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Chiral Recognition of Derivatives Based on the Ergot Alkaloid Terguride

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Intermolecular forces have always been object of interest, but, how they act, in concert, to discriminate between molecules, has been increasingly studied with the development of the concept of molecular recognition. An aspect of molecular recognition is chiral recognition. Here molecules are not expected to differentiate on the basis of physicochemical properties. They can only be discerned when they give rise to slightly different diastereomeric interaction once they associate with another chiral molecule. Chiral recognition is the basis of chiral chromatography. In fact, liquid chromatography requires a chiral stationary phase that interacts in an enantio- discriminative way with passing analyte in the mobile phase. The enantioselective absorption can be fairly understood, when the nature of the interactions between the species involved can be specified.

Here, the forces, that occur in the formation of the molecular complex between the selector and the more retained enantiomer of the analytes, are investigated from combining chromatographic studies and the analysis of structures in the solid state. This method is employed to derive a model of discrimination for the chiral selector (5*R*,8*S*,10*R*)-N1-allyl-N2'-diethyl-terguride, **1**, and for the analogous derivatives N2'-dimethyl, **2**, and N2'-diisopropyl, **3**, since they show different efficiency in the separation of racemates of the same classes of carboxylic acids. The crystal structures of the molecular complexes **1**/(**S**)-dansyl-tryptophan and **3**/(**S**)-naproxen will be discussed with other complexes to determine the differences in the mechanism of the enantiodiscriminative process.

Keywords: crystal structures, molecular complexes, chiral recognition

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Spectroscopic Investigation of Some Azo-azomethine Compounds

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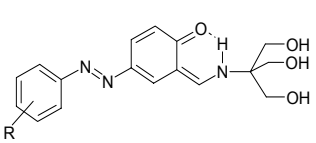
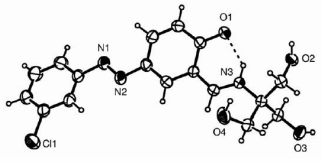
The azo-azomethine compounds investigated with UV-VIS, IR, ^{1}H-NMR, ^{13}C-NMR and X-RAY spectroscopic methods were prepared by condensation of the corresponding azo dye derivatives of salicylaldehyde with tris(hydroxymethyl)aminomethane and then crystallized in suitable solvents.

The structure of Schiff bases derived from the salicylaldehyde generally exist in the *enol* form while others derived from the condensation of salicylaldehyde with tris(hydroxymethyl) aminomethane exists only in the *keto* form. Azo-azomethine compounds obtained as single crystals were found to prefer *keto* form as well.



R = H, 2-Cl, 3-Cl, 4-Et



The molecule with R=3-Cl

[1]

IR spectrums show that azo-azomethine compounds in solid state prefer keto form whereas they are in *keto-enol* equilibrium, the *enol* form being dominant in solution according to UV-VIS analysis.

[1] Odabaşoğlu M., Albayrak Ç., Büyükgüngör O., Goesman H., *Acta Cryst*., 2003, **C59**, o234-o236.

Keywords: dye compounds, tautomerism, hydrogen bonds

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Electrostatic Potential of AaRS Navigates tRNA on its Pathway to the Binding Site

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In the first stage of diffusion-controlled enzymatic reaction, aminoacyl-tRNA synthetases (aaRSs) interact with cognate tRNA's forming nonspecific encounters. The aaRSs catalyzing the same overall aminoacylation reaction vary greatly in subunit organization, structural domain composition and amino acid sequence. The diffusional association of aaRS and tRNA was found to be governed by long-range electrostatic interactions when negative potential of tRNA fits to the patches of positive potential produced by aaRS: one patch for each tRNA molecule. Considering aaRS as a molecule with anisotropic reactivity and based on the Smoluchowski's theory, the reaction conditions for tRNA-aaRS diffusional encounters are formulated. The significance of multipole electrostatic potential components to the tRNA steering process is conditioned by subunit organization of aaRS. Enzymatically relevant domains appeared to be nonessential for field sculpturing at long distances. On the other hand, set of complementary domains exerts primary control on the aaRS's isopotential surface formation. Subdividing the aaRS's charged residues into native, conservative and non-conservative subsets we evaluated the contribution of each group to long-range electrostatic potential. Surprisingly, the electrostatic potential landscapes generated by native and non-conservative subsets are fairly similar, thus suggesting the non-conservative subset being specifically developed for efficient tRNA attraction.

Keywords: tRNA, aminoacyl-tRNA synthetase, recognition

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Structural Characterization of Functionalized β-Cyclodestrins

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β-Cyclodextrins (β-CD) have received considerable attention for their suitability to serve as relatively low molecular weight models for drug delivery and for artificial enzymes. In fact, β-CD shows remarkable ability to form inclusion complexes with various natural and synthetic molecules that fit inside the β-CD cavity. The inclusion process is influenced by the interaction between the guest molecules and the cavity, and also by the shape and size of the guest. This process can change the chemical and physical properties of the guest. In particular, pharmacological properties, such as stability, solubility, and toxicity, can be improved. Then, the rational design of functionalized β-CDs with bioactive moieties can represent an important step for the development of new drugs.

In this work, we report a detailed conformational analysis at atomic resolution by x-ray diffraction data and computational techniques on several functionalized β-CDs to understand the structural requirement to modulate the binding properties and basic phenomena governing the inclusion process for β-CDs.

[1] Di Blasio B., Pavone V., Nastri F., Isernia C., Saviano M., Pedone C., Cucinotta V., Impellizzeri G., Rizzarelli E., Vecchio G., *PNAS*, 1992, **89**, 7218.

Keywords: functionalized β-cyclodextrin, X-ray diffraction, molecular recognition