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Computational Thermochemistry and Benchmarking of Reliable Methods

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April 2006

MSCF
Molecular Science Computing Facility

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Number of hours allocated for the past three years

- FY99: 600,000 node hours
- FY00: 600,000 node hours
- FY01: 600,000 node hours

Number of hours actually used in the past three years

- FY99: 494,591 node hours
- FY00: 504,433 node hours
- FY01: 470,117 node hours

Overview of the past three years' accomplishments and activities

During the first and second years of the Computational Thermochemistry and Benchmarking of Reliable Methods project, we completed several studies using the parallel computing capabilities of the NWChem software and Molecular Science Computing Facility (MSCF), including large-scale density functional theory (DFT), second-order Møller-Plesset (MP2) perturbation theory, and CCSD(T) calculations. The calculations performed on the IBM SP housed in the MSCF have led to a number of publications (see listing below). Topics of these publications include:

- a study of the binding energy of a water molecule to single-layer graphite
- predictions of the heats-of-formation of furan, tetrahydrofuran (THF) and several THF-derived radicals
- a study of the binding energies of the alkali cations to 15-crown-5
- a conformational study of 9-thiacrown-3, 12-thiacrown-4, 15-thiacrown-5, and 18-thiacrown-6
- a study of the binding energies of the alkali cations to benzene
- continued studies in computational thermochemistry.

Many of these studies share a common goal: to reliably calculate a property (*e.g.*, a total dissociation energy) near the complete basis-set limit, where the error associated with the use of a finite Gaussian basis-set expansion goes to zero. Our approach is to use coupled-cluster theory with single and double excitations and a perturbative correction for the triples (CCSD(T)) to treat the n-particle problem in conjunction with extrapolations to the complete basis set limit of correlation-consistent basis sets to treat the 1-particle problem. For chemical systems that can be qualitatively described by a single configuration wavefunction, such as the molecules examined in the present study, CCSD(T) is an excellent method for recovering a significant fraction of valence correlation energy when combined with large basis sets. We obtained initial energetics within the frozen core (FC) approximation in which the inner shell electrons of the carbon and fluorine 1s orbitals are excluded from the correlation treatment. Nonetheless, even with such large basis sets, the errors in thermodynamic properties can still be unacceptably large. Attacking the residual basis set truncation error via brute-force techniques is usually not practical. Fortunately, the convergence of the total energies derived from the correlation-consistent basis sets is sufficiently uniform to warrant some type of extrapolation to the complete basis set (CBS) limit. Having estimated total energies at the CCSD(T)(FC)/CBS level of theory, we then included a number of additional corrections to account for core/valence , atomic spin-orbit, and molecular scalar relativistic effects. Zero-point vibrational energies were also carefully considered. The effect of higher-order correlation contributions to diatomic dissociation energies was measured in a study that required the estimation of full-configuration interaction energies for a collection of three molecules using nontrivial basis sets.

During the third year, we continued to pursue the computational thermodynamic and benchmarking studies outlined in our proposal. With the issues affecting the robustness of the coupled cluster part of NWChem resolved, we pursued studies of the heats-of-formation of compounds containing 5 to 7 first- and/or second-row elements and approximately 10 to 14 hydrogens. The size of these systems, when combined with the large basis sets (cc-pVQZ and aug-cc-pVQZ) that are necessary for extrapolating to the complete basis set limit, creates a formidable computational challenge, for which NWChem on NWMPP1 is well suited. We explored other molecular torsional potentials as well as weak hydrogen bonds from C-H to acceptors such as O and N. We will continue our DFT, MP2, and CCSD(T) studies of the hydrocarbon isomer, $C_nH_{(2n+2)}$, and then move on to n=6-8 systems using local and gradient-corrected functionals as time permits. With the new CCSD(T) code in NWChem, we hope to be able to study larger radicals and examine the β-scission of CH_3CHO* and CF_3CHFO* and several radical reactions of hydrocarbons. In addition, we will continue our studies of alkali metal cation/ligand complexes and fluoride affinity studies (*i.e.*, the generation of the Lewis acidity scale). In terms of the project focused on obtaining high-accuracy binding energies for water to graphite and, ultimately, single-walled, carbon-based nanotubes, we plan to begin MP2 calculations on the actual water/nanotube system. Although the quality of the basis sets used in this study will normally not reach the level used in the thermochemical calculations on small organic compounds, the overall size of the system (*i.e.*, the total number of atoms) will make these some of the largest correlated calculations ever attempted.

