A detailed study of tautomeric properties of uric acid and its different anions were performed at the Density Functional Theory level employing B3LYP functional. Initially, the relative stability of different possible neutral tautomers were determined using 3-21G(d,p) basis set and this was followed by computation with 6-31G(d,p) basis set for selected stable tautomers. To different possible anions and radicals the 6-31++G(d,p) basis set was used. The effect of aqueous solvation on the relative stability of neutral, anionic, and radical species was considered using Tomasi’s polarized continuum model. The keto form of the molecule is found to be most stable in the gas phase and in aqueous medium. Different properties of neutral tautomers, neutral transition states, anionic and radical form of the uric acid in the gas phase and in aqueous media are discussed.
Computational Studies on Novel Steroid-Nucleoside Conjugates

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In an attempt to develop potent anti-HIV agents devoid of serious toxic effects, H. J. Lee et. al. developed these three novel compounds along the antedrug scheme; AZT conjugated to Cholenic Acid (Conjugate 1), P-16 acid (Conjugate 2) (where P is an abbreviation for Prednisolone), and P-21-oic acid (Conjugate 3). These compounds make a unique class of drugs; which have been formed through ester bonds (conjugates) between AZT and the steroid and non-steroid carboxylic acids. Cholenic acid, P-16 acid, and P-21-oic acid will also be referred to as Acid 1, 2, and 3, respectively. Through H9 cell line tests it was determined that the only Conjugate 1 possessed anti-tumor behavior. In an earlier work the structural characteristics of the active compound were compared to those of the inactive compounds and their constituent components; several differences were determined. That work was done in vacuum, while this work will attempt to make similar comparisons after solvating the molecules. Particular focus will be on the position of various functional groups at the ends of the compounds. The work will be conducted using a Tripos forcefield and conformational searches while varying the dielectric constants of the model solvent system between 2 and 10. This is to examine structural changes due to solvation. The work presented here was done at the Molecular Mechanics and quantum mechanics levels.
Theoretical Studies of Analogs of the Roger Brown Rearrangement

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Three structures involved in the Roger Brown rearrangement are shown below: butadiyne (1), ethynylvinylidene (2), and trialene (3). We have recently discovered analogs of trialene (3) in our laboratory, and a systematic study of the structures involved in the Roger Brown rearrangement is underway. These studies will include structures 1-3 shown below as well as their Si, Ge, and Sn derivatives. We present here some preliminary results of calculations on the species 1-3 and their Si-analogs. At this stage of the project the calculations have been carried out at the SCF and DFT-levels of theory, but after the main features of the potential surface has been mapped, significantly more accurate calculations will be carried out.

Reference
Review of QR-SC-MEH-MO Calculations of $M_2$ Molecules
($M = \text{Cr, Mo, W, Sg}$)

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Calculations of the electronic structures and bonding in the molecules $\text{Cr}_2$, $\text{Mo}_2$, $\text{W}_2$ and $\text{Sg}_2$ have been carried out via the QR-SC-MEH-MO method. It has been found that antiferromagnetic coupling dominates the bonding in $\text{Cr}_2$, but this accounts for only about one third of the bonding in $\text{Mo}_2$.

In the case of $\text{W}_2$, the HOMO is an open shell triplet, but antiferromagnetic coupling is found to be nil in this molecule. All of the bonding is attributed to the 5d, and to a lesser extent, 6s orbitals.

The $\text{Sg}_2$ molecule has a closed shell ground state, in which the HOMO is totally 7s in character. However, the bonding is due almost exclusively to the 6d orbitals. Of course strong relativistic effects are predominant as well.
Theoretical Calculation of the Ionization Potentials of the DNA Bases in Aqueous Solution

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It has been a goal for some time now to establish the threshold energies necessary to ionize nucleotides. The experimental determination of the ionization potentials of nucleotides presents two challenging problems. It is difficult to prepare intact gas-phase nucleotides, and one expects that the large number of valence orbitals in a nucleotide with similar energy would give rise to poorly resolved ionization spectra. Previous work has therefore focused on the components of a nucleotide, the bases, and the deoxyribose-phosphates.

One would like to use theoretical calculations to estimate the ionization potentials of the nucleotides. Theoretical IP’s have successfully calculated the gas phase IP’s of the DNA bases. The most accurate results have been obtained using ab initio electron propagator calculations in the partial third order (P3) approximation with the 6-311G(d,p) basis set. P3 calculations and some more familiar calculations using Hartree-Fock and Density Functional Theory will be presented.

The next step is to ask what are these ionization potentials in a biologically relevant environment. Here one has only limited experimental data. One knows for example that reported ionizations with 250 nm light (which corresponds to energies of 4.9 eV) involve a biophotonic process. On the other hand, 193 light (6.4 eV) does monophotonically ion-ize purines. This information can be used to bracket the threshold energies required for DNA ionization in aqueous solution to lie in the range of 4-7 eV.

To study how an aqueous environment would affect IP’s, one needs to repeat these calculations in a dielectric continuum. Presently the P3 methods cannot be used to do these calculations. So one must look back at MP2, or DFT techniques in the gas phase to see which technique yields the best results. Then one can perform IP calculations in a dielectric continuum. All the calculations presented suggest that the trend in IP’s in aqueous solution is T>C>A>G, with the pyrimidines having significantly higher IP’s than the purines. Guanine has the lowest IP, and therefore would be the easiest to oxidize.

The calculations presented are for the canonical bases with N1-H for the pyrimidines and N9-H for the purines. In looking ahead of the situation in DNA, it was decided to repeat the calculations with N1-CH₃ or N9-CH₃ to mimic the glycosidic bond in DNA. These calculations show a small downward shift in IP’s for the methylated bases. In this same vein it should be pointed out that new calculations have been performed on C5 methylated cytosine. This results in a cytosine base that has an IP more like a purine, and may therefore have to be considered in competition with guanine as a hole trap.

Thanks to Leonid Gorb for helpful suggestions in the course of this work. This work is supported by PHS Grant CA36810-16 awarded by National Cancer Institute, DHHS.
Tricyclo[3.2.0.0\(^1,3\)]heptane - a New Hypothetical Molecule with Unusual Spatial Structure

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Hydrocarbons with nonstandard spatial structure are exciting objects since, in addition to contradiction with van’t Hoff and LeBel hypothesis on the tetrahedral arrangement of atoms around a tetravalent carbon atom, they exhibit unusual reactivity [1]. According to MP2 calculations using cc-pVTZ basis set, tricyclo[3.2.0.0\(^1,3\)]heptane 1 the configuration at C1 (Fig. 1) is very close to the intermediate structure between the tetrahedral and pyramidal arrangement of bonds. The energy of the latter molecule calculated at the MP2/6-311G** level is intermediate between its known syn- 2 and anti- 3 isomers [2]. Therefore, the titled molecule exhibiting unusual configuration at the quaternary carbon atom seems to be a plausible synthetic target.

References
Molecular Modeling Study of Stabilization of C\textsubscript{20} inside the Cavities of Higher Fullerenes

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Recently Prinzbach \textit{et al}. [1] reported an observation of the unstable smallest possible fullerene, C\textsubscript{20}. Similar to the encapsulation of highly unstable molecules inside a ‘molecular flasks’ [2], C\textsubscript{20} could be stabilized by encapsulation inside a bigger fullerene forming onion-like complex. Such complexes (called buckyonions or nested fullerenes) with C\textsubscript{60} as the inner shell have been observed by Iijima [3] even before the discovery of fullerenes. The intershell distance in nested fullerenes is similar to that between graphite planes (3.34 – 3.5 Å) [4, 5]. The ease of formation of nested fullerenes was recently shown in our group to be mainly driven by nonbonded interactions [6].

In this study a search of a stable endohedral complexes of C\textsubscript{20} with icosahedral fullerenes from C\textsubscript{60} to C\textsubscript{240} was undertaken by means of molecular mechanics calculations, MM, using CVFF and ESFF force fields. Then molecular dynamics, MD, simulations were run for the most stable structures found in MM.

A comparison of the stabilization energies (as a difference between the energy of the complex and that of its constituent parts) for both force fields applied revealed that the complexes of C\textsubscript{20} with C\textsubscript{60} and C\textsubscript{80} are strongly destabilized while those with C\textsubscript{140}, C\textsubscript{180} and C\textsubscript{240} undergo considerable stabilization which is smaller for the last host than for the former ones. This trend in stabilization energies is accompanied by significant changes in the values of intershell distances \(d\). For the first two destabilized complexes the \(d\) values are significantly smaller than the intershell graphite distance while for the last three stable complexes it is comparable to the graphite value (Table 1).

\textbf{Table 1.} Stabilization energies (in kcal/mol) and intershell distances (in Å) for endohedral complexes of C\textsubscript{20} with icosahedral C\textsubscript{60}, C\textsubscript{80}, C\textsubscript{140}, C\textsubscript{180} and C\textsubscript{240} calculated using CVFF and ESFF force fields.

<table>
<thead>
<tr>
<th>Complex</th>
<th>C\textsubscript{20}@C\textsubscript{60}</th>
<th>C\textsubscript{20}@C\textsubscript{80}</th>
<th>C\textsubscript{20}@C\textsubscript{140}</th>
<th>C\textsubscript{20}@C\textsubscript{180}</th>
<th>C\textsubscript{20}@C\textsubscript{240}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E) (CVFF)</td>
<td>4856</td>
<td>2389</td>
<td>-131</td>
<td>-130</td>
<td>-92</td>
</tr>
<tr>
<td>(\Delta E) (ESFF)</td>
<td>2063</td>
<td>835</td>
<td>-58</td>
<td>-56</td>
<td>-41</td>
</tr>
<tr>
<td>Intershell distance, (d)</td>
<td>2.7</td>
<td>2.8</td>
<td>3.6</td>
<td>4.1</td>
<td>3.6*</td>
</tr>
</tbody>
</table>

* - fullerene C\textsubscript{20} is not situated at the center
The MM stabilization energies for the complexes of \( \text{C}_{20}\text{@C}_{140} \) and \( \text{C}_{20}\text{@C}_{180} \) are found to be very close. Therefore, MD simulations for them were carried out in an attempt to establish their relative stability. The result of the simulations seems to indicate that in both CVFF and ESFF the \( \text{C}_{20}\text{@C}_{180} \) complex is more stable than the \( \text{C}_{20}\text{@C}_{140} \) one.

To summarize, the MM and MD results indicate that the stable fullerene complexes involving \( \text{C}_{20} \) as a guest can only be formed if the outer fullerene consists of at least 140 carbon atoms. However, at present only fullerenes with less than 100 carbon atoms are produced in bulk. Therefore, the methods of obtaining of considerably bigger fullerenes should be mastered that could stabilize the exciting \( \text{C}_{20} \) structure.

References
Homology Modeling of Horse Butyrylcholinesterase on a Torpedo Acetylcholinesterase Template Using Molecular Dynamics Simulation

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Despite a wealth of structural information on acetylcholinesterases from a number of sources, little structural information is available for the homologous enzyme, butyryl (pseudo)-cholinesterase.1 Butyrylcholinesterase is an enzyme found in erythrocytes which shows greater specificity for longer-chain O-acylcholines than does acetylcholinesterase,2 and most sequenced butyrylcholinesterases to date show high levels of sequence similarity to acetylcholinesterases.

In the present work, butyrylcholinesterase sequences were collected from the San Diego Supercomputer Center’s Non-Redundant (SDSC-NR) protein sequence database, and compared to acetylcholinesterase sequences for which crystallographic structures existed in the Protein Data Bank (Research Collaboratory for Structural Bioinformatics). Each of the ten subject butyrylcholinesterase sequences was aligned to the database of sequences for proteins in the Protein Data Bank using the Biology Workbench (San Diego Supercomputer Center) BLASTP program;3 the butyryl-/acetylcholinesterase pair of greatest similarity was horse (Equus caballus) butyrylcholinesterase aligned to the acetylcholinesterase from the Pacific electric ray, Torpedo californica (PDB entry 2ack).4,5 The two sequences were then paired in the Biology Workbench’s ALIGN program,6 and residue homologies were identified from that alignment.

The segments of amino acid sequence in horse butyrylcholinesterase not corresponding to polypeptide chain segments appearing in the 2ack structure4,5 were modeled, using the program RIBOSOME (Antony Crofts, University of Illinois), as extended (β-sheet-type conformation) segments, in order to avoid biasing the molecular-dynamics energy-minimization by engineering excessive stability into them. Once the butyrylcholinesterase dimer was constructed, it was subjected to repeated cycles of energy minimization and short molecular-dynamics trajectories using the molecular dynamics package NAMD27 (Klaus Schulten, University of Illinois) in order to identify structurally stable regions and incorporate mutations, in small groups, which slowly convert the acetylcholinesterase residues to those of butyrylcholinesterase. The short molecular dynamics trajectories were chosen to identify transient high-energy structures containing spaces, allowing larger-residue substitutions to be carried out without atomic-level overlap. Using these repeated cycles of small-group multiple-residue substitutions and short minimization/molecular-dynamics trajectories, an energy-minimized structure containing strong sequence and structural homology to Torpedo acetylcholinesterase was constructed.

Theoretical *ab Initio* Study of the Effects of Methylation on Structure and Stability of Watson–Crick Base Pairs

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Methylation of DNA occurs most readily at N(3), N(7), and O(6) of purine bases and N(3) and O(2) of pyrimidines. Methylated bases are continuously formed through endogenous and exogenous mechanisms. The results of a theoretical *ab initio* study on the methylation of Watson–Crick base pair components are reported. The geometries of the local minima were optimized without symmetry restrictions by the gradient procedure at DFT level of theory and were verified by energy second derivative calculations. The standard 6-31G(d) basis set was used. The single-point calculations have been performed at the MP2/6-31G(d,p), MP2/6-31++G(d,p), and MP2/6-311++G(2d,2p) levels of theory. The geometrical parameters, relative stability and counterpoise corrected interaction energies are reported. Also, using a variation-perturbation energy decomposition scheme we have found the vital contributions to the total interaction energy.
Methylation of Isolated and Paired Nucleic Acid Fragments

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Methylation of nucleic acid bases occurs most readily at N(3), N(7), and O(6) of purine bases and N(3), O(4) and O(2) of pyrimidines. The results of theoretical ab initio on these methylated species are presented.

