

erties. Such simulations can also indicate the effects of including different kinds of intermolecular forces, and so can help to model the real system with greater fidelity.

The present work will demonstrate, using molecular graphics, and discuss hydration structures around amino acid residues as they would appear in a peptide chain. Future work will address the importance of cooperative effects (i.e., explicit polarization forces) on the hydration structures and energetics.

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Modeling and Measuring DNA Deformation

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Experimental evidence on the biological role of fine structure within DNA is rapidly accumulating. In principle, theoretical modeling should be able to help in deciphering this new “code”; however, the size and complexity of the molecular systems involved has hindered progress in this area.

Recent developments in our laboratory have led to two new methodologies that should improve the situation. First, we have developed an energy minimization procedure, specifically oriented to the treatment of nucleic acids, which directly uses helicoidal parameters as variables. We are thus able to describe DNA oligomers with 10 times fewer variables than are necessary in classical molecular mechanics. At the same time, we are able to study much more easily the energy dependence of structural deformations. Second, we have formulated an algorithm for rigorously describing the conformation of irregular nucleic acid oligomers and, in particular, their curvature. We will present applications of these techniques to studying the influence of base sequence on the fine structure, the flexibility and the conformational transitions of DNA.

Modeling Organometallic Reactivity Using Quantum Chemistry and Molecular Graphics Techniques

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A new formalism has been developed in order to evaluate the intermolecular interaction energy between an organometallic or inorganic substrate S and an incoming reactant R in the framework of the extended Hückel (EH) method. Approximate procedures are used to estimate electrostatic (E_{es}), charge transfer (E_{ct}) and exchange repulsion (E_{ex}) components, which leads to short response times that make it possible to use the model as a routine tool on an interactive molecular graphics facility. Test calculations performed for ferrocene and iron pentacarbonyl have indeed shown that a model based on the electrostatic component alone is not adequate for describing electrophilic or nucleophilic attack. Therefore, in addition to the electrostatic potential of S, evaluated using EH wavefunctions and the NDDO or the Mulliken approximations for the one-electron integrals, we have derived a model based on the S–R orbital interactions at the EH level to estimate the E_{ct} component. Finally, the short range E_{ex} exchange repulsion energy is approximated using the hard spheres model for S–R interaction on the molecular surface of S. The total S–R interaction energy is then used as a reactivity index and evaluated at selected points belonging to the molecular envelope of S, a proton with an empty 1s orbital being chosen as the model electrophile, and an H^- hydride ion with two 1s electrons as the model nucleophile.

Color-coded three-dimensional Connolly dot surfaces are used for the graphics representation of the reactivity index of the substrates, together with special procedures we have recently developed on the PS-390 in order to generate solid models clipped so as to allow the simultaneous visualization of the structural skeleton. On the basis of the results obtained for a large series of organometallic reactions, this model is shown to describe adequately the initial stage of electrophilic and nucleophilic addition or substitution mechanisms. In particular, ferrocene and iron pentacarbonyl are correctly predicted to undergo an electrophilic attack on metal, whereas for arene- $M(CO)_3$ species and their derivatives, the nucleophilic attack takes place as expected on the exo-face of the ligand ring. Finally, it will be shown that regioselectivity may even be properly predicted in the case of competing sites on the same ligand, as exemplified by the nucleophilic attack to the meta position of the substituted ring in anisole- $Cr(CO)_3$ and to the internal carbon of diene in butadiene- $Fe(CO)_3$. When applied to the modeling of organometallic reaction mechanisms, the combination of simple quantum chemistry methods and molecular graphics techniques seems therefore able to bring an interesting contribution toward a better understanding of the processes of specific interactions between chemical species.

Molecular Modeling of Protein-Polymer Interactions

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