<b>T</b> • O	I.40433	5.00500	0.05005	

Table	75	-	Methyl	Cyanoform	mate, C <sub>s</sub> ,	Energy: -376.78433
С О О И И И И И И Н Н Н Н Н			6.0 6.0 8.0 7.0 6.0 1.0 7.0 1.0 1.0 1.0 1.0	-1.47301 -0.73161 0.57986 -1.27341 -2.11971 1.42222 2.43222 3.46108 2.47835 1.21412 1.21412 3.88029 3.88029	-0.77120 0.49697 0.24591 1.58460 -1.75893 1.43332 1.03286 -1.18080 -1.44492 2.02517 2.02517 -1.62369 -1.62369	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.89140\\ 0.89140\\ 0.891425\\ 0.81425\\ 0.81425 \end{array}$
Table	76	_	Dimeth	ylcarbona	te, C <sub>1</sub> , E	nergy: -398.99274
О С О С С Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н			8.0 6.0 8.0 6.0 6.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1	-1.71595 -0.66748 0.32101 -0.86388 -2.84908 0.23999 -3.54950 -0.08140 -3.29192 -2.56146 0.39780 1.14739 3.05507 3.27864 2.33736 3.88902	-1.64567 -0.81514 -1.11461 0.34335 -1.20995 1.27555 -2.04128 2.14169 -0.31311 -1.01547 1.54388 0.83630 -0.71645 -1.51546 -1.02664 -0.52819	$\begin{array}{c} -0.34681 \\ -0.46796 \\ -1.10910 \\ 0.18726 \\ 0.42601 \\ 0.08546 \\ 0.37647 \\ 0.65991 \\ -0.00759 \\ 1.45935 \\ -0.95969 \\ 0.49912 \\ 0.47509 \\ 1.06409 \\ -0.17824 \\ -0.07662 \end{array}$

Table	77	-	Dimet	hylurethan	e, C <sub>1</sub> ,	Energy	-379.16693
ОС N О H С С H H H H H H H H H H H H H H H H			8.0 6.0 7.0 8.0 1.0 6.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	0.04191 -0.00425 -1.10517 1.10629 -0.99067 2.31080 -2.37522 -3.16768 -2.43288 -2.52691 3.09582 2.23378 2.51772 -0.20802 -0.07207 0.67082	1.63 0.43 -0.29 -0.38 -1.27 0.31 0.38 -0.36 0.92 1.09 -0.43 0.76 1.09 -3.07 -3.45 -2.64 2.85	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.12268 .10942 .40633 .08147 .67022 .25469 .57605 .54944 .52439 .23628 .23699 .24627 .47424 .02144 .95418 .74028
11			1.0	0.30903	5.05	0 100	
Table	78	-	Methy	l Acetamid	e, C <sub>1</sub> ,	Energy	-304.12207
С			6.0	-0.58441	-1.75	116 -0	.33760
С			6.0	0.69427	-0.98	409 -0	.60803
0			8.0	1.74947	-1.55	792 -0	.89954
Ν			7.0	0.59695	0.36	353 -0	.50903
С			6.0	1.76516	1.18	265 -0	.75155
Ν			7.0	-1.99959	1.82	192 0	.20970
H			1.0	-0.83598	-2.33	883 -1	.22328
H			1.0	-0.40745	-2.45	155 0	.48152
Н			1.0	-1.42418	-1.10	112 -0	.08357
Н			1.0	1.48857	2.22	927 -0	.61446
Н			1.0	2.57168	0.92	838 -0	.05857
Н			1.0	2.14185	1.03	875 -1	.76797
Н			1.0	-2.20075	1.79	949 1	.20697
Н			1.0	-2.83095	1.47	116 -0	.26089
Н			1.0	-1.91824	2.80	368 -0	.04643
Н			1.0	-0.29005	0.80	918 -0	.26822

