2016

Computational studies of paradifluorobenzene cations and hydrogen cyanide molecule

John C. Rowe IV
University of Richmond

Recommended Citation

Rowe, John C. IV, "Computational studies of paradifluorobenzene cations and hydrogen cyanide molecule" (2016). *Honors Theses*. 931.
https://scholarship.richmond.edu/honors-theses/931

Computational Studies of Paradifluorobenzene Cations and Hydrogen Cyanide Molecules

by

John C. Rowe, IV

Honors Thesis

in

Program in Biochemistry and Molecular Biology
University of Richmond
Richmond, VA

4.22.16

Advisor: Dr. Samuel Abrash

This thesis has been accepted as part of the honors requirements
in the Program in Biochemistry and Molecular Biology.

Samuel A Allen
(advisor signature)

4/21/2016
(date)

Julia A Pollock
(reader signature)

4/22/16
(date)

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are hypothesized to comprise a significant portion of interstellar carbon identified from the Diffuse Interstellar Bands (DIBs). Gas phase cation-molecule reactions between compounds that previously existed as weakly bound species provides the best explanation for the emergence of PAHs in the interstellar medium (ISM). In this work, we use computational methods to characterize one of these weakly-bound systems. We discovered that intramolecular charge distribution (calculated using the Natural Population Analysis) dictate the complexes formed between a paradifluorobenzene cation and either one or two HCN molecules. Additionally, the relative stabilities of the complexes and the binding energies released upon their formation are also determined by the molecular charge distribution. Ultimately, this finding helps us better understand the properties that dictate weakly-bound species that potentially serve as precursors for reactive systems in the ISM.

Introduction

The Diffuse Interstellar Bands (DIBs) are absorption lines seen from the spectra of nearby stars following light's pass through the interstellar medium (ISM). The absorption lines observed in these spectra, observed as early as 1922 *(1)*, correspond to compounds of a uniquely stable nature that exist in the harsh environment of the ISM (with a temperature of approximately 4 Kelvin). Despite the efforts of the scientific community since the discovery of the DIBs, the first absorption lines were not conclusively identified as C_{60}^{+} until quite recently *(2)*. Therefore, the specific identity of the remaining DIBs remains an area of focused study in current research. Additionally, the presence of these compounds in the ISM engenders questions regarding the unique stability of these species and their formation from smaller molecules in an environment unfavorable for reactions.

Current researchers have hypothesized that the majority of the DIBs correspond to carbonaceous gases in the ISM *(3 - 5)*. Furthermore, it is hypothesized that the majority of these carbonaceous gases are large carbon molecules, such as fullerenes (further supported by the recent identification of C_{60}^{+}), diamond, and polycyclic aromatic hydrocarbons (PAHs). Specifically, the documented evidence of smaller organic molecules in the ISM provides support for the hypothesis that some of the DIBs correspond to PAHs. These smaller molecules could serve as precursors for PAH synthesis in the ISM. Moreover, PAHs have the ability to exist in the ISM because of the overall stability, while these molecules have strong potential for electron transitions (due to their aromatic rings) that would lead to the absorption lines observed in the spectra. For these reasons, researchers have focused on how PAHs could emerge from reactions between smaller molecules in the ISM.

The majority of the PAHs in the ISM most likely emerged from gas phase reactions between small molecules *(4)*. Gas phase reactions between one cationic species and another neutral species are more likely to occur than neutral-neutral reactions because of the lower activation energy required for the initiation of the reaction *(5 - 7)*. Since the smaller organic compounds required for PAH formation exist in space, cation-molecule reactions between these species present a possible pathway for PAH synthesis in the ISM. Therefore, in order to understand the reactions that lead to the presence larger PAH molecules, scientists need to understand the properties that dictate weakly bound interactions between smaller precursor molecules. Indeed, small molecules could exist in these weakly-bound states in the ISM for substantial periods of time before obtaining the energy from an outside source that induces the reaction. Therefore, understanding the weakly bound interactions between small molecules in the ISM provides a frame of reference for understanding interstellar chemistry.

