Investigating the Properties of Electropositive Holes in Double-Bonded Chalcogen Donors

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Here we probe the energetic, structural, and vibrational properties in a series of substituted chalcogen σ/π-hole bond donors and the properties given different prototypical structures and functional groups. Full geometry optimizations and harmonic vibrational frequency computations are performed on each ChB donor with the M06-2X density functional in conjunction with a triple-ζ quality correlation consistent basis set augmented with diffuse functions on all atoms and a psuedopotential on selenium and tellurium centers (aug-cc-pVTZ for H, C, N, O, F and aug-cc-pVTZ-PP for Se, Te; denoted aVTZ). The nature of the σ/π-holes in the ChB donors are probed with bond critical point (BCP), and electrostatic potential surface (ESP) analysis. To gain insight into the relationship between the strength of the σ/π-hole and electron orbitals in the donor, the occupation of atomic and bonding orbitals is evaluated using full NBO analyses on the M06-2X/aVTZ optimized geometries. Connections between select geometrical parameters, σ/π-hole strength, and angular dependence of the ChB donors will be discussed.