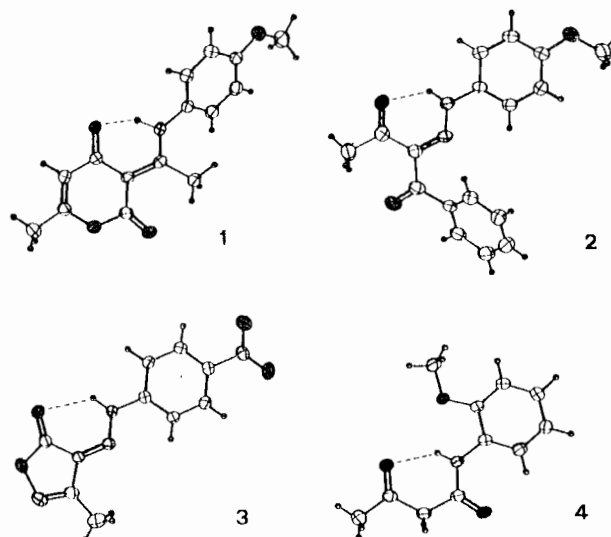


Fig. 1 Model of Crystal Types



**PS-06.04.06** INTRAMOLECULAR N-H...O HYDROGEN BOND ASSISTED BY RESONANCE. By Valeria Ferretti<sup>\*</sup>, 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 enaminoone fragment.

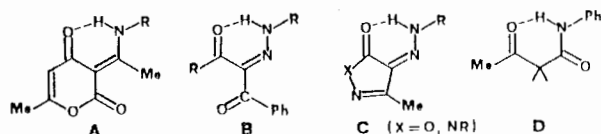
Accordingly we have undertaken the crystal structure determination of molecules containing the enaminoone fragment (class A, 4 compounds) and related diketo-hydrazone (class B, 11 compounds) and keto-hydrazone (class C, 3 compounds) fragments. As a reference point, the structure of another compound able 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:  $2.51 \leq d(\text{N} \cdots \text{O}) \leq 2.56$  Å, Fig.1

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

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

Class D:  $d(\text{N} \cdots \text{O}) = 2.748$  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  $\pi$ -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  $\pi$ -conjugated systems is greater the shorter the hb is.
- 4) IR and <sup>1</sup>H-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  $\beta$ -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<sup>\*</sup>, 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<sup>+</sup>...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  $d(\text{O} \cdots \text{O}) = 2.42$  Å) in non-strained neutral molecules where the two O atoms are connected by a system of  $\pi$ -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).

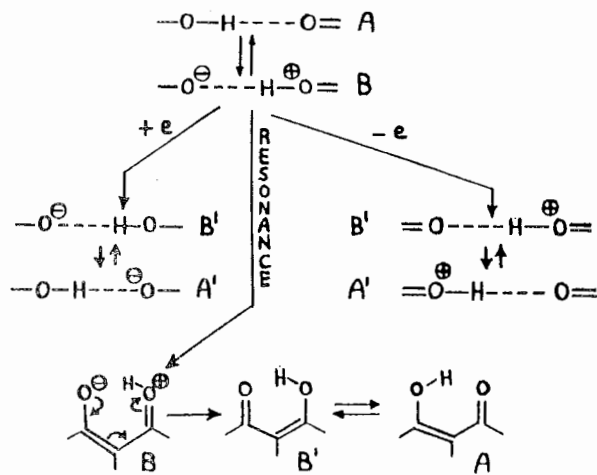
It is clear that previous theories based on the preminent role of positive and negative charges need to be revised. The new model we suggest is based on the idea that very short O-H...O bonds must overcome a very strong O...O repulsion which cannot be compensated by the electrostatic attraction which is known to cause weak or medium range hbs (Umeyama, H. & Morokuma, K. (1977). *J. Am. Chem. Soc.*, 99, 1316-1333). This implies 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<sup>+</sup> 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

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connecting the two O atoms by a resonant system able to transmit the charges; (ii) by adding an electron to B; (iii) by removing an electron from B (see scheme). Experimental proves of such statement will be given at the meeting for all strong O-H...O bonds retrievable from the Cambridge Structural Database.

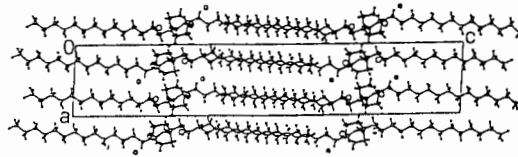


**PS-06.04.08** QUATERNARY ALKYL HALIDE SALTS OF 1,4-DIAZABICYCLO[2.2.2]OCTANES WITH HALIDE ANION CONDUCTIVITY. By M. Yasui<sup>1</sup>, R. Yamazaki<sup>1</sup>, F. Iwasaki<sup>1</sup>, T. Nogami<sup>1</sup>, N. Kamiya<sup>2</sup> and H. Iwasaki<sup>2</sup>, <sup>1</sup>Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu, Tokyo 182, Japan, <sup>2</sup>The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan.