Ionic hydrogen bonding interactions, formed between a cation and a polar molecule capable of hydrogen bonding, could dictate the arrangement of small molecule species in the ISM. Ionic hydrogen bonds (IHBs), which are of particular importance in some biological and organic molecules *(8 - 10)*, are a particularly strong intermolecular interaction *(11)*. IHBs have also been shown to dictate the arrangements of weakly bound species in the gas phase *(12 - 14)*. Additionally, the stepwise formation of species consisting of a single cationic hydrocarbon and multiple small organic molecules held in place due to IHBs has also been demonstrated *(7, 12, 15 - 17)*. Therefore, the complexes formed between small carbonaceous gases and small molecules in the gas phase due to

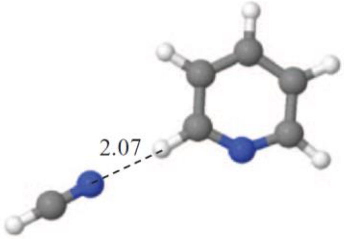


Figure 1: Ionic hydrogen bond between HCN and pyridine$^+$. Calculated IHB structures of pyridine$^+$ and HCN *(17)*. In this case, the attractive force is particularly strong because of the system's ability to form an IHB due to presence of cation. Distances shown are in angstroms.

IHBs could serve as precursors for reactions that lead the formation of PAHs in the ISM. Importantly, the overall stability of these species due to the strength of IHBs suggests that small molecules could form these species in the ISM and exist in that arrangement until overcoming the requisite activation energy barrier.

Benzene-like cations and hydrogen cyanide (HCN) can form IHBs and exist as stable weakly bound species. For that reason, we computationally analyzed weakly bound species formed between paradifluorobenzene cations and $(HCN)_n$ (n = 1 and 2) in order to better understand the properties that dictate the interactions between these molecules. Moreover, the presence of HCN in space in both comet dust and planetary nebula has been well established *(18-21)*. Additionally, the fact that paradifluorobenzene is the most stable of the two-fluorine benzene like ring species made it the focus of this work. Similar to HCN, evidence of the existence of both $C_6H_6^+$ and F_2 in space has been documented *(22 - 24)*. From our computational analysis, we report that the weakly-bound interactions between paradifluorobenzene cations and HCN, in addition to these species relative stabilities, are dictated by the charge distributions of the two molecules.

Theoretical Methods

Gaussian 09 was used to carry out Density Functional Theory calculations on complexes formed between a single paradifluorobenzene cation and either one or two HCN molecules. Numerous combinations of starting positions between these molecules were initially drawn using the ArgusLab software package. These calculations were performed at Truhlar's M062X level of theory *(25)* using Dunning's aug-cc-pVTZ basis set *(26)*. From these calculations, the zero point vibrational energies were determined. Frequency calculations for all species were also performed in order to confirm the lack of imaginary frequencies. Additionally, the Boys and Bernardi counterpoise method *(27)* was used to correct the basis set superposition error, leading to the determination of a zero point counterpoise corrected energy for each species. Counterpoise corrected binding energies were also calculated for each complex based upon the counterpoise corrected vibrational energies of the independent paradifluorobenzene cation and HCN molecules. Optimized geometries, relative zero point counterpoise corrected energies, and counterpoise corrected binding energies were compared in order to determine the stability of the species. The stability of these species was further justified using the charge distribution for each molecule calculated using the Natural Population Analysis (NPA) at the same level of theory and basis set *(28)*.

Results and Discussion

Table 1 displays the stable geometries obtained following our calculations for complexes formed with only one HCN molecule. From the numerous initial geometries that we used as an input, we identified only these three structures as stable arrangements between the two molecules. Therefore, we see that the HCN can occupy one of three stable positions relative to the cation. Based on the relative stabilities of these positions, we saw that the most stable complex forms when the HCN binds the cation in an out-of-plane fashion where the HCN is positioned above the carbon molecule bound to the fluorine in the cation. The two other positions, both of which form in-plane IHBs, are less stable the out-of-plane position. From the amount of starting arrangements inputted, it is clear that these are the only three positions the HCN can occupy that form stable complexes with the paradifluorobenzene$^+$.

