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Examination of Solvent-Room Temperature Ionic Liquid Interactions using 2D NMR and Computational Chemistry

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Introduction

Current methods for electrochemical processing of Rare Earth Metals (REMs) require high temperatures (i.e. energy intensive) and produce an abundance of hazardous fluoride waste. Room temperature ionic liquids (RTILs) are an alternative electrolyte as they allow for a low-temperature, energy-efficient electrochemical process. The viscosity and conductivity of the RTIL determine how effective they can be in this process. Since viscosity is directly related to molecular structure and forces, this study sets out to investigate intra- and intermolecular interactions in the RTIL, Trihexyltetradecylphosphonium dicyanamide (Cyphos 105). As seen here, 2-dimensional nuclear magnetic resonance (2D NMR) spectroscopy suggests a close interaction between the hydrogen atoms on the tetradecyl tail and the phosphorus atom of the Cyphos 105 ionic liquid. Density Functional Theory (DFT) computations were performed to determine if the optimized geometries of the Cyphos 105 are consistent with a close approach of H and P atoms via a strong inter- or intramolecular interaction in the Cyphos RTIL.

Method

- 2D NMR of Cyphos 105 were taken (H-NOESY and P-31/H-1 HOESY)
- Straight geometries of Cyphos 105 were modelled in Avogadro, with the dicyanamide anion in different positions around the phosphorus atom of the phosphonium cation.
- A DFT geometry optimization calculation was performed on the different geometries using Gaussian 16.
- All optimization calculations were done using the B3LYP theory, 6-31G(d) basis set and the PCM solvation model.
- The most stable geometry was identified. Similar geometries were modelled, with their tetradecyl tails at different distances from the P atom and then optimized.
- Then to begin investigating intermolecular interactions, geometry optimization calculations were initiated on a Cyphos 105 to measure the intermolecular distance.