First, ab initio techniques were used to determine the effects of protonation and methylation on cytosine’s molecular geometry, molecular affinities, relative stability, and structural rigidity. The geometries of local minima were fully optimized by the gradient procedure at DFT and MP2 levels of theory with the medium size 6-31G(d,p) basis set. The results of energetic analysis indicate that N(3)-methyl-cytosine and C(5)-methyl-cytosine are the most stable derivatives for monocationic and neutral species, respectively. The structural rigidity of each species was assessed by an analysis of normal out-of-plane frequencies, the amplitudes, and by the contribution of internal coordinates to the potential energy distributions. The obtained evidence suggests that methylation increases the overall structural flexibility of cytosine and that all molecules in this study populate a non-planar conformation 50% of the time.

Secondly, the results of a theoretical ab initio study on the effects of methylation on the stability of rare tautomers of the pyrimidines, cytosine, uracil, and thymine, and the purines, guanine and adenine are presented. The geometries of the local minima were optimized without symmetry restrictions by the gradient procedure at DFT and MP2 levels of theory and were verified by energy second derivative calculations. The standard 6-31G(d,p) basis set was used. The relative stability and relevant geometrical parameters are reported.
Ab initio Comparison of Modified Adenine Derivative in tRNA

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Within the matrix of the nucleus, tRNA, the key molecule involved in the translation of genetic information to proteins, behaves as a control center for translation and other cell activities. In protein synthesis, a ribosome moves along an mRNA molecule, reading the codon for protein assembly as it goes. As it moves, the ribosome assembles amino acids into a gradually lengthening protein chain. At the end of the coded message, translation stops, the ribosomal subunits separate and detach from the mRNA, and the completed protein is released. Transfer RNA (tRNA) molecules function as the lexicon in the translation mechanism. Each of the 20 amino acids used in protein synthesis is linked to a specific kind of tRNA. The tRNA is capable of recognizing and binding the nucleic acid code word specifying its attached amino acid in an mRNA molecule. The translation of genetic information is thereby mediated by adaptor molecules in tRNA. The interactions of modified adenine derivatives were investigated by nonempirical ab initio calculations. Optimizations were carried out on adenine and three derivatives using the second-order Moller-Plesset (MP2) method and the 6-31 G(d) basis set. The optimizations were performed with no symmetry. The stabilization energies and dipole were studied for each molecule for their importance in tRNA structure and function.
Double Proton Transfer in DNA Base Pairs and Prototypic Complexes

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Two basic molecular mechanisms are considered for the formation of point mutations for the period of DNA replication. Firstly, base mispairs may occur between the canonic and ‘rare’ tautomeric forms of nucleobases during catalytic incorporation of the new base into growing DNA strand. In this case the frequency of the mutation event is governed by the concentration of free nucleotide triphosphates in their minor tautomeric forms. The second possibility does not require the presence of the free ‘rare’ tautomers. It results from ‘rare’ tautomers being formed in the template via the concerted transfer of two protons in the GC and AT base pairs.

We have applied high level of ab initio theory (up to CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p)) to investigate the second aforementioned possibility. For this purpose we have calculated two-dimensional adiabatic potential energy surface for the double proton transfer in formamidine-formamide (FIFA), adenine-thymine and guanine-cytosine complexes and located corresponding local minima and transition states.

The following issues are discussed.

1. Relative energies, including relative Gibbs free energies.
2. Proton transfer coordinate.
3. Geometries of the complexes.
4. Possible biological relevance including replication fidelity.
Nonadiabatic Evolution of Electronic States by Electron Nuclear Dynamics Theory

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The adiabatic approximation has been successful in describing numerous classes of molecular motion and interaction phenomena /1/. It relies on the concept of the Potential Energy Surface (PES) and assumes that a molecular system adopts its parameter dependent ground state at any stage of its evolution. Within the confines of the adiabatic approximation, the molecular motion is computationally predictable if the ground state PES of the respective system is known. This approach, however, meets its limits wherever highly dynamic situations are involved, such as in fast collisions or scattering reactions at high energy. Further, the adiabatic approximation loses its validity in cases of degenerate or near-degenerate electronic ground states, as is encountered in the vicinity of a conical intersection /1/.

A formalism that transcends the limits of the adiabatic approximation is available with the Electron Nuclear Dynamics (END) Theory /2/, which has been designed to provide a full description of the dynamic development of the electronic system. A particular strength of the END Theory consists in its independence of any PES constructions. Since the processes studied in this contribution are characterized by a sizeable dynamic coupling between electrons and nuclei, any use of the PES concept appears artificial or, in the best case, computationally unnecessarily extensive, requiring the implementation of a complex scheme of multiple PES.

The present work addresses the problem how to determine accurately the nonadiabatic content of any given dynamic process involving molecular motion. More specifically, we attempt to cast the dynamic END wave function into the language of electronic excitations. This is achieved by adiabatic transport of an electronic basis along the classical nuclear trajectories of the studied molecular system. This basis is chosen as the static UHF molecular ground state determinant of the system in conjunction with all determinants that arise from the ground state by single and double substitutions. Projecting the dynamic wave function into this basis yields a natural distinction between adiabatic and nonadiabatic components of the motion considered. We will discuss this concept by the examples of bound systems at the dissociation threshold as well as scattering situations.


Acknowledgment.
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Theoretical Modeling of Cisplatin and Cisplatin Analogs

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Studies of structures, energetics, and charge distribution were performed for ground and lowest excited electronic states of MeCl_{2}(NH_{3})_{2}, Me=Pd and Pt complexes. Despite the similarity of the Pd and Pt elements, the differences in isomerization energies, ground-excited state separation energy, and electronic density distribution are significant. The Me-N and Me-Cl bonds possess a different nature with the Cl accepting and the NH_{3} group donating electrons to the central metal. The bonds are more polarized in Pt based complexes. The electronic excitations involve mostly the metal atom, and although they do not change the structure drastically, the excitations do, however, impact the charge distribution. Interaction energy decomposition for the ground state indicates that ammonia-metal interactions are dominated by the energy delocalization term.

Comprehensive ab initio calculations are performed on Cis-diamminedichloropalladium (cispd) and Cis-diamminedichloronickel (cisni) at the HF, DFT, and MP2 levels of theory. The results are compared to those obtained for cisplatin. The characteristics of the interactions of cispd with Guanine and Guanine-Cytosine base pair are also evaluated and compared to the interactions of cisplatin. Cispd causes similar geometric changes of the base as cis-platinum when complexed to guanine. The palladium and platinum complexes also show similar characteristics when complexed to GC base pair. However, this study revealed lower dissociation energy of the chlorine ligands and lower interaction energy of the cispd with guanine, which indicates areas of differences between the title Pd and Pt complexes. Study of cisni revealed higher dissociation energy of the chlorine ligands that indicate areas of differences between the title Ni and Pt and Pd complexes. Similar interaction energy of the cispd with guanine to that of cispt indicates areas of differences between the title Ni and Pd complexes.

A theoretical DFT study of the interactions of cisplatin and cis-palladium with DNA fragments consisting of two stacked guanines with and without the sugar phosphate backbone was carried out. The obtained molecular parameters indicate that the considered model is consistent with the crystal structure elucidated by Lippert. Our calculations also suggest that palladium binding is similar to that of the platinum. The interaction energy is found to be reliant upon the backbone involvement although the order of binding remains the same as the one from calculations without the backbone. The interaction becomes weaker with the backbone included. A study of the energy components suggest that the dispersion term is greatly affected by the binding of the platinum. There is also significant change in the electrostatic term between the two guanine conformations. The backbone is found to be an important stabilizing factor to offset geometric and energetic changes.
Conventional Strain Energy in the Diazetidines and the Diphosphetanes

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The conventional strain energies for 1,2-diazetidine, 1,3-diazetidine, 1,2-diphosphetane, and 1,3-diphosphetane, each of which have a cis and trans conformation, are determined within the isodesmic, homodesmotic and hyperhomodesmotic models. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory, and density functional theory (DFT). The DFT functional employed is Becke’s three parameter hybrid functional using the LYP correlation functional. Two basis sets, both of triple-zeta quality on valence electrons, are employed: 6-311G(d,p) and 6-311+G(2df,2pd). Finally, the conventional strain energies of these systems are compared to those of azetidine, phosphetane, cyclopropane, cyclobutane, 1,2,3-oxadiazetidine, and 1,2,4-oxadiazetidine. We gratefully acknowledge support from NSF EPSCoR (EPS-0132618).
A Multicentered Approach to Integrated QM/QM Calculations: Applications to Multiply Hydrogen Bonded Systems

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A multicentered integrated QM/QM technique has been developed. By separating high level calculations in separate regions of molecules, the multicentered approach supplants a single large high level calculation with several smaller calculations. Due to the steep polynomial scaling of traditional ab initio quantum chemical methods, this separation significantly decreases the computational cost typically associated with integrated QM/QM methods. Successful applications to large aliphatic diols and tetrols are presented, demonstrating the accuracy and cost savings possible with the method. The limitations of the new approach are also discussed.
Theoretical AM1 Studies of Inclusion Complexes of 2-Hydroxypropyl-β-Cyclodextrins with Methylated Phenols

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Semi-empirical quantum mechanical (AM1) calculations have been performed on the inclusion complexes of 2-hydroxypropyl-β-cyclodextrins (HPβCD) with methylated phenols in two orientations, the “head-first” and “tail-first” positions. In the former, the OH group points toward the primary hydroxyls of the HPβCD. In the latter, it points away from them. In all we have studied the fifteen different methylated phenols (mono-methyl-phenols, dimethyl-phenols, and trimethyl-phenols) and phenol with two different HPβCDs. There are a total of 64 inclusion complexes. The stabilization energies are defined as the differences between the heats of formation of the inclusion complexes and the sum of the heats of formation of the host (HPβCDs) and guest (methylated phenols) molecules. The relative stabilization energies have been carefully compared. The stabilization energies are being analyzed in terms of intermolecular and intramolecular hydrogen bonds and the hydrophobicity and the size of the guest.
The Reactivity of Methanediazonium Ion and AT Base Pairs

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N-nitroso compounds have been widely studied and found to exhibit carcinogenic and mutagenic properties. Diazonium ions, converted forms of N-nitroso compounds, are sturdy alkylating agents for the nucleophilic sites in DNA bases. It is believed that diazonium ions are chiefly responsible for the carcinogenic behavior of N-nitroso compounds due to the binding of alkanediazonium ions to DNA base molecules.

Leao & Pavao recently used molecular orbital calculations to analyze the bonds formed between DNA bases and N-nitroso compounds (1997). Since these investigations are based on the simple frontier orbital theory, they do not include information responsible for the quantitative study of DNA base alkylation by N-nitroso compounds.

Many previous reports provide information on the carcinogenic behavior of alkanediazonium ions. Investigations on diazonium ions themselves were conducted by Vincent & Radom (1978) and Glaser & Choy (1993). Reynolds and Thomson performed analyses on diazohydroxide as a precursor of diazonium ion (1986; 1987).

Nakayama, Tanaka, and Kikuchi studied methylation reactions at ten nucleophilic sites in four DNA base molecules (2002). This characteristic methylation by methanediazonium ion (N₂Me⁺) was studied by ab initio MO/GB calculation which includes the solvent effect with the continuum model using the generalized Born formula. That study included the energy profiles of methylation of DNA base molecules by N₂Me⁺. Nakayama elucidates why the fraction of DNA base alkylation by N-nitroso compounds is unique.

In Figure 1, the schematic energy profile of nucleophilic addition reaction of methanediazonium ion with DNA bases is presented. The stabilization energy of the ion-dipole complex (ΔEₜₜ) in addition to the energy of transition state (ΔEₜₜ) is important in the study of reaction mechanism of alkylating species with the nucleophilic site. Eₜₜ represents the ability of the nucleophile to electrostatically capture the cation; hence, Eₜₜ may be an effective descriptor for the experimental fractions of total methylation.

In this study, the energy profiles of the methylation of base-paired adenine-thymine (AT) molecules by methanediazonium ion are examined by using *ab initio* techniques. In this paper, nucleophilic addition reactions of N₂Me⁺ for five selected sites of this conventional DNA base pair (N1, N3, and N7 sites of adenine, and O2 and O4 sites of thymine, see Fig 2.) are studied.
Conventional Ring Strain in Unsaturated Four-Membered Rings

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In order to study the effect of unsaturation on the ring strain in small cyclic molecules, the conventional strain energies for cyclobutene, azetidine-1-ene (Figure 1), phosphetane-1-ene (Figure 2), azetidine-2-ene (Figure 3), and phosphetane-2-ene (Figure 4) are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular system using SCF theory, second-order perturbation theory, and density functional theory (DFT). The DFT functional employed is Becke’s three parameter hybrid functional using the LYP correlation functional. Two basis sets, both of triple-zeta quality on valence electrons, are employed: 6-311G(d,p) and 6-311+G(2df,2pd).

Figure 1

Figure 2

Figure 3

Figure 4
Gas–Phase Conformations of RDX: A DFT Study

Olexandr K. Isayev, Leonid Gorb, and Jerzy Leszczynski

*Computational Center for Molecular Structure and Interactions*
*Department of Chemistry, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217*

The development of cleanup technologies for a disposal of explosives is a challenge for environmental science. Such development involves the coordination of experimental and theoretical investigations to integrate both the technological and fundamental aspects of key processes. Although the major processes affecting the natural and engineering treatment of explosives have been investigated qualitatively, many issues regarding the physical and chemical properties of explosives remain unsolved.

One of the properties which currently are investigated rather poorly is the conformation(s) of RDX molecule. To investigate them in the gas phase, we have performed a quantum-chemical study at the DFT (B3LYP) level of theory using standard 6-31G(d,p) basis set.

