

1122 - Using natural bond orbital methods to investigate organic reaction mechanisms

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Computational chemists frequently use electronic structure calculations to explore reaction pathways. Calculations yield a detailed, molecular-level description of the various elementary steps that constitute a reaction mechanism. Additional insight into bond breaking and forming processes can be gained from natural bond orbital (NBO) analysis, a set of methods for calculating properties (e.g. atomic charges, hybridization, Lewis structures) that are central to our understanding of molecular structure and stability. We report here on our recent efforts to characterize a number of fundamental organic reaction mechanisms using the NBO methods. Gaussian-03 calculations generated a series of structures along the minimum energy pathways for SN₂, E₂, and hydrogen abstraction reactions. Analysis of the electron density at each structure yielded a sequence of orbital images that animate electron redistribution during the course of the reaction.

1202 - Origin of hydrocarbon stability: Extension and application of the vicinal interactions model

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The vicinal interactions (VI) model was developed to predict and interpret the stability of straight chain, branched, and cyclic alkanes. Electronic structure calculations and natural bond orbital analysis of the alkanes reveal highly localized CC and CH bonds that participate in important steric and delocalizing interactions. The VI model incorporates two-center bond energies and four-center vicinal bond interactions to reproduce standard heats of formation for the alkanes to within a few tenths of a kcal/mol. Alkane isomers and conformers are treated simultaneously. We report here on our recent efforts to extend the VI model to treat gas-phase alkyl radicals and alkenes.

1123 - Vicinal interactions model: Predicting and interpreting the stability of amines

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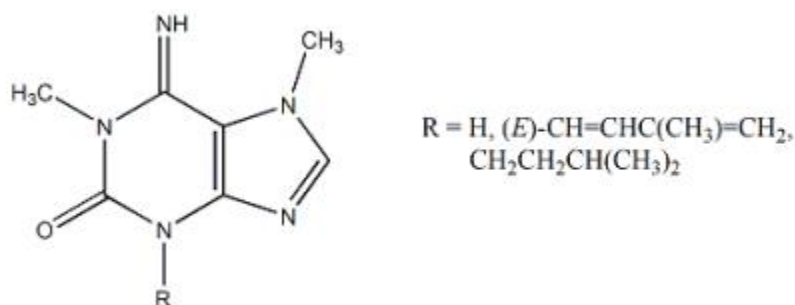
Accurate estimates of reaction thermochemistry can be obtained using group additivity methods. Although these methods are useful for predicting energetics, they provide limited insight into the factors that influence molecular stability. Several bond additivity methods have been recently proposed by us and others that may overcome this limitation. We have proposed the vicinal interactions (VI) model in which the heat of formation for an organic molecule is represented by a combination of bond energies and vicinal bond interactions. Theoretical support for this model stems from ab initio electronic structure calculations that reveal the essential role of steric bond-bond and delocalizing bond-antibond interactions in unstrained organic molecules. We have demonstrated that the VI model can be used to accurately predict heats of formation for

hydrocarbons and to interpret the origin of the differing stabilities of hydrocarbon isomers and conformers. We discuss the VI model and its extension to amines in this presentation.

1170 - Dioicine: Chemical ecology, synthetic, and biological studies

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We recently reported dioicine, a prenylated purine alkaloid from the Kentucky coffeetree, *Gymnocladus dioicus*. Dioicine possesses a structure similar to caffeine and exhibits neurotoxic and developmental effects in mouse and zebrafish models. We are now pursuing the synthesis of dioicine and derivatives for biological evaluation, as well as examining the abundance and distribution of dioicine as a function of season, light level, altitude and tree gender. Our results to date will be presented.



1158 - Synthetic studies toward adamantane based dendrimers for biological applications

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We are interested in adamantane based dendrimers with hydrophilic amine-terminated PEG-based backbones for use in biological systems. Such polymers may be useful for preparing biomolecule terminated dendrimers. Initial studies approached the synthesis of adamantane tetracarboxylic acid using the method of Newkome. Tether chemistry is focused on the preparation of bifunctional linkers based on 4,7,10-undecane-1,13-diamine containing Boc protection at one end and CDI activation at the other. Our results to date will be presented.

