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

J. E. DEL BENE, *Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555*; J. ELGUERO, *Instituto de Química Médica,CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain*.

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 ($^{2h}J_{N-N}$) are positive, and decrease as the N-N distance increases. All one-bond N-H coupling constants ($^{1}J_{N-H}$) are negative ($^{1}K_{N-H}$ are positive). $^{1}J_{N-H}$ is related to the N-H distance and the hybridization of the donor N atom. One bond H...N coupling constants ($^{1h}J_{H-N}$) are positive ($^{1h}K_{H-N}$ are negative) for traditional hydrogen bonds, but $^{1h}J_{H-N}$ becomes negative when the hydrogen bond acquires sufficient proton-shared character. The N-N and H...N distances at which $^{1h}J_{H-N}$ changes sign are approximately 2.71 and 1.62 Å, respectively. Predictions are made of the values of $^{2h}J_{N-N}$ and $^{1}J_{N-H}$, and the signs of $^{1h}J_{H-N}$ for those complexes that are too large for EOM-CCSD calculations.