We have found that the global energy minimum is the chair conformation of RDX possessing two nitro-groups in axial and remaining one in equatorial orientations (Chair AAE). In addition four less stable conformations (two chair, boat and twist) have been located within the range of 2 kcal/mol above global minima.

To estimate the probability of possible transitions between these conformations, the corresponding transition states were localized and the vibrational frequencies for both the local minima and transition states were predicted. From these data the characteristic vibrations which are responsible for the transitions from one conformation to another were located. Their combined analysis together with the values of relative energies suggests that only two conformations (Chair AAE and Chair AAA) will populate the conformational space at room temperature.
Direct Ab Initio Molecular Dynamics Study of C\(^+\) + H\(_2\)O

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P. O. Box 23346, San Juan, PR 00931-3346, USA.

An ab initio direct molecular dynamics study of the reaction of C\(^+\) with water has been performed and the mechanism of reaction examined. Ab initio energy and gradient evaluations were done at the QCISD/6-31+G* level. The primary products of reaction are isoformyl cation, HOC\(^+\), and H atom. The reaction proceeds through two principal channels. The first is a direct “knock out” of a hydrogen atom, and the second involves a relatively high-energy intermediate, H\(_2\)OC\(^+\), an isomer of formaldehyde cation. The intermediate mechanism differs from that posited in previous experimental and theoretical studies of the reaction, which have assumed formation of more stable intermediates. The simulations predict that most product HOC\(^+\) molecules are internally energetic enough to isomerize to formyl cation, HCO\(^+\). The distribution of product kinetic energies and the product angular distribution gathered from 579 trajectories agree well with experiment.
Determination of Octanol–Water Partition Coefficients from Chemical Potential Calculations

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The octanol-water partition coefficient is the ratio of the concentration of a chemical in octanol and in water at equilibrium. This parameter is useful for the prediction of the transport properties of chemicals. Partition coefficients are used extensively in environmental science. Octanol-water partition Coefficients can be determined using various techniques. These methods include experiments and Quantitative Structure Activity Relationships (QSAR). In a number of cases, the values obtained using these methods have a large uncertainty. It appears that the use of the molecular dynamics method of statistical mechanics to obtain partition coefficients has been used only once. This application was successful. The results from this application were relatively accurate. The uncertainty associated with these molecular dynamics results is in the same range as the experimental uncertainties.

We are utilizing a molecular dynamics method to determine the octanol-water partition coefficient for a number of chemical compounds. Our method consists of the AMBER software package to generate molecular trajectories and the Molecular Mechanics Poission-Boltzman Surface Area (MM-PBSA) method to obtain chemical potentials from these trajectories.
Ab initio Study Non Watson-Crick Like Hydrogen-Bonding of Pyramidine in tRNA

Cynthia Jeffries, Tomekia Simeon, Glake Hill, Gareth Forde, Jerzy Leszczynski

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The study of nucleic acid base pair is crucial to the understanding of genetics and heredity. The most common types of base pairing are that of the Watson-Crick Model. This model shows two hydrogen-bonds for A-T base pair and three hydrogen-bonds of G-C base pair. Watson-Crick base pair is primarily found in DNA. Other combinations have been located however in RNA structures, specifically tRNA. The base pairing patterns are unique in both structure and energy. Our present research focuses on structural and energetic difference between Watson-Crick base pair involving pyramidine and hydrogen-bonding in irregular interaction of pyramidine in tRNA. We will show trends in binding and energy to suggest the role of this non-classical binding.
Exploring the Relationships between Molecular Surface Electrostatic Potentials, Local Ionization Energy and Local Polarizability

Pin Jin, Jane S. Murray and Peter Politzer

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Berkowitz and Parr have suggested that the molecular electrostatic potential is related to local hardness, which would mean to local polarizability as well. We have proposed that the latter is in turn related to the average local ionization energy. In this presentation, we explore the implied relationship between the local ionization energy and both the electronic and the total electrostatic potential, all computed on molecular surfaces.
Atomic Radial Functions from Molecular Densities

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Quantum chemical calculations on large molecules, though becoming increasingly feasible, have not yet reached the sophistication and accuracy required in many areas of molecular sciences. Consequently, there has been a steady interest in simple methods for predicting electrostatic properties of macromolecules from those of constituent functional groups or atoms.

The central property in this respect is the molecular electron density (\( \rho \)) and the key question is how to partition a known density into atomic fragments that possesses chemical transferability necessary to construct unknown densities [1].

The approach presented here, invokes the nucleus-centered multipole expansion technique (pseudoatom formalism) that has been used very efficiently to derive experimental charge densities from X-ray diffraction intensities [2]:

\[
\rho_A(r) = \sum_{l,m} P_{lm+} R_{lm+}(r_A) d_{lm+}(\Omega_A, \varphi_A)
\]  

(1)

In this expression \( P_{lm+}'s \), \( R_{lm+}'s \) and \( d_{lm+}'s \) are, respectively, multipole populations, radial functions and density normalized real spherical harmonics [2] referred to a local coordinate system centered at nucleus (A).

However, instead of a direct least-squares (LS) projection of the molecular density into pseudoatoms, we adopt a two-steps procedure: the total density is partitioned according to the stockholder scheme [3]

\[
\hat{\rho}_A(r_A) = \frac{\rho^o(r)}{\rho^o(r)} \rho(r) = W_A(r) \rho(r), \quad \sum_A \hat{\rho}_A(r_A) = \rho(r)
\]

(2)

( \( \rho^o \) is the promolecule being a superposition of spherical atomic densities \( \rho^o_A \)), followed by a fit of each constituent stockholder atom \( \hat{\rho}_A(r_A) \) independently. The corresponding LS conditions leads to angular integrals

\[
\hat{\rho}_{lm+}(r) = \int \hat{\rho}(r)d_{lm+}d\Omega = P_{lm+}\gamma_{lm+}(r)
\]

(3)

exhibiting the spherical-harmonics content of each pseudoatom.

In this contribution we demonstrate the efficiency and accuracy of the method by reconstruction of theoretical molecular densities in terms of eq. (1) where the radial functions are fitted by simple Slater-type functions.

References
Quantum-Chemical Research of Chemical Scavenging Effects in Radical Reactions

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Improvements in techniques to control fires may aid in ameliorating fire problems. Water, the extinguishing of antiquity, remains the major material applied. However, water additives, to produce foams, inert gases such as CO₂ and N₂, chemical suppressants containing halogens and dry powders of various types have countered increasing utility. Improved knowledge of mechanisms by which these agents operate may help in advancing suppression strategies. The scope of the theoretical research is limited to chemical suppressants acting mainly on the hydrogen flames. It is well known that the flame propagation mechanism on hydrogen-air flames at the pressure above one atmosphere the clue role plays hyper equilibrium concentration atoms and radicals connecting with chain branching reaction. Addition a few inhibitor amount, which able to catch (scavenge) the radicals can significant to reduce combustion speed. It is known that addition of halogens to flames promotes extinction at least partially through modification of the chemical kinetics. There are experimental and theoretical evidences [1, 2], that reaction products of CF₃Br must be directly responsible for this chemical inhibition. Since similar effects are produced by other bromine-containing compounds, it is reasonable to assume that product molecules containing Br interact with the chain mechanism of combustion to slow the overall rate. It would be useful to have overall kinetic parameters that describe the inhibition effect of Br.

In this paper C₂F₄ClF and C₂F₄ClCl (242) and also well known flame inhibitor C₂F₄Br₂(2402) have been investigated Choice of objects have been caused such fact that the similarity of the compounds isn’t provided analogical inhibition effect. The quantum-chemical calculations by the SCF MO LCAO in the frame approximation MNDO [3] by program [4] the destruction ways a number of known and studying inhibitors have been carried to study effect of the substance composition and structure on inhibition activity in hydrogen flame and also for investigation inhibition mechanism.

At first the destruction ways of all investigated fire suppressants have been calculated for proof the radical mechanism of probable interactions. The analysis has been carried out by the comparison of enthalpies of particles.

For the next stage the collision complexes between destruction products and active centers of flame (H, OH, O) have been calculated to research scavenging effectiveness of these substances. The interaction probability has been estimated by the depth of minimum on the potential curves (dependence potential energy from distance between particles). The relative stability of the short living complexes have been determined by the comparative analysis of bind lengths and energies.
### Table. Destruction products’ enthalpies ($\Delta H_f \text{kJ/mol}$) of investigated fire suppressants

<table>
<thead>
<tr>
<th>Fire suppressants</th>
<th>Destruction products</th>
<th>$\Delta H_f \text{kJ/mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. CF$_3$-CF$_3$</td>
<td>CF$_3^+$ + CF$_3^-$</td>
<td>221.68</td>
</tr>
<tr>
<td></td>
<td>CF$_3^+$ + CF$_3^-$</td>
<td>22.16</td>
</tr>
<tr>
<td></td>
<td>F$^+$ + CF$_2$F$_5^-$</td>
<td>86.7</td>
</tr>
<tr>
<td>II. CF$_2$Cl-CF$_2$Cl</td>
<td>C$_2$F$_4$Cl + Cl$^-$</td>
<td>44.69</td>
</tr>
<tr>
<td></td>
<td>CF$_2$Cl$^+$ + CF$_2$Cl$^-$</td>
<td>19.29</td>
</tr>
<tr>
<td>III. CF$_2$Br-CF$_2$Br</td>
<td>CF$_2$Br$^+$ + CF$_2$Br$^-$</td>
<td>54.63</td>
</tr>
<tr>
<td></td>
<td>C$_2$F$_4$Br + Br$^-$</td>
<td>66.37</td>
</tr>
<tr>
<td>IV. CF$_3$-CF$_2$Br</td>
<td>C$_2$F$_5$Br$^+$ + Br$^-$</td>
<td>30.01</td>
</tr>
<tr>
<td></td>
<td>C$_2$F$_4$Br + F$^-$</td>
<td>79.21</td>
</tr>
<tr>
<td></td>
<td>CF$_2$Br$^+$ + CF$_3^-$</td>
<td>16.21</td>
</tr>
<tr>
<td>V. CF$_3$-CF$_2$Cl</td>
<td>C$_2$F$_5^+$ + Cl$^-$</td>
<td>44.84</td>
</tr>
<tr>
<td></td>
<td>CF$_3^+$ + CF$_2$Cl$^-$</td>
<td>18.39</td>
</tr>
</tbody>
</table>

As we can see from the table, the homolitical decay much more preferable for all investigated fire suppressants. Therefore, we can suggest the possibility of participation of these particles in branch radical flame spreading reactions. Among the all substances, C$_2$F$_4$Br$_2$ gives more active inhibiting particles which have smaller values of enthalpies. Apart from that the two bromine atoms can to catch atomic hydrogen by reaction: H$^+$ + Br$^-$ → HBr. By these facts we can explain the strong inhibiting effect of this suppressant. But contrary for traditional point of view our research also shows that the most important particle for all investigated compounds is CF$_3^-$. The enthalpy has the least values for all cases of destruction. And besides this particle well interacts with all active centers of flame. The binding energy CF$_3$-OH, for example, is 6, 67 eV. By the substitution only one atom on Cl and Br, lead to inert behavior of CF$_2$Cl and CF$_2$Br to active radicals, which promote to spreading of flame.

We can do some conclusions about stabilizing acting of substituents by analyzing of interatomic distances C-halogen. Thus, distance C-Cl in molecule C$_2$F$_5$Cl is R=1,227 Å, and C-F is R=1,346 Å. As we can see, $R_{C-Cl}$ at 0,119 Å less, than C-F, in spite of known fact that radius of chlorine atom some more. Thus, we can conclude that chlorine atom stronger binds in molecule. Fluorine as more mobile substituent can light abstract and scavege atomic hydrogen to stable molecule HF. All this results is in agreement with experimental date.

### References

Binding Energies of Monovalent and Divalent Cations with TNT

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Trinitrotoluene is considered a major environmental hazard because it can seep into groundwater and sterilize soil. And yet, TNT is prevalent at artillery ranges, bomb sights, and anywhere explosives are used for any purpose, military or civil. The only current EPA-approved method for remediating TNT from soil is incineration, which is quite expensive. However, other treatments are currently being investigated involving base hydrolysis of TNT. Base hydrolysis always occurs in the presence of high concentrations of monovalent and divalent cations. In the present study, we begin our investigation of this process by calculating the binding energy of TNT to such cations using ab initio and density functional methods.
Conformational Energetics of Naphthylquinoline Derivatives

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A library of naphthylquinoline derivatives which satisfy the hypothesized structural criteria for triplex DNA selectivity have been designed and synthesized by Dr. Lucjan Strekowski of Georgia State University. The criteria included a large aromatic surface area, unfused flexible ring system, cationic, and crescent shape. High-throughput competition dialysis experiments were performed to investigate selectivity of each compound to fourteen different nucleic acid structures. Results from this experiment demonstrated that replacement of the secondary amine function (LS8) with an ether oxygen (MHQ12) drastically improved selectivity towards triplex DNA.

Recently, a predictive receptor-independent (RI) 4D-QSAR has been developed using apparent equilibrium constants measured from the competition dialysis assay. From this study, a series of "active conformations" were identified. With these active conformations as starting points, we are investigating the validity of these conformers identified from molecular mechanics using semi-empirical, density functional, and ab initio methods. Initially, we are investigating the flexibility of LS8 and MHQ12 by computing rotational energy barriers about the ring-ring and ring-chain dihedral angles. Combining computed molecular properties with results of experimental binding thermodynamics, we hope to develop accurate structure activity relationships in order to design, and eventually synthesize, the best naphthylquinoline compound to bind selectively to triplex DNA. We gratefully acknowledge support from NSF EPSCoR (EPS-0132618).
The Effects of Substitutions within the Ring and Substituents on the Ring to the Computation of Conventional Strain Energy

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Internal strain energy [1-2] in a cyclic molecular system is the sum of Baeyer strain [3], Pitzer strain [4-5], Dunitz-Shoemaker strain [6], and bond distortion strain [7]. Conventional strain energy [8] includes any additional stabilization effects and destabilization effects in addition to the internal strain energy. We have computed conventional strain energies for numerous homocycles and heterocycles within the isodesmic [9-10], homodesmotic [11] and hyperhomodesmotic [12-13] models. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies were computed for all pertinent molecular systems using SCF theory, second-order perturbation theory, and density functional theory with Becke’s three parameter hybrid functional using the LYP correlation functional (B3LYP). Two basis sets, both of triple-zeta quality on valence electrons, were employed in all studies: 6-311G(d,p) and 6-311+G(2df,2pd). The effect of replacing CH2 with NH, PH, and/or O in cyclopropane and cyclobutane is discussed, and the effect of adding substituents to a cyclic system is addressed. In this latter topic, the role of strain energy and the gem-dimethyl effect is specifically discussed. We gratefully acknowledge support from NSF EPSCoR (EPS-0132618).

