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Tautomerism from X-ray powder data? The challenging case of CLT acid, $C_7H_8ClNO_3S$.

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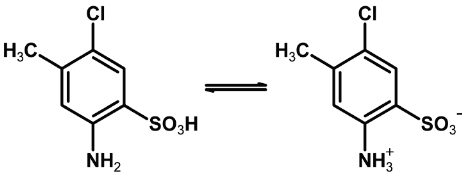
CLT acid is an industrial intermediate in the synthesis of laked red azo pigments used for newspaper printing [1] and industrially produced in an amount of several 10,000 t per year. Up to date no solid state structure of this compound is known.

The compound can exist in two tautomers:



non-zwitterionic zwitterionic

The crystal structure was solved from laboratory X-ray powder diffraction data by means of real-space methods using the program *DASH 3.1* [2]. Subsequently the structure was refined by the Rietveld method with *TOPAS 4.1* [3].

The compound crystallises in the monoclinic space group *Ia*, $Z = 4$ with $a = 5.49809(7)$ Å, $b = 32.8051(5)$ Å, $c = 4.92423(7)$ Å, $\beta = 93.5011(7)$ ° and $V = 886.50(2)$ Å^3 [4].

The Rietveld refinements revealed on the basis of *R*-values as well as by refining the occupancies of the H atoms that the compound exists as the zwitterionic tautomer in the solid state. The tautomeric state was confirmed by solid-state NMR and IR spectroscopy. Finally the structure was confirmed by lattice-energy minimisations using dispersion-corrected density-functional calculations [5] with the program *GRACE* [6].

[1] Herbst, W., Hunger, K., Industrial Organic Pigments, 3rd ed., Wiley-VCH, Weinheim, 2004. [2] David, W. I. F., Shankland, K., van de Streek, J., Pidcock, E., Motherwell, W. D. S., Cole, J. C, *J. Appl. Cryst.*, 2006, 39, 910-915. [3] Coelho, A. A., TOPAS Academic version 4.1 (Computer Software), Brisbane 2007. [4] Bekö, S. L., Thoms, S. D., Brüning, J., Alig, E., van de Streek, J., Lakatos, A., Glaubitz, C., Schmidt, M. U., *Z. Krist.*, 2010, *submitted*. [5] Neumann, M. A., Perrin, M.-A., *J. Phys. Chem.*, 2005, B109, 15531-15541. [6] GRACE (http://www.avmatsim.eu).

Keywords: X-ray powder diffraction, tautomerism, dispersion-corrected DFT calculations

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Halogen bonding in DABCO-I_2 complexes and *N*-substituted 3-iodopyridinium halides.

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Predicting and designing non-covalently bound supramolecular complexes and assemblies is difficult because of the weakness of the interactions involved, most recent of these being the interaction between polarized iodine atoms and nucleophilic atoms (N, O, S) or anions (iodide, bromide, etc.), *viz.* the halogen bonding [1]. Our research interest has been focused on the studies of weak non-covalent intermolecular, *viz.* supramolecular interactions as the driving force in self-assembly and molecular recognition, especially in the solid state by single crystal X-ray diffraction. In addition to studies of well-known non-covalent forces (*e.g.,* hydrogen bonds), recognition, characterization and understanding of less-studied halogen bonding [2,3] and derived systems is also one of our aims. The presentation will show some of our recent results on halogen bonding in DABCO-iodine (I_2, $2I_2$) complexes and *N*-substituted 3-iodopyridinium halide salts.

[1] a) Metrangolo P., Resnati G., Pilati T., Biella S., in Halogen Bonding Fundamentals and Applications (eds. Metrangolo P., Resnati G.), Springer, Berlin, 2008, pp. 105-136; b) Metrangolo P., Meyer F., Pilati T., Resnati G., Terraneo G., *Angew. Chem. Int. Ed.* 2008, 47, 6114; c) Metrangolo P., Neukirch H., Pilati T., Resnati G., *Acc. Chem. Res*. 2005, 38, 386. [2] a) Russo L., Biella S., Lahtinen M., Liantonio R., Metrangolo P., Resnati G., Rissanen K., *CrystEngComm.* 2007, 9, 341; b) Rissanen K., *CrystEngComm.* 2008, 10, 1107; c) Raatikainen K., Rissanen K., *CrystEngComm.* 2009, 11, 750; d) Raatikainen K., Huuskonen J., Lahtinen M., Metrangolo P., Rissanen K., *Chem. Comm.* 2009, 2160; e) Metrangolo P., Carcenac Y., Lahtinen M., Pilati T., Rissanen K., Vij A., Resnati G., *Science* 2009, 323, 1461. [3] Raatikainen K., Cametti M., Rissanen, K., *Beilstein J. Org. Chem.* 2010, 6, no. 4.

Keywords: halogen bonds, amines, pyridinium halides

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Investigation of hydrogen bonds at low temperatures using polarized Raman spectroscopy and single-crystal X-ray diffraction.

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The properties of strong hydrogen bonds are widely discussed in recent literature. This interest is related to the role of these bonds in the processes of enzymatic catalysis, in the interactions between drugs and biological molecules, and in determining the properties of molecular materials for non-linear optics. Besides, the formation of hydrogen bonds determines the secondary structure of proteins, the structure of molecular crystals, and can account for delivery of drugs to the desired area of the cell, using the mechanisms of molecular recognition.

Strong hydrogen bonds are present in many of the crystalline amino-acid salts. From this class of compounds, for the present study we have selected bis(DL-serinium) oxalate dihydrate and DL-alaninium semioxalate hydrate. Geometry of hydrogen bonds (D-A distance and angles of the bonds) was studied using single-crystal X-ray diffraction in the temperature range 100-300 K. Considering this data, polarized Raman spectra with polarization along crystallographic axes have been measured for the single crystals in the temperature