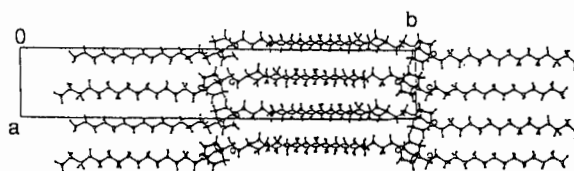
A series of quaternary alkyl halide salts of 1,4-diazabicyclo[2.2.2]octanes (DABCO) exhibited first-order phase transition in the temperature range of 62-100°C and showed halide anion conductivity in the high temperature phase (Shimizu, J. *et al.*, 1986, Bull. Chem. Soc. Jpn, **59**, 1443-1448). The phase transition temperature (T<sub>c</sub>) and heats of transition showed a so-called even-odd number effect of carbon number which was also observed for a series of long chain alkanes and alcohols. In this study, we have investigated the crystal structures of *N,N'*-ditetradecyl-1,4-diazabicyclo[2.2.2]octane dibromide (I) and a dipentadecyl derivative (II). In each crystal, one dimension of the unit cell was very long and crystals showed instabilities against the X-ray irradiation, so that the intensity data from single crystals were collected on the IPD-WAS (Weissenberg type diffractometer with Imaging Plate, N. Kamiya *et al.*, 1990, Acta Cryst. **A46** Suppl., C10). The molecular structures of (I) and (II) have similar features. Two alkyl chains have *trans*-zigzag conformation, and dihedral angles between the planes of alkyl carbons are 128 and 157° for (I) and (II), respectively. Two bromide anions reside near the DABCO ring. Alkyl chains form sheet-like structures in crystals. In spite of the difference of chain length, the number of van der Waals contacts between alkyl chains in (I) is slightly larger than that in (II). This fact may explain the even-odd number effect that the heat of transition of (I) was greater than that of (II). In the powder X-ray diffraction patterns for (I) and (II) which were measured at the temperature near T<sub>c</sub>, sharp diffraction peaks for the high temperature phase appeared at lower 2θ angles. At the temperature beyond the T<sub>c</sub>, diffraction peaks assigned for short axes directions disappeared, although the sharp peaks for long axis direction still remained. Thus disorder along short axes just as the liquid-crystal arose from the phase transition.

## Crystal Data

	(I)	(II)
Formula	2Br <sup>+</sup> C <sub>34</sub> H <sub>70</sub> N <sub>2</sub> <sup>2-</sup> · 0.5H <sub>2</sub> O	2Br <sup>+</sup> C <sub>36</sub> H <sub>74</sub> N <sub>2</sub> <sup>2-</sup>
Fw	666.75	694.80
Color	Colorless	Colorless
Crystal system	monoclinic	orthorhombic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	8.720(1)	8.792(5)
b	8.789(2)	52.046(7)
c	49.298(8)	8.727(2)
β/°	93.83(2)	90.00
V/Å <sup>3</sup>	3770(1)	3993(1)
Z	4	4
Reflections measured	9499	10125
observed	3675	2385
R	0.0650	0.0650



(I)



(II)

**PS-06.04.09** POLYMORPHIC STRUCTURES AND PHASE TRANSITIONS OF N-PICRYLANILINE DERIVATIVES By K. Taguchi, M. Hirota, K. Maeda, M. Yasui and F. Iwasaki\*, Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu-shi, Tokyo 182, Japan

N-picryl-p-toluidine (I) and N-(2,4-dinitrophenyl)-o-anisidine (II) crystallize in two modifications, orange and red forms. The condition to crystallize each form is very subtle, so that it is by chance which form can be obtained and the coexistence of these forms is often observed. The orange crystals of both I and II turns red just below the melting points. After the orange crystals melt completely, the red crystals are obtained by cooling. Crystal structures of these polymorphic forms have been determined in order to study on the relationships between molecular interactions and polymorphic transition.

	I <sub>o</sub>	I <sub>r</sub>	II <sub>o</sub>	II <sub>r</sub>
Color	Orange	Red	Orange	Red
Cr. system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Sp. group	P2 <sub>1</sub> /a	P2 <sub>1</sub> /c	P2/a	P2 <sub>1</sub>
a / Å	16.475(3)	13.107(4)	15.546(8)	15.693(2)
b	6.007(1)	17.739(4)	4.220(1)	10.981(3)
c	15.203(3)	6.090(2)	16.747(4)	3.842(1)
β / °	114.12(1)	102.16(3)	122.31(1)	98.39(2)
V / Å <sup>3</sup>	1373.2(4)	1384.2(8)	1287.0(7)	655.0(2)
Z	4	4	4	2
Dx / gcm <sup>-3</sup>	1.539	1.527	1.493	1.467
Radiation	MoKα	MoKα	CuKα	MoKα
No. ref.	2188	1434	1234	866
R	0.052	0.106	0.120	0.079
Solvent	acetone	acetone+CCl <sub>4</sub>	benzene+EtOH	acetone

The molecular structures of I<sub>o</sub> and I<sub>r</sub> are very similar. Intramolecular NH...O hydrogen bond is formed between anilino and nitro groups. On the other hand the molecules of II<sub>o</sub> and II<sub>r</sub> are rotational isomers. In II<sub>r</sub> NH group is hydrogen-bonded to nitro and methoxy groups bifurcatedly, while in II<sub>o</sub> the hydrogen