Table	79 -	- Me	ethyl	Trifluor	coacetamide,	, C <sub>1</sub> ,	Energy:	-601.21078
С		(	5.0	-0.82875	-0.56153	0.1	5288	
0		8	3.0	-0.80045	-1.77822	-0.0	3209	
Ν		-	7.0	-1.85164	0.26359	-0.1	1855	
Н		-	L.O	-1.77164	1.27590	0.0	5920	
С		(	5.0	0.38976	0.16714	0.7	3801	
F		(	9.0	1.35475	-0.68472	1.0	8379	
F		(	9.0	0.05156	0.89101	1.8	3585	
F		(	9.0	0.90633	1.04679	-0.1	6086	
С		(	5.0	-3.06416	-0.27987	-0.6	9897	
Н		-	1.0	-3.77324	0.53671	-0.8	3466	
H		-	1.0	-3.50126	-1.03572	-0.0	4201	
Н		-	1.0	-2.85776	-0.74710	-1.6	6533	
Ν		-	7.0	-1.40375	3.13233	0.4	2482	
Н		-	1.0	-1.44356	3.29561	1.4	2829	
H		-	L.O	-0.42197	3.19100	0.1	6428	
Н		-	1.0	-1.87974	3.91178	-0.0	2372	
Table	80 -	- Me	ethyl	cyanoform	namide, $C_s$ ,	Energ	gy: -356.	96347
N		-	7 0	-1 83570	-1 50407	0 0	0000	
C		(	5 0	-0 74073	-1 06034	0.0	0000	
C			5.0	0 63723	-0 51063	0.0	0000	
0		\$	3.0	1 62091	-1 25131	0.0	0000	
N		-	7.0	0.63991	0.83336	0.0	0000	
C		(	5.0	1.90428	1.54385	0.0	0000	
H		-	1.0	-0.26184	1.33637	0.0	0000	
H		-	1.0	1.69447	2.61327	0.0	0000	
N		-	7.0	-2.10406	1.92527	0.0	0000	
H		-	L.O	-2.60719	1.03890	0.0	0000	
Н		-	1.0	-2.42393	2.44214	-0.8	1642	
Н		-	1.0	-2.42393	2.44214	0.8	1642	
Н		-	1.0	2.49159	1.28779	-0.8	8526	
Н		-	1.0	2.49159	1.28779	0.8	8526	

Table	81	-	Methyl	Succinim	ide,	$C_1$ ,	Energy:	-455.18368
С			6.0	0.52917	-1.2	2629	1 -0.862	215
С			6.0	1.76042	-0.8	8320	2 -0.08	551
Ν			7.0	1.38135	0.1	1477	1 0.814	472
С			6.0	0.02188	0.	4567	6 0.76	478
С			6.0	-0.61973	-0.	4420	0 -0.27	780
0			8.0	-0.52583	1.	3005	4 1.45	442
0			8.0	2.90039	-1.2	2587	4 -0.223	177
С			6.0	2.31425	0.	8138	9 1.71	023
Ν			7.0	4.66504	-1.	6481	6 2.40	933
H			1.0	0.70344	-1.	0704	3 -1.92	439
H			1.0	0.40072	-2.	3424	6 -0.748	822
H			1.0	-1.38283	-1.	0525	8 0.212	272
H			1.0	-1.13219	0.1	1832	3 -1.013	348
H			1.0	1.71974	1.	3814	3 2.42	535
H			1.0	2.93544	0.0	0738	1 2.21	649
H			1.0	2.95198	1.	4953	0 1.142	227
H			1.0	4.30095	-1.	6296	5 1.45	794
H			1.0	4.64012	-2.	6181	9 2.71	474
H			1.0	5.64806	-1.3	3926	5 2.35	189

Table 82 - 1,3-Propanesultone,  $C_1$ , Energy: -796.58767

С	6.0	-3.84229	0.75631	-0.06952
С	6.0	-2.58632	0.41009	-0.85058
С	6.0	-1.99255	-0.81172	-0.13710
0	8.0	-3.07688	-1.58382	0.44439
S	16.0	-4.53908	-0.86358	0.19264
0	8.0	-5.30841	-0.98887	1.42085
0	8.0	-5.08698	-1.34937	-1.07484
N	7.0	-6.48769	1.37912	-1.88668
Н	1.0	-4.58130	1.35214	-0.61505
Н	1.0	-3.62600	1.18153	0.91458
Н	1.0	-1.87349	1.23697	-0.87655
Н	1.0	-2.85960	0.15626	-1.87649
Н	1.0	-1.44270	-1.46802	-0.81361
Н	1.0	-1.34769	-0.51631	0.69471
Н	1.0	-7.38886	1.55983	-1.45017
Н	1.0	-6.39456	0.36670	-1.95086
Н	1.0	-6.55907	1.72724	-2.84003

