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A Computational Study to Understand the Electronic Effect on Ion Recognition of Diaminomalenonitrile based Molecular Receptor Systems

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Abstract

In this work, the optimized molecular structure, bond parameters, Mulliken charge distribution analysis of methyl (M), ethyl (E), phenyl (P) and naphthyl (N) fragments tagged with diaminomaleonitrile (DMN) receptors were studied with the help of density functional theory (DFT) and time-dependent density functional theory (TD-DFT) method. Since, all the receptors have been explored as ion receptors for F− via absorption recognition signal. Thus here we have tried to understand these sensing modulations theoretically before (neutral) and after the interaction of receptors with F−ions (deprotonated). The absorption spectra of neutral as well as deprotonated forms were calculated using 6-311++G (d,p) basis set in DFT/TD-DFT method. The theoretical results of all receptors were compared with each other.

Keywords: Optimized; Receptor; DMN; DFT; TD-DFT; ICT; PET

Abbreviations: DFT: Density Functional Theory; TD-DFT: Time-Dependent Density Functional Theory; DMN: Diaminomaleonitrile; THF: Tetrahydrofuran; PCM: Polarized Continuum Model.

Introduction

The design and synthesis of receptors capable of binding and sensing anions selectively have received significant attention in recent years because anions play an important role in a wide range of biological, environmental, and chemical processes [1-7]. This can be attributed to the fact that molecular receptors are highly valuable tools to perform *ion recognition* amid high selectivity and sensitivity. Most importantly, synthetic receptors are easy to prepare, operate and realize high sample through output [8]. A number of interactions, such as hydrogen bonding, electrostatic force, metal-ligand coordination, hydrophobic and vander Waals forces have been employed to develop novel and effective receptors [9-11]. In the present study, the combined use of DFT/TD-DFT (B3LYP) functional and standard basis sets 6-311++G(d,p) provides an excellent theoretical information. The literature survey reveals that, no intensive observation of theoretical [DFT/TD-DFT] investigation has been reported so far with types of receptors possessing free -NH_2 based recognition site. Therefore, the present investigation was undertaken to study the optimization, bond lengths and Mulliken charge distribution of neutral and deprotonated states of methyl (M), ethyl (E), phenyl (P) and naphthyl (N) diaminomaleonitrile (DMN) based receptors (Figures 1 & 2).

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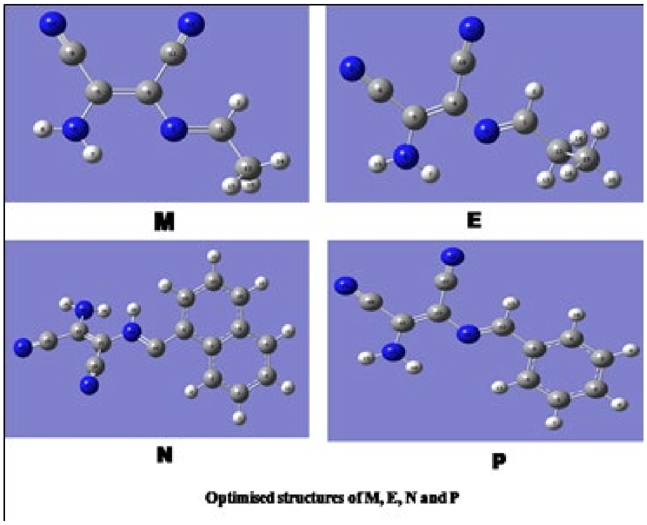

Figure 1: Optimized structures of Molecular Receptors labeled as M, E, N and P.

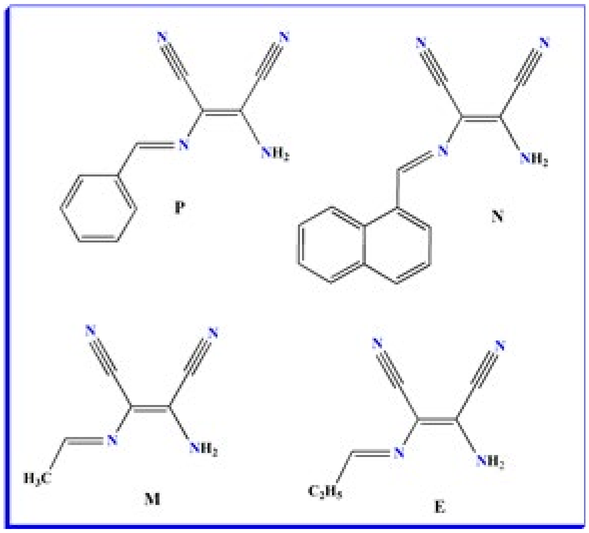

Figure 2: General structures of Molecular Receptors (M, E, N and P) with Diaminomalenonitrile as recognition site.

Methodology

All calculations were performed using Gaussian 09 program. The hybrid density functional theory (DFT) and Time Dependent DFT (TD-DFT). B3LYP/6-311G+ (d,p) was used to obtain the geometry optimization of the various receptors as it is moderate and suitable for such large organic compounds. To investigate the solvent effect of tetrahydrofuran (THF), PCM (Polarized Continuum Model) calculation was performed.