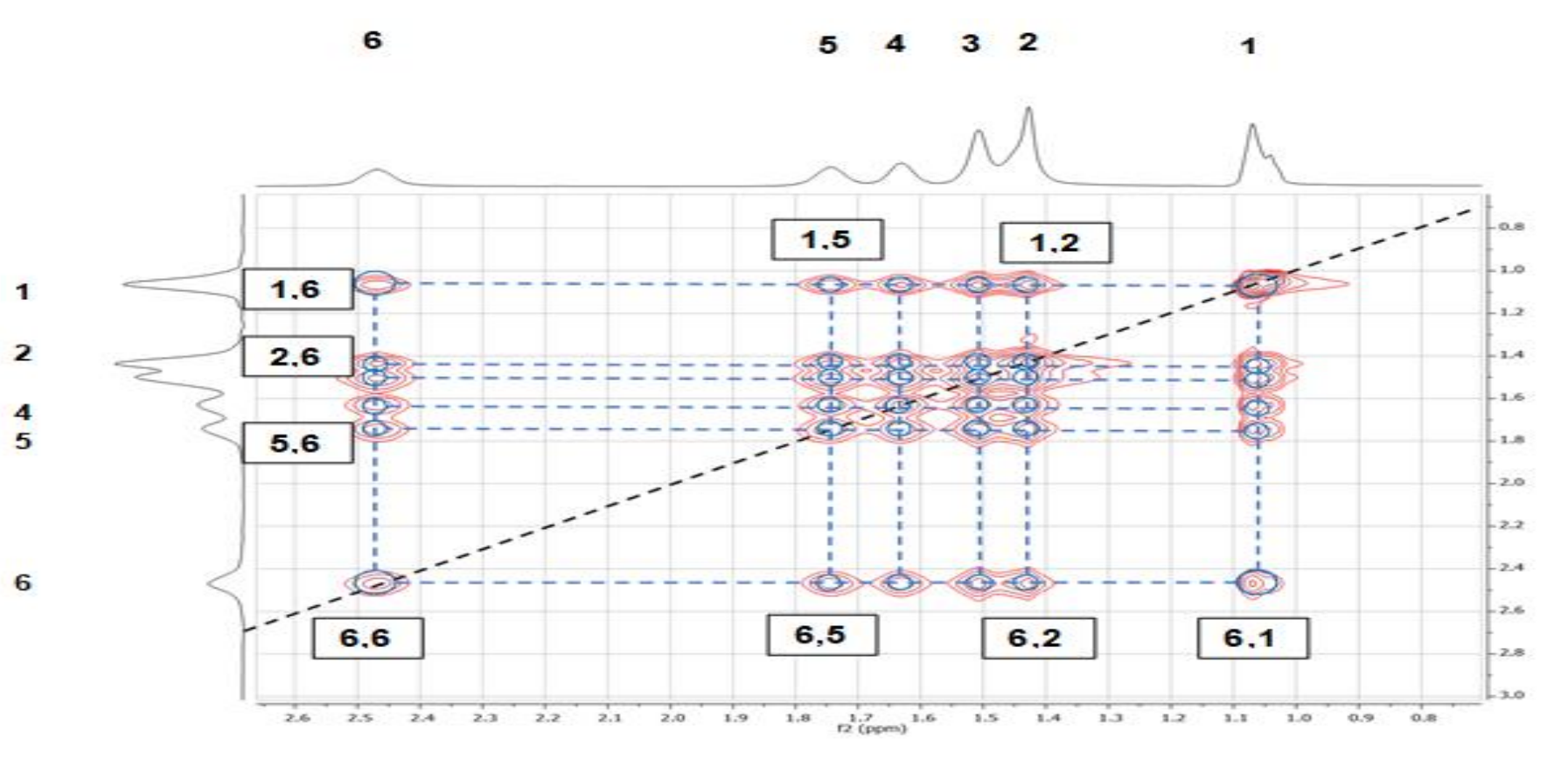
Results

Phosphonium Cation Showing the Different H Atoms

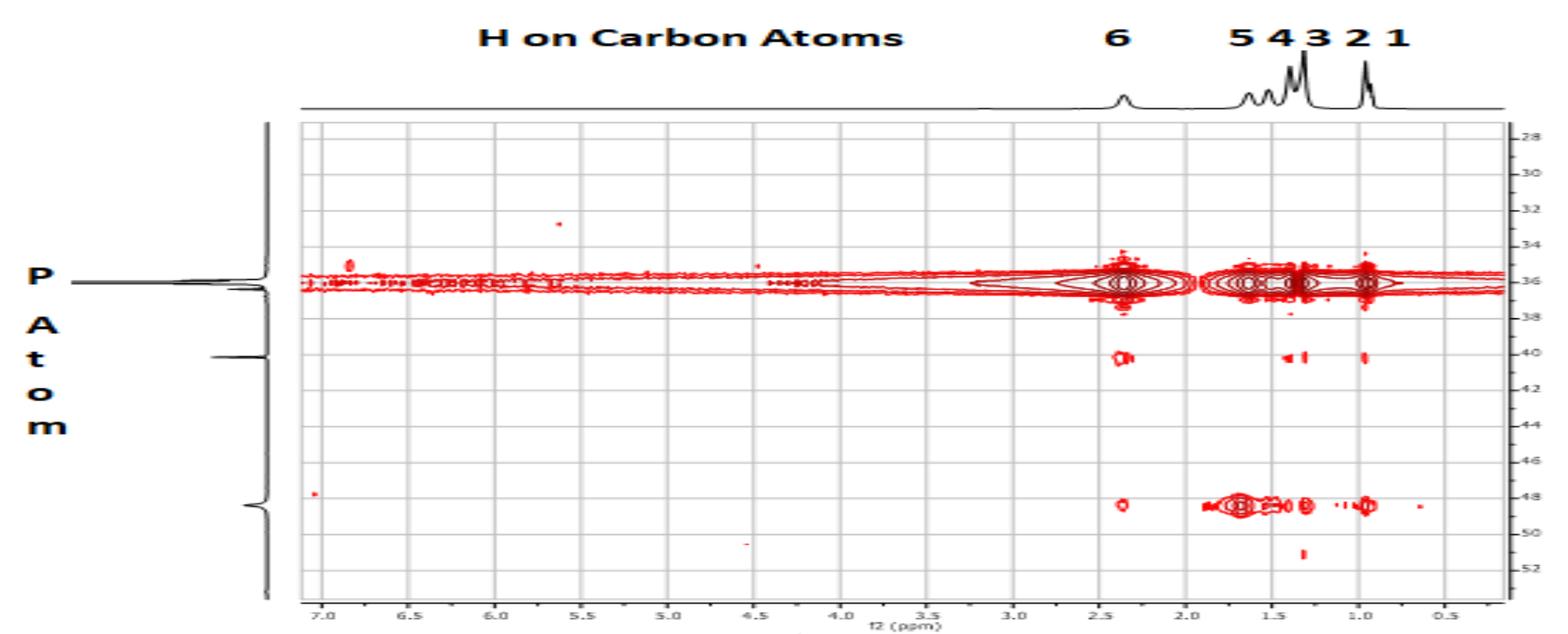
$(CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2CH_2)_3 - P^+ - CH_2CH_2CH_2(CH_2)_4(CH_2)_6CH_3$

