

Condensed-Phase Effects on the Structural Properties of FCH_2CN-BF_3 and $ClCH_2CN-BF_3$

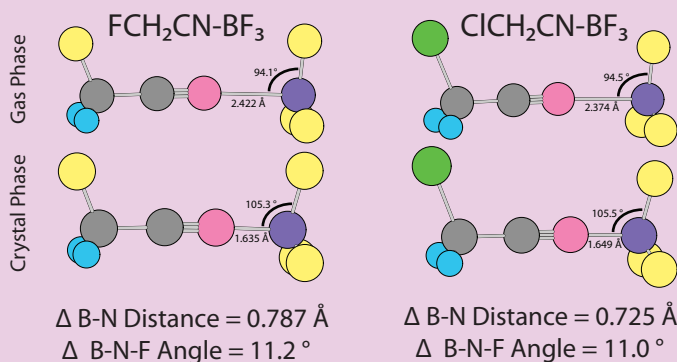


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Context: Large Gas-Solid Differences¹



Now:

What is the effect of a bulk, condensed-phase environment? (i.e. solid neon, argon, etc.)

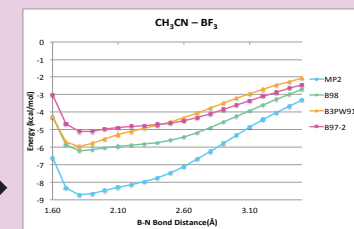
Potential Curves: Energy vs. B-N Distance

• CH_3CN-BF_3 :

~Large gas-solid structure differences occur²:

$$\left. \begin{array}{l} \text{Crystal} = 1.63 \text{ \AA} \\ \text{Gas} = 2.01 \text{ \AA} \end{array} \right\} \Delta \text{ B-N Distance} = 0.38 \text{ \AA}$$

~Flat potential, but global minimum is in interior of flat region



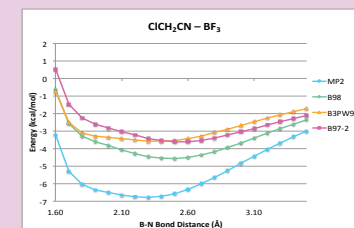
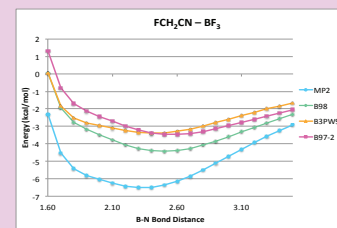
• FCH_2CN-BF_3 and $ClCH_2CN-BF_3$

~More significant broad, flat region

~Global minima at longer bond lengths

~Greater potential for medium effects

~Constant with even inert environments causing shift in bond length

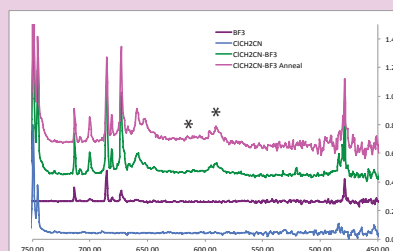
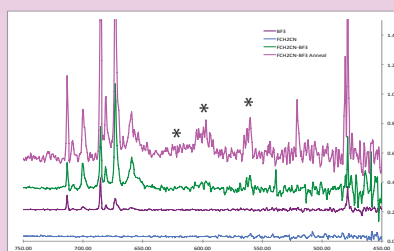


Experimental: FTIR Spectra in Neon Matrices

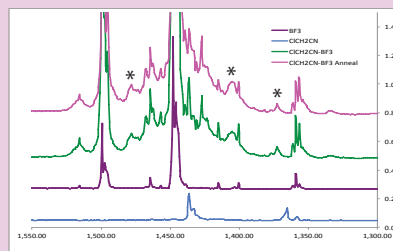
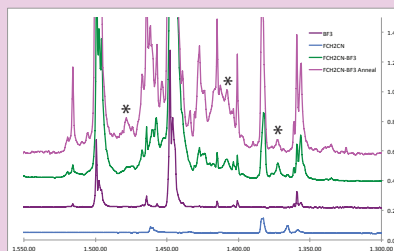
FCH_2CN-BF_3

$ClCH_2CN-BF_3$

750-450 cm^{-1}



1550-1300 cm^{-1}

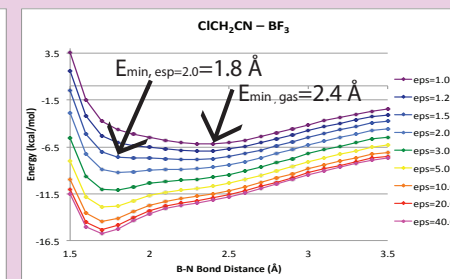
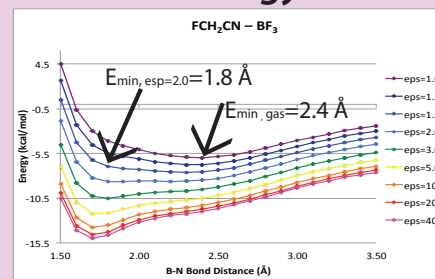


Mode	Neon (B3PW91/aug-cc-pVTZ)	Gas (B3PW91/aug-cc-pVTZ)	Mode	Neon (B3PW91/aug-cc-pVTZ)	Gas (B3PW91/aug-cc-pVTZ)
¹¹ B-Asymmetric Stretch	1408.417	1424.41	¹¹ B-Asymmetric Stretch	1405.225	1419.11
¹¹ B-Umbrella Mode	598.697	607.506	¹¹ B-Umbrella Mode	591.252	596.481

~ Shifts observed between calculated and measured frequencies

Conclusion: Even neon compresses the bond length! (frequencies coincide with 2.1 Å)

Solvation Energy: Shift in E_{min}



Conclusion: Even very low dielectric media can affect the structure.

Sources

- "Large Gas - Solid Structural Differences in Complexes of Halo-acetonitriles with Boron Trifluoride"; Phillips, J.A.; Halfen, J.A.; Wrass, J.P.; Knutson, C.K.; Cramer, C.J. *Inorganic Chemistry* **2006**, 45, 722.
- "The B-N Distance Potential of CH_3CN-BF_3 Revisited". C.J. Cramer, J.A. Phillips, *Journal of Physical Chemistry B* **2007**, 111, 1408. (b) A.A. Eigner,* J.A. Pohde,* C.C. Knutson,* J.A. Phillips, *Journal of Physical Chemistry B* **2007**, 111, 1402.

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