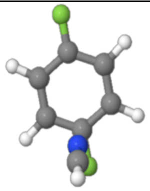
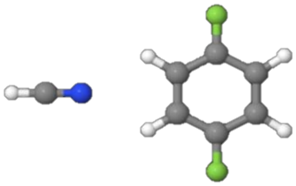
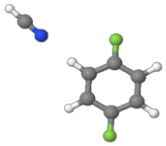
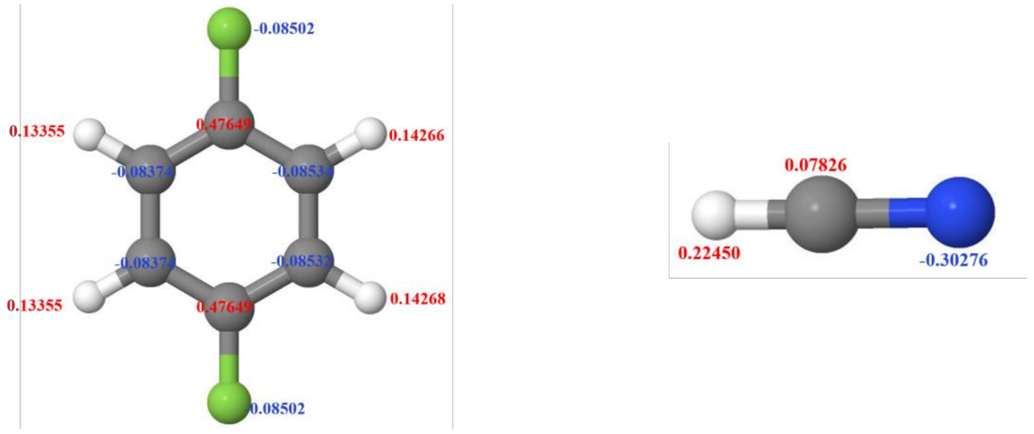
	Optimized Geometry	Zero-Point Counterpoise Corrected Relative Energy	Counterpoise Corrected Binding Energy
1		0	-12.34
2		1.168	-11.27
3		2.280	-10.11

Table 1: Paradifluorobenzene cations with one HCN molecule. Table displays the optimized geometries obtained using the M062X/aug-cc-pVTZ level of theory and basis set. Zero-Point Counterpoise Corrected Relative Energy indicates scaled energy of the overall complex. Counterpoise Corrected Binding Energy represents energy change due to complex formation based upon the Counterpoise Corrected energies of the standalone paradifluorobenzene cation and HCN molecule. All energies calculated in kcal/mol.

In order to explain the presence of only three complexes and their relative stabilities, we calculated the charge distributions for the cation and the HCN molecule using both the Mulliken Distribution and NPA. As shown in Fig. 1, both calculations predicted the same sign of charge for the molecules in the paradifluorobenzene$^+$, however, the Mulliken calculation produced more extreme values. Additionally, the Mulliken calculation assigned the carbon atom in HCN a negative charge, which violated our chemical intuition based upon the polar nature of the molecule. Mulliken charge distributions are known to be heavily dependent upon the basis set used, therefore, given our results, we decided to proceed with our analysis using the NPA charge distribution *(29)*. As shown in Fig. 1, this calculation indicated that the two carbon atoms in the cation bound to the fluorine atoms were positively charged, while the remaining carbons in the molecule were negatively charged.