1 2 3 4 5 6 6 5 4 3 2 1

2D NMR Spectra of Cyphos105



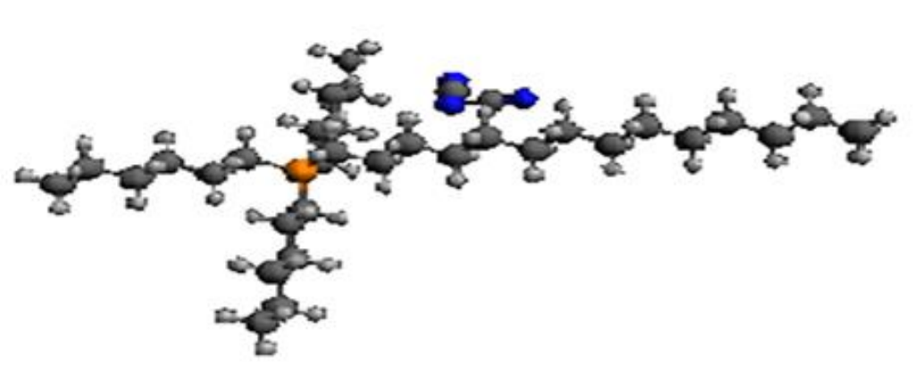
^{1}H-NOESY NMR



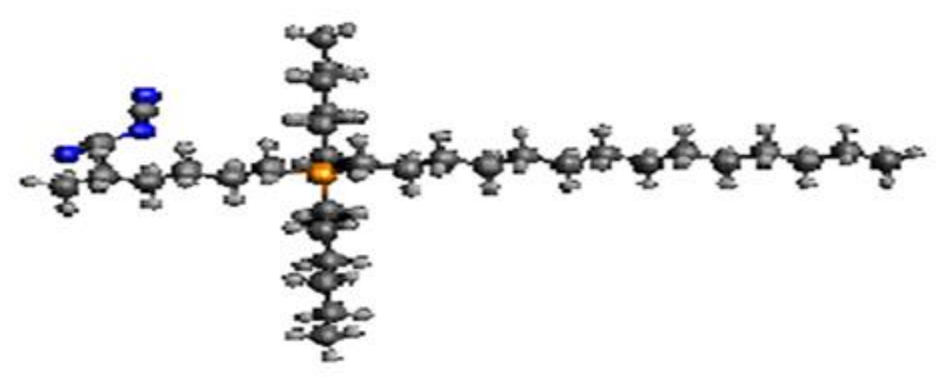
P-31/H-1 HOESY

The 2D NMR for Cyphos 105 showed interactions between the different types of H atoms. The diagonal dotted line represents the correlation of peaks to themselves, while off diagonal signals show correlation between two signals. It can be seen that H atoms on the tetradecyl tail and other terminal H atoms interact with H atoms very close to the P atom. There is also interaction between the H atoms and the P atom. Based on the Nuclear Overhauser Effect (NOE), the P & H and H & H atoms must be about 5 Å or less apart for this to happen.

