SPIN-SPIN COUPLING CONSTANTS ACROSS N-H^{+}-N HYDROGEN BONDS

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A systematic ab initio EOM-CCSD study of ^{15}N-^{15}N and ^{15}N-^{1}H spin-spin coupling constants has been carried out for a series of complexes formed from 11 nitrogen bases with experimentally measured proton affinities. When these complexes are arranged in order of increasing proton affinity of the proton-acceptor base, and for each proton acceptor, increasing order of proton affinity of the protonated N-H donor, trends in distances and signs of coupling constants are evident which are indicative of the nature of the hydrogen bond. All two-bond spin-spin coupling constants ($^{2h}\mathrm{J}_{N-N}$) are positive, and decrease as the N-N distance increases. All one-bond N-H coupling constants ($^{1}\mathrm{J}_{N-H}$) are negative ($^{1}\mathrm{K}_{N-H}$ are positive). $^{1}\mathrm{J}_{N-H}$ is related to the N-H distance and the hybridization of the donor N atom. One bond H...N coupling constants ($^{1h}\mathrm{J}_{H-N}$) are positive ($^{1h}\mathrm{K}_{H-N}$ are negative) for traditional hydrogen bonds, but $^{1h}\mathrm{J}_{H-N}$ becomes negative when the hydrogen bond acquires sufficient proton-shared character. The N-N and H...N distances at which $^{1h}\mathrm{J}_{H-N}$ changes sign are approximately 2.71 and 1.62 Å, respectively. Predictions are made of the values of $^{2h}\mathrm{J}_{N-N}$ and $^{1}\mathrm{J}_{N-H}$, and the signs of $^{1h}\mathrm{J}_{H-N}$ for those complexes that are too large for EOM-CCSD calculations.