The binding energy of water to single-layer graphite

As a first step toward understanding how molecular processes are altered inside a nanotube, we have begun to develop molecular models for carrying out reliable computer simulations of water in nanotubes (Figure 1). For this purpose, it is essential to develop good water-nanotube classical force fields for use in classical molecular dynamics or Monte Carlo simulations. Unlike the situation with water-water potentials, where the state-of-the-art is well advanced, the literature contains no high-quality water-nanotube potentials. Since the interior of nanotubes is characterized by a large surface area/volume ratio, and preliminary electronic structure calculations (Feller and Jordan, 2000) show the fundamental interaction between a single water molecule and graphite is on the order of 6 kcal/mol (compared with 5 kcal/mol for water-water), it appears essential to describe the interaction between the solvent and the walls of the tube accurately. Because of the scarcity of experimental data, high-quality electronic structure calculations must be used to develop the force fields. Calculations on various-sized single-layer graphite fragments (up to $C_{96}H_{24}$) with basis sets as large as quadruple-*zeta* demonstrate both the accuracy of a second-order perturbation theory and the computational feasibility of the approach on massively parallel computers (Figure 2).

Reference

Feller D and KD Jordan. 2000. "Estimating the Strength of the Water/Single-Layer Graphite Interaction." *Journal of Physical Chemistry A* 104(44):9971-9975, DOI: 10.1021/jp001766o.

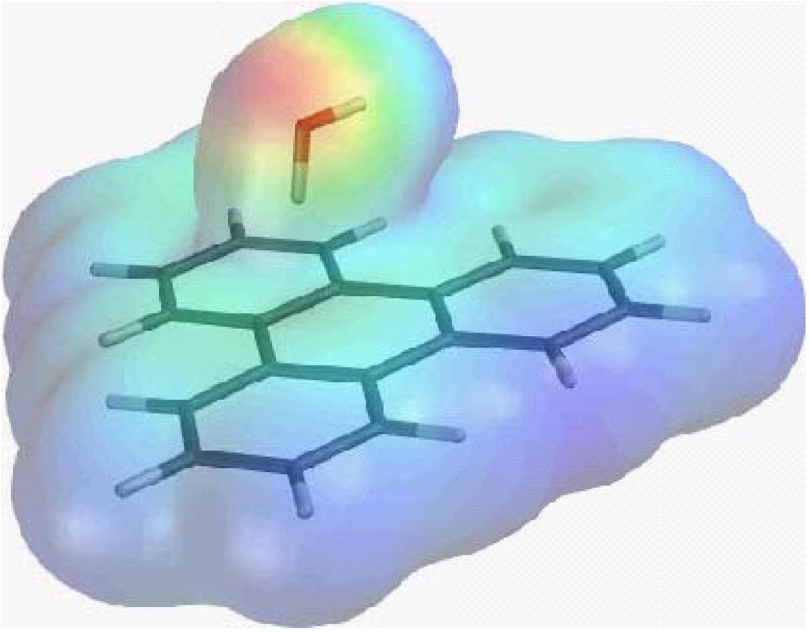


Figure 1. The electrostatic potential of water as it binds to a fragment of single-layer graphite.

