# Condensed-Phase Effects on the Structural Properties of $C_6H_5CH_2CN–SiF_4$ and $CH_3CH_2CN–SiF_4$

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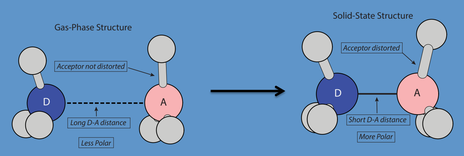
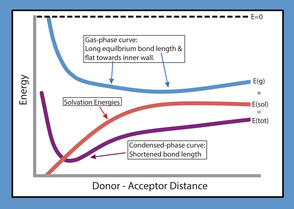
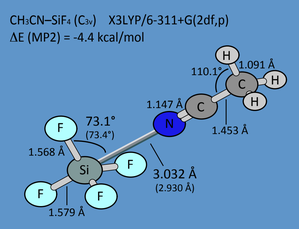
## Introduction: $CH_3CN–SiF_4$

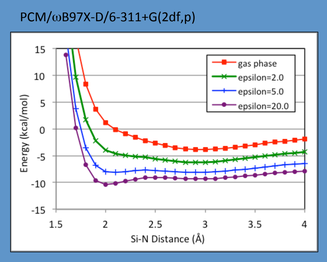
Our research involves the identification of molecular complexes that change structure when the chemical environment is altered, e.g., gas-phase to solid-state (left below). The plot (right below) conveys a general mechanism for bulk condensed-phase effects. The key is a long bond length in the gas phase with a very slight energy rise towards the shorter donor-acceptor distances. The addition of solvation energies can shift the bond length inward.




This project stems from a previous study on $CH_3CN–SiF_4$ (below), in which condensed-phase structural changes were predicted but not observed [1].




## Present: $C_6H_5CN–SiF_4$ and $CH_3CH_2CN–SiF_4$

In the present case, we are dealing with two specific complexes: $CH_3CH_2CN–SiF_4$ and $C_6H_5–SiF_4$. We expect the larger carbon groups to enhance the bonding interaction and lead to more significant structural change in the condensed phase.

## Computational Methods

All computations were performed using Gaussian 09 version B.01:

- Methods: M06 (preferred), MP2, and ωB97X-D
- Basis set: 6-311G+(2df,2pd)
- Solvation energies: Polarized Continuum Model (PCM)

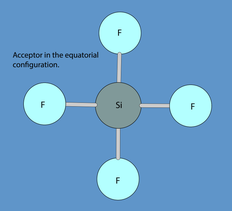
We computed the following properties:

- Equilibrium geometries: opt=tight
- Binding energies
- Frequencies
- Gas-Phase Si-N potential curves: 1.6-3.6Å (0.1Å increments)
- Condensed-Phase Si-N potential curves: 1.6-3.6Å (0.1Å increments)

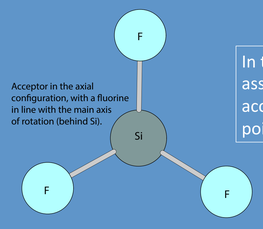
## Results

### *Equilibrium Geometries*

Conformational analysis: We considered 4 possible isomers in our search for the most stable structure. The first consideration was coordination geometry; how the donor would approach the acceptor ($SiF_4$). The two possibilities are depicted below: Equatorial (left) & axial (right). There are two possible conformations for each.



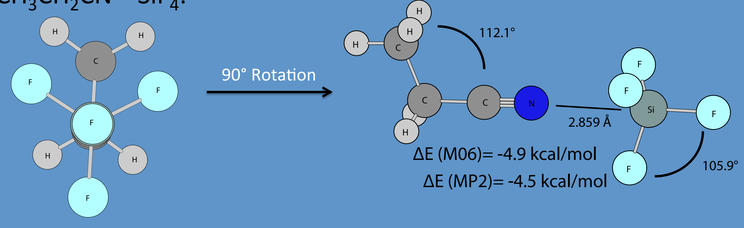

OR




In the figures (left), the donor is assumed to be approaching the acceptor head-on from our point of view.

For $CH_3CH_2CN–SiF_4$ we found the axial staggered isomer (below, left) to be the most stable (lowest energy, no imaginary frequencies). This isomer has the substituents offset, rather than overlapped like an eclipsed form.

