

# Peculiarities of Intramolecular Hydrogen Bonds in Porphyrin Isomers

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Owing to (a) differences in symmetry and geometrical parameters of the inner macrocycle cavity and (b) possibility of existence of various tautomeric forms, porphyrin (porphine) and its isomers: porphycene, corphycene, hemiporphycene, and isoporphycene are very good models for understanding the relationship between geometry and intramolecular H-bond strength.

I will present the results of experimental and theoretical studies that show the importance of the N–N distance and the NHN angle for proper characterization of intramolecular H-bonds. In contrast to the intermolecular H-bonds, where these parameters adjust to optimal values, the geometry of the intramolecular bonds is imposed by the topology of the inner macrocycle cavity. This may lead to such unusual phenomena as short H-bonds being weaker than longer ones. Moreover, tautomers that exhibit the strongest H-bonds may not correspond to the lowest energy structures, because of unfavorable effects related to electron density redistribution upon tautomeric conversion. Finally, the apparent strength of the intramolecular H-bond may either increase or decrease with excitation of certain vibrational modes.

## Keywords

### This abstract is submitted for....

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