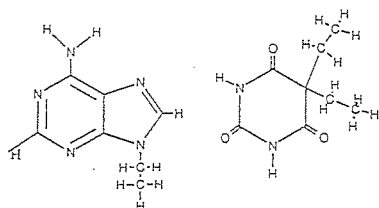


PS09.01.20 THE CHARGE DENSITY OF 9-ETHYLADENINE-5,5-DI-ETHYLBARBITURIC ACID. M. Niederhut and B.M. Craven. Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260

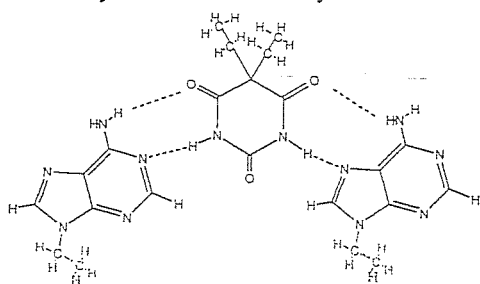
Barbital is a molecule that binds with many biological compounds. In binding with adenine, as shown by Voet, (1972, JACS, 94:23, 8213-8222.), it forms layers of hydrogen bonds of both Watson-Crick and Hoogsteen types.

New low temperature data of the adenine-barbital complex, space group P1, were collected using MoK α radiation ($\lambda=0.7093\text{\AA}$). Multipole refinements and charge density plots will be presented and discussed.

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9-ethyladenine 5,5-diethylbarbituric acid



PS09.01.21 MULTIPOLE ELECTRON DENSITY MODELING IN ACENTRIC SPACE GROUPS? PERIODIC AB INITIO CALCULATIONS ON HEXAMETHYLENETETRAMINE. Henrik Birkedal and Sine Larsen, Centre for Crystallographic Studies, University of Copenhagen, Denmark

The multipole formalism for modeling of experimental electron densities is a well established method, but problems are encountered in acentric space groups due to the lack of general phase restrictions. To obtain a quantitative measure of the quality of phase reconstruction in acentric space groups periodic *ab initio* Hartree-Fock calculations on hexamethylenetetramine (HMT) have been performed making use of the CRYSTAL 92 package¹. The atomic parameters were taken from a 15 K neutron diffraction study². X-ray structure factors were calculated from the HF electron density. From the experimental atomic displacement parameters an overall displacement parameter was estimated, which was used to calculate pseudo-dynamic structure factors, that display the decrease of the intensities with $\sin \theta/\lambda$ due to the effects of thermal motion.

The static and pseudo-dynamic structure factors are used as observations in a least squares refinement with the generalized structure factor (gsf) formalism³. Three different sets of static and pseudo-dynamic structure factors were used. They correspond to the maximum resolution with the wavelengths 0.71073 \AA (MoK α), 0.56087 \AA (AgK α), and 0.24 \AA (synchrotron radiation). The resulting gsf phases are compared to the original *ab initio* phases.

The quality of the total multipole modeled electron density has been examined by mapping of the difference density (*ab initio*

- multipole model) and by comparing its characteristic topological features with those found with the TOPOND program⁴ from the *ab initio* electron density.

¹R. Dovesi, V.R. Saunders, and C. Roetti *Crystal 92 An Ab initio Hartree-Fock LCAO program for periodic systems, User Manual*, 1992

²Kampermann, Sabine, Craven, and McMullan. *Acta Cryst.* A51, 489-497

³R.F. Stewart, M.A. Spackman, and C. Flensburg. *Valray Manual*, 1995

⁴C. Gatti, V.R. Saunders, and C. Roetti. *J. Chem. Phys.* 101, 10686 (1994)

PS09.01.22 EXPERIMENTAL AND THEORETICAL CHARGE DENSITIES IN A MODEL "PROTON SPONGE" COMPLEX. Paul R. Mallinson, Kirsty L. McCormack, Chemistry Department, University of Glasgow, UK, and Krzysztof Wozniak, Chemistry Department, University of Warsaw, Poland

Substituted 1,8-diaminonaphthalenes show a wide range of basic strengths, with observed pK_a values up to 16.3 [1]. On methylation of 1-dimethyl,8-methylaminonaphthalene to form 1,8-bis(dimethylamino)naphthalene (DMAN) there is a decrease of six orders of magnitude in the acidity constant K_a of the conjugate acid: the pK_a value changes from 6.4 to 12.1. The ammonium ion, for comparison, has pK_a = 9.25.

The acid salt formed by DMAN with 1,2-dichloromaleic acid contains two strong, asymmetric hydrogen bonds [N-H...N]⁺ and [O-H...O]⁻ [2]. For the cation, *ab initio* MO calculations [3] predict an asymmetric H bond to be 25kJ/mol more stable than a symmetric one. Directionality of the H-bond acceptor lone pairs towards the hydrogen nuclear position is observed in Laplacian distributions of the charge density in both cation and anion, obtained from X-ray and neutron diffraction data. On protonation of DMAN, density in the bonds to the carbon at the 9-position increases, while the density in the C-N bonds decreases.

[1] H. A. Staab and T. Saupe, *Angew. Chem.* 27 (1988), 885-879.

[2] K. Wozniak, H. He, J. Klinowski, W. Jones, and T.L. Barr, *J. Phys. Chem.* 99 (1995), 14667-14677.

[3] J.A. Platts and S.T. Howard, *J. Org. Chem.* 59 (1994), 4647-4651.

PS09.01.23 ELECTRON DENSITY STUDIES ON 2,3-PYRIDINEDICARBOXYLIC ACID Márcia D. D. Costa, Nelson G. Fernandes, Department of Chemistry - Federal University of Minas Gerais CP 702, 31270-901 - Belo Horizonte - Brazil

The present work reports a deformation refinement from X-ray data for quinolinic acid, C₇H₅NO₄. The compound adopts the zwitterion form in the crystalline state and has a short asymmetric hydrogen bond with O—O' distance of 2.401(4) \AA . This is one of the shortest intramolecular hydrogen bonds known. In addition, neutron diffraction data at room and low temperatures are available. These are the reasons that motivated us to study 2,3-pyridinedicarboxylic acid.

Data collection was performed on a SIEMENS-P4 diffractometer, in θ - 2θ scan mode, $(\sin\theta/\lambda)_{\max} = 1.20 \text{\AA}^{-1}$, MoK α . Data were corrected for absorption, Lorentz and polarization effects; no extinction correction was necessary. 6856 reflections collected, 4817 unique. Deformation density refinement was performed following the Hirshfeld procedure, that allows the charge-density redistribution accompanying molecule formation to be incorporated into the crystallographic model for least-squares refinement, together with the usual positional and thermal parameters. This resulted in wR=0.0556 (F²) for 218 parameters refined, of which 109 were deformation parameters.

Deformation density map through the short hydrogen bond shows two maxima peak heights of approximately 0.3 e/ \AA^3 localized in the bonds O-H and O'-H. One of them is at 0.6 \AA from O and 0.7 \AA from H. The other is located at 0.7 from O' and 0.5 \AA from H. It is clear from the data that there are two different C-O bond orders with maxima of 0.3 and 0.6 e/ \AA^3 .