A Quantitative Analysis of the Electron Withdrawing Strength of Polyatomic Groups

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Electron withdrawing power is a property of atoms and molecules that is important in chemical interactions, as it governs the way in which structures form after a bond is created. Though its effects are central to many theories of bonding, such as Lewis's theory of acids and bases, a quantitative catalogue of the electron withdrawing power for molecular fragments (analogous to Pauling's and other measures of electronegativity) has not been developed so far. In this work, computational analyses at the MP2 level with the cc-pVTZ basis set have been performed using the Gaussian suite of programs in order to set up a numerical index of electron withdrawing power for common molecular fragments. As the basis for the characterization we turned to halogen bonding because of its extreme sensitivity and directionality, which is absent from other common forms of weak interactions. Each group to be tested was optimized as a substituent bonded to the nitrogen in a CF_3I---NH_2X complex. Our group has demonstrated that the I---N bond is extremely sensitive to the identity of X. The optimized bond length for the minimum energy structures were then used as the basis for quantifying the electron withdrawing power. Our work is still ongoing, but this strategy and other currently under consideration shows promise as a means of assigning actual and meaningful values for the electron withdrawing power of substituents.