

Crystal Engineering: Hydrogen Bonded Chains

A Proposal to the ISIS Facility of the Rutherford Appleton Laboratories by

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In engineering molecular crystals it is often necessary to produce polar materials. This is easiest to arrange for linear structures and, especially, structures that can be interconverted by proton exchange. This is the case for linear chain hydrogen bonded networks.

Several organic species are known to form linear chain hydrogen bonded networks. These materials have interesting properties such as ferroelectric phases or unusually short hydrogen bonds attributed to resonance stabilization. One example to be investigated is 1,3-cyclohexanedione (below) which, as the enol tautomer, has the linear chain structure shown with an O...O distance of 2.56 Å [1], considerably shorter than the van der Waals distance of 3.0 Å and suggesting a strong H-bond. Such H-bonded chains, particularly, the covalent contributions to their stability, has been discussed by Gilli [2]. Other examples to be investigated in this study are the five-membered ring analog, 1,3-cyclopentanedione [3] and phenylmalonaldehyde.

NH...N systems of this type are salts of 1,4-diazabicyclo[2.2.2]octane. The structure of the BF₄ salt [5] is shown above right. The ClO₄ salt has a very similar structure. The N...N distance is 2.84 Å in each case. These materials have a ferroelectric phase transitions at about 377 K.

These systems are attractive for study both because of their intrinsic interest and because the hydrogen bonding system is one-dimensional permitting reliable simulations of the material without the excessive size of a three-dimensional arrangement.

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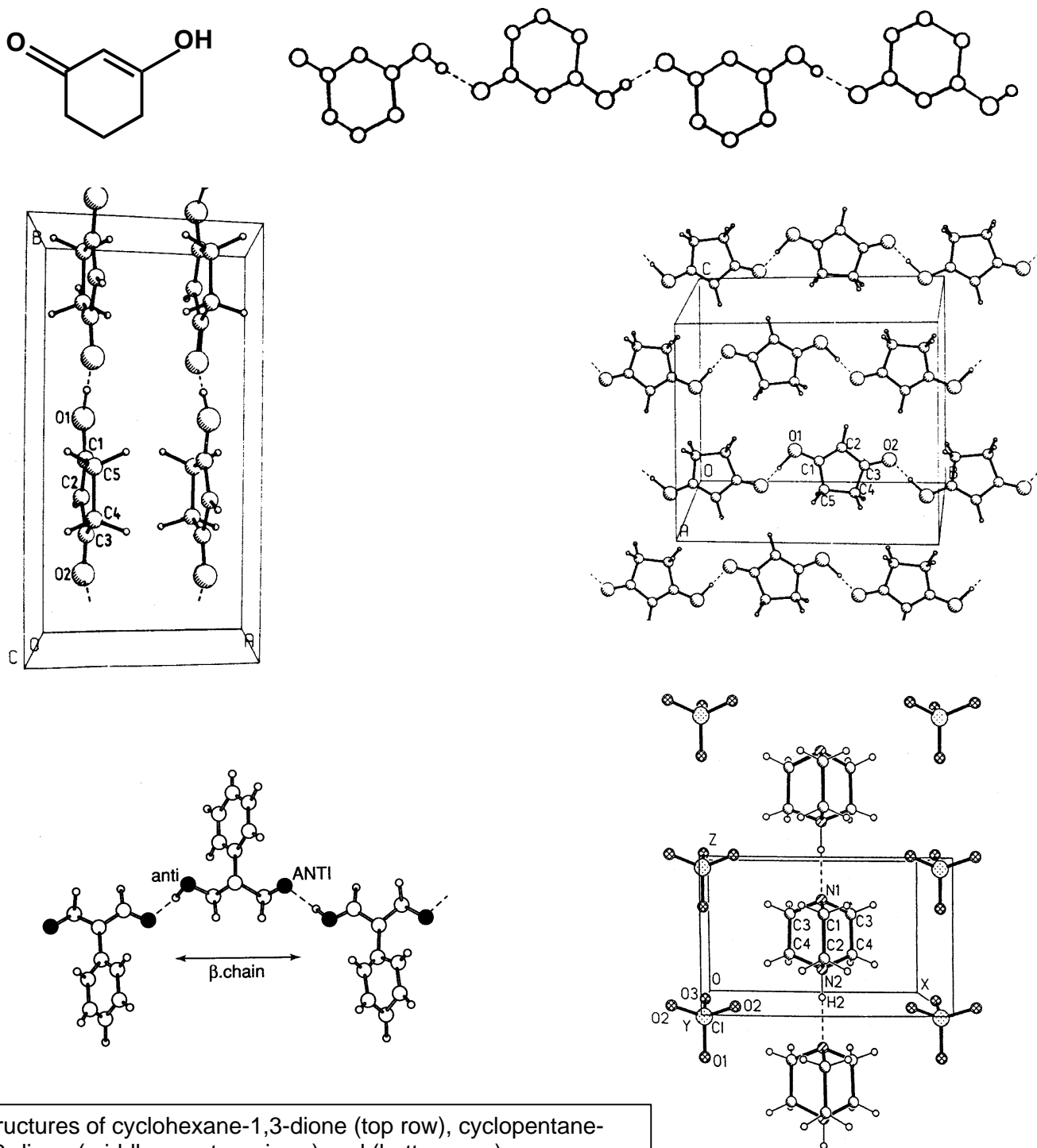
[2] Bertolasi, Valerio; Gilli, Paola; Ferretti, Valeria; Gilli, Gastone. Intramolecular O-H...O hydrogen bonds assisted by resonance. Correlation between crystallographic data and ¹H NMR chemical shifts. *J. Chem. Soc., Perkin Trans. 2* (1997), 945-952; Gilli, Paola; Ferretti, Valeria; Bertolasi, Valerio; Gilli, Gastone. A novel approach to hydrogen bonding theory. *Adv. Mol. Struct. Res.* (1996), 2, 67-102; Bertolasi, Valerio; Gilli, Paola; Ferretti, Valeria; Gilli, Gastone. Resonance-assisted O-H...O hydrogen bonding: its role in the crystalline self-recognition of β-diketone enols and its structural and IR characterization. *Chem.--Eur. J.* (1996), 2, 925-934.

[3] Structure of 1,3-cyclopentanedione. Katrusiak, Andrzej. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* (1990), C46, 1289-93.

[4] Szafranski, M.; Katrusiak, A. Thermodynamic behaviour of bistable NH⁺-N hydrogen bonds in monosalts of 1,4-diazabicyclo[2.2.2]octane. *Chem. Phys. Lett.* (2000), 318(4,5), 427-432.

[5] Katrusiak, Andrzej; Szafranski, Marek. Ferroelectricity in NH...N Hydrogen Bonded Crystals. Phys. Rev. Lett. (1999) 82, 576-579.

[6] Katrusiak, Andrzej; Ratajczak-Sitarz, Malgorzata; Grech, Eugeniusz. Stereochemistry and transformations of NH-N hydrogen bonds. Part II. Proton stability in the monosalts of 1,4-diazabicyclo[2.2.2]octane. J. Mol. Struct. (1999), 474, 135-141.



Structures of cyclohexane-1,3-dione (top row), cyclopentane-1,3-dione (middle row; two views) and (bottom row) phenylmalonaldehyde (left) and 1,4-diazabicyclo[2.2.2]octane HBF₄ (right).