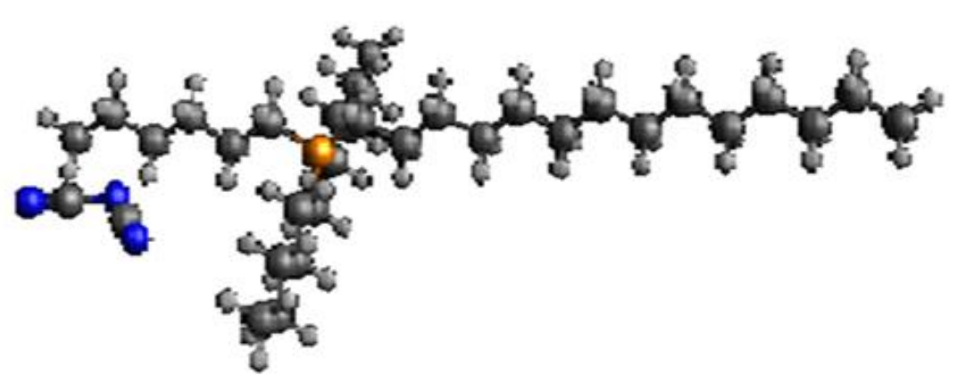
Before Optimization (Straight Geometry)



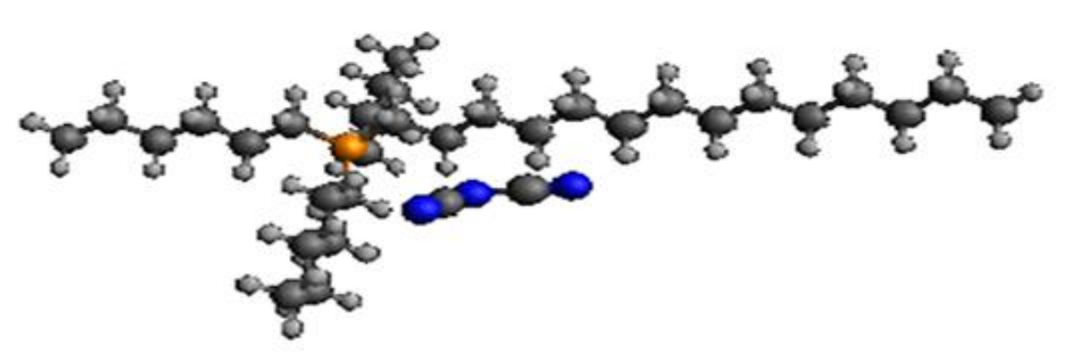
Geometry 1



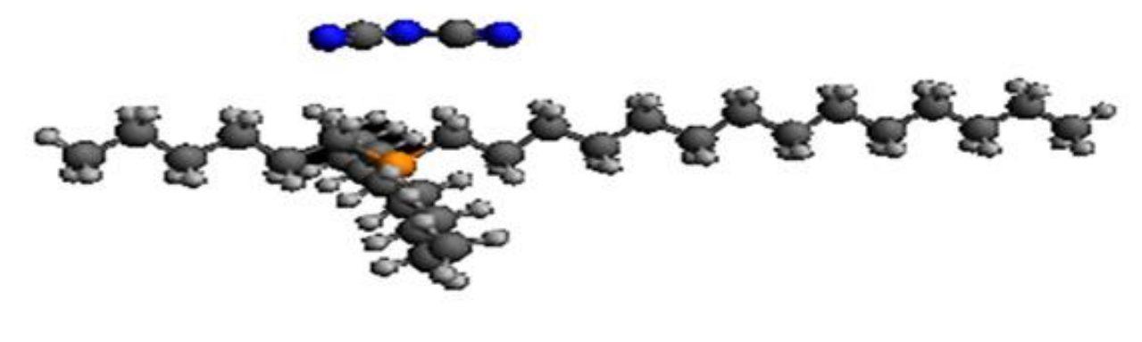
Geometry 2



Geometry 3



Geometry 4



Geometry 5

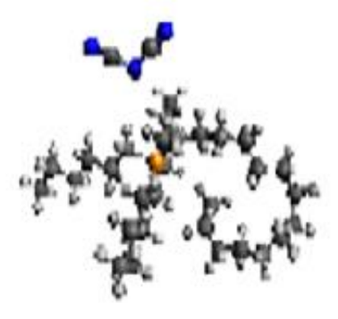
Energies of the Optimal Geometries

Molecule	Energy (kJ/mol
Geometry 1	-4,839,770.510
Geometry 2	-4,839,771.540
Geometry 3	-4,839,758.510
Geometry 4	-4,839,768.593
Geometry 5	-4,839,793.044

Optimal Dist. Between the Cation and Anion

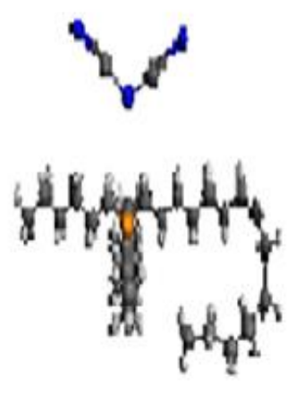
Molecule	Distance Between Phosphonium ion and Dicyanamide ion BEFORE Optimization (Å)	Distance Between Phosphonium ion and Dicyanamide ion AFTER Optimization (Å)	Energy (kJ/ mol)
Geometry 5_1	4.020	5.042	-4,839,806.989
Geometry 5_2	8.000	5.042	-4,839,701.185
Geometry 5_3	10.032	4.588	-4,839,671.255
Geometry 5_4	12.029	4.588	-4,839,650.818

Before Optimization (Bent Geometry)