Natural Population Analysis



Mulliken Distribution

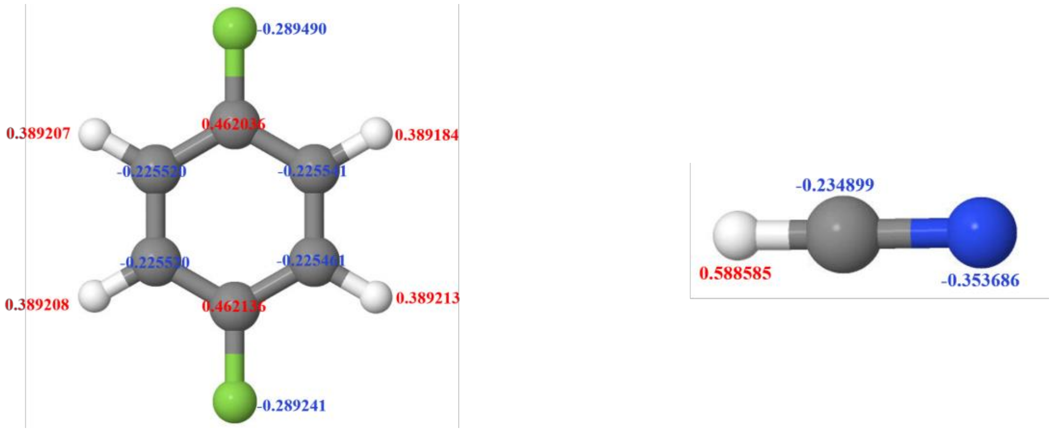
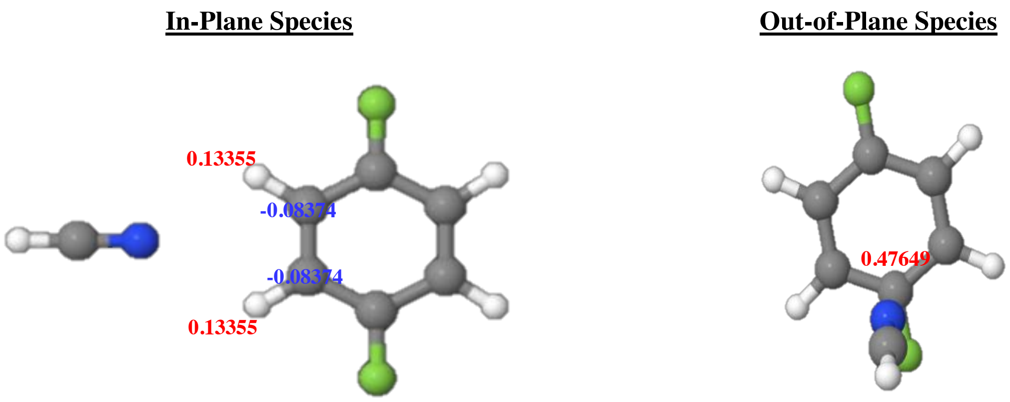


Figure 2: Calculated charge distributions of paradifluorobenzene⁺ and HCN. Charges assigned to each atom in the molecules based upon the Natural Population Analysis and Mulliken Distribution methods. All charges calculated at the M062X/aug-cc-pVTZ level of theory and basis set.

Using the NPA charge distribution, we can explain the stable positions occupied by the HCN. The three stable positions we observed correspond to regions in the cation where the negatively charged nitrogen atom in the HCN can access the regions of positive charge in the paradifluorobenzene$^+$. Correspondingly, the most stable complex forms when the HCN accesses the most positive region in the cation: the positively charged carbon in the ring that is bound to the fluorine atoms. Therefore, the relative stability and binding energy changes observed for these complexes also relate to the regions of charge within the paradifluorobenzene cation.

As shown in Fig. 2, the influence of the charged regions in the paradifluorobenzene$^+$ have different impacts on the HCN depending upon whether it bends in an in-plane or out-of-plane position. When the HCN occupies one of the two in-plane positions, the sum of the charges the HCN faces (due to the hydrogen atoms) is positive. Therefore, the HCN is still able to occupy this spot, in spite of the negatively charged carbon atoms. By contrast, when the HCN binds in out-of-plane position, the only atom nearby with a positive charge is the carbon atom directly underneath the HCN. Therefore, the out-of-plane species does not depend on the sum of the charges faced, but rather the individual charge of the carbon atom. Additionally, as indicated by the calculated energies, the out-of-plane position is the most stable because of the direct access to the most positive region in the molecule. This access is exhibited by the shorter distance between the nitrogen and the carbon in the out-of-plane species (278.5 pm) than in the in-plane species (314.2 pm). This distance corresponds to the two molecules ability to interact due to their charged regions, which relates to the increased stability in the out-of-plane complex.