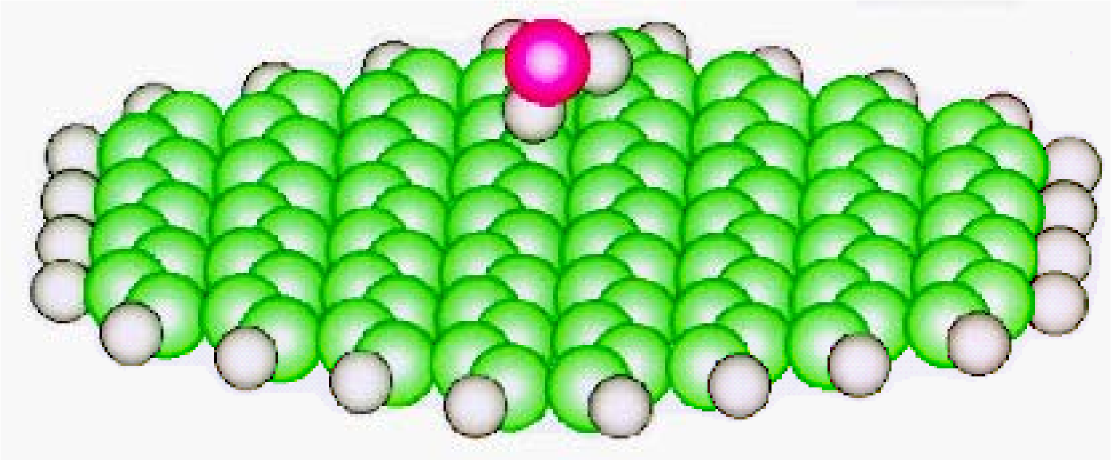


Figure 2. Water binding to $C_{96}H_{24}$, the largest graphite fragment for which MP2 calculations were run.

Heats-of-formation of furan, tetrahydrofuran (THF), and several THF-derived radicals

The free-radical reactivity of tetrahydrofuran (THF) is of interest as a prototype for the reactivity of cyclic ethers of biological importance in radical-induced oxidation reactions. Large basis-set coupled-cluster calculations, with corrections for core/valence, atomic spin-orbit, and scalar relativistic effects, have been used to determine the atomization energies of furan ($^1A_1$, C_4H_4O), tetrahydrofuran (^1A, C_4H_8O), and the THF-2-yl (^2A, C_4H_8O) and THF-3-yl (^2A, C_4H_8O) radicals (Figure 3). For furan and tetrahydrofuran, where gas-phase experimental data are available, the level of agreement between experiment and theory is very good. The 0-K heats-of-formation for the four systems are:

- ΔH_f(furan)= -4.6±0.5 (calc.) vs. -5.2±0.2 (expt.)
- ΔH_f(tetrahydrofuran)= -37.6±0.7 (calc.) vs. -37.6±0.2 (expt.)
- ΔH_f(THF-2-yl)= 5.1±1.0 (calc.)
- ΔH_f(THF-3-yl)= 8.9±1.0 (calc.).

At 298K, the comparable values are:

- ΔH_f(furan)= -7.7±0.5 (calc.) vs. -8.3±0.2 (expt.)
- ΔH_f(tetrahydrofuran)= -44.0±0.5 (calc.) vs. -44.0±0.2 (expt.)
- ΔH_f(THF-2-yl)= -0.5±1.0 (calc.)
- ΔHϕ(THΦ−3−ψλ)= 3.6±1.0 (χαλχ.).