References
Application of Designer Polynomials to the Soft-Coulomb Potential in One-Dimension

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Department of Physics, Florida A&M University

In a recent article [C.A. Weatherford, E. Red, A. Wynn III, International Journal of Quantum Chemistry 90, 1289-1294 (2002)], an algorithm was described whereby a “synthetic” weighted polynomial basis may be constructed which is adapted (designed) to a particular potential. It was applied therein to the Schrödinger equation with a coulomb potential in one dimension ($-1/|x|$). A weighted polynomial basis with weight function $w(x) = \exp(-\alpha |x|)$ was employed. It was observed that this potential had no even parity solutions—only odd parity solutions. The question arises as to the relationship of the solutions (eigenfunctions and eigenvalues) for this “hard” coulomb potential to the solutions for the “soft” coulomb potential ($-1/\sqrt{x^2 + \beta^2}$). In particular, since the soft coulomb potential is clearly expected to possess both even and odd parity solutions, how do these solutions behave as $\beta \to 0$ and thus what happens to the even solutions. This problem is deceptively difficult—none of the standard basis sets produce a variational minimum as a function of $\alpha$ for nonzero $\beta$. This is apparently why this problem has never been done before. A new orthonormal basis was designed with weight function $\exp(-\alpha \sqrt{x^2 + \beta^2})$ which did produce a variational minimum for variable $\alpha$ and arbitrary fixed $\beta$. The present paper describes these solutions and clearly indicates how they behave as $\beta \to 0$.

*Directed by Professor C.A. Weatherford.

This work was supported in part by the Army High Performance Computing Research Center under the auspices of the Department of the Army, Army Research Laboratory cooperative agreement number DAAD19-01-2-0014, the content of which does not necessarily reflect the position or the policy of the government, and no official endorsement should be inferred. It was also partially supported by NASA Grant NAG5-10148.
Adsorption of Sarin and Soman on Dickite: ab initio ONIOM Study

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\textsuperscript{b}Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, 1400 Lynch Street, P. O. Box 17910, Jackson, MS 39217, USA
\textsuperscript{c}Scientific Research Department of Alkali Halide Crystals, STC “Institute for Single Crystals”, National Academy of Sciences of Ukraine, 60 Lenina ave., 61001 Kharkov, Ukraine

The study of adsorption of Sarin (GB) and Soman (GD) on the octahedral (o) and tetrahedral surfaces (t) of dickite (D) using the two-level ONIOM(B3LYP/6-31G(d,p):PM3) and the ONIOM(B3LYP/6-31G(d,p):HF/3-21G) methods and cluster model approximation has been performed. The optimized structure of Sarin on the octahedral surface of dickite obtained at the ONIOM(B3LYP/6-31G(d,p):PM3) level is illustrated in Figure 1.

Formally, GB and GD can be adsorbed on the octahedral and the tetrahedral surfaces of dickite so that they cover the octahedral and ditrigonal cavity. The analysis of the topological characteristics of electron density distribution in the inner part of D-GB and D-GD systems at the B3LYP/6-31G(d,p) level of theory reveals that the adsorption of Sarin and Soman on the surface of dickite occurs through the formation of multiple hydrogen bonds. These hydrogen bonds were found between the oxygen atom and methyl groups of GB and GD and hydroxyl groups (the adsorption on the octahedral surface, see Figure 1) and between the methyl groups of GB and GD and basal oxygen atoms (the adsorption on the tetrahedral surface). The oxygen atom of GB and GD plays the crucial role in the formation of hydrogen bonds and in the stabilization of the organic molecule on the surface. The arrangement of three atoms of formed H-bonds is mostly linear and predicted hydrogen bond distances are within the range of such H-bonds.

The analysis of electron density transfer between Sarin, Soman and the mineral confirms the formation of conventional O-H...O and weak C-H...O hydrogen bonds predicted by the “Atoms in Molecules” analysis. The adsorption results in changes of geometric parameters, in the polarization of adsorbed molecules and the surface of dickite and in the charge density transfer between Sarin and Soman and the surface of mineral. This corresponds to the formation of the attractive contacts between GB and GD and the surface of dickite. The polarization of the organic molecule and the surface of dickite is more significant in the case of adsorption on the octahedral side. The amount of electron density, transfer from the mineral to Sarin and Soman, is proportional to the binding strength.
The values of interaction energies reveal that the binding energy of C-H…O is about a fraction of kcal/mol. Interaction energies of adsorption system with the organic molecule on the octahedral surface are almost two times larger than interaction energies of adsorption systems on the tetrahedral surface (see Table 1). Therefore, we concluded that the Sarin and Soman will adsorb most preferably on the octahedral surface of dickite.

In the case of adsorption on the octahedral surface, an analysis of interaction energy components indicates the significant importance of electrostatic and delocalization binding contribution. In the case of adsorption on the tetrahedral surface, the contribution of the SCF term to the total interaction energy is repulsive. It originates from repulsive interactions between P=O oxygen atom of Sarin and basal oxygen atoms of the tetrahedral surface of dickite. The stabilization of Sarin and Soman adsorbed on the tetrahedral surface is secured by the correlation forces.

Table 1. BSSE Corrected Interaction Energies (kcal/mol) of the D-GB and D-GD Systems Calculated using ONIOM(B3LYP/6-31G(d,p):PM3) and ONIOM(B3LYP/6-31G(d,p):HF/3-21G) Method.

<table>
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<tr>
<th>System</th>
<th>D(o)-GB</th>
<th>D7(o)-GB</th>
<th>D(t)-GB</th>
<th>D(o)-GD</th>
<th>D7(o)-GD</th>
<th>D(t)-GD</th>
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<td>LL method</td>
<td>PM3</td>
<td>HF</td>
<td>PM3</td>
<td>PM3</td>
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<td>PM3</td>
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<tr>
<td>Int. Energy</td>
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<td>-16.5</td>
<td>-3.9</td>
<td>-4.9</td>
<td>-7.4</td>
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Table 1. BSSE Corrected Interaction Energies (kcal/mol) of the D-GB and D-GD Systems Calculated using ONIOM(B3LYP/6-31G(d,p):PM3) and ONIOM(B3LYP/6-31G(d,p):HF/3-21G) Method.

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<td>-4.9</td>
<td>-7.4</td>
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</table>
Theoretical Study of Adsorption and Decomposition of Sarin on Magnesium Oxide

A. Michalkova\textsuperscript{a, b}, M. Ilchenko\textsuperscript{b}, L. Gorb\textsuperscript{b}, J. Leszczynski\textsuperscript{b}

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\textsuperscript{b}Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, 1400 Lynch Street, P. O. Box 17910, Jackson, MS 39217, USA

The adsorption and decomposition of Sarin — isopropyl methylphosphonofluoridate (C\textsubscript{4}H\textsubscript{10}FO\textsubscript{2}P) on the surface of magnesium oxide (MgO) was investigated at the B3LYP/6-31G(d) and MP2/6-31G(d) levels of theory. The representative small (in the case of decomposition, see the A model in Figure 1) and large (in the case of adsorption, see the B model in Figure 1) cluster models have been used to simulate the surface of MgO. Sarin was allowed to fully relax. The geometry of MgO fragment was kept frozen.

1. Adsorption. The location and orientation of adsorbed GB on the surfaces of MgO was found. The adsorption of GB on the surface of MgO occurs due to the formation of C-H…O hydrogen bond between C-H group of the molecule and oxygen atom of the oxide surface and ionic type interactions between Mg cation of the surface and O and F atoms of Sarin. The adsorption energy of MgO-GB complex corrected by the basis set superposition error, obtained using large cluster models of metal oxide, is predicted in range of -10 kcal/mol. The adsorption results in electron density transfer between Sarin and the oxide surface and in the polarization of Sarin and the surface of MgO.

2. Decomposition. Using the small model of MgO, the decomposition of Sarin on the surface has been modeled. The fluorine atom was transferred from Sarin to the MgO surface and placed in a bonding distance with Mg atom of the surface. The removal of fluorine atom is more preferable reaction in comparison with the interactions of whole Sarin with the oxide surface since according to values of the interaction energy of these systems this system is more stable than the system presented in Figure 1 as the A model.
Figure 1. The optimized structure of Sarin on the surface of MgO obtained using small (A) and large (B) model of MgO
Density Functional Theory Study of Regiochemical Aspects of Trimethylsilyloxirane and tert-Butiloxirane Methanolysis Reaction

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2Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217, USA

The opening of the epoxide ring in neutral and basic medium is nucleophilic substitution at carbon atom which undergoes by S_N2-like mechanism. As a rule the nucleophile attacks the less-substituted carbon atom (Krasuski’s rule). However, there are some examples where nucleophile attacks more hindered carbon atom. One of them is silicon-substituted oxiranes with preferable nucleophilic attack of α-carbon atom in relation to silicon, despite of its larger steric hindering.

\[
\begin{array}{cccc}
1 & 2 & 3 & 4 \\
\end{array}
\]

<table>
<thead>
<tr>
<th></th>
<th>(\Delta G_{\text{act}}, \text{kcal/mol} ) (B3LYP/6-31+G*)</th>
</tr>
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<tbody>
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<td>Gas phase</td>
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<td>Supermolecular</td>
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<td>approach</td>
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</tbody>
</table>

In order to investigate the relation between steric and electronic factors on the regiochemistry of methanolysis reaction of monosubstituted oxiranes we have performed quantum-chemical study of the methanolysis reactions of trimethylsilyloxirane and tert-butiloxirane in basic medium with methanol as a solvent. Calculations have been performed at the B3LYP/6-31+G(d) level of theory in vacuo as well as with taking into account solvent effects using supermolecular approach and SCRF Onsager’s model. The first solvent shell has been modeled using supermolecular approach where three methanol molecules have been connected with methoxy-anion and one with epoxidic oxygen atom.

Calculated values of activation barriers correctly reproduce the regiochemistry for both of epoxides with preference of \(\alpha\)-opening for trimethylsilyloxirane and \(\beta\)-opening for tert-butiloxirane. Natural bond analysis for optimized transition states revealed that in the case of trimethylsilyloxirane the direction of opening determines by stabilization of \(\alpha\)-transition state (1) due to significant donation of lone pair of methoxy-anion’s oxygen atom to Si-C bond.
An Investigation of the $^1$H and $^{13}$C NMR Chemical Shifts in Oxiranes Using Magnetically Corrected Basis Sets

S.I. Okovytyy, L.I. Kasyan, V.V. Rossikhin, L.K. Umrikhina, J. Leszczynski

1 National University, Dnepropetrovsk, 49050, Ukraine
2 National Technical University, Dnepropetrovsk, 49010, Ukraine
3 Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217, USA

The accuracy of ab initio calculation of NMR parameters has increased significantly over the past few years. Recently we have proposed for calculations of magnetic shielding the magnetically consistent basis sets 6-31G## and demonstrated their advantages over standard basis sets on the example of $^{17}$O NMR chemical shifts for the number of oxiranes.\(^1\),\(^2\)

Here we report the calculated $^{13}$C and $^1$H NMR chemical shifts as obtained in vacuo and in chloroform, both at various computational levels for epoxides (1-12).

The calculated chemical shifts are compared with experimental solution data, focusing on the agreement with spectral patterns and spectral trends. The influence of different basis sets (6-31G## and 6-311++G(3d,2p)), methods (GIAO and CSGT) and levels of theory (HF and DFT) was investigated systematically by exhaustive calculations on the epoxidic compounds. The solvent dependence of the NMR chemical shifts is accounted for, and it is described using PCM method. The chemical shifts obtained with 6-31G## (II) basis set are of above the same quality or better as those obtained with larger Pople’s 6-311++G(3d,2p) basis set. The GIAO and CSGT procedures yielded very similar results in conjunction with both basis sets. The analysis of the solvent dependence of the shielding constants for $^1$H and $^{13}$C nuclei shows that the main experimental trends are well reproduced at the PCM-CSGT level.

Identification of the Stereoisomers of Tetrahydroindene Diepoxide: A Combined Experimental and Theoretical $^1$H and $^{13}$C NMR Study

S.I. Okovytyy, L.I. Kasyan, M.F. Seferova, V.V. Rossikhin, L.K. Umrikhina, J. Leszczynski

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3Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217, USA

NMR spectroscopy has proven to be an exceptional tool for investigation of the structure and conformational properties of organic compounds. However in some cases it is very difficult or even impossible to make signal assignments or identify the structure of synthesized compounds based only on experimental NMR spectra alone. In these cases quantumchemical calculations can provide valuable assistance, since direct comparison of experimental and accurately predicted theoretical spectra allows one almost unambiguously accept or decline suggested structure.

The purpose of present work is experimental and theoretical study of stereochemistry of tetrahydroindene (TGI) (1) epoxidation reaction by monoperoxyphthalic acid (MPPA). The following stages has been done during investigation: (i) epoxidation of TGI by MPPA; (ii) chromatographical separation of obtained diepoxides of tetrahydroindene (DOTGI); (iii) experimental investigation of $^1$H and $^{13}$C specters of diepoxides (iv) theoretical investigation of conformational properties and $^1$H and $^{13}$C chemical shifts of DOTGI; and, finally, (v) comparison of experimental and theoretical results and identification of stereoisomeric diepoxides.

Molecular structures and conformations for all of possible stereoisomeric diepoxides 2 have been investigated at MP2/6-311G(d) level of theory and the most stable conformers for each isomer (structures 2A-D) have been selected for further theoretical investigation of $^1$H and $^{13}$C chemical shifts.

