

06-Crystallography of Organic Compounds

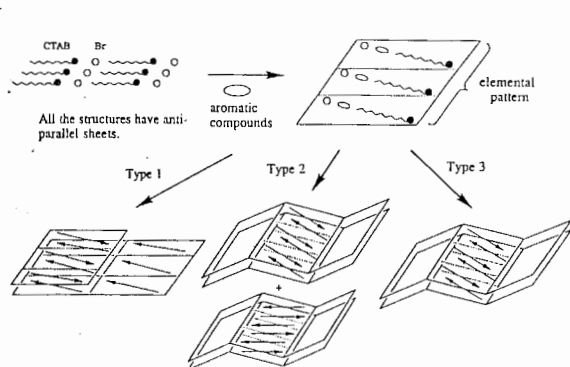
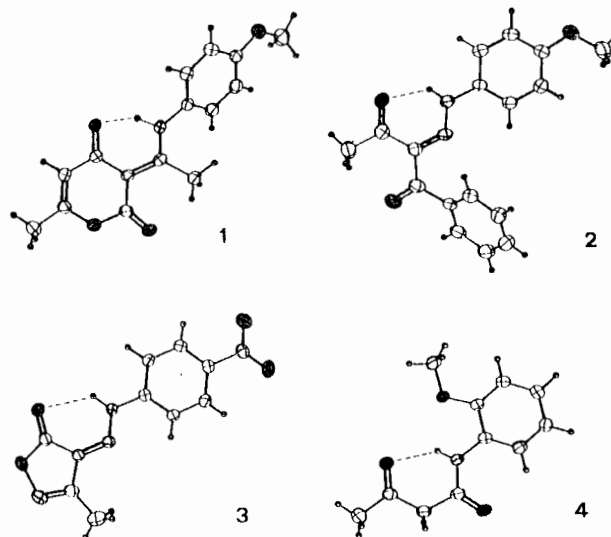


Fig. 1 Model of Crystal Types



PS-06.04.06 INTRAMOLECULAR N-H...O HYDROGEN BOND ASSISTED BY RESONANCE. By Valeria Ferretti^{*}, Valerio Bertolasi, Luca Nanni and Paola Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffraattometrica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy.

The phenomenon of RAHB (Resonance Assisted hb) has been so far studied essentially in the intra- and inter-molecular hb of the O=C-C=C-OH group (Bertolasi *et al.* (1991). *J. Am. Chem. Soc.*, 113, 4917; Gilli *et al.* (1993). *Acta Cryst.*, B49, in the press). It should be, however, generalizable to other heteroconjugated systems such as the O=C-C=C-NH enamionone fragment.

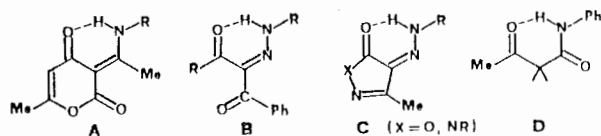
Accordingly we have undertaken the crystal structure determination of molecules containing the enamionone fragment (class A, 4 compounds) and related diketo-hydrazone (class B, 11 compounds) and keto-hydrazone (class C, 3 compounds) fragments. As a reference point, the structure of another compound able to form hb but unable to assist it by resonance (D) has been determined. All compounds studied form the expected 6-membered intramolecular N-H...O hb but with different d(N...O) distances.

Class A: $2.51 \leq d(N...O) \leq 2.56$ Å, Fig.1

Class B: $2.56 \leq d(N...O) \leq 2.61$ Å, Fig.2

Class C: $2.78 \leq d(N...O) \leq 2.92$ Å Fig.3

Class D: $d(N...O) = 2.748$ Å Fig.4



The following points are to be remarked:

- 1) The rather long distance observed for D (2.748 Å) is typical of an usual intramolecular N-H...O bond.
- 2) When hb donor and acceptor atoms are part of a π -conjugated system the hb should be shortened by the resonance. This should happen in classes A, B and C but actually happens only in A and B because of the steric restraints caused by the 5-membered ring in C.
- 3) The delocalization of the π -conjugated systems is greater the shorter the hb is.
- 4) IR and ¹H-NMR spectroscopic data of the aminic proton are in perfect agreement with the observed pattern of N...O distances.
- 5) In conclusion: The behaviour observed for the O-H...O hb formed by O=C-C=C-OH β -diketone enols and interpreted by us through the RAHB model is essentially reproduced by other heterodienes (O=C-C=C-NH and O=C-C=C-N-NH) suggesting that it will hold for all hbs forming heteroconjugated systems A-C-(C=C)-N-DH, N=O,1,...

PS-06.04.07 A GENERALIZED MODEL FOR THE STRONG O-H...O HYDROGEN BOND. By Paola Gilli^{*}, Valerio Bertolasi, Valeria Ferretti and Gastone Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffraattometrica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy.

In spite of the extraordinary wealth of data on the O-H...O hb, the true chemical reasons determining its strength remain widely unknown. So far it was believed that such strong bonds were to be related either to severe intramolecular strain or to systems containing -O-H...O- or =O-H⁺-O= groups (Jeffrey, G.A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*, p.112. Berlin: Springer). It has been recently discovered, however, that there are very strong -O-H...O- bonds (up to $d(O...O) = 2.42$ Å) in non-strained neutral molecules where the two O atoms are connected by a system of π -conjugated double bonds. Such bond has been addressed to as RAHB (Resonance Assisted Hydrogen Bonding) (Gilli, G., Bellucci, F., Ferretti, V. & Bertolasi, V. (1989). *J. Am. Chem. Soc.*, 111, 1023-1028; Gilli, G. & Bertolasi, V. (1990). *The Chemistry of Enols*, Z. Rappoport ed., ch.13. New York: John Wiley; Bertolasi, V., Gilli, P., Ferretti, V. & Gilli, G. (1991). *J. Am. Chem. Soc.*, 113, 4917-4925; Gilli, G., Bertolasi, V., Ferretti, V. & Gilli, P. (1993). *Acta Cryst.*, B49, in the press).

It is clear that previous theories based on the preminent role of positive and negative charges need to be revised. The new model we suggest is based on the idea that very short O-H...O bonds must overcome a very strong O...O repulsion which cannot be compensated by the electrostatic attraction which is known to cause weak or medium range hbs (Umeyama, H. & Morokuma, K. (1977). *J. Am. Chem. Soc.*, 99, 1316-1333). This imply that very strong O-H...O bonds must have a relevant covalent component or, in VB terms, be a mixture of the two canonical forms A: -O-H...O= and B: =O-H...O⁺ with the greatest possible contribution of form B. Usually, the contribution of B is small because dissociation of charges enhances its energy with respect to A. Any chemical situation able to make comparable the energies of A and B is then the origin of the short O-H...O bond.

It is easy to show that A and B energy equalization can be produced only by three chemical situations:(i) by