Table 8	83 -	N-Tri	flylpropan	esultam,	C <sub>1</sub> , Energy:	-1660.66338
С		6.0	-6.53875	0.6944	6 1.10123	
С		6.0	-5.68805	1.16524	4 2.26912	
С		6.0	-4.38491	0.37093	1 2.17801	
Ν		7.0	-4.08139	0.30374	4 0.73124	
S		16.0	-5.42434	0.80259	9 -0.28481	
0		8.0	-5.21655	2.20223	3 -0.64154	
0		8.0	-5.69217	-0.1959	5 -1.31100	
S		16.0	-2.78151	-0.57133	3 0.21035	
0		8.0	-3.01004	-1.08554	4 -1.12846	
0		8.0	-2.32875	-1.4014	6 1.32047	
С		6.0	-1.54199	0.77269	9 0.03454	
F		9.0	-1.96431	1.65378	8 -0.87233	
F		9.0	-0.37569	0.25072	2 -0.35214	
F		9.0	-1.38165	1.39053	3 1.21390	
Ν		7.0	-5.52432	-2.52894	4 0.86250	
Н		1.0	-6.80796	-0.36070	0 1.19574	
Н		1.0	-7.40418	1.32330	0.88038	
Н		1.0	-6.18426	0.97369	9 3.22347	
Н		1.0	-5.49594	2.23828	8 2.18494	
Н		1.0	-3.56541	0.86523	1 2.70334	
Н		1.0	-4.52252	-0.6428	6 2.55743	
Н		1.0	-5.44561	-2.32132	2 -0.13276	
Н		1.0	-4.61498	-2.8906	6 1.14725	
Н		1.0	-6.17549	-3.30833	1 0.94198	
Table 8	84 -	Methy	l Chloride	, C <sub>3v</sub> , En	ergy: -555.	73069
С		6.0	0.00000	0.0000	0 1.91852	
Н		1.0	-0.51302	0.88858	8 1.56196	
Н		1.0	-0.51302	-0.88858	8 1.56196	
Н		1.0	1.02604	0.0000	0 1.56196	
Н		1.0	0.47000	-0.8140	6 -1.71285	
Н		1.0	0.47000	0.8140	6 -1.71285	
Н		1.0	-0.94000	0.0000	0 -1.71285	
Cl		17.0	0.00000	0.0000	3.70220	
Ν		7.0	0.00000	0.0000	0 -1.32406	

## MP2(full)/6-31G(d) Geometries and Energies of Methyl Transfer Agents

Table	85 -	Methyl	Mesylate,	C <sub>s</sub> , Energ	gy: -702.219	14
S O C H H H H H O O		16.0 8.0 6.0 1.0 1.0 1.0 1.0 1.0 1.0 8.0 8.0	-0.48793 0.74189 2.05024 -1.78750 -2.72724 2.75493 -1.70452 -1.70452 2.17258 2.17258 -0.48327 -0.48327	0.59518 -0.48079 0.14658 -0.60331 -0.04971 -0.68149 -1.21272 -1.21272 0.75409 0.75409 1.32550 1.32550	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ -0.89869\\ 0.89869\\ -0.89797\\ 0.89797\\ -1.26391\\ 1.26391\\ 1.26391 \end{array}$	
Table	86 -	Dimeth	ylsulfate,	C <sub>1</sub> , Energ	gy: -777.243	77
C O S O C O H H H H H H		6.0 8.0 16.0 8.0 6.0 8.0 8.0 1.0 1.0 1.0 1.0 1.0	-1.94327 -1.26787 0.29230 0.41024 1.78363 1.08668 0.45285 -2.95766 -1.93144 -1.46981 1.69338 2.25226 2.34201	-1.54122 -0.26138 -0.32041 1.27809 1.75545 -0.78435 -0.95375 -1.34542 -1.85542 -2.28940 2.82986 1.52071 1.31405	0.02882 0.16975 -0.21263 -0.33405 -0.32370 0.91383 -1.51198 0.36629 -1.01440 0.66698 -0.46080 0.63166 -1.15122	

Table 87 - Methyl Triflate, C1, Energy: -999.28488

S	16.0	0.25159	0.41701	0.83473
0	8.0	0.07720	1.75046	0.28263
0	8.0	0.96943	0.13787	2.05924
0	8.0	0.81877	-0.58589	-0.29120
С	6.0	0.71707	-0.15875	-1.68227
С	6.0	-1.42711	-0.29711	1.03422
F	9.0	-2.08031	-0.24174	-0.13658
F	9.0	-2.09407	0.41557	1.94346
F	9.0	-1.34499	-1.56608	1.43089
Н	1.0	1.21648	-0.95207	-2.23302
Н	1.0	-0.32836	-0.08190	-1.97734
Н	1.0	1.22784	0.79245	-1.81832

Table 88 - Methylfluorosulfonate, C1, Energy: -762.07625

S	16.0	-0.60047	0.32365	1.04387
0	8.0	-0.88595	1.67695	0.65859
0	8.0	0.30024	-0.05308	2.10684
0	8.0	-0.27758	-0.48448	-0.28811
С	6.0	0.14692	-1.86719	-0.10985
F	9.0	-2.00395	-0.37244	1.39800
Н	1.0	0.32409	-2.22029	-1.12209
Н	1.0	1.05819	-1.89960	0.48505
Н	1.0	-0.65152	-2.43862	0.36382

