

A Study of Charge-Shift Bonding in Neutral and Protonated Alcohols, Amines, and Related Molecules R-X and RXH⁺ (R=Me, Et, iPr, tBu; X=OH, NH₂, F, SH, PH₂, Cl)

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The quantum theory of atoms-in-molecules (QTAIM) was used first to survey more than 120 diverse molecules to develop an understanding of the relationships among properties of the electron density topology, including the electron density (ρ) and the Laplacian of the electron density ($\nabla^2\rho$) at the bond critical point (BCP) and the delocalization index (DI) of the bond, with the type of bond, including covalent, polar covalent, ionic, and charge-shift bonds. Then alcohols, amines, and related molecules were investigated and some of the protonated species were found to be examples of charge-shift bonds (CSB). A novel form of bond, related to but different from covalent bonds, the CSB is characterized by values of $\rho > 0.1 \text{ e}\cdot\text{bohr}^{-3}$, $\nabla^2\rho \cong 0.1 - 0.5 \text{ e}\cdot\text{bohr}^{-5}$, and $\text{DI} \cong 0.5 - 0.7$. Further, when protonated, the charges on the alcohol O and amine N do not increase, while the charges on the central carbons decrease and those on the peripheral H's increase, demonstrating hyperconjugation from the substituents to minimize the charge on carbon in the charge-shift resonance structure (R⁺:OH₂, for example). The sum of bond angles around the central carbon also demonstrates rehybridization, reflecting the significance of the charge-shift resonance structure. Overall, charge-shift bonding is shown to occur in these "normal" molecules, alongside examples of polar covalent and ion-dipole bonds, in the molecules R-X and R-XH⁺ (R=Me, Et, iPr, tBu; X=OH, NH₂, F, SH, PH₂, Cl).