In-Plane Species

Out-of-Plane Species

Figure 3: Difference in interaction between in-plane and out-of-plane complexes. Most stable in-plane species and out-of-plane species shown here with relevant charges of paradifluorobenzene$^+$ atoms displayed. The in-plane position is stable because of the sum of the charges the HCN molecule faces. By contrast, the out-of-plane species is a stable location because of the single positive charge accessible to the HCN.

Following the analysis of the complexes with a single HCN molecule, we performed similar calculations with species containing two HCN molecules. As shown in Table 2, the complexes formed by adding an additional HCN are simply combinations of the stable positions observed in the single HCN species. Furthermore, as seen in complexes three and seven, the HCN molecules can also form a dimer and position themselves in a single, stable location relative to the cation. This analysis did not reveal any other stable positions the HCN molecules can occupy that were not previously identified in the single HCN calculations.

Applying the NPA charge distribution to these species explains the relative stabilities of the resulting compounds. The most stable species are those where the HCN molecules access separate regions of positive charge in the cation. Furthermore, we can see that more stable complexes form when the molecules occupy individual positions instead of forming a dimer in single location. This corresponds with the greater attractive force due to the IHB between the paradifluorobenzene$^+$ and the HCN, which is greater than the attractive force of a typical hydrogen bond that the HCNs form independently. Interestingly, complex four has a lower relative energy than complex three, in spite of the fact that it has a higher binding energy. This indicates that the presence of a single HCN in the out-of-plane position may negatively impact the ability of another HCN to bind in the other out-of-plane position on the same side of the paradifluorobenzene$^+$. However, once both those HCN molecules do form IHBs with the cation, a more stable complex is formed than some others with greater binding energies.

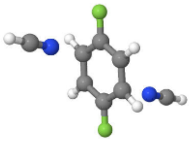
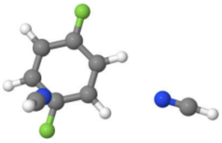
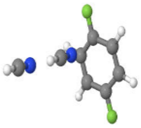
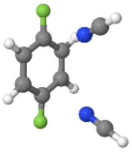
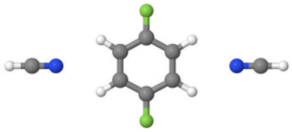
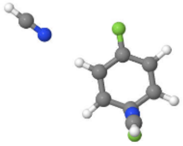
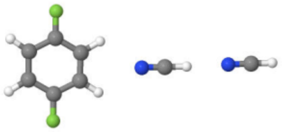
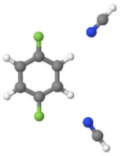
	Optimized Geometry	Zero-Point Counterpoise Corrected Relative Energy	Counterpoise Corrected Binding Energy
1		0	-23.02
2		1.203	-22.34
3		1.470	-22.27
4		1.407	-21.99
5		1.511	-21.72
6		2.006	-21.72
7		2.933	-20.54
8		3.948	-19.01

Table 2. Paradifluorobenzene cations with two HCN molecules. Table displays the optimized geometries obtained using the M062X/aug-cc-pVTZ level of theory and basis set. Zero-Point Counterpoise Corrected Relative Energy indicates scaled energy of the overall complex. Counterpoise Corrected Binding Energy represents energy change due to complex formation based upon the Counterpoise Corrected energies of the standalone paradifluorobenzene cation and HCN molecules. All energies calculated in kcal/mol.

The stable species identified contain only some of the predicted combinations of two HCN species based upon the stable positions identified in the previous calculations. Given the HCN molecules ability to form dimers in each stable location, we would expect to see seven additional species with the two HCN molecules. We hypothesize that we did not observe these complexes due to a change in the charge distribution of the cation following the formation of the first IHB between the paradifluorobenzene$^+$ and one HCN. We expect that this initial interaction alters the charge in the cation and eliminates the second stable location, which prevents the second HCN from occupying that position. The fact that the calculated binding energies for the two HCN complexes are not direct sums of the binding energies from the one HCN species (in fact, the binding energies in the two HCN complexes are approximately 1 kcal/mol less than the sums of the appropriate one HCN species) supports this hypothesis. This suggests that the IHB formed with the first HCN alters the other stable positions in the cation, making the energy gained from the second HCN's attraction slightly less than expected.

