

[s9.m1.p5] **Evidence for Intramolecular N-H...O Resonance-Assisted H-Bond in  $\beta$ -Enaminones and Related Heterodienes**. P. Gilli\*, V. Ferretti, V. Bertolasi, *Chemistry Department and Centro di Strutturistica Diffraattometrica, Ferrara University, Via Borsari 46, I-44100 Ferrara, Italy; E-mail: paola.gilli@unife.it*  
 Keywords: Hydrogen Bonding, RAHB, N-H...O.

Resonance-Assisted H-Bond (RAHB) is a syner-gistic interplay between  $\pi$ -delocalization and H-bond strengthening introduced<sup>1,2</sup> for explaining strong O-H...O bonds formed by the ...O=C-C=C-OH... fragment **I** in  $\beta$ -diketone enols. Its applicability to intra-molecular N-H...O bonds formed by other heterodienes (...O=C-C=C-NH...  $\beta$ -enaminones **II**, ...O=C-C=C=N-NH... ketohydrazones **III**, and ...O=N-C=C-NH... nitrosoenamines **IV**) is now investigated by X-ray crystallography, CSD (Cambridge Structural Database) search, and comparative analysis of IR  $\nu_{\text{NH}}$  stretching frequencies and <sup>1</sup>H NMR  $\delta_{\text{NH}}$  chemical shifts. It is shown that all descriptors of H-bond strength [ $d(\text{N}...O)$  shortening, decrease of  $\nu_{\text{NH}}$ , increase of  $\delta_{\text{NH}}$  and increase of  $\pi$ -delocalization] are mutually intercorrelated according to RAHB 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, how-ever, distinctive features. Their strength is partially hampered by the proton affinity difference ( $\Delta\text{PA}$ ) between the N and O atoms, so that very strong H-bonds ( $2.65 \geq d(\text{N}...O) \geq 2.48 \text{ \AA}$ ;  $3200 \geq \nu_{\text{NH}} \geq 2340 \text{ cm}^{-1}$ ;  $13 \leq \delta_{\text{NH}} \leq 18 \text{ ppm}$ ) can occur only when  $\pi$ -delocalization is associated with substituents able to decrease  $\Delta\text{PA}$  by increasing NH acidity. Moreover, at variance with strong O-H...O RAHBs, whose protons are mostly symmetric, even the strongest N-H...O RAHBs are highly dissymmetrical in spite of the very similar changes undergone by both IR and <sup>1</sup>H 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 (EChBM) previously developed for the homonuclear case<sup>3,4</sup>. 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<sup>-1</sup> for non-resonant **V**, and 5.22, 6.12 and 7.03 kcal mol<sup>-1</sup> for unsubstituted resonant **II**, **III** and **IV**, respect-ively. Proper substitutions of  $\beta$ -enaminone **II** nearly double H-bond energies making them comparable with those calculated for homonuclear O-H...O RAHB in  $\beta$ -diketone enols ( 9.51 and 13.08 kcal mol<sup>-1</sup> for malondialdehyde and acetylacetonone, respectively).

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[s9.m1.p6] **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, Universitetetsparken 5, DK-2100 Copenhagen, Denmark.*  
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The hydrogen malcate 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 malcate in some cases, it is not a general behaviour. There appears to be no obvious structural reasons for this difference between hydrogen malcate 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.