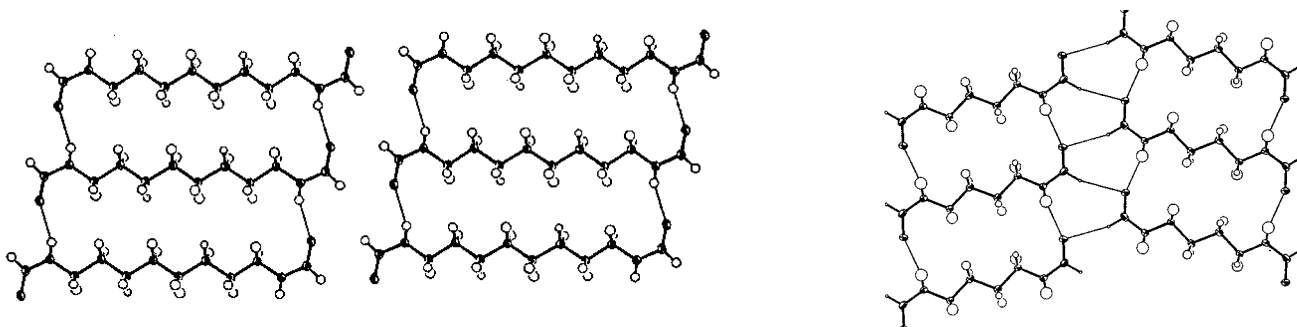
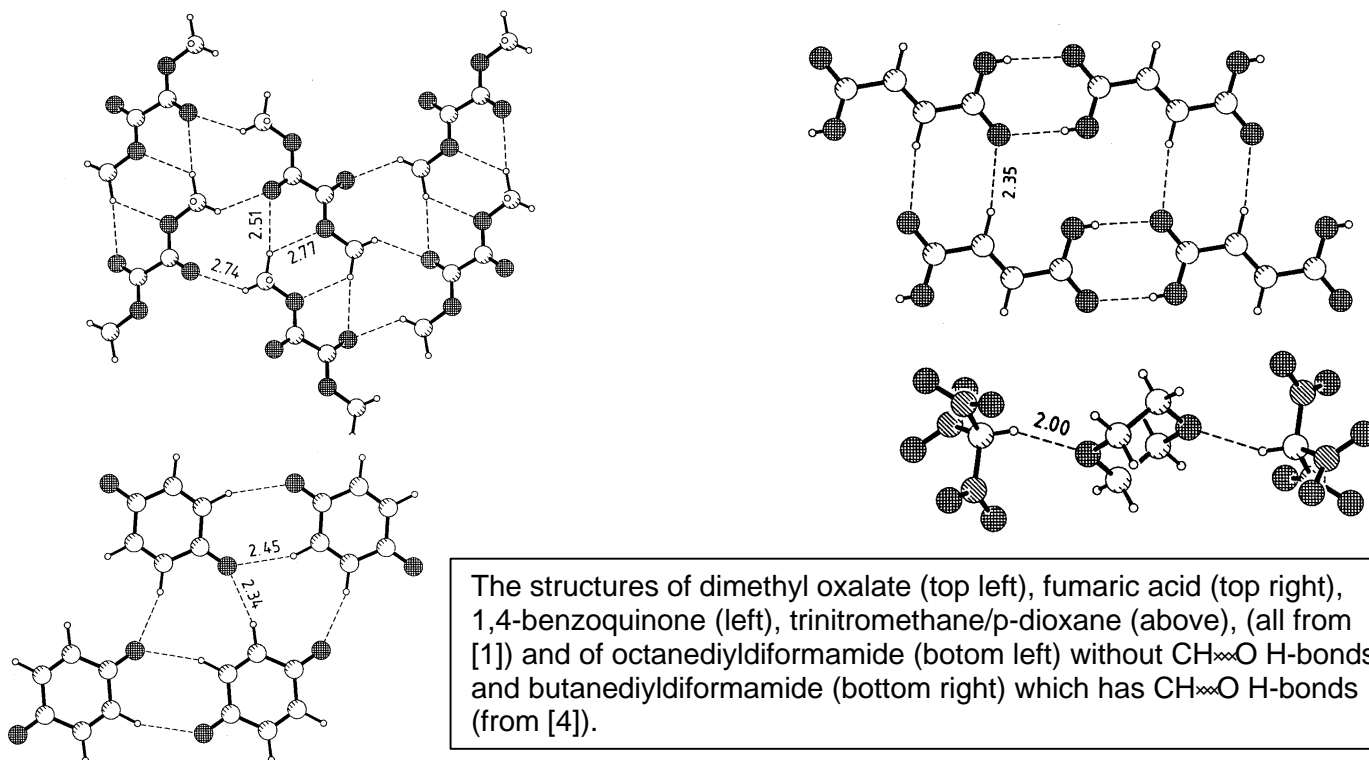


Crystal Engineering: CH \cdots O Hydrogen Bonds

A Proposal to the ISIS Facility of the Rutherford Appleton Laboratories by
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There is growing evidence for the importance of weak intermolecular interactions in the determination of crystal structures and drug receptor interactions [1]. One such interaction is the CH \cdots O hydrogen bond. Understanding this interaction is essential in any attempt to engineer crystalline materials or effective pharmaceuticals.