Based on the comparison of calculated (GIAO-PCM/PBE1PBE/6-31G## level of theory) and experimental $^1$H and $^{13}$C chemical shifts synthesized diepoxides have been assigned to corresponding stereoisomers.
Development of New Computational Program for the Second–Order Magnetic Properties Calculations

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1Dnepropetrovsk National University, Dnepropetrovsk, 49050, Ukraine
2National Technical University, Dnepropetrovsk, 49010, Ukraine
3Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217, USA

The new computational program for performing of ab initio calculations of the second-order molecular magnetic properties is proposed. The main future is to address calculations of the paramagnetic part of magnetizability and magnetic shielding tensors. The algorithm is based upon the idea of simultaneous account of analytical dependence of both the density matrix and initial basis functions on corresponding perturbation parameters within of the coupled Hartree-Fock perturbation theory. Needful explicit expression for the first-order density (bond order) matrix \( P^{(1)} \) to the zero-order one \( P^{(0)} \) has been received in [1]:

\[
P^{(1)} = \sum_{a=1}^{n} \sum_{b=a+1}^{m} (C_{b}^{(0)} K_{ba} \tilde{C}_{a}^{(0)}) + C_{a}^{(0)} \tilde{K}_{ba} \tilde{C}_{b}^{(0)}) - S^{-1} \mu P^{(0)} - P^{(0)} \mu S^{-1}
\]

where \( K_{ba} = (\varepsilon_{a} - \varepsilon_{b})^{-1} [\tilde{C}_{b}^{(0)} (F^{(1)} - \varepsilon_{a} \mu - \varepsilon_{b} \mu) C_{a}^{(0)}],\varepsilon_{a}, \varepsilon_{b} \) are one-electron energies, \( F^{(1)} \) is the first-order correction to the Fock operator matrix, \( \mu \) is the matrix with elements \( \langle \chi_{p}^{(1)}, \chi_{q}^{(0)} \rangle, \chi_{p}^{(1)} \) is the first-order correction functions to the basis functions \( \chi_{p}^{(0)} \), \( S^{-1} \) is the matrix reverse to an overlap matrix, \( C_{a}^{(0)} \) is the molecular orbital expansion coefficient.

It is necessary to underline that if \( \chi^{(1)} = 0 \) the expression for \( P^{(1)} \) is reduced to the form corresponding to standard perturbation theory which is used in almost all software packages for calculation of the molecular properties.

Determination of explicit form of the first-order correction functions \( \chi^{(1)} \) [2] to initial basis set AO’s \( \chi^{(0)} \) is based upon the solution of inhomogeneous Schrödinger equation

\[
[-\frac{1}{2} \Delta + V(r) - E] \chi(r) = \lambda \hat{W}(r) \chi(r), \tag{1}
\]

where \( V(r) \) is a potential which defines the form of basis set AO’s, \( \hat{W}(r) \) is the perturbation operator.
The differential equation (1) can be reduced to the integral equation of the second kind, from
the solution of which it follows that the first-order correction to the solution \( \chi^{(0)}(r) \)
corresponding to the homogeneous form of equation (1) \( (\lambda \hat{W}(r) \equiv 0) \) is determined by relation:

\[
\chi^{(1)}(\vec{r}) = \int G_E(\vec{r}, \vec{r}') \hat{W}(\vec{r}') \chi^{(0)}(\vec{r}') \, d\vec{r}'.
\]  
(2)

Here \( G_E(\vec{r}, \vec{r}') \) is the Green’s function [3] for the nonrelativistic homogeneous Schrödinger equation.

For the spherically symmetrical potential \( V(r) \) the Green’s function can be expressed in closed form:

\[
G_E(\vec{r}, \vec{r}') = \sum_{l,m} g_l(r, r'; E) Y_{lm}(r_0) Y_{lm}^*(r_0'),
\]

where \( Y_{lm} \) are spherical functions of the argument \( r_0 = \vec{r}/r \), \( g_l(r, r'; E) \) is a radial part of the Green’s function.

In the case the magnetic field operator \( \hat{W}(r) \) depends on the choice of the coordinate system wherein the vector potential is expressed for the molecular problem, \( \hat{W}(r) = (e \hbar /2mc) (\vec{r} - \vec{R}) \times \vec{V} = \hat{W}_0 - (e \hbar /2mc) \cdot \vec{R} \times \vec{\nabla} \),

where \( \vec{r} \) is the electron position vector relative to a nucleus, \( \vec{R} \) is the nucleus position vector relative to the molecular reference system. Since the influence of the \( \hat{W}_0 \) operator on the basis function \( \chi^{(0)} \) is reduced to the modification of the magnetic quantum number \( m \), the contribution of this operator to (2) vanishes. Thus the operator \( -(e \hbar /2mc) \cdot \vec{R} \times \vec{\nabla} \) is the appropriate perturbation operator.

Above-described relation leads in natural manner to the physically justified improvement of the approximate wave function in those regions of the configuration space that give the dominant contribution to the molecular properties under consideration.

It should be noted that size of all matrix used in calculations coincide with the one for the unperturbed zero-order basic set functions.

The advantages of developed program in comparison with standard CHF calculations with different basis sets are shown by the test calculations of the magnetic susceptibilities (see Table) for the number of molecules.
Table. Magnetic Susceptibilities of the First-Row Hydrides (ppm cgs/mol)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>6-31G (0)^a</th>
<th>6-31G(d,p) (0)^a</th>
<th>6-311++G(3d,3p) (0)^a</th>
<th>6-31G (1)^b</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dia</td>
<td>-10.48</td>
<td>-10.38</td>
<td>-10.89</td>
<td>-10.48</td>
<td>-11.01</td>
</tr>
<tr>
<td>para</td>
<td>0.44</td>
<td>0.48</td>
<td>0.46</td>
<td>0.78</td>
<td>0.61</td>
</tr>
<tr>
<td>total</td>
<td>-10.04 (11)^c</td>
<td>-9.90 (20)^c</td>
<td>-10.43 (48)^c</td>
<td>-9.70 (11)^c</td>
<td>-10.4</td>
</tr>
<tr>
<td>H2O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>para</td>
<td>0.95</td>
<td>1.26</td>
<td>1.41</td>
<td>1.97</td>
<td>1.51</td>
</tr>
<tr>
<td>total</td>
<td>-14.11 (13)^c</td>
<td>-13.64 (25)^c</td>
<td>-13.98 (58)^c</td>
<td>-13.09 (13)^c</td>
<td>-13.12±1.78</td>
</tr>
<tr>
<td>NH3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dia</td>
<td>-20.79</td>
<td>-20.62</td>
<td>-21.07</td>
<td>-20.79</td>
<td>-20.2</td>
</tr>
<tr>
<td>para</td>
<td>1.82</td>
<td>2.87</td>
<td>3.66</td>
<td>4.02</td>
<td>3.923</td>
</tr>
<tr>
<td>total</td>
<td>-18.97 (15)^c</td>
<td>-17.75 (30)^c</td>
<td>-17.41 (71)^c</td>
<td>-16.76 (13)^c</td>
<td>-16.3±0.8</td>
</tr>
<tr>
<td>CH4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>-24.10 (17)^c</td>
<td>-21.38 (35)^c</td>
<td>-19.03 (84)^c</td>
<td>-19.02 (17)^c</td>
<td>-17.4±0.8</td>
</tr>
</tbody>
</table>

^aCalculated at standard CHF level; ^bCalculated using new procedure; ^cNumber of basis functions.

Film Growth in Aqueous Solution of Hydrophobic and Polar Groups on an Adsorbing Substrate by Monte Carlo Simulation

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Department of Physics & Astronomy, University of Southern Mississippi
Hattiesburg, MS 39406-5046

Using a computer simulation model, growth of film on a discrete lattice is studied in a multi-component system. The substrate is designed by placing a layer of absorbing constituents (S) at the bottom of the lattice. Components include: water solvent (A), polar (B), and hydrophobic (C) constituents. Nearest neighbor interaction among these constituents are considered along with their molecular weight. Sample is initialized by mixing these components with a stochastic stirring simulation. Metropolis algorithm is used to move these constituents. Periodic boundary conditions are used for each components except the water constituents which are allowed to evaporate, i.e., escape the sample from the top. As the simulation proceeds, concentration of water reduces and the mobility of B and C decreases accordingly. Precipitation and phase separation between B and C components occur simultaneously with water constituents trapped in between. Preliminary simulations show that the roughness of the film increases with the solvent concentration. Snaps and figures will be presented to monitor the surface growth as the data will become available.
High-Level \textit{ab initio} Comparison Study of the Hydrogen–Bonded Cyclic Complexes

Yevgeniy Podolyan and Jerzy Leszczynski

\textit{Computational Center for Molecular Structure and Interactions,\newline Jackson State University, Jackson, MS 39217-0510}

Hydrogen bonding attracted attention of the scientists for many years. We have performed the comparison study of the formic acid, formamide, and formamidine dimers and formamide-formamidine complex (fig.1). These complexes are of special interest due to close resemblance of the hydrogen bonding of the base pairs in DNA.

Optimizations and vibrational frequency calculations have been performed at MP2 level with 6-31G(d,p) and aug-cc-pVDZ basis sets and single-point calculations have been done at CCSD(T) level with the same basis sets. The structural parameters, hydrogen bonding parameters (length and strength) and IR vibrational frequencies are compared for all studied compounds.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures of the studied complexes.}
\end{figure}
A Survey of both Fundamental and Applied Aspects of Atomic and Molecular Electrostatic Potentials

Peter Politzer

University of New Orleans, Department of Chemistry, New Orleans, LA 70148

The electrostatic potential that is created in the surrounding space by the nuclei and electrons of a system is a very fundamental property. It is related by Poisson's equation to the electronic density, the essential nature of which was established by the Hohenberg-Kohn theorem. Atomic and molecular energies can be expressed rigorously in terms of the electrostatic potentials at the nuclei, as can the chemical potential (electronegativity). The minimum in the potential along the internuclear axes of bonded atoms permits realistic determination of their covalent radii, while the radial minimum for anions is a good measure of their ionic radii.

The electrostatic potential is also extremely useful in quantifying noncovalent interactions. When computed on a molecular surface and characterized in terms of such features as its maxima and minima, average deviation, variance, etc., it is possible to develop relationships that correlate and predict with good accuracy a variety of macroscopic condensed-phase properties that depend upon noncovalent interactions. These include boiling points, critical constants, heats of vaporization, fusion and sublimation, partition coefficients, diffusion constants, viscosities, surface tensions, and solubilities and solvation energies.
Theoretical Predictions of Chemical Degradation Reaction Mechanisms of Cyclic (RDX HMX) and Caged Nitramines (ONC, TNTAC) as Related to Their Molecular Structures

Mohammad (Mo) M. Qasim,1 Herbert Frederickson,1 Chris McGrath,1 John Furey,1 Rakesh Bajpai2

1ERDC-MS
2University of Missouri, Columbia

Although the geometrical structure of 2,4,6,8,10,12-hexanitrohexaazoiso-wurtizane (CL-20) is more complex than that of hexahydro-1, 3, 5-trinitro-1, 3, 5-s-triazine (RDX), they have the same basic structural components. Hence our prediction that, under equivalent conditions, certain chemical degradation schemes successful with RDX should also be successful with CL-20 in that CL-20 degradation is expected to follow mechanisms comparable to those of RDX after the breaking of its carbon-carbon (C-C) bonds. Other structurally similar nitramines, as octonitrocubane (ONC) and 2,4,6,8-tetranitro-1,3,5,7-tetraaza-cubane (TNTAC) can be expected to follow the predicted mechanisms.

Depending upon conditions, RDX follows the competitive modes of degradation mechanisms shown in the accompanying diagram. Nucleophilic substitution of the nitro group utilizes addition of hydroxide ions. Base proton abstraction, due to addition of alkali concentrations of hydroxide ions, forms double bonds via 2nd order rate elimination (E2). Reductive degradation (chemical and biochemical) of RDX nitro groups leads to the formation of nitroso and nitro-aromatic amine derivatives. Free radical oxidation reactions, in which symmetrical bond breaking/cleavage occurs upon addition of hydroxyl (and other, as hydroperoxide radicals), attack the bonds either in sequence or simultaneously (concerted mechanism).

Preliminary calculations indicate that the free radical mechanism (symmetrical bond-breaking) is more apt to occur with the increase in number of symmetrical C-C (preferred), then N-N bonds contained within the molecule. The less polar the bond—such as C-C and, to a lesser extent, N-N—the greater the tendency toward free radical bond-breaking. Therefore, the higher the ratio of these bonds the more likely that degradation will proceed via free radical oxidation. In general, free radical reactions are most apt to take place where bonds are between the same type of atom. Conversely, the more polar C-N bonds are more prone to follow hydroxylation or reductive degradation pathways. Because under similar conditions, the free radical ring-breaking pathway competes effectively with nucleophilic/base degradation, transformation
mechanics for C-N bonding can tend toward either free radical cleavage or toward nucleophilic/base abstraction.

Depending on conformer, calculations show some C-C bonds of CL-20 become elongated, thus producing sites of possible reactivity in which bond-breaking takes place, resulting in heterocyclic-heptagonal rings as opposed to RDX heterocyclic hexagonal rings. Energy calculations show that additional sites of reactivity result at CL-20 and ONC bonds, where stretching, symmetrical bond-breaking, and production of intermediates occur. Here, C-C bond cleavage is most apt to occur due to free radical attack. ONC has 12 C-C, 8 C-N bonds and no N-N bonds. Since C-C bonds comprise the ONC cage, it is predicted that the free-radical C-C symmetrical bond-breaking degradation mechanism will prevail as indicated by the HOMO/LUMO molecular orbitals. (ONC supportive material in manuscript.)