Overall, our calculations indicate that the existence of these stable complexes between the paradifluorobenzene cation and HCN molecules, in addition to their relative stabilities, are dictated by the charge distribution of the two molecules. Future work will help us further develop the influence of HCN addition to the overall charge distribution of the system, which will help us understand the absence of several expected complexes. These findings help us understand the properties that dictate the formation of these weakly bound species that could serve as precursors for cation-molecule chemical reactions. Ultimately, this work contributes to our overall understanding of the characteristics of systems that may ultimately be responsible for the presence of large interstellar molecules.

Acknowledgements

I would like to thank Dr. Samuel Abrash for his remarkable assistance with this research. I would also like to thank all of the members of the Abrash Lab for their support. Additionally, I would like to thank the Faculty Research Committee and Spider Research Funds at the University of Richmond for their financial support of this work. Finally, I would like to thank Dr. René Kanters of the University of Richmond and Dr. Samy El-Shall of Virginia Commonwealth University for their assistance and advice with this project.

References

1) Hager, M.L. The spectra of certain class B stars in the regions of 5630Å – 6680Å and 3280Å - 3380Å. *Lick Obs. Bull.* **1922,** *10*, 146-147.
2) Campbell, E.K.; Holz, M.; Maier, J.P. Laboratory confirmation of C_{60}^{+} as the carrier of two diffuse interstellar bands. *Nature.* **2015,** *523*, 322-323.
3) Herbig, G.H. The diffuse interstellar bands. *Annu. Rev. Astrophys.* **1995,** *33*, 19-73.
4) Ehrenfreund, P.; Charnley, S.B. Organic molecules in the interstellar medium, comets, and meteorites: a voyage from the dark clouds to the early earth. *Annu. Rev. Astrophys.* **2000,** *38*, 427-483.
5) Snow, T.P.; Le Page, V.; Keheyan, Y.; Bierbaum, V.M. The interstellar chemistry of PAH cations. *Nature.* **1998**, *391*, 259-260.
6) Bohme, D.K. PAH and fullerene ions and ion/molecule reactions in interstellar and circumstellar chemistry. *Chem. Rev.* **1992,** *92*, 1487-1508.
7) Attah, I.K.; Hamid, A.M.; Meot-Ner, M.; El-Shall, M.S.; Aziz, S.G.; Alyoubi, A.O. Substituent effects of noncovalent bonds: complexes of ionized benzene derivatives with hydrogen cyanide. *J. of Phys. Chem.* **2013,** *117*, 10588-10597.
8) Perrin, C.L.; Nielson, J.B. "Strong" hydrogen bonds in chemistry and biology. *Annu. Rev. Phys. Chem.* **1997,** *48*, 511-544.
9) Dominiak, P.M.; Grech, E.; Barr, G.; Teat, S.; Mallinson, P.; Wozniak, K. Neutral and ionic hydrogen bonding in schiff bases. *Chem. Eur. J.* **2003,** *9*, 963-970.
10) Cerny, J.; Hobza, P. Non-covalent interactions in biomacromolecules. *Phys. Chem. Chem. Phys.* **2007,** *9*, 5291-5303.
11) Meot-Ner, M. Update 1 of: Strong ionic hydrogen bonds. *Chem. Rev.* **2012,** *112*, PR22-PR103.
12) Ibrahim, Y.; Alsharaeh, E.; Dias, K.; Meot-Ner, M.; El-Shall, M.S. Stepwise hydration and multibody deprotonation with steep negative temperature dependence in the benzene^{*+} - water system. *J. Am. Chem. Soc.* **2004,** *126*, 12766-12767.
13) Mabrouki, R.; Ibrahim, Y.; Xie, E.; Meot-Ner, M.; El-Shall, M.S. Gas phase hydration and deprotonation of cyclic $C_3H_3^{+}$ cation. Solvation by acetonitrile, and comparison with the benzene radical cation. *J. Phys. Chem.* **2006,** *110*, 7334-7344.
14) Momoh, P.O.; El-Shall, M.S. Gas phase hydration of organic ions. *Phys. Chem. Chem. Phys.* **2008,** *10*, 4827-4834.
15) Hamid, A.M.; Soliman, A.R.; El-Shall, M.S. Assembly of HCN hydrogen bonding chains in the gas phase. Binding energies and structures of phenylacetylene$\bullet^{+}$(HCN)$_n$ cluster, n = 1-4. *Chem. Phys. Let.* **2012,** *543*, 23-27.
16) Hamid, A.M.; Soliman, A.R.; El-Shall, M.S. Stepwise association of hydrogen cyanide and acetonitrile with the benzene radical cation: structures and binding energies of $(C_6H_6\bullet^{+})(HCN)_n$, n = 1-6, and $(C_6H_6\bullet^{+})(CH_3CN)_n$, n = 1-4, clusters. *J. of Phys. Chem.* **2013,** *117*, 1059-1078.

