Sigma Holes and Sigma Gaps: Non-Covalent Interactions between Group 14 Halomethane Analogues and Lewis Bases

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The characterization of the patterns of halogen bonding interactions between Group 14 halomethane analogues and a series of Lewis bases has been the focus of our work. We are interested in halogen bonds, which are weak non-covalent interactions between an area of positive electrostatic potential on a halogen and a negative site, because research in this field has led to a deeper understanding of weak interactions and has opened up doors in the fields of supramolecular chemistry and crystal engineering. In this project, we are using the MP2(full) level of theory and the cc-pVTZ basis sets to explore the possibility of halogen bonding interactions in various systems. We have tested eight different halomethane analogues as Lewis bases, those of the form CF_3X, where X=F, Cl, Br, I; and those of the form MF_3I, where M=Si, Ge, Sn, Pb. We have paired all of these compounds with 18 unique Lewis bases, and have gathered data on their interactions energies and the halogen bond distances. Preliminary findings indicate that halogen bonds become stronger when the size of X in CF_3X systems or the size of M in MF_3I systems is increased, across all bases. We have also determined that the substitution patterns on nitrogen and oxygen can be decisive for the strength of the halogen bond, with the strongest bonds occurring when the least electron-withdrawing groups are used as substituents. We have investigated the MF_4 systems, too, in their interactions with common bases. The presence of an area of positive electrostatic potential on the center of M, the so-called "sigma gap," leads to a strong interaction that distorts the bond angles of the MF_4 tetrahedral geometry.