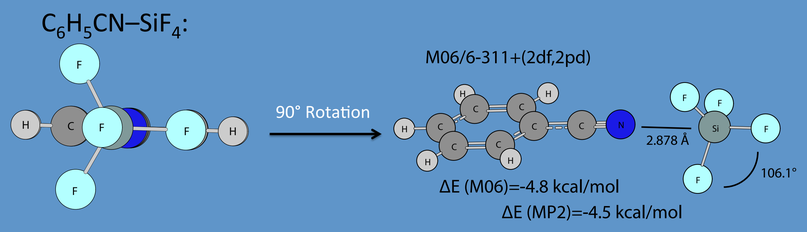
$CH_3CH_2CN—SiF_4$:




- This is a weak complex with a long N-Si bond.
- The $SiF_4$ subunit is only slightly distorted from a tetrahedral geometry (<F-Si-F=105.9°).
- Results are very similar to $CH_3CN–SiF_4$, for which the N-Si distance is 2.874 Å and the binding energy is -4.8 kcal/mol (M06).

For the $C_6H_5CN–SiF_4$ complex we found the axial eclipsed isomer (below, left) to be the most stable (lowest energy, no imaginary frequencies). One of the fluorines overlaps with the phenyl ring.

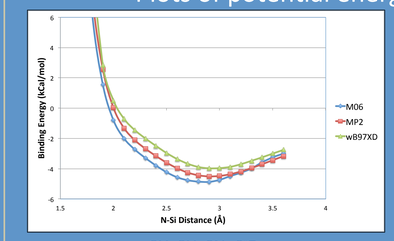
$C_6H_5CN–SiF_4$:



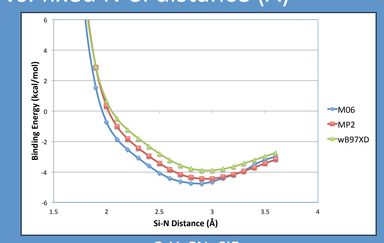

- This is a weak complex with a long N-Si bond.
- The $SiF_4$ subunit is only slightly distorted from a tetrahedral geometry (<F-Si-F=106.1°).
- Results are very similar to $CH_3CN–SiF_4$, for which the N-Si distance is 2.874 Å and the binding energy is -4.8 kcal/mol (M06).

### *Gas-Phase Si-N Potential Curves*

Plots of potential energy vs. fixed N-Si distance (Å)



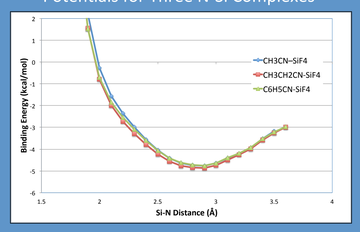

$CH_3CH_2CN–SiF_4$




$C_6H_5CN–SiF_4$

- These potentials show the key characteristics: A long bond length in the gas phase, and a very slight energy rise towards the shorter donor-acceptor distances.
- Results for three computational methods are consistent.
- The potentials for both compounds differ very little from $CH_3CN–SiF_4$, for which condensed-phase effects were not observed.

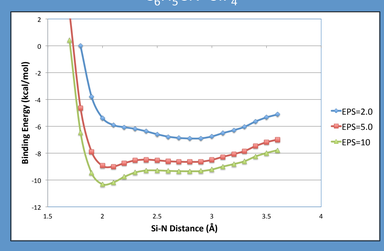
Potentials for Three N-Si Complexes




Left is a comparison of N-Si potential energy curves for $CH_3CN–SiF_4$, $CH_3CH_2CN–SiF_4$, and $C_6H_5CN–SiF_4$. There is a subtle substituent effect. The inner wall of the curve is slightly lower in energy with larger organic substituent.

### *Condensed-Phase Si-N Potential Curves*

$C_6H_5CN–SiF_4$




Left is a plot of the potential energy curve in bulk dielectric media. The dielectric constant (EPS) reflects charge-stabilizing ability of the medium (i.e., polarity). Note that the shape of the curve changes dramatically in condensed phases.

- For $C_6H_5CN—SiF_4$, the shape of the PE curve changes dramatically with increasing dielectric constant (ε), and the minimum energy point shifts from 2.8 Å at ε=2 to 2.0 Å at ε=10.
- But a similar effect was noted for $CH_3CN–SiF_4$ and we did not see any experimental evidence.
- Future work will involve Infrared Spectroscopy of nitrile/$SiF_4$ thin-films, in an attempt to observe condensed-phase effects.

## Acknowledgments

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## Literature Cited

1. Helminiak, H. M.; Knauf, R. R.; Danforth, S. J.; Phillips, J. A. *J. Phys. Chem. A* **2014**, *118 (24)*, 4266–4277.