Objectives, to: 1) compare structural similarities between simulated molecules of CL-20 and RDX as well as other such nitramines as ONC and TNTAC; 2) relate chemical/physical properties to reactivities; 3) identify possible sites of hydroxyl radical (OH•) oxidation and of hydroxide ion (OH−) elimination as well as other reduction reactions, our preliminary approach consisted both of the use of MOPAC approximation (quantum mechanical) methods AM1, MNDO, and PM3; and classical force field molecular mechanics (MM2) to calculate chemical/physical properties that characterize nitramine molecules Quantum mechanical calculations of RDX and CL-20 included studies of the structure: formation and steric energies; energies of highest occupied and lowest unoccupied molecular orbitals; bond lengths and angles; partial and electrostatic potential charges; cosmo solvation; and possible reaction sites. Similar MOPAC approximation and quantum mechanical methods are being used on ONC and TNTAC. The initial results of this study are presented in the following graphs and tables.
Important Modes Of RDX Degradation

- HYDROXYL IONS — addition of base utilizes hydrogen abstraction
- HYDROXYL IONS — addition of base initiates nucleophile substitution of nitro groups and 2nd order rate elimination
- REDUCTIVE — both chemical and biochemical degradation
- FREE RADICAL — added agents produce hydroxyl radicals (and other radicals such as hydroperoxide radicals)

RDX Oxidation

Oxidation of RDX results in the formation of nitroso groups, which can further oxidize to form nitro groups.

RDX Reductive Mechanism

Proposed Mechanism of Reduction

Third Tier Reductive Products

Energy profile of third tier RDX reducible reduction products.

Some Cyclic Nitro Amines

- RDX
- CL20
- ONC
- TNTAC
<table>
<thead>
<tr>
<th>RDX -- APPROXIMATION METHODS OF CALCULATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steric and Formation Energies = kcal/mole; LUMO and</td>
</tr>
</tbody>
</table>

### Heats of Formation

<table>
<thead>
<tr>
<th>Method</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 104.8850</td>
<td>LUMO → -1.1008</td>
<td>-1.0978</td>
<td>-0.2168 N = 43</td>
</tr>
<tr>
<td>MNDO = 100.8966</td>
<td>HOMO → -12.1057</td>
<td>-12.3302</td>
<td>-11.0842 N = 42</td>
</tr>
<tr>
<td>PM3 = 42.1098</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Steric Energy (MM2) = -1.899

**Dipole Moment** = 6.964 Debye

### RDX Reduction Products -- First Tier

#### RDX -- Mononitroso

<table>
<thead>
<tr>
<th>Method</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 88.8247</td>
<td>LUMO → -0.8675</td>
<td>-0.8998</td>
<td>-0.6856 N = 40</td>
</tr>
<tr>
<td>MNDO = 73.3264</td>
<td>HOMO → -11.3769</td>
<td>-11.6232</td>
<td>-10.6531 N = 39</td>
</tr>
<tr>
<td>PM3 = 56.3635</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Steric Energy (MM2) = 8.6644

**Dipole Moment** = 6.398 Debye

### RDX -- Monohydroxylamine

<table>
<thead>
<tr>
<th>Method</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 89.610</td>
<td>LUMO → -0.5772</td>
<td>-0.6948</td>
<td>-0.352 N = 41</td>
</tr>
<tr>
<td>PM3 = 39.933</td>
<td></td>
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<td></td>
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</tbody>
</table>

### Steric Energy (MM2) = 2.75

**Dipole Moment** = 6.803 Debye

### Monoamino RDX

<table>
<thead>
<tr>
<th>Method</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 103.1976</td>
<td>LUMO → -0.5534</td>
<td>-0.5381</td>
<td>-0.3426 N = 38</td>
</tr>
<tr>
<td>MNDO = 92.5067</td>
<td>HOMO → -10.6059</td>
<td>-11.008</td>
<td>-9.454 N = 37</td>
</tr>
<tr>
<td>PM3 = 50.4463</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

### Steric Energy (MM2) = 8.30

**Dipole Moment** = 5.961 Debye

### RDX Hydroxylation Products -- First Tier

#### RDX -- Nucleophilic OH-- Substitution for NO2

<table>
<thead>
<tr>
<th>Method</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 66.0237</td>
<td>LUMO → -0.648</td>
<td>-0.7573</td>
<td>-0.4199 N = 38</td>
</tr>
<tr>
<td>MNDO = 56.3390</td>
<td>HOMO → -11.0344</td>
<td>-11.315</td>
<td>-10.752 N = 37</td>
</tr>
<tr>
<td>PM3 = 19.2703</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Steric Energy (MM2) = 7.35

**Dipole Moment** = 5.871 Debye

#### RDX - OH Proton Abstr/NO2 Elim; Form of C=N

<table>
<thead>
<tr>
<th>Method</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 93.4747</td>
<td>LUMO → -1.2319</td>
<td>-1.0505</td>
<td>-0.8632 N = 34</td>
</tr>
<tr>
<td>MNDO = 83.5432</td>
<td>HOMO → -11.2436</td>
<td>-11.4885</td>
<td>-10.7783 N = 33</td>
</tr>
<tr>
<td>PM3 = 44.6176</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Steric Energy (MM2) = 1.46

**Dipole Moment** = 4.164 Debye

### RDX Free Radical Oxidation

#### RDX with 1 Ring C-N Bond Broken

<table>
<thead>
<tr>
<th>Method</th>
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<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 81.9344</td>
<td>LUMO → -0.9574</td>
<td>-0.9544</td>
<td>-0.6921 N = 44</td>
</tr>
<tr>
<td>MNDO = 90.4041</td>
<td>HOMO → -11.4487</td>
<td>-11.7472</td>
<td>-11.0979 N = 43</td>
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<tr>
<td>PM3 = 30.4820</td>
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</tbody>
</table>

### Steric Energy (MM2) = -3.0

**Dipole Moment** = 2.245 Debye

#### RDX1 Ring C-N Bond Bro/Form of Term C=N

<table>
<thead>
<tr>
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<th>PM3</th>
</tr>
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<tbody>
<tr>
<td>AM1 = 112.9147</td>
<td>LUMO → -1.6718</td>
<td>-1.5424</td>
<td>-1.4013 N = 43</td>
</tr>
<tr>
<td>MNDO = 104.4508</td>
<td>HOMO → 11.7426</td>
<td>11.7478</td>
<td>-11.042 N = 42</td>
</tr>
<tr>
<td>PM3 = 46.1728</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Steric Energy (MM2) = -3.2

**Dipole Moment** = 7.081 Debye

---

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CL-20—APPROXIMATION METHODS OF CALCULATION
Steric and Formation Energies = kcal/mole; HOMO and LUMO = eV

<table>
<thead>
<tr>
<th>Heats of Formation</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 278.0814</td>
<td>LUMO → -2.304</td>
<td>-2.0466</td>
<td>2.7189</td>
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<tr>
<td>MNDO = 233.4438</td>
<td>HOMO → -12.2423</td>
<td>-12.5675</td>
<td>-11.5628</td>
</tr>
<tr>
<td>PM3 = 107.8881</td>
<td>Steric Energy (MM2) = 343</td>
<td>43.504</td>
<td>Dipole Moment = 1.016 Debye</td>
</tr>
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</table>

CL-20 Reduction Reactions

CL-20 - Mononitroso

<table>
<thead>
<tr>
<th>Heats of Formation</th>
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<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 258.9145</td>
<td>LUMO → -2.1116</td>
<td>-1.9569</td>
<td>-1.463</td>
</tr>
<tr>
<td>MNDO = 203.9329</td>
<td>HOMO → -11.9888</td>
<td>-12.2391</td>
<td>-11.13</td>
</tr>
<tr>
<td>PM3 = 122.3562</td>
<td>Steric Energy (MM2) = 46.5</td>
<td>46.9411</td>
<td>Dipole Moment = 2.901 Debye</td>
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</tbody>
</table>

CL-20 - Monohydroxylamine

<table>
<thead>
<tr>
<th>Heats of Formation</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 270.8444</td>
<td>LUMO → -1.9884</td>
<td>-1.808</td>
<td>-1.4108</td>
</tr>
<tr>
<td>MNDO = 261.7489</td>
<td>HOMO → -11.5847</td>
<td>-11.9457</td>
<td>-10.6585</td>
</tr>
<tr>
<td>PM3 = 106.2330</td>
<td>Steric Energy (MM2) = 38.3</td>
<td>38.3423</td>
<td>Dipole Moment = 3.71 Debye</td>
</tr>
</tbody>
</table>

CL-20 Hydroxylation Reactions

CL-20 - NO2 + OH- Nucleophilic Substitution

<table>
<thead>
<tr>
<th>Heats of Formation</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 238.4936</td>
<td>LUMO → -1.9908</td>
<td>-1.8495</td>
<td>-1.3325</td>
</tr>
<tr>
<td>MNDO = 187.4229</td>
<td>HOMO → -11.7158</td>
<td>-11.9125</td>
<td>-11.0868</td>
</tr>
<tr>
<td>PM3 = 85.6708</td>
<td>Steric Energy (MM2) = 48.6</td>
<td>48.6164</td>
<td>Dipole Moment = 4.532</td>
</tr>
</tbody>
</table>

CL-20 OH- Proton Abstract/NO2 Elimin; Formation of C=N

<table>
<thead>
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<th>Heats of Formation</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 329.5995</td>
<td>LUMO → -3.1231</td>
<td>-3.0378</td>
<td>-2.4194</td>
</tr>
<tr>
<td>MNDO = 270.2762</td>
<td>HOMO → -11.8908</td>
<td>-12.263</td>
<td>-11.353</td>
</tr>
<tr>
<td>PM3 = 161.1986</td>
<td>Steric Energy (MM2) = 38.7</td>
<td>38.8854</td>
<td>Dipole Moment = 1.483</td>
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CL-20 Free Radical Reactions

CL-20 with 1 Broken C-C Bond

<table>
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<tr>
<th>Heats of Formation</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 276.4934</td>
<td>LUMO → -2.4269</td>
<td>-2.431</td>
<td>-1.544</td>
</tr>
<tr>
<td>MNDO = 261.8335</td>
<td>HOMO → -12.0484</td>
<td>-12.4485</td>
<td>-11.226</td>
</tr>
<tr>
<td>PM3 = 127.6483</td>
<td>Steric Energy (MM2) = 45.7</td>
<td>45.702</td>
<td>Dipole Moment = 4.033 Debye</td>
</tr>
</tbody>
</table>

CL-20 with 2 Broken C-C Bonds

<table>
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<tr>
<th>Heats of Formation</th>
<th>AM1</th>
<th>MNDO</th>
<th>PM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1 = 259.5870</td>
<td>LUMO → -1.4168</td>
<td>-2.0537</td>
<td>-1.6838</td>
</tr>
<tr>
<td>MNDO = 259.9882</td>
<td>HOMO → -11.0833</td>
<td>-12.3457</td>
<td>-11.5151</td>
</tr>
<tr>
<td>PM3 = 119.8098</td>
<td>Steric Energy (MM2) = 38.5</td>
<td>38.944</td>
<td>Dipole Moment = 2.023 Debye</td>
</tr>
</tbody>
</table>

CL20 w2 broken C-C bonds
Conventional Strain Energy and the *gem*-dimethyl Effect

Ashley L. Ringer, Patricia L. Honea, and David H. Magers

*Department of Chemistry and Biochemistry, Mississippi College, Clinton, Mississippi*

The *gem*-dimethyl effect is the acceleration of cyclization by substituents in the chain and is often used in organic synthesis as a ring-closing effect. In the current study, calculations on methylcyclobutane (Figure 1) and 1,1-dimethylcyclobutane (Figure 2) are performed to determine if this effect is a thermodynamic effect due to lower strain energy or a kinetic effect that simply lowers the activation barrier. 1,1-dimethylcyclobutane is a four-membered carbon ring with *gem*-dimethyl substituents.

One hypothesis suggests that the strain energy is lower because the methyl groups have more freedom to move in the ring than in the open chain. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory and density functional theory (DFT). Comparisons are made between the conventional strain energy of cyclopropane and cyclobutane and the methylcyclobutane and 1,1-dimethylcyclobutane. We gratefully acknowledge the support of NSF EPSCoR (EPS-0132618).
Expansion of Force Field for Considering the Nonrigidity of Amino Group in DNA bases. Preliminary Data

Teri Robinson¹, Leonid Gorb¹, Valeri Poltev² and Jerzy Leszczynski¹

¹Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217
²Facultad de Ciencias Fisico-Matematicas, Benemerita, Universidad Autonoma de Puebla, Puebla, Mexico

The understanding of the mechanisms of biological functioning and the search of new biologically active compounds with desired properties is impossible without the development of the models describing the process at molecular level. It is well known that the information provided by experimental methods themselves is insufficient for construction of such models. Therefore, to build detailed picture of biopolymers and in the area of supra-molecular complexes, molecular mechanics computations are widely used. However, according to molecular mechanics calculations the NH₂- groups of DNA bases are practically planar. This results in somewhat inadequate description of the structure of oligonucleotides and DNA duplexes.

On another hand, the phenomenon of nonplanarity of these amino groups has important biological relevance, therefore it should be included in the parameters of the force fields that are used for modeling of DNA interactions. Conversely, to our knowledge, the available versions of AMBER and CHARMM force fields have so far failed to include this effect.

To fill this gap, we started a project whose final aim is to develop such a force field. We present the data on the ab initio torsion potentials of the NH₂-group that will be considered as benchmarks for developing such a force field for the cytosine. The data has been obtained at the MP2 level of ab initio theory with the optimization of geometry using 6-31G(d,p) basis set.
Charge Exchange in Highly Charged Ion-Atom Collisions

Bidhan C. Saha

Department of Physics, Florida A&M University, Tallahassee, FL-32307.

The physics of highly charged ions has become an extremely active field of research in recent years. Charge exchange becomes most the important mechanism to explain various phenomena occurring in planetary atmosphere, in supernova explosion in interstellar medium, in energetic solar flare, and most recently in the X-ray emission data. The process of electron capture is an important technique for producing Rydberg atoms in the laboratory.