Results and Discussion

Mulliken Charge Distribution Analysis

The Mulliken charge is used to understand the charge distribution or density on the chemical bond between nitrogen and hydrogen because it facilitates positive and negative regions in the molecular space, at which the protons and electrons concentrate. Thus chemically significant regions; bonds can be identified; also gives the narration of the mechanism of electrophilic and nucleophilic substitutions. Normally, the charges are distributed evenly over the molecule which leads to be neutral. But after interaction with F^- ions leads to deprotonation of the all receptors i.e neutral as well as deprotonated and hence leads to increase or decrease of charge density. Usually, the negative Mulliken populated over the highly electronegative atoms which splits the positive charges among hydrogen atoms. The N and H of the molecule have negative and positive space respectively. The Mulliken charges of N and H atoms of amine (NH_2) of chemosensors are graphically presented in Figure 3.

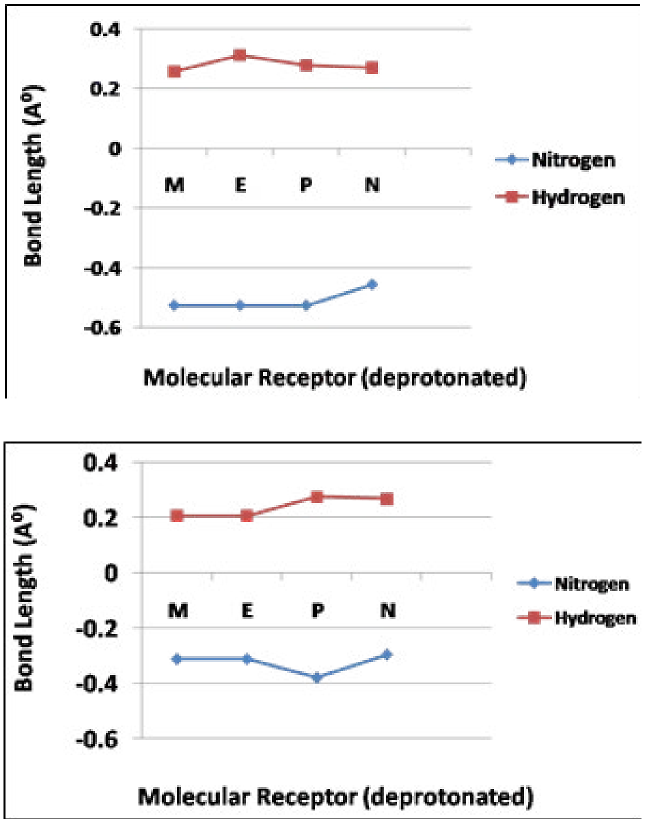

Figure 3: Charge density on Nitrogen and hydrogen of neutral and deprotonated receptors M, E, P and N.

Bond Length Analysis

The calculation of bond lengths of different bonds of receptors M, E, P and N in neutral as well as deprotonated state. In the current study, a large variation of bond lengths has been observed in deprotonated as well in neutral states in E, P and N but however in M. This may be due to the delocalization of π-electrons and hence extended conjugation. Except NH bond (in NH_2 moiety) where the bond length remains constant in neutral as well as deprotonated state. But however the bond length of all other bonds increases may be because of the extended conjugation (Figure 4).

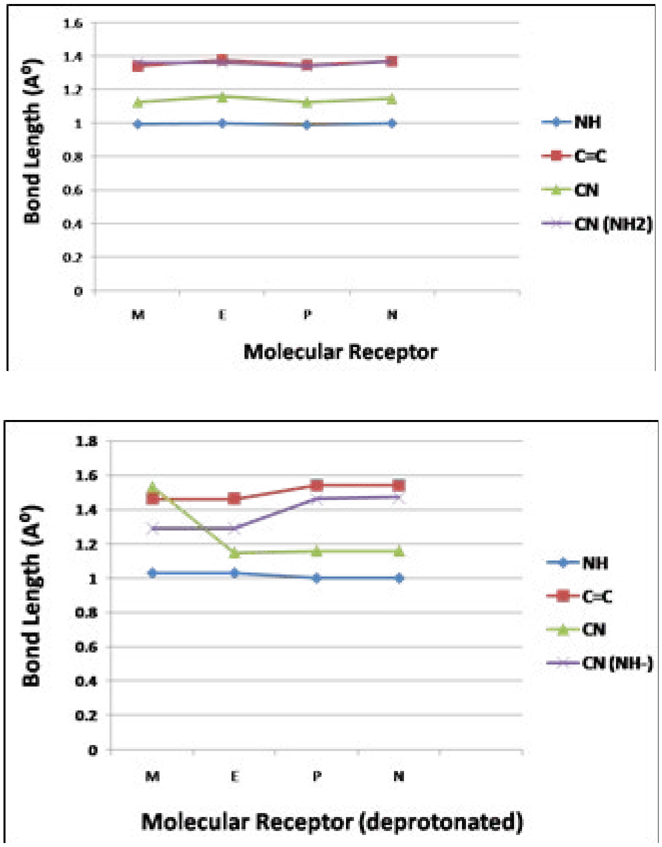

Figure 4: Bond length of different bonds of neutral (above) and deprotonated receptor (below) M, E, P, N and Py.

Conclusion

In this article, the optimized molecular structure, bond parameters, Mulliken charge distribution analysis of methyl (M), ethyl (E), phenyl (P) and naphthyl (N) fragments tagged with diaminomaleonitrile (DMN) receptors have been presented. All the receptors have been explored as ion receptors for F^- to understand these sensing modulations theoretically before (neutral) and after the interaction of receptors with F^- ions (deprotonated) using 311++G (d,p) basis set in DFT/TD-DFT method. The theoretical results of all receptors were compared with each other.

Conflict of Interest

The Authors declare that there is no conflict of interest regarding the publication of this article.

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