Table 89 - Methyl TFSI (anti)  $C_1$ , Energy: -1863.35495

Ν	7.0	0.17552	0.23493	0.17590
S	16.0	0.43900	-1.37755	0.62715
S	16.0	-1.01820	0.70063	-0.93931
0	8.0	-0.59558	1.99214	-1.45403
0	8.0	-1.40403	-0.41878	-1.77282
0	8.0	1.17721	-1.34640	1.87842
0	8.0	-0.77508	-2.13839	0.42166
С	6.0	-2.41875	1.03803	0.20971
F	9.0	-3.45702	1.46415	-0.50953
F	9.0	-2.05184	1.99210	1.07545
F	9.0	-2.74842	-0.06349	0.87714
С	6.0	1.65825	-1.89764	-0.65200
F	9.0	1.12524	-1.81351	-1.86777
F	9.0	2.02968	-3.15258	-0.40263
F	9.0	2.72495	-1.08941	-0.57754
С	6.0	1.11958	1.28464	0.63431
Н	1.0	0.54846	2.14726	0.97208
Н	1.0	1.79542	1.57006	-0.17071
Н	1.0	1.67563	0.87380	1.47449
- 1 1	0.0 14 1	1 = a = - a	_	1 2 0 0 2 4 2 0

Table 90 - Methyl FSI, C1, Energy: -1388.93439

Ν	7.0	0.12598	0.85721	-0.43711
S	16.0	0.17991	-0.74351	0.10271
S	16.0	-1.35861	1.54537	-0.78570
0	8.0	-1.09995	2.82832	-1.38785
0	8.0	-2.21553	0.52898	-1.33205
0	8.0	-0.96600	-1.06044	0.91471
0	8.0	1.54614	-0.98483	0.49304
F	9.0	-1.88279	1.85606	0.69869
F	9.0	-0.04132	-1.46132	-1.30164
С	6.0	1.24220	1.74979	-0.04756
Н	1.0	1.17936	2.63172	-0.68081
Н	1.0	2.17296	1.22368	-0.24244
Н	1.0	1.17679	2.03019	1.00543

Table 91 - Methyl MSI (anti) C<sub>1</sub>, Energy: -1269.22819

Ν	7.0	0.18569	0.23527	-0.72916
S	16.0	-0.02526	-1.44459	-0.89703
S	16.0	-1.19470	1.24290	-0.57807
0	8.0	-0.68432	2.59692	-0.77402
0	8.0	-2.27211	0.71724	-1.41653
0	8.0	-1.10049	-1.80835	0.02067
0	8.0	1.31052	-2.02036	-0.78488
С	6.0	-1.63882	1.02999	1.12318
H	1.0	-2.51134	1.66215	1.29904
H	1.0	-0.79905	1.35384	1.73718
H	1.0	-1.87133	-0.02041	1.28927
С	6.0	-0.59449	-1.68216	-2.56249
Н	1.0	0.16590	-1.30695	-3.24863
H	1.0	-0.72473	-2.75684	-2.70243
H	1.0	-1.53800	-1.15121	-2.68209
С	6.0	1.39738	0.84298	-1.31282
H	1.0	1.59453	1.77865	-0.79397
Н	1.0	1.28781	1.04332	-2.38254
Н	1.0	2.21657	0.14727	-1.14029
- 1 1		1 1/07 0	_	

Table 92 - Methyl MSA,  $C_1$ , Energy: -682.37105

С	6.0	-0.46679	-0.98040	1.39584
Ν	7.0	0.60191	-0.06732	1.00427
Н	1.0	1.51463	-0.47669	0.82176
S	16.0	0.27618	1.19746	-0.01451
0	8.0	-0.92965	1.84720	0.49174
0	8.0	1.54382	1.90088	-0.18715
С	6.0	-0.15223	0.48393	-1.59370
Н	1.0	-0.14236	-1.52469	2.28386
Н	1.0	-1.33902	-0.38197	1.65753
Н	1.0	-0.73913	-1.70185	0.61542
Н	1.0	-0.39272	1.30803	-2.26707
Н	1.0	-1.02420	-0.16124	-1.47872
Н	1.0	0.70035	-0.07500	-1.98104

Table 93 - Methyl FSA, C1, Energy: -742.23853

С	6.0	-0.47591	-1.08472	0.63071
N	7.0	0.77742	-0.37593	0.35091
H	1.0	1.15876	-0.49957	-0.58501
S	16.0	0.91353	1.17616	0.83132
0	8.0	0.46777	1.28713	2.19914
0	8.0	2.15882	1.69964	0.32390
F	9.0	-0.24927	1.89708	-0.04507
H	1.0	-0.31366	-2.13860	0.40637
H	1.0	-0.69531	-0.97950	1.69189
H	1.0	-1.31405	-0.70311	0.04073

