Analyzing Halogen Bonding and Hydrogen Bonding by a Point-Charge Approach: Rigorous Separation of Polarization and Charge-Transfer

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Halogen and hydrogen bonding are important intermolecular interactions that are classified as σ-hole interactions [1]. Central to the σ-hole concept is a region of positive surface electrostatic potential that is associated with the σ -hole, and it has been found that the strength of σ -hole interactions is largely governed by electrostatics and polarization. However, several studies have pointed towards the importance of charge-transfer for halogen bonding and hydrogen bonding; in particular for interactions where the σ -hole donor interacts with a soft Lewis base [2, 3]. These findings have led to controversies as it has been argued that there is no rigorous approach for distinguishing charge transfer from polarization. In some recent studies, we have investigated halogen bonding and hydrogen bonding by a point-charge approach, where the Lewis base is replaced by a point charge, or a distribution of point charges, in the Hamiltonian of the interacting system [4]. The approach allows polarization to be rigorously separated from charge transfer, as the interacting system has no electrons that can be transferred from the Lewis base to the halogen or hydrogen bond donor. We have applied the point-charge approach to a number of complexes where charge-transfer has been argued to be significant for the interaction strength. In all cases, we have found that the interaction energy of the point-charge approach is linearly related to the full quantum chemical interaction energy, and there is no indication of charge transfer to be of any importance. Halogen bond interaction energies are found to have a large contribution from polarization; a contribution that in some cases is even larger than the contribution from electrostatics. Polarization is mediated by the chemical bonds and is in general larger in conjugated systems. Hydrogen bonds, on the other hand, are dominated by electrostatics and generally the interaction energy has only a minor polarization component.

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