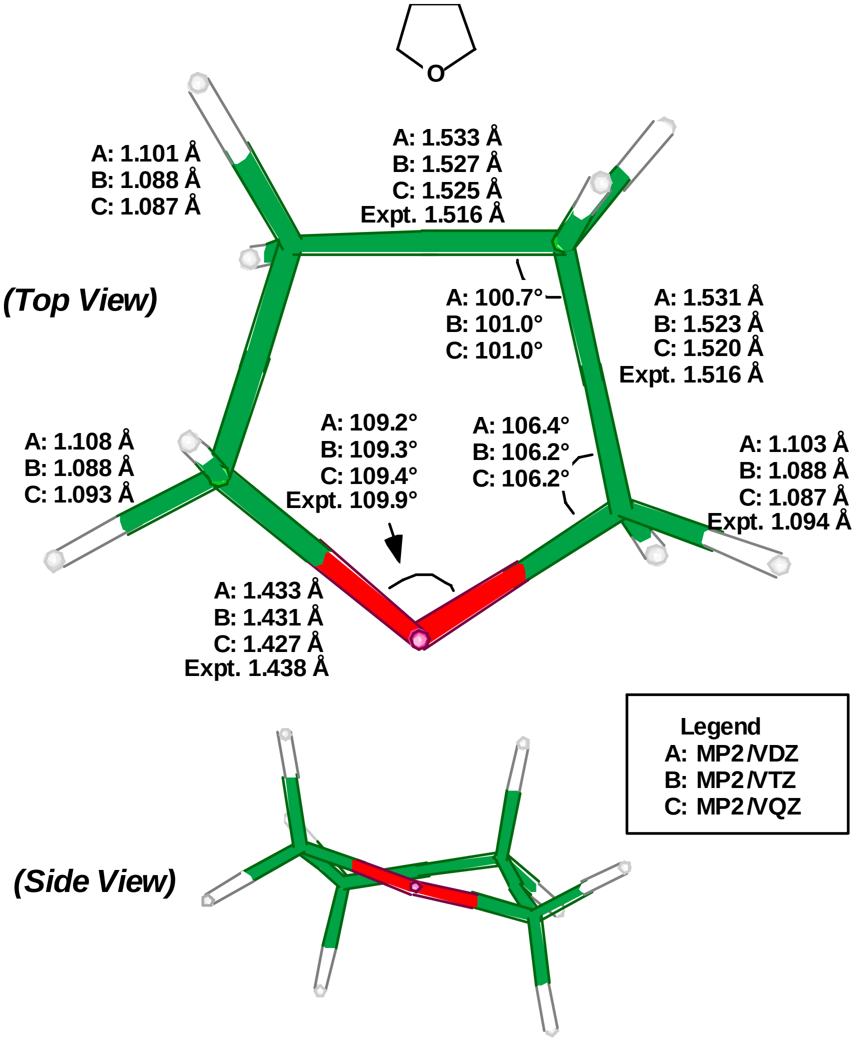


Figure 3. The optimized structure of tetrahydrofuran.

Binding enthalpies of the alkali cations to benzene

The binding enthalpies of metal cation-benzene complexes using the alkali cations Li, Na, K, Rb, or Cs, have been the subject of several gas-phase experimental and theoretical studies. These studies have been motivated by the importance of alkali cation-ligand interactions in chemically related systems of biological or chemical separations importance. In the case of Na^+(benzene), which is the most extensively studied of the complexes, the strength of the interaction exceeds that of the corresponding interaction in $Na^+(H_2O)$, despite the presence of a substantial dipole moment in water and the lack of a permanent dipole in benzene. The geometries and binding enthalpies of the metal cation-benzene complexes with Li, Na, K, Rb, or Cs, were obtained from large basis-set, second-order perturbation theory and coupled-cluster theory calculations (Figure 4). The best ΔH_{298} estimates (in kcal/mol) are:

- Li^+(benzene)=-35.5±0.2 (theory) vs. -37.9 (expt.)
- Na^+(benzene)=-24.7±0.3 (theory) vs. -28.0±1 and -21.5 (expt.)
- K^+(benzene)=-20.1±0.4 (theory) vs. -19.2 (expt.)
- Rb^+(benzene)=-16.4±0.2 (theory)
- Cs^+(benzene)=-12.5±0.2 (theory).

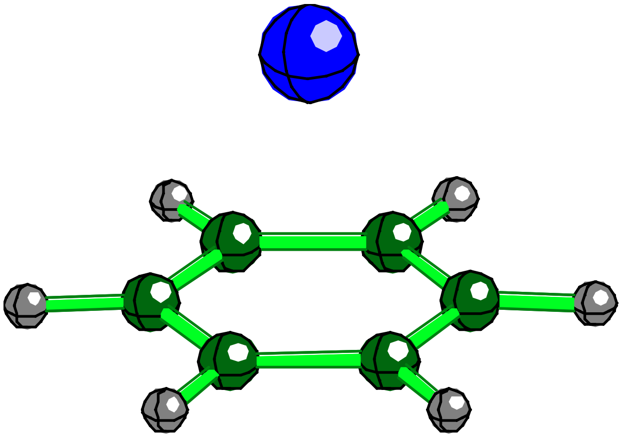


Figure 4. The optimized structure for K^+(benzene) from large basis-set MP2 calculations.

Binding enthalpies of the alkali cations to 15-crown-5

A combination of classical force-field molecular dynamics and electronic structure calculations were used to identify the low-lying, gas-phase conformations of isolated 15-crown-5 and the complexes it forms with a single alkali cation (Li^+, Na^+, K^+, Rb^+, and Cs^+; Figure 5). The computed binding enthalpies are compared with recent gas-phase, collision-induced dissociation measurements. While agreement is reasonably good for sodium and potassium, it worsens for the larger cations, where theory and experiment differ by as much as 20 kcal/mol. Tests of the sensitivity of the predicted binding enthalpies to the size of the basis sets were conducted with large, diffuse-function-augmented, correlation consistent basis sets. Despite the increase in size and flexibility of the basis sets, they resulted in relatively little change in the computed binding energies. A possible explanation of these differences, first