INDIRECT READOUT OF THE PurF OPERATOR BY THE PURINE REPRESSOR (PurR)

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The PurR-hypoxanthine-purF operator complex structure has been solved to 2.5 Å resolution and revealed several features key to specific DNA recognition, including an introduced kink in the DNA at the central CpG step. However, the structure does not reveal the strict conservation of certain DNA bases. Specifically, PurR binds 21 known operators, which can be described as 42 half-sites due to the pseudopalindromic nature of these binding sites; of these, 41 have an adenine at the 7 position, and one has a cytosine. Surprisingly, the PurR-hypoxanthine-purF operator structure shows no direct contacts between adenine7 and the protein. Equilibrium binding experiments using fluorescence anisotropy with substituted operators revealed a striking result, whereby substitution of adenine7 by cytidine, thymine or guanine resulted in 12, 30 and 107 fold higher Kd values, respectively. The crystal structures of the Escherichia coli PurR bound to operator sites mutated at the 7 position have been solved by molecular replacement and two separate effects were observed: mutation of the highly conserved base in the cytidine and thymine structures altered neighboring base contacts to Lysine 55 due to altered electrostatics in the minor groove. Moreover, inherent base stacking preferences of the wild type purine-purine step over the pyrimidine-purine steps of the cytidine and thymine substituted purF operators also play a role in PurR binding preference of Adenine at position 7. Observed in the lowest affinity guanine substituted operator was a distortion of the DNA backbone as a result of the sequence change: indirect readout.

Keywords: TRANSCRIPTION FACTOR INDIRECT READOUT PURINE REPRESSOR

MOLECULAR RECOGNITION OF THE PLANT HORMONE AUXIN IS STILL A PUZZLE

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The plant hormone auxin is involved in almost every aspect of plant development; auxin homeostasis and auxin signaling are thus of crucial importance. The wider auxin family includes endogenous growth promoters, such as indole-3-acetic acid (IAA), and chemically diverse synthetic analogues; minor structural modifications afford growth inhibitors (antiauxins). As proper classification is of technological relevance (growth regulators, herbicides) we developed a classification by interaction similarity indices, based on evaluation of two distinctive molecular conformations (planar and tilted) of indole-3-acetic acid in comparison with optimized conformations of 50 compounds. Then we extended a method to a larger set of compounds using similarity of molecular interaction fields and lipohilicity predictions (log P). In addition to theoretical approaches based on the evaluation of molecular conformations of possible relevance for binding to the auxin receptor(s), we used experimental methods, such as X-ray structure analysis and spectroscopic methods to characterize the molecules of interest: alkylated IAAs, halogenated IAAs (F, Cl, Br), and dihalogenated IAAs. Systematic analysis of physico-chemical and structural properties provided indirect insight into the topology of the substrate-binding site of the, so far hypothetical, common auxin receptor. Our findings are in reasonable accord with the models proposed by previous researchers. The question of molecular fit to the receptor active site will, however, remain open until the coordinates of the first structurally characterized auxin binding protein ABP1, will be at public domain.

Keywords: **MOLECULAR RECOGNITION, AUXINS**

POLYMORPHISM IN LONG-CHAIN N-ALKYLAMMONIUM CHLORIDES

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The n-alkylammonium halides are used in industry as detergents and surfactants. A large number of crystalline phases can form, depending on temperature and crystallization method. The room temperature polymorphs crystallize from the melt or from different solvents. The homologous series of alkylammonium halides ($C_nH_{2n+1}NH_3X$; X= Cl, Br, I) exhibit polymorphism and pseudo polymorphism and interesting solid-solid phase transitions.
We investigated the structural and thermal behaviour of saturated n-alkylammonium chlorides, for chains with $10 < n < 18$. These compounds have been investigated by various techniques, including single crystal X-ray diffraction, powder diffraction, solid state NMR, hot-stage microscopy and differential scanning calorimetry (DSC).
We determined the crystal structures of two polymorphs of n-octadecylammonium chloride by single crystal and powder methods. The structures of n-decylammonium chloride, n-dodecylammonium chloride and n-undecylammonium chloride monohydrate have been reported previously. By extrapolation on cell dimensions and thermal behavior, it was possible to assign structure types to most of the phases studied.
In all of the crystal structures studied, polar layers are formed by alternating ammonium and chloride ions interacting through hydrogen bonds. Each ammonium group is bonded to three chloride anions that surround it. The non-polar layers contain parallel hydrocarbon chains, tilted relative to the ionic layer and interacting through van der Waals forces. Covalent N-C bonds link the polar and non-polar layers. The aliphatic chains can be interdigitated (with all-trans conformations) or non-interdigitated (with the C2-C3 bond in a gauche conformation). A phase transition sequence for this class of compound could be formulated.

Keywords: **POLYMORPHISM ALKYL AMMONIUM HALIDES THERMAL ANALYSIS**

STRUCTURES, LATTICE ENERGIES AND FLUORESCENCE OF DIPHENYL MALEIC ACID ANHYDRIDE (IMIDE) POLYMORPHS

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In 1912 Drugmann described an orthorhombic stable and a monoclinic metastable phase of 2,3-diphenyl maleic acid anhydride $C_{16}H_{10}O_3$ (α- and β-DA) and their different fluorescence. The structure of α-DA was determined 1995 by Yoon et al.. Crystallographic data of 2,3-diphenyl maleic acid imide $C_{16}H_{11}O_2N$ (DI) were not known until now. Crystals of both compounds were precipitated from solutions in various solvents and by slow and rapid supercooling of the melts. For DA, in addition to crystals of the α- and β-modifications described by Drugman, a second metastable phase, γ-DA, was found. For all polymorphs, except for γ-DA, single crystals suitable for structure determination were obtained. From melts, the stable phases crystallize by slow, the metastable phases by fast (i.e. high) supercooling. X-ray structure determinations, lattice energy calculations (program HABIT95, Scheraga force field), and fluorescence measurements (excitation source: Nd:YAG laser) were performed. The results are (quoted in the sequence α-DA, β-DA, α-DI, β-DI): Space groups: *Pbca*; $P2_1/c$; *P*-1; *C*2/*c*. Densities (g cm^{-3}): 1.334; 1.351; 1.307; 1.297. Melting points (degree Celsius): 156; 146; 216; 212 Total lattice energies (kcal mol^{-1}): -30.58; -31.85; -33.41; -33.39. Wavelengths (nm)/wave numbers (cm^{-1}) of maximum fluorescence intensity (broad emmission bands): 468/(21368); 461/(21692); 490/(20408); 509/(19646).
Unexpectedly the density and the calculated (intermolecular) lattice energy of stable α-DA are lower than for β-DA. Stabilisation of α-DA is possibly achieved by changes in the intramolecular energy in the solid due changes in dihedral angles compared to the free molecule in the gas phase.

Keywords: **POLYMORPHISM LATTICE ENERGIES FLUORESCENCE**