Computational and Experimental Nitrogen and Halogen Chemistry

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The $\mathbf{CS_2N_3^{\cdot}}$ radical has been shown to fulfil the criteria for being classed as a **pseudohalogen**. It is a strongly bound planar univalent radical ($CS_2N_3^{\cdot}$), which can form the corresponding anion ($[CS_2N_3]^-$), hydracid (HNNNSC=S), neutral dipseudohalogen species ($(CS_2N_3)_2$), the interpseudohalogen compound (CS_2N_3-CN), and the alkyl derivative (CS_2N_3-CH_3). The structures of various isomers have been computed ab initio and have been compared and contrasted with the experimental findings.

Adducts between boron triazide, $\mathbf{B(N_3)_3}$ and nitrogen bases as well as salts of the tetraazidoborate anion, $\mathbf{[B(N_3)_4]^-}$, have been structurally characterized (X-ray). Quantum chemical calculations were carried out for $[B(N_3)_4]^-$, $B(N_3)_3$, $C_5H_5N{\cdot}B(N_3)_3$, $(N_3)_3B{\cdot}NC_4H_4N{\cdot}B(N_3)_3$, and the hypothetical $C_3H_3N_3{\cdot}[B(N_3)_3]_3$ at HF, MP2, and B3LYP levels of theory. The structure of tetraazidoborate was optimized to S_4 symmetry and confirmed the results obtained from the X-ray diffraction analysis. The dissociation enthalpies for the pyridine as well as for the pyrazine adduct were also calculated.

The reaction of $[N_2H_5]^+{}_2[SO_4]^{2-}$ with barium-5,5´-azotetrazolate results in a new high-energy material based on the 5,5´-azotetrazolate dianion. The dihydrazinium salt of $\mathbf{[N_4C\text{-}N{=}N\text{-}CN_4]^{2-}}$ was prepared in high yield. This compound, which is reported for the first time, represents a new high-nitrogen HEDM with one of the highest nitrogen contents reported to date ($[N_2H_5]^+{}_2[N_4C\text{-}N{=}N\text{-}CN_4]^{2-}$:**N 85.2 %**. The standard heat of formation of the solvate free compound was computed at MP2(FULL)/6-311+G(d,p) level of theory to be $\Delta H°_f$ = 264 kcal mol^{-1} which translates to 1147 kcal kg^{-1} and is one of the highest ever reported.

The **fluorine plus (F^+) detachment energy** values (*FPDE* values) of the oxidative fluorinators $C_3N_3X_3F^+$ (X = H, F, Cl) (structurally based on the 1,3,5-trihalogenotriazine moiety) and $C_5NX_5F^+$ (X = H, F, Cl) (based on pyridine or pentahalogeno pyridine) have been computed quantum-chemically at the density functional B3LYP hybrid level of theory using a 6-31G(d,p) basis set. The gas phase fluorine plus detachment energy values (*FPDE*) have been additively calibrated by an experimental value for KrF^+ and have been determined to be: ΔH_{FPDE} [$(FCN)_3F^+$] = 212 kcal mol^{-1}, ΔH_{FPDE} [$(ClCN)_3F^+$] = 227 kcal mol^{-1}, ΔH_{FPDE} [$(HCN)_3F^+$] = 240 kcal mol^{-1}, ΔH_{FPDE} [$C_5H_5NF^+$] = 266 kcal mol^{-1}, ΔH_{FPDE} [$C_5F_5NF^+$] = 219 kcal mol^{-1}, and ΔH_{FPDE} [$C_5Cl_5NF^+$] = 227 kcal mol^{-1}.