Quantum mechanical calculation involving highly excites states encounters enormous complication owing the presence of large number of oscillation in the final state wave functions of the formed atoms. In this talk we will present a simple but straightforward method to evaluate the scattering amplitude in the first Born Approximation (FBA) taking the effect of the full interaction potential. This is a well-known method, which has enjoyed many applications in collision physics as a whole. We plan to report the following charge-transfer reaction:

\[ \text{X}^\text{q+1} + \text{H}(100) \rightarrow \text{X}^{\text{q-1}}(n,l,m)^* + \text{H}^0 \]

where \( \text{X}^\text{q+1} \) is the incident multiply charged ion and \( \text{X}^{\text{q-1}}(n,l,m)^* \) is the formed ions into any quantum \((n: \text{pricipal}, l: \text{orbital and } m: \text{magnetic})\) states after the collision. Before the collision the target H atoms remain in its ground state \((n=1, l=0 \text{ and } m=0)\).

After the collision the projectile captures the electron from the target to form a bound state \((\text{X}^\text{q+1} + e)\) leaving the bare nucleus of the target H atoms alone (see Fig. 1). Let \( \textbf{K}_i \) and \( \textbf{K}_f \) represent, respectively, the initial and final momenta in the center of mass system. The scattering amplitude in the FBA can be written as

\[ g(k_f, k_i) = -\frac{\mu_f}{2\pi} (I_{\omega\omega} + J_{\omega\omega}) \]

where,

\[ I_{\omega\omega} = -\int F(r, r_i) \frac{1}{r_i} dr_i dr \]

and

\[ J_{\omega\omega} = \int F(r, r_i) \frac{1}{|r_i - r|} dr_i dr \]

where

\[ F(r, r_i) = \exp[i(\alpha \cdot r_i - \beta \cdot r)] \phi_i(r) \phi_i^*(r) \]
The vectors $\alpha$ and $\beta$ are given by

$$\alpha = \frac{M}{M+1} k_i - k_f$$

and

$$\beta = k_f - \frac{M}{M+1} K_f$$

The initial and final bound state wave functions are given by

$$\phi(I) = \sqrt{\frac{1}{\pi}} \exp(-\gamma_1 r_1) \text{with } \gamma_1 = 1$$

and

$$\phi_f(r) = N_{n\ell m} R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

where

$$R_{n\ell}(r) = r^n \exp(-\gamma_2 r) L_{\ell+\frac{1}{2}}^n(2\gamma_2 r)$$

with

$$L_{\ell+\frac{1}{2}}^n(x) = -\frac{(n+\ell)!}{2\pi i} \int dt \exp\{-xt/(1-t)\} (1-t)^{\ell+\frac{1}{2}} t^{\ell+1}$$

The contour $C$ in the above integral encloses the origin. The normalization constant $N_{n\ell m}$ is given by

$$N_{n\ell m} = \frac{1}{2\pi i} \int dt \exp\{-xt/(1-t)\} (1-t)^{\ell+\frac{1}{2}} t^{\ell+1}$$

We will show in details how to evaluate $I_{n\ell m}$ integral analytically and reduces the $J_{n\ell m}$ integral into a single dimension convenient for numerical integration.

**The Coordinate System**

![Coordinate System](image)
Theoretical Study on Molecular Structures and Thermodynamical Properties of Selected Lanthanide Halides

Julia Saloni\textsuperscript{1,2}, Szczepan Roszak\textsuperscript{1,2}, and Jerzy Leszczynski\textsuperscript{1}

\textsuperscript{1}The Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, 1400 J.R. Lynch Street, P.O. Box 17910, Jackson, Mississippi 39217
\textsuperscript{2}Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland

Lanthanide halides LnX\textsubscript{3}, where Ln = Ce, Nd, Gd, Tb, Dy, Ho, Er, Tm and X = F, Cl, Br, I were investigated experimentally by Knudsen effusion mass spectrometry. [1-2] In high temperatures gaseous molecules of LnX\textsubscript{3} follows processes of ionization and fragmentation. As a result a number of different ions: LnX\textsubscript{3}\textsuperscript{+}, LnX\textsubscript{2}\textsuperscript{+}, LnX\textsuperscript{+}, and Ln\textsuperscript{+} was obtained. [3]

In this project theoretical study on structures and thermodynamical properties (such as $\Delta H$, $EA$, $IP$) of these species was performed. Calculations were carried out using RSC 1997 ECP basis set for Dy and RLC ECP basis set, augmented by polarization and diffusions functions for halides. HF method as implemented in Gaussian 98 program was applied. Ground state molecular geometries were obtained for all studied species. An example of the results obtained for dysprosium is discussed.

Calculations of properties of molecular systems that include lanthanides are very interesting because of their various multiplicities (Table 1.). [4]

<table>
<thead>
<tr>
<th>Ln</th>
<th>Ce</th>
<th>Nd</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>3</td>
<td>5</td>
<td>9</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Singly ionized</td>
<td>4</td>
<td>6</td>
<td>10</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

References:
Theoretical Study of Gas Phase Tautomerization Reactions for the Ground and First Excited Electronic States of Adenine

Latasha M. Salter a,b and Galina M. Chaban c

aTougaloo College, 500 West County Line Road, Tougaloo, Mississippi 39174
bDepartment of Chemistry and Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217
cNASA Ames Research Center, Mail Stop T27B-1, Moffett Field, California 94035-1000

Geometrical structures and energetic properties for different tautomers of adenine are calculated in this study, using multi-configurational wave functions. Both the ground and the lowest singlet excited-state potential energy surface are studied. Four tautomeric forms are considered, and their energetic order is found to be different on the ground and the excited state potential energy surfaces. Minimum energy reaction paths are obtained for hydrogen atom transfer (tautomerization) reactions in the ground and the lowest excited electronic state. It is found that the barrier heights and the shapes of the reaction paths are different for the ground and the excited electronic state, suggesting that the probability of such tautomerization reaction is higher on the excited state potential energy surface. This tautomerization process should become possible in the presence of water or other polar solvent molecules and may play an important role in the photochemistry of adenine.
Ultrafast Auger Spectroscopy of Quantum Well Excitons in Strong Magnetic Field

Tigran Shahbazyan

Department of Physics, Jackson State University, Jackson, MS 39217

We study theoretically the coherent ultrafast dynamics of quantum well excitons in strong magnetic field. We address the role of many-body correlations originating from inter-Landau level (LL) transitions. In the linear response, the processes involving transitions between different LL's are suppressed due to a large LL separation. Our main observation is that, in strong magnetic field, the nonlinear optical response is dominated by resonant Auger processes: e.g., two electrons, excited to n=1 LL, can scatter to n=0 and n=2 LL's. We perform numerical calculations for the third-order four-wave-mixing (FWM) polarization which incorporate the Auger processes nonperturbatively. We find, in particular, that the time-integrated FWM signal at negative time delays exhibits oscillations with period determined by the characteristic interaction energy.
The Molecular Structures and Nature of Interactions in N$_2$H$^+$-X$_n$ (X = He, Ne, n = 1 - 17) Complexes

Yinghong Sheng, Szczepan Roszak, and Jerzy Leszczynski

1 The Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, 1400 J. R. Lynch Street, Jackson, Mississippi 39217
2 Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyspianskiego 27, 50-370 Wrocław, Poland

The N$_2$H$^+$-X$_n$ (X=He, Ne) complexes were investigated for n up to 17. The molecular structures were optimized without any structural constraint using the second-order Möller-Plesset (MP2) perturbation level of theory. The harmonic vibrational frequencies were obtained at the same level of theory. The coupled cluster theory including single and double substitutions and non-iterative triplet contributions CCSD(T) method was also applied for complexes with n up to 6.

The N$_2$H$^+$-X (X=He, Ne) dimers have linear proton-bound structures, and further He or Ne ligands fill three equatorial solvation rings around the linear dimer core, each of them containing up to five rare gas atoms. Unlike their analogues N$_2$H$^+$-X (X=Ar, H$_2$) in which the first salvation shells are composed of 12 argon or hydrogen molecule, the first solvation shells of N$_2$H$^+$-X (X=He, Ne) are completed when the 17th helium or neon atoms are attached.

The change of the calculated dissociation energies, and vibrational frequencies is related to the increasing size of the studied complexes. The nature of interactions is discussed by analyzing the charge distribution and the energy decomposition scheme.
An \textit{ab initio} Study of Non-Classical Purine Interactions of tRNA

Tomekia Simeon, Glake Hill, Gareth Forde, and Jerzy Leszczynski

\textit{The Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, 1400 J. R. Lynch Street, Jackson, Mississippi 39217}

In DNA, it is solely the hydrogen bonding of base pairs in Watson-Crick formation that keeps the polynucleotide chains of the double helix aligned. On the other hand, non-classical base pairing is significant to the 3-dimensional structure of tRNA. Moreover, tRNA binds to a number of different codons specifying the same amino acid. This observation is explained by the non-classical “wobble hypothesis”. According to this model, the first two codon-anticodon pairings follow the standard Watson-Crick base-pairing. However, the third pair can exhibit a certain amount of play or wobble, enabling a variety of specific non-Watson-Crick weak pairings. Weak interactions in tRNA are the central point in studying non-classical base-pairing. This study will provide insight into the wobble type base pair interactions of tRNA which could be parallel to previous studies of DNA. Our purine binding comparison will determine factors regulating tRNA structure and function. Nucleic acid structure moieties were calculated at the Hartree Fock level using the Gaussian program.
Applications of the Theory of Intermolecular Interactions in Molecular Modeling

W. Andrzej Sokalski

Molecular Modeling Laboratory, Institute of Physical & Theoretical Chemistry I-30
Wrocław University of Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland

Numerous properties of matter essential in nanotechnology, materials science, biotechnology, catalysis, molecular biology or pharmacology are determined by intermolecular forces. Precise knowledge of the physical nature of such interactions opens the possibility to derive entire hierarchy of approximate theoretical models aiding rational design of new materials, drugs, pesticides, catalysts, adsorbents, etc.

The utility of various currently available methods used for calculations of intermolecular interaction energy components will be briefly reviewed. Hybrid variation-perturbation approach [1-2] enabling nonempirical analysis of interactions in relatively large molecular systems of practical interest, like enzyme [3-4] or zeolite [5] active sites, will be presented in more detail. The same concerns more approximate models based on multicenter multipole expansion applicable in macromolecular systems with dominant electrostatic effect [6].

Sample applications of various approximate theoretical models in crystal packing simulations [7] and drug design [4,8] will be discussed more extensively.

References
The Effects of Non-Classical Triad Binding on Watson-Crick GC Interactions in t-RNA

Chi-Cobi Speaks, Tomekia Simeon, Glake Hill, Gareth Forde, Jerzy Leszczynski

Department of Chemistry, Jackson State University, Jackson, Mississippi 39217

The nucleic acids, long-chain polymers of nucleotides, are made up of sugar, phosphoric acid, and several nitrogen-containing bases. The sugar in nucleic acid can be ribose or deoxyribose, giving two forms: RNA and DNA. The molecules guanine and cytosine were bonded together to form triple hydrogen bonds. Base pairs should be used with guanine and cytosine because they are favorable for combining with each other. Transfer RNA includes four standard nucleotides which are adenine, uracil, guanine, and cytosine. This gives some explanation as to why we use t-RNA. The methods that were used to describe this project were to learn, understand, and draw the structure and elements that pertain to guanine and cytosine. In computational chemistry the research is targeted at molecules by calculating their characteristics using the basic laws of quantum mechanics and experimental knowledge. These molecules are part of the reason why we use computational chemistry. With this project I hope to achieve the best satisfaction of knowing that this was a successful experimentation of chemistry. Also that I have learned, understood, and retained the information that I have collected for this project.
We describe two different approaches to exploiting parallel computing architectures that have been used successfully for reactive molecular simulation using bond-order potentials. These potentials are based on the Tersoff bond-order formalism, and allow accurate treatment of covalent bonding reactions in the framework of a classical potential. They include Brenner’s reactive empirical bond order (REBO) potential and Stuart’s adaptive intermolecular version of this potential (AIREBO). Traditional spatial- and atom-based parallel decomposition techniques have been employed in the RMD-CE program developed for parallel molecular dynamics simulations with a variety of reactive potentials. Key features of this implementation, including the object-oriented approach and novel algorithms for the integrator and pair lists will be discussed. The resulting code provides efficient scaling down to system sizes of ~400 atoms per processor, and has been applied to systems of half a million atoms. For smaller systems, Voter’s parallel replica dynamics algorithm has been successfully applied to take advantage of parallelism in the time domain for rare-event systems. This approach takes advantage of the independence of different parts of a dynamics trajectory, and provides excellent parallel efficiencies for systems as small as tens of atoms, where other parallel simulation techniques are not applicable. This technique has been used to model the pyrolysis of hexadecane for timescales of microseconds, at more realistic temperatures than are achievable with other simulation methods.
Structure and Property of Polyhydrated Complexes of Guanine: A Density Functional Study

Oleg S. Sukhanov, a,b Oleg V. Shishkin, a,b Leonid Gorb, b and Jerzy Leszczynski b

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bComputational Center for Molecular Structure and Interactions, Department of Chemistry Jackson State University, P.O. Box 17910, 1325 Lynch Street, Jackson, MS 39217 USA

Structure and properties of the polyhydrates of Guanine, containing 12, 13, 14, 16 and 17 water molecules, are investigated at the B3LYP/6-31G(d,p) level of theory, using topological analysis of the electron density distribution and the NBO (Natural bond orbital) theory.

Fig. 1 The structure of Guanine surrounded by 12 water molecules.

The following issue are discussed.