Table 94 - MeiprFSA, C1, Energy: -859.75289

С	6.0	-1.80722	-0.85772	0.47214
Ν	7.0	-0.79726	0.15979	0.14298
С	6.0	0.59710	-0.15701	0.57192
S	16.0	-1.04159	0.95216	-1.25824
0	8.0	-2.43176	1.33359	-1.36381
0	8.0	0.05565	1.85854	-1.51026
F	9.0	-0.86695	-0.24180	-2.35604
Н	1.0	-1.59199	-1.81629	-0.01234
Н	1.0	-1.80916	-0.98511	1.55533
Н	1.0	-2.78819	-0.50207	0.16115
С	6.0	1.41497	-0.88805	-0.48732
Н	1.0	0.43285	-0.84411	1.40886
С	6.0	1.30135	1.07545	1.12054
Н	1.0	2.23665	0.77053	1.59903
Н	1.0	0.67519	1.56923	1.86713
Н	1.0	1.52976	1.78580	0.32701
Н	1.0	2.35797	-1.22087	-0.04512
Н	1.0	1.64644	-0.22725	-1.32439
Н	1.0	0.88618	-1.76480	-0.86857

Table	95	-	Methyl	Acetate,	C <sub>s</sub> , Energ	y: -267.59323	
С О О С Н Н Н Н Н Н Н			6.0 6.0 8.0 6.0 1.0 1.0 1.0 1.0 1.0	2.68274 1.23130 0.79414 0.44331 -0.96736 3.29585 -1.45462 -1.24089 -1.24089 2.90425 2.90425	-0.19511 0.19417 1.33134 -0.90962 -0.62359 0.70458 -1.59632 -0.05332 -0.05332 -0.80029 -0.80029	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 -0.88859 0.88859 -0.88168 0.88168	
Table	96	_	Methyl	Trifluor	pacetate,	C <sub>s</sub> , Energy:	-564.66942
С О О С Н Н Н F F F			$ \begin{array}{c} 6.0\\ 6.0\\ 8.0\\ 6.0\\ 1.0\\ 1.0\\ 9.0\\ 9.0\\ 9.0\\ 9.0 \end{array} $	2.68783 1.21056 0.82365 0.45829 -0.96475 -1.42554 -1.24147 -1.24147 2.97136 2.97136 3.46795	-0.18717 0.21533 1.36512 -0.88853 -0.63202 -1.61614 -0.06886 -0.92258 -0.92258 0.89761	0.00000 0.00000 0.00000 0.00000 0.00000 -0.89130 0.89130 -1.09071 1.09071 0.00000	
Table	97	_	Methyl	Cyanoforr	mate, C <sub>s</sub> ,	Energy: -320.	41939
С С О С Н Н Н			6.0 6.0 8.0 6.0 1.0 1.0	1.37723 0.01780 -0.21986 -0.87322 -2.25169 -2.83598 -2.45105 -2.45105	-0.16951 0.38172 1.57342 -0.61542 -0.17089 -1.08702 0.42337 0.42337	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 -0.89167 0.89167	
Ν			7.0	2.49554	-0.54781	0.0000	

Table	98 -	- Dimetl	nylcarbona	te, C <sub>s</sub> , i	Energy: -342.62576
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		8.0 6.0 8.0 6.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	$1.32894 \\ -0.01437 \\ -0.67479 \\ -0.51325 \\ -1.95315 \\ 2.02034 \\ 3.07540 \\ 1.77468 \\ 1.77468 \\ -2.20380 \\ -2.34489 \\ -2.$	-0.4549 -0.4514 -1.4668 0.8076 0.8493 0.8066 0.5401 1.3840 1.3840 1.9079 0.3561 0.3561	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Table	99 -	- Dimetl	nylurethan	e, C <sub>1</sub> , E	nergy: -322.79444
0 C N 0 H C C H H H H H H		8.0 6.0 7.0 8.0 1.0 6.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	-1.68705 -1.68319 -2.75114 -0.59305 -2.55723 0.57467 -3.98495 -3.99845 -4.82779 -4.08382 1.35224 0.85481 0.39661	2.7085 1.4871 0.6952 0.7054 -0.2847 1.4561 1.2690 1.3521 0.6552 2.2662 0.7104 2.1457 2.0212	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
Table	100	- Meth	yl Acetami	de, C <sub>1</sub> , 1	Energy: -247.75036
C C N O C H H H H H H		6.0 6.0 7.0 8.0 6.0 1.0 1.0 1.0 1.0 1.0	-2.63278 -1.32164 -0.21658 -1.26543 1.12159 -2.58313 -3.39653 -2.92879 -0.33358 1.69942 1.01750	-0.4188 0.3382 -0.4219 1.5442 0.1312 -1.3657 0.2165 -0.6210 -1.4115 -0.2582 1.2099	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
Н		1.0	1.65173	-0.0910	0 1.16051

