Evidence for Intramolecular N-H...O Resonance-Assisted H-Bond in β-Enaminones and Related Heterodienes. P. Gilli*, V. Ferretti, V. Bertolasi, Chemistry Department and Centro di Strutturistica Diffrattometrica, Ferrara University, Via Borsari 46, I-44100 Ferrara, Italy; E-mail: paola.gilli@unife.it

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Resonance-Assisted H-Bond (RAIIB) is a synergistic interplay between π-delocalization and H-bond strengthening introduced for explaining strong O-H...O bonds formed by the OC=C=O-1... fragment in β-diketone enols. Its applicability to intramolecular N-H...O bonds formed by other heterodienes (OC=C=N-NH... β-enaminones II, OC=C=O-NH... ketohydrazones III, and OC=N=C=N-NH... nitrosochromes IV) is now investigated by X-ray crystallography, CSD (Cambridge Structural Database) search, and comparative analysis of IR νSH stretching frequencies and 1H NMR δHH chemical shifts. It is shown that all descriptors of H-bond strength (Δd(N...O) shortening, decrease of νSH, increase of δHH and increase of π-delocalization) are mutually intercorrelated according to RAIIB rules which can then account for heteronuclear N-H...O bonds in II-IV as well as for homonuclear O-H...O bonds in I. Heteronuclear N-H...O bonds have, however, distinctive features. Their strength is partially hampered by the proton affinity difference (ΔPA) between the N and O atoms, so that very strong H-bonds (2.65 ≥ Δd(N...O) ≥ 2.48 Å; 3200 ≥ νSH ≥ 2340 cm⁻¹; 13 ≤ δHH ≤ 18 ppm) can occur only when π-delocalization is associated with substituents able to decrease ΔPA by increasing NH acidity. Moreover, at variance with strong O-H...O RAIIBs, whose protons are mostly symmetric, even the strongest N-H...O RAIIBs are highly dissymmetrical in spite of the very similar changes undergone by both IR and 1H NMR spectra in O-H...O and N-H...O H-bonded systems. Heteronuclear H-bonds are shown to be interpretable by the Electrostatic-Covalent H-Bond Model (ECIBM) previously developed for the homonuclear case. The conclusions drawn are corroborated by extended DFT quantum-mechanical calculations at the B3LYP/6-31 +G(d,p)//B3LYP/6-31+G(d,p) level of theory and full geometry optimization. Calculations allow to estimate H-bond energies that are found to be some 2.75 kcal mol⁻¹ for non-resonant V, and 5.22, 6.12 and 7.03 kcal mol⁻¹ for unsubstituted resonant II, III and IV, respectively. Proper substitutions of β-enaminone II nearly double H-bond energies making them comparable with those calculated for homonuclear O-H...O RAIIB in β-diketone enols (9.51 and 13.08 kcal mol⁻¹ for malondialdehyde and acetylacetone, respectively).


The influence of cations on the formation of the intramolecular hydrogen bond in hydrogen phthalates. A. Langkilde, S. Larsen, Centre for Crystallographic Studies, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark.

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The hydrogen maleate ion is characterised by having a very short intramolecular hydrogen bond with O-O distances close to 2.4 Å.

Though hydrogen phthalate ions form intramolecular hydrogen bonds similar to those in the hydrogen maleate in some cases, it is not a general behaviour. There appears to be no obvious structural reasons for this difference between hydrogen maleate and hydrogen phthalate ions.

We have examined if this difference is linked to the nature of the counter cation and present a comparative study of the salts of hydrogen phthalate ion with and without an intramolecular hydrogen bond.