1) The influence a hydration shell on geometry and electron density distribution in Guanine molecule.
2) The nature and specific of the hydrogen bonds.
3) Thermodynamic properties of considered complexes.
4) Effect of water environment (IPCM “Isodensity surface polarized continuum” models) on the character of hydrogen bonds in polyhydrates of Guanine.
5) The possibility the formation of unusual hydrogen bonds of the following type: OH…N(3)...HO, OH…N(7)...HO, OH…π, C-H…O and N(H 2)...H-O.
Molecular Properties of Protonated Homogenous and Mixed Carbon Oxide and Carbon Dioxide Clusters

Jaroslaw J. Szymczak$^{1,2}$, Szczepan Roszak$^{1,2}$, and Jerzy Leszczynski$^1$

$^1$The Computational Center for Molecular Structure and Interactions Department of Chemistry, Jackson State University, 1400 J.R. Lynch Street, P.O. Box 17910, Jackson, Mississippi 39217
$^2$Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland

The molecular structures and characteristics of CO and CO$_2$ protonated homogenous and mixed complexes were studied by theoretical, \textit{ab initio} calculations. The study reveals similarities and differences between homogenous protonated carbon oxide and protonated carbon dioxide clusters. The structural differences between (CO)$_n$H$^+$ and (CO$_2$)$_n$H$^+$ clusters are the consequence of the symmetry of protonated dimers – constituting the cationic core of clusters. The OCH$^+$ as well as OCOH$^+$ fragments are stabilized by the cluster formation. The structures and energetics of complexes emerge as a balance between competing electrostatic, exchange, and covalent interactions. The directional covalent forces prevail and enforce the structure of complexes, however.
Modeling of the Zn\(^{2+}\) and Mn\(^{2+}\) Aquacomplexes Electroreduction Reaction

V.F. Vargalyuk, V.A. Seredyuk

Dnepropetrovsk National University, Department of Chemistry, Dnepropetrovsk, Ukraine

Electrochemical reactions of d-metal aquacomplexes are considered to be the most widely spread in theoretical and applied electrochemistry. Numerous experimental data show that a part of ions is reduced to metals comparatively easily (Cu\(^{2+}\), Pb\(^{2+}\), Zn\(^{2+}\) and others), while the reduction of Cr\(^{3+}\), Mn\(^{2+}\), Fe\(^{2+}\) ions out of aqueous solutions is much more complicated.

Quantum-chemical modeling of the reaction

\[
\text{Me}^{2+} \cdot \text{aq} + e^- \rightarrow (\text{Me}^+) \cdot \text{aq} \rightarrow \text{Me}^+ \cdot \text{aq}
\]

\[
\text{Me}^+ \cdot \text{aq} + e^- \rightarrow (\text{Me}^0) \cdot \text{aq} \rightarrow \text{Me}^0 \cdot \text{aq}
\]

for Mn\(^{2+}\) and Zn\(^{2+}\) ions as the typical representatives of these ion groups has been carried out.

The calculated system contains a metal ion surrounded by 32 water molecules. Electrons were introduced in succession into the system until a full [Me\(_m\)\(^{2+}\)] cation reduction. The total interaction energy of all the particles making up the (E, kcal/mol) system, this energy gradient on the reaction route coordinate, coordinates of all the atoms and effective charge on them (Z) were determined. The investigation was carried out by way of computer modeling with GAMESS program being used. The system was calculated at unrestricted Hartree-Fock level of theory using 3-21G basis set. In the process of calculation, arbitrarily oriented solvent molecules were placed around the cation being in the +2 oxidation degree. Then the system was optimized. The obtained coordinates of the systems optimized were the initial approximations for the calculations on the next stage of electroreduction.

Besides, transitional complexes with structural starting (marked with an asterisk) were calculated. These structures appear at the moment of electron transition when the atom nuclei have not changed their position yet.

**Figure.** Energy diagram of Me(H\(_2\)O)\(_m\)\(^{2+}\) + 2e\(^-\) = Me(H\(_2\)O)\(_n\) reaction route.
The analysis of the calculation results shows that Mn\(^{2+}\) ions form, together with water, solid (\(\Delta H = -52.62 \text{kcal/mol}\)) complexes their structure practically does not change during the reaction. Zinc, *vice versa*, being in +2 condition, connects with water into tetrahedral complex (\(\Delta H = -36.72 \text{kcal/mol}\)) which is transformed, after electron being transmitted on it, into \([\text{Zn(H}_2\text{O)}_3]^+\) pyramidal structure. The latter is preserved at the stage of formation of formally zero-valent Zinc complexes.

The comparison of energy diagrams of Zinc and Manganese aquacomplexes electroreduction reaction routes (Figure) reveals the number of peculiarities. Electron transition on \([\text{Mn(H}_2\text{O)}_6]^2+\) particle results in energy increasing of the system, while \([\text{Zn(H}_2\text{O)}_4]^2+\) one-electron discharge occurs without energy effects. Thus, the probability of Mn\(^{2+} + \text{e}^- \rightarrow \text{Mn}^+\) reaction should be considerably less than that of Zn\(^{2+} + \text{e}^- \rightarrow \text{Zn}^+\) reaction.

**Table.** The change of central ion and aquacomplex charge in Me\((\text{H}_2\text{O})_m\)^\(^{2+} + 2\text{e}^-\) reaction

<table>
<thead>
<tr>
<th>Central atom</th>
<th>Mn(^{2+})</th>
<th>(Mn(^{+}))^*</th>
<th>Mn(^{+})</th>
<th>(Mn(^{0}))^*</th>
<th>Mn(^{0})</th>
<th>Zn(^{2+})</th>
<th>(Zn(^{+}))^*</th>
<th>Zn(^{+})</th>
<th>(Zn(^{0}))^*</th>
<th>Zn(^{0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z(Me)</td>
<td>0.529</td>
<td>-0.475</td>
<td>-0.404</td>
<td>-1.295</td>
<td>-1.176</td>
<td>0.472</td>
<td>-0.169</td>
<td>-0.084</td>
<td>-0.850</td>
<td>-0.763</td>
</tr>
<tr>
<td>Z(Me(H(_2\text{O})_m))</td>
<td>0.790</td>
<td>-0.161</td>
<td>-0.128</td>
<td>-0.969</td>
<td>-0.812</td>
<td>0.655</td>
<td>-0.004</td>
<td>0.081</td>
<td>-0.513</td>
<td>-0.402</td>
</tr>
</tbody>
</table>

The lower value of relaxed Zn\(^{+}\) aquacomplex energy in comparison with that of (Zn\(^{0}\))^* aquacomplex points out that in the process of Zn\(^{2+}\) aquacomplexes electroreduction in the region of small polarization, Zn\(^{+}\) ions may be accumulated in the system in a noticeable amount. The electrolysis rate being high,

\[
(Zn^{+})^{*}\cdot \text{aq} + \text{e}^- \rightarrow (Zn^{0})^{*}\cdot \text{aq},
\]

reaction should dominate because its kinetic ability is considerably higher than that of \(\text{route. (Zn}^{+})^{*}\cdot \text{aq} \rightarrow Zn^{+}\cdot \text{aq, Zn}^{+}\cdot \text{aq} + \text{e}^- \rightarrow (Zn^{0})^{*}\cdot \text{aq.}
\]

The instability of structures, which appear in Manganese aquacomplexes, is revealed by the way the charge is being distributed in them. As it can be seen from the Table, Mn\(^{2+}\) cation is characterized by high ability to charge accentuation. The transition of two electrons here results in Z (Me) changes by 1.705 e. For comparison, \(\Delta Z(\text{Me})\) for Zinc makes up 1.235 e. Besides, the charge of all Mn\((\text{H}_2\text{O})_6\)^0 aquacomplex is twice as big as that of Zn\((\text{H}_2\text{O})_3\)^0 aquacomplex: -0.812 and -0.402 correspondingly.
Interactions of Fasciculin 2 with AChE: A DFT-Based Molecular Dynamics and Quantum Chemical Study

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Acetylcholinesterase (AChE) is an especially efficient serine hydrolase to terminate synaptic transmission at cholinergic synapses through catalyzing the breakdown of the neurotransmitter acetylcholine (ACh). It has an active site gorge with the depth of 20 Å, which has two separate ligand binding sites: the acylation site and the peripheral site. The acylation site lies at the bottom of the gorge, containing a catalytic triad (H440, E327, and S200). The peripheral site locates at the entrance of the gorge, including residue W279.

Fasciculin 2 (FAS2), a peptidic three-finger snake toxin (61 residues) from green mamba venom, is found to be a neurotoxin inhibitor of AChE. The crystal structure of AChE binding with FAS2 reveals that FAS2 caps the entrance of the gorge with excellent complementarity and many polar and hydrophobic interactions.

Site-specific mutant studies indicate that W279 on the rim of the active site gorge is a key component of the peripheral site and is essential for high-affinity FAS2 binding. Accordingly, two models were selected from the crystallographical structure (with code 1FSS in the Protein Data Bank), for AChE and for FAS2 bounded AChE, respectively. A Model contains only the selected fragment of AChE, including residue W279 with its neighbouring negative charged residue E278. B Model adds residue P31 of FAS2 compounded to the A Model (Fig. 1).

![Models selected for simulations](image)

Fig. 1 Models selected for simulations
Applying DFT-based molecular dynamics approaches, the two models are simulated at the simulated temperature of 300K. During the simulation processes, A Model was noticed to poorly retain its initial structure chosen from the crystal data. The peptide chain rotated easily, resulting in the considerable change of the relative orientation for residue W279 and E278. For B Model with the FAS2’s binding, the structure of the AChE moiety appeared to be less flexible. The relative orientation of W279 and E278 remained almost the same as the initial structure while a proton transfer was observed from the N6 of W279 to the O2 of E278, leading to an intramolecular hydrogen bond between H41 and O2, which stabilized the AChE moiety.

Based on the molecular dynamics results of the two models, the FAS2 moiety and the AChE moiety are fully optimized using the B3LYP/6-311G(d,p) level of theory. Vibrational frequency analyses which reveal no imaginary frequency suggests that both species are energy minima on the potential energy surface. For the AChE moiety, the atomic distance between H41 and O3 is predicted to be 1.55 Å, suggesting a strong H-bonding interaction between W279 and E278. The molecular structures, energies and the electrostatic potential are depicted in Figure 2. The binding energy of FAS2 and AChE will be further characterized.

**Fig. 2** Optimized structures and electrostatic potential maps (mapping onto the surface of the electron density of 0.002 unit) for AChE and FAS2 moiety. (The data in bracket are energies in a.u., at B3LYP/6-311G(d,p) level of theory.)
Molecular Structure, Vibrational Frequencies, Energetics, and Excited States of the HOONO\(^{+}\) Ion

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Equilibrium geometries have been optimized and harmonic vibrational frequencies obtained for neutral peroxynitrous acid (HOONO) and its cation employing quadratic configuration interaction and coupled-cluster methods with correlation-consistent basis sets. The lowest energy structure of HOONO\(^{+}\) is a planar conformer on the \(^{2}\)A\(^{'}\) potential energy surface with a cis-trans arrangement \(\tau(OONO) = 0^\circ\) and \(\tau(HOON) = 180^\circ\). This is quite the opposite from neutral HOONO, which prefers a cis-cis arrangement because of hydrogen bonding. The adiabatic ionization potential for HOONO is predicted to be 260.0 ± 1 kcal mol\(^{-1}\) (11.3 eV) at the estimated complete basis set limit. Planar ion-molecule complexes formed from the ground states of HO\(_{2}\) and NO\(^{+}\) have been located on the \(^{2}\)A\(^{''}\) surface. The binding energy of the most stable complex is estimated to be 18.1 ± 1 kcal mol\(^{-1}\) at the complete basis set limit. Excited states of the HOONO\(^{+}\) ion were calculated with quasi-restricted Hartree-Fock and unrestricted Hartree-Fock coupled-cluster methods including connected triple excitations.
Molecular Dynamics Studies of Interactions between Calcium–Containing Crystals and Phospholipid Membranes

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In the past it has been shown that calcium-containing crystals may bind to several types of cells. This binding often leads to pathological conditions, frequently resulting in cell damage. The nature of the crystal-cell interaction is of considerable interest since the understanding of the mechanism of the crystal-cell sticking can be used in developing inhibitors that would diminish the adhesion of calcium-containing crystals to cells. It has been proposed that cell adhesion occurs due to interactions between calcium-containing crystals and phospholipid membranes.

In this study using the methods of CHARMM molecular dynamics, we investigate the molecular mechanism of crystal-induced membranolysis. We show that the interactions between the surface of Calcium Pyrophosphate Dihydrate Crystal (CPPD) and the extracellular layer of the hydrated dimyristoyl phosphatidylcholine (DMPC) phospholipid bilayer may lead to decoupling of this external layer from the intracellular side of the membrane. In turn, a local thinning of the layer on the intracellular side of the membrane occurs which favors water penetration of this layer, leading to membranolysis.
The Effects of cis-Pt(LH3)2Cl2 (L = N, P, As) on the Structure of Nucleic Acid Bases

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In 1959, Dr. Bartlett Rosenberg changed the history of the cancer drug through his discovery of a square planar compound called cisplatin. Cisplatin is well established to bind to DNA [1-6], thereby causing damage and subsequently cell death. Its main positions of binding are the O6, N7 sites of guanine and/or the N7, N7 sites on two adjacent guanines of the DNA strand [7]. Crystal structures have shown that this linkage causes significant structural abnormalities in the DNA chain. In this study, we examine the role that the ammine leaving group plays in the overall properties of cisplatin. We also examine this ligand effect on subsequent guanine binding. Lastly, we examine the electronic properties of such binding to develop theories as to the significance of the ammine group.

Quantum Transport in Nanostructures

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The main feature of electronic devices is that they are open systems with respect to electron flow. A theoretical consideration of such devices should be done in terms of statistically mixed states which address the problem to quantum kinetic theory [1].

A review of contemporary developments in the computational approach to quantum transport theory is presented.

An application of *ab initio*, semiempirical and model schemes to C\textsubscript{60}, adenine-thymine DNA base pair and benzene-1,4-dithiolate molecule is discussed

MCSCF Study of the Thermal Isomerization of Quadricyclane to Norbornadiene

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The isomerization of quadricyclane to norbonadiene was investigated using ab initio calculations at MCSCF theory level. Single point energy corrections were performed with MCQDPT2 and CCSD(T) methods. The isomerization process was found to proceed through a concerted, asynchronous pathway characterized as a disrotatory ring opening of the cyclobutane moiety. The activation energy was calculated to be 32.9 kcal/mol. A multiconfigurational wavefunction is necessary to describe the reaction path on the potential energy surface correctly because of the biradical character of the transition state.