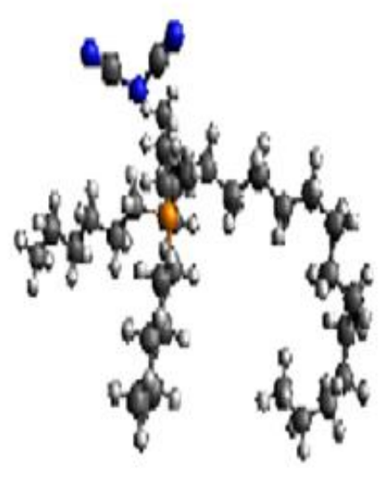


Geometry 6

Geometry 7

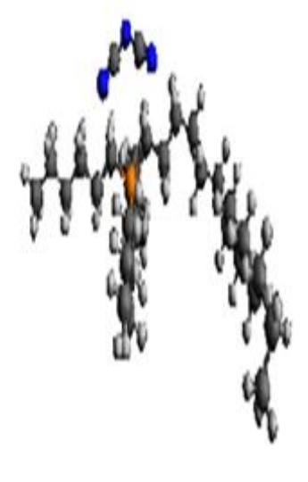


Geometry 8

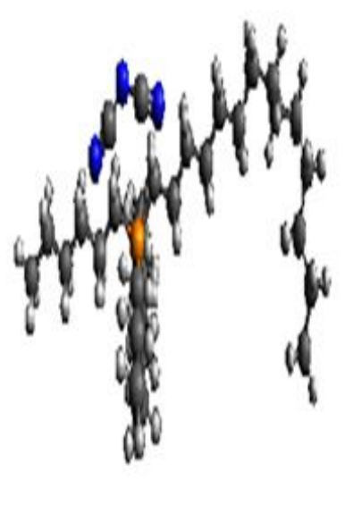


Geometry 9

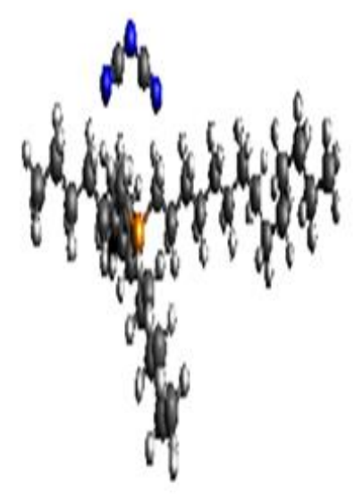
After Optimization



Geometry 10



Geometry 11



Geometry 12

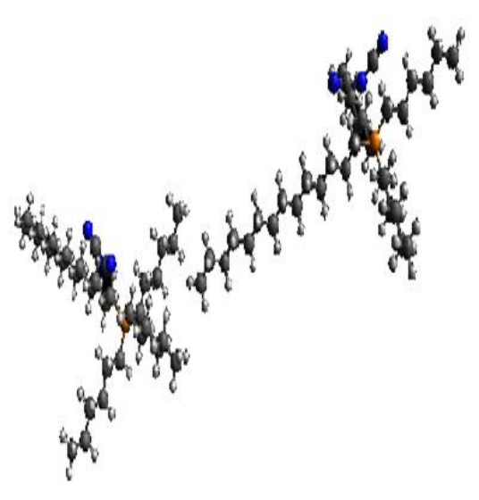
Geometry 13

Distance & Energy Between the P atom & Tetradecyl Tail After Optimization

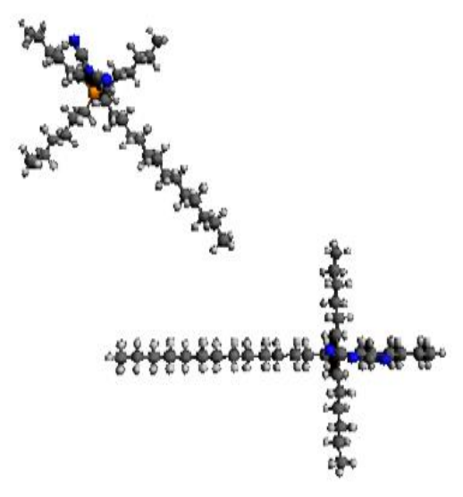
Molecule	Distance Between P atom and the End of the Tetradecyl tail BEFORE Optimization (Å)	Distance Between P atom and the End of the Tetradecyl tail AFTER Optimization (Å)	Energy after Optimization (kJ/ mol)
Geometry 10	2.999	13.27	-4,839,566.589
Geometry 11	4.105	11.935	-4,840,030.133
Geometry 12	5.792	12.914	-4,835,669.573
Geometry 13	7.721	9.379	-4,839,663.857