Table 101 - Methyl Trifluoroacetamide,  $C_s$ , Energy: -544.83515

С	6.0	0.49401	-0.00687	0.00000
С	6.0	-1.03527	0.07587	0.00000
0	8.0	-1.58336	1.17432	0.00000
Ν	7.0	-1.66595	-1.11551	0.00000
F	9.0	0.94330	-1.29065	0.00000
Н	1.0	-1.12087	-1.96561	0.00000
F	9.0	0.99271	0.59792	1.08865
F	9.0	0.99271	0.59792	-1.08865
С	6.0	-3.11718	-1.16451	0.00000
Н	1.0	-3.42912	-2.20812	0.00000
Н	1.0	-3.51399	-0.66427	0.88576
Н	1.0	-3.51399	-0.66427	-0.88576

Table 102 - Methylcyanoformamide,  $C_{\rm s},$  Energy: -300.58450

С	6.0	2.61562	-0.18309	0.00000
С	6.0	1.19688	0.22863	0.00000
0	8.0	0.86457	1.41048	0.00000
N	7.0	0.34474	-0.82117	0.00000
N	7.0	3.76025	-0.47562	0.00000
H	1.0	0.71669	-1.76205	0.00000
С	6.0	-1.09068	-0.59470	0.00000
H	1.0	-1.38667	-0.03003	-0.88642
H	1.0	-1.38667	-0.03003	0.88642
Н	1.0	-1.59166	-1.56190	0.00000

Table 103 - Methyl Succinimide, C<sub>s</sub>, Energy: -398.81698

Ν	7.0	-0.02919	0.96204	0.00000
0	8.0	2.26482	0.70480	0.00000
0	8.0	-2.32393	0.63450	0.00000
С	6.0	1.14492	0.21891	0.00000
С	6.0	-1.18736	0.18999	0.00000
С	6.0	0.76407	-1.25124	0.00000
С	6.0	-0.76528	-1.26945	0.00000
Н	1.0	1.20551	-1.72785	0.87928
Н	1.0	1.20551	-1.72785	-0.87928
Н	1.0	-1.19543	-1.75653	0.87916
Н	1.0	-1.19543	-1.75653	-0.87916
С	6.0	-0.03046	2.41152	0.00000
Н	1.0	-1.07105	2.73425	0.00000
Н	1.0	0.48307	2.78389	-0.88801
Н	1.0	0.48307	2.78389	0.88801

Table 104 - Methyl Chloride,  $C_{3v}$ , Energy: -499.36908

С	6.0	0.00000	0.00000	1.91773
Н	1.0	-0.51467	0.89144	1.56476
Н	1.0	-0.51467	-0.89144	1.56476
Н	1.0	1.02934	0.00000	1.56476
Cl	17.0	0.00000	0.00000	3.69460

## MP2(full)/6-31G(d) Geometries and Energies of Anions

Table	105	- Mesy	late (-	) C <sub>3v</sub> ,	Energy	: -662	.53310	
C S O O H H H		$ \begin{array}{r} 6.0\\ 16.0\\ 8.0\\ 8.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0 \end{array} $	0.000 0.000 -0.721 -0.721 1.442 0.515 0.515 -1.031	00 C 00 C 21 1 21 -1 42 C 66 -C 66 C 32 C	.00000 .00000 .24918 .24918 .00000 .89315 .89315 .00000	0.15 1.95 2.37 2.37 2.37 -0.20 -0.20 -0.20	5191 5361 1290 1290 1290 0542 0542 0542	
Table	106	- Meth	ylsulfa	te (-)	C <sub>s</sub> , En	ergy:	-737.57487	7
О S О С H О О H H		8.0 16.0 8.0 6.0 1.0 8.0 8.0 1.0 1.0	1.622 0.508 -0.815 -2.056 -2.837 0.334 0.334 -2.155 -2.155	57 C 38 -C 10 C 06 -C 68 C 47 -1 47 -1 25 -C 25 -C	.37580 .58274 .48061 .21083 .55435 .36721 .36721 .83840 .83840	0.00 0.00 0.00 0.00 -1.24 1.24 -0.89 0.89	0000 0000 0000 0000 4145 4145 9199 9199	
Table	107	- Trif	late (-	) C <sub>3v</sub> ,	Energy	: -959	.63081	
C S O O O F F		6.0 16.0 8.0 8.0 8.0 9.0 9.0	0.000 0.000 -0.722 -0.722 1.444 0.627 0.627	00 C 00 C 10 1 10 -1 20 C 44 -1 44 1	.00000 .00000 .25071 .25071 .00000 .08676 .08676	0.20 2.04 2.35 2.35 2.35 -0.29	0921 4431 5488 5488 5488 9674 9674	
F.		9.0	-1.254	89 (	.00000	-0.29	96/4	

