SPIN-SPIN COUPLING ACROSS INTERMOLECULAR F-Cl...N HALOGEN BONDS

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Ab initio EOM-CCSD calculations have been performed to determine one- and two-bond spin-spin coupling constants ^{1}J(F-Cl), ^{1X}J(Cl-N), and ^{2X}J(F-N) across F-Cl...N halogen bonds in complexes with F-Cl as the Lewis acid and N_2, FCN, HCN, $(CH_3)CN$, LiCN, Z-HNNH, H_2CNH, NH_2F, NH_3, cyclic $NH(CH_2)_2$, and $NH_2(CH_3)$ as Lewis bases. The structures of these complexes were optimized at MP2 with the aug'-cc-pVTZ basis set. The absolute value of ^{2X}J(F-N) increases in these complexes as the F-N distance decreases, a behavior similar to that of ^{2h}J(F-N) for complexes stabilized by F-H...N hydrogen bonds. ^{1X}J(Cl-N) also tends to increase in absolute value with decreasing F-N distance. ^{1}J(F-Cl) is always positive, decreases upon complex formation as the F-Cl distance increases, and appears to be sensitive to the nature of the nitrogen base. The relatively large differences in the values of these coupling constants in the various complexes and their variation along the chlorine-transfer coordinate for F-Cl...NH_3 suggest that they should be amenable to experimental investigation.