17) Hamid, A.M.; El-Shall, M.S.; Hilal, R.; Elroby, S.; Aziz, S.G. Unconventional hydrogen bonding to organic ions in the gas phase: stepwise association of hydrogen cyanide with the pyridine and pyrimidine radical cations and protonated pyridine. *J. of Chem. Phys.* **2014,** *141*, 054305.

18) Snyder, L.E.; Buhl, D. Observations of radio emission from interstellar hydrogen cyanide. *The Astrophys. J.* **1971,** *163*, L47-L52.

19) Boonman, A.M.S.; Stark, R.; Van Der Tak, F.F.S.; Van Dishoeck, E.F.; Van Der Wal, P.B.; Schaefer, F.; De Lange, G.; Laauwen, W.M. Highly abundant HCN in the inner hot envelope of GL 2592: probing the birth of a hot core? *The Astrophys. J.* **2001,** *553*, L63-L67.

20) Mumma, M.J.; DiSanti, M.A.; Magee-Sauer, K.; Bonev, B.P.; Villanueva, G.L.; Kawakita, H.; Russo, N.D.; Gibb, E.L.; Blake, G.A.; Lyke, J.E.; Campbell, R.D.; Aycock, J.; Conrad, A.; Hill, G.M. Parent volatiles in comet 9P/Tempel 1: before and after impact. *Science***, 2005,** *310*, 270-274.

21) Matthew, C.N.; Minard, R.D. Hydrogen cyanide polymers, comets and the origin of life. *Faraday Discuss.* **2006,** *133*, 393-401.

22) Mowlavi, N.; Jorissen, A.; Arnould, M. Fluorine production in intermediate-mass stars. *Astron. Astrophys.* **1996***,* *311*, 803-816.

23) Neufeld, D.A.; Wolfire, M.G.; Schilke, P. The chemistry of fluorine-bearing molecules in diffuse and dense interstellar gas clouds. *The Astrophys. J.* **2005,** *628*, 260-274.

24) Momoh, P.O.; Abrash, S.A.; Mabrouki, R.; El-Shall, M.S. Polymerization and ionized acetylene clusters in covalent bonded ions: evidence for the formation of the benzene radical cation. *J. Am. Chem. Soc.* **2006,** *128*, 12408-12409.

25) Zhao, Y.; Truhlar, D.G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Che. Account.* **2008,** *120*, 215-241.

26) Kendall, R.A.; Dunning, Jr, T.H.; Harrison, R.J. Electron affinities for the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992,** *96*, 6796-6806.

27) Boys, S.F.; Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Molec. Phys.* **1970,** *19*, 553-566.

28) Reed, A.E.; Weinstock, R.B.; Weinhold, F. Natural population analysis. *J. Chem. Phys.* **1985,** *83*, 735-746.

29) Guerra, C.F.; Handgraaf, J.W.; Baerends, E.J.; Bickelhaupt, F.M. Voronoi deformation density (VDD) charges: assessment of the Mulliken, Bader, Hirshfeld, Weinhold, and VDD Methods for charge analysis. *J. of Comp. Chem.* **2004,** *25*, 189-210.