Table	108	- Fluo	rosulfonate	(-) C <sub>3v</sub> ,	Energy: -722.42035
F S O O O		9.0 16.0 8.0 8.0 8.0	0.00000 0.00000 -0.71849 -0.71849 1.43697	0.00000 0.00000 1.24445 -1.24445 0.00000	0.29520 1.95804 2.26366 2.26366 2.26366
Table	109	- TFSI	(anti)(-)	C <sub>2</sub> , Energ	y: -1823.69893
N S S O O O C C F F F F F F		$7.0\\16.0\\16.0\\8.0\\8.0\\8.0\\6.0\\6.0\\9.0\\9.0\\9.0\\9.0\\9.0\\9.0\\9.0\\9.0\\9.0$	0.00000 1.41490 -1.41490 1.41448 -1.41448 2.42973 -2.42973 1.80301 -1.80301 2.98193 0.86056 -0.86056 1.90555 -1.90555	0.00000 0.02268 -0.02268 0.48851 -0.48851 0.52762 -0.52762 -1.76885 1.76885 1.93558 1.93558 -2.42617 2.42617 -2.33443 2.33443	0.87210 0.11185 0.11185 -1.27785 -1.27785 1.03850 1.03850 -0.01609 -0.01609 -0.64993 -0.64993 -0.70840 1.19802 1.19802
Table	110	- FSI	$(-)C_2$ , Energy	gy -1349.	28297
N S F		7.0 16.0 16.0 9.0	0.00000 1.34747 -1.34747 1.79459	0.00000 0.31716 -0.31716 -1.15425	0.90199 0.10686 0.10686 -0.44979

S	16.0	1.34747	0.31716	0.10686
S	16.0	-1.34747	-0.31716	0.10686
F	9.0	1.79459	-1.15425	-0.44979
F	9.0	-1.79459	1.15425	-0.44979
0	8.0	1.19740	1.11481	-1.10277
0	8.0	-1.19740	-1.11481	-1.10277
0	8.0	2.37985	0.65209	1.07274
0	8.0	-2.37985	-0.65209	1.07274

Table	111	- MSI	(anti)(-)	$C_2$ , Energy:	-1229.53832
N S S O O O O C C H H H H H H H		$7.0\\16.0\\8.0\\8.0\\8.0\\6.0\\6.0\\1.0\\1.0\\1.0\\1.0\\1.0\\1.0\\1.0$	0.00000 1.39569 -1.39569 1.36940 -1.36940 2.46813 -2.46813 1.63809 -1.63809 2.58701 -2.58701 0.80040 1.66567 -1.66567	0.00000 0.05051 -0.05051 0.93808 -0.93808 0.27777 -0.27777 -1.59984 1.59984 -1.61728 1.61728 -1.83034 1.83034 -2.29000 2.29000	1.19069 0.37946 0.37946 -0.80902 -0.80902 1.36210 1.36210 -0.26067 -0.26067 -0.80014 -0.91775 0.91775 0.58283 0.58283
Table	112	- MSA	(-) C <sub>1</sub> , En	ergy: -642.	63252
N H S O O C H H H		$7.0 \\ 1.0 \\ 16.0 \\ 8.0 \\ 6.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 $	0.57006 1.48921 0.38777 -0.62712 1.66059 -0.39514 -0.57377 -1.34108 0.26538	-0.10099 -0.50957 1.03873 2.02699 1.59170 0.32181 1.11028 -0.13545 -0.43491	0.96594 0.77668 -0.09430 0.34904 -0.65248 -1.56133 -2.29622 -1.26657 -1.99171
Table	113	- FSA	(-) C <sub>1</sub> , En	ergy: -702.	52414
N H S O F		7.0 1.0 16.0 8.0 8.0 9.0	0.56722 0.97222 0.52061 0.19381 1.54857 -0.85883	-0.19330 -0.42577 1.35184 1.84129 2.08606 1.81386	0.15548 -0.75429 0.22419 1.56672 -0.54186 -0.63337