The X-H \cdots A hydrogen bond forms when A has a lone pair and X is electronegative. Common examples are A, X = N, O, F and Cl. The case where X = C, i.e., the C-H \cdots A hydrogen bond, has been the subject of considerable controversy [1]. Neutron diffraction has played a crucial role in rehabilitating this hypothesized interaction with the high point being the analysis by Taylor and Kennard of 113 neutron diffraction structures [2]. Vibrational spectroscopy has played a significant role in studies of C-H \cdots A hydrogen bonds but primarily for C $^\circ$ C-H bonds which are relatively acidic. There do not appear to be any INS studies of this interaction. The present proposal consists of a study of the best characterized systems that contain CH \cdots O hydrogen bonds where it is expected that this interaction will result in a recognizable feature in the INS spectrum. These are dimethyl oxalate, fumaric acid, p-benzoquinone, the adduct of trinitromethane with p-dioxane and the bis-formamides HCONH-(CH $_2$) $_n$ NHCHO, n = 4-8. The crystal structures of these materials are shown below.



The melting point of dimethyl oxylate (COOCH₃)₂, 54° C, is ca. 100° higher than that of related carboxylic acid esters. This has been ascribed to the formation of numerous CH...O H-bonds of the methyl groups in this compound. The determination of the CH₃ torsional frequency in this material in comparison with that of, for example, dimethylmalonate (CH₂(COOCH₃)₂), mp -62° C, will immediately establish the validity of this assertion and permit estimation of the strength of this interaction.

The triclinic form of fumaric acid shows the usual centro-symmetric ring structure of carboxylic acids but in an unusual C=O, *antiplanar* geometry. This is attributed to the formation of C=CH...O=C hydrogen bonds. In this case we will investigate the species with the exchangeable protons replaced by D so as to leave only the pair of H atoms hypothesized to be involved in CH...O H-bonds..

1,4-Benzoquinone has been the subject of a previous INS study [3] aimed at location of inactive modes. There appear to be large discrepancies between the calculated and observed intensities based on an isolated molecule refined force field. This work [3] points out that the molecular structure is different for the gas phase and crystal. This structure is particularly suitable to a cluster calculation of the type we have recently applied to oxamide because of its planar arrangement. This should reveal the importance of the CH...O=C hydrogen bonds which involve all of the H atoms to the structure and dynamics.

The trinitro methane/p-dioxane co-crystal provides an interesting case of a very short (2.00 Å C -O) H-bond. The p-dioxane-d₈ complex with only the CH...O H-bond H atom will be investigated and modeled as an isolated unit using density functional methods.

The bis-formamides, HCONH-(CH₂)_nNHCHO, exhibit a 35° alternation in melting point with n, the odd numbered species being much lower in melting point than the n even compounds except for n = 8 which has a low value. The structure of these compounds [4] reveals that CH...O=C H-bonds form in the high-melting n = 4 and 6 cases but not in the n = 8 case and, presumably, not in the n-odd cases. A direct comparison of the INS spectra of the HCOND-(CD₂)_nNDCHO spectra for various n should reveal the effects of the CH...O=C bonds on the vibrational dynamics.

[1] Desiraju, Gautam R.; Steiner, Thomas. "The Weak Hydrogen Bond" (IUCr/Oxford, Oxford, 1999) Chapter 2 (pages 29-121).

[2] Taylor, Robin; Kennard, Olga. "Crystallographic evidence for the existence of CH...O, CH...N and CH...Cl hydrogen bonds", J. Am. Chem. Soc. (1982), 104(19), 5063-70.

[3] Penfold, J.; Tomkinson, J., "First observation of the optically inactive modes in solid 1,4 benzoquinone" J Chem Phys 85 6296 (1986).

[4] Chaney, J. D.; Goss, C. R., Folting, F.; Santarsiero, B. D.; Hollingsworth, M. D., "Formyl CH...O Hydrogen Bonding in Crystalline Bis-Formamides?", J. Am. Chem. Soc. 1996, 118, 9432.