Dimer

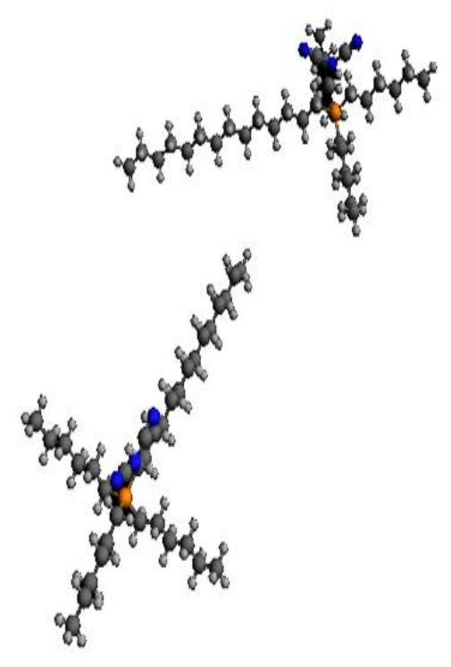
Before optimization



Geometry 14

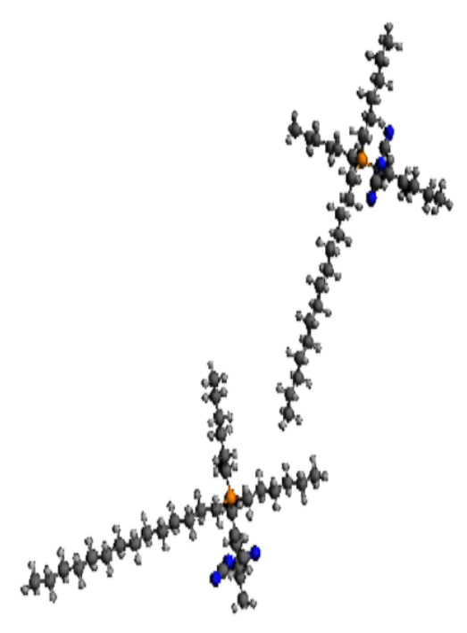


Geometry 15

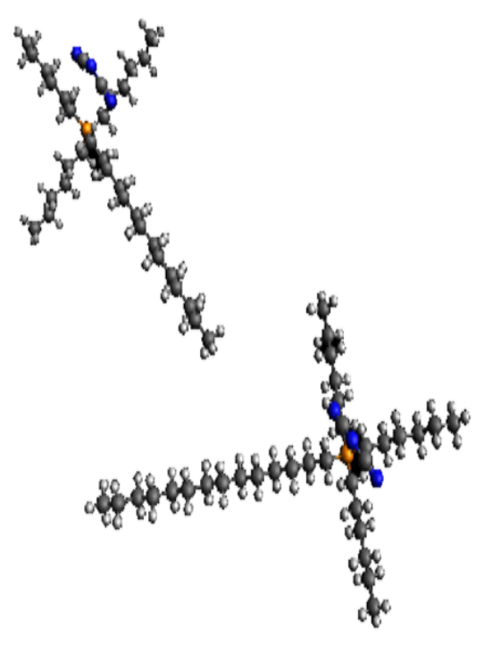


Geometry 16

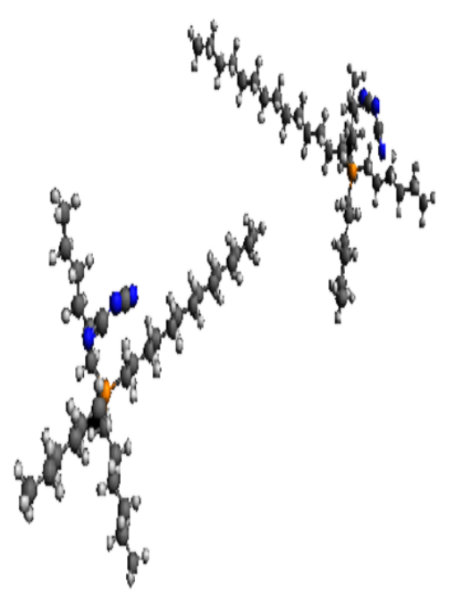
After optimization



Geometry 17



Geometry 18



Geometry 19

Interaction in the Dimer Molecules After Optimization

Dimer	Distance Between P Atom & Tetradecyl Tail Before Optimization (Å)	Distance Between P Atom & Tetradecyl Tail After Optimization (Å)	Energy (KJ/ mol)
Geometry 17	6.971	6.808	-9,680,093.172
Geometry 18	12.389	11.760	-9,679,642.661
Geometry 19	11.811	11.697	-9,679,642.915

Conclusion

- The optimal position of the dicyanamide anion was found to be about 4.5 to 5 Å above the P atom in the trihexyltetradecylphosphonium cation.
- In each instance, the tetradecyl tail was pushed further away from the P atom after optimization calculations suggesting minimal intramolecular interaction between the P atom and terminal methyl protons.
- In some cases, the distance between the tetradecyl tail protons of one dimer molecule and the P atom of the other dimer molecule decreased after optimization calculations, suggesting some sort of intermolecular interactions. However, there were other cases in which the distance increased rather than decrease. Further calculations are still being done in order to have a better understanding of what is going on.

Acknowledgement

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