Table	114	-	Isop	ropyl	FSA	( - )	C1,	-82	0.03	3729			
N C S O O F C H C H H H H H H		1	7.0 6.0 8.0 8.0 9.0 6.0 1.0 1.0 1.0 1.0 1.0 1.0	-1.1 0.1 -1.3 -2.7 -0.2 -1.0 1.1 0.0 0.8 1.7 0.1 1.0 2.0 1.3 0.6	6986 7441 1598 0600 6330 6232 0384 0632 4000 8322 6790 3613 3381 5160 1212	-0. -0. 0. 1. 1. -0. -1. 0. 0. 1. 1. -1. 0. 0. -1. -1. -1. -1. -1. -1. -1. -1	.124 432 715 116 708 371 067 187 .770 483 .181 .543 .407 .342 .920	12 54 00 78 67 09 78 38 93 69 88 66 54 15	$\begin{array}{c} 0 \\ 0 \\ -1 \\ -1 \\ -1 \\ -2 \\ 0 \\ 1 \\ 1 \\ 2 \\ 0 \\ 0 \\ -1 \\ 0 \end{array}$	1032 5924 1833 4198 4945 4584 4453 3744 2647 7487 0233 5208 0276 2236 9184	4 6 2 4 8 4 2 3 6 9 8 7 8 9 0		
Table	115	_	Acet	ate (	-) C	<sub>s</sub> , En	ergy	y: -	227.	854	13		
С С О Н Н Н			6.0 6.0 8.0 8.0 1.0 1.0	1.4 -0.1 -0.8 -0.5 1.7 1.8 1.8	1889 3047 1068 1302 0293 4816 4816	0. -0. 1. -1. 1. -0.	.170 .010 .053 .214 .226 .322 .322	15 33 06 48 74 79 79	0. 0. 0. 0. -0. 0.	0000 0000 0000 0000 0000 8799 8799	0 0 0 0 1		
Table	116	-	Trif	luoro	acet	ate	( – )	Cs,	Enei	gy:	-5	24.9	96954
C C O F F F			6.0 6.0 8.0 8.0 9.0 9.0 9.0	-1.3 0.1 0.7 0.5 -1.9 -1.9 -1.8	9578 5647 8477 1389 6620 6620 5640	-0. 0. -1. 0. 0. -1.	.131 .010 .073 .212 .465 .465 .411	02 14 86 94 61 61 09	0. 0. 0. -1. 1. 0.	0000 0000 0000 0000 0892 0892 0000	0 0 0 5 5 0		
Table	117	-	Cyan	oform	ate	(-) (	2v,	Eneı	rgy:	-28	30.7	7302	23
C C N O O			6.0 6.0 7.0 8.0 8.0	0.0 0.0 0.0 0.0	0000 0000 0000 0000 0000	0. 0. 0. -1. 1.	.000 .000 .000 .149 .149	00 00 00 98 98	-0. 1. -1. 2. 2.	0255 5198 2097 0099 0099	5 2 9 1		

Table 118 -	Methylcarbonate (-) C <sub>s</sub> , Energy: -302.90805
О С О С Н Н Н	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Table 119 -	Methylurethane (-) C <sub>s</sub> , Energy: -283.02333
О С О N С Н Н Н Н	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
Table 120 -	Acetamide (-) C <sub>s</sub> , Energy: -207.96859
N O C H H H	7.0 $-0.02089$ $-1.42154$ $0.00000$ $8.0$ $1.13446$ $0.59077$ $0.00000$ $6.0$ $0.06986$ $-0.09681$ $0.00000$ $6.0$ $-1.22754$ $0.76548$ $0.00000$ $1.0$ $-1.02004$ $-1.65591$ $0.00000$ $1.0$ $-1.21978$ $1.41923$ $0.87947$ $1.0$ $-1.21978$ $1.41923$ $-0.87947$ $1.0$ $-2.16072$ $0.18718$ $0.00000$
Table 121 -	Trifluoroacetamide (-) C <sub>s</sub> , Energy: -505.08677
C C O N F H F	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

Table	122	-	Cyano	oformamide	( - )	$C_{s}$ ,	Energ	у: -	260.84632
N C O N H			7.0 6.0 6.0 8.0 7.0 1.0	2.12924 0.94410 -0.58354 -1.08719 -1.16580 -0.42817	-0.0 0.0 -0.0 -1.3 1.3	0045 0112 0042 1545 1811 8925	7 0. 8 0. 3 0. 6 0. 2 0. 0 0.		0 0 0 0 0
Table	123	_	Succi	inimide (-)	C <sub>2v</sub>	, En	ergy:	-359	9.07164
N			7.0	0.00000	0.0	0000	0 0.	3428	6
0			8.0	-2.29645	0.0	0000	0 -0.	0749	8
0			8.0	2.29645	0.0	0000	0 -0.	0749	8
С			6.0	-1.11121	0.0	0000	0 -0.	4460	5
С			6.0	1.11121	0.0	0000	0 -0.	4460	5
С			6.0	-0.75752	0.0	0000	0 -1.	9564	9
С			6.0	0.75752	0.0	0000	0 -1.	9564	9
Н			1.0	-1.20887	0.8	8803	1 -2.	4274	4
Н			1.0	1.20887	0.8	8803	1 -2.	4274	4
Н			1.0	-1.20887	-0.8	8803	1 -2.	4274	4
Н			1.0	1.20887	-0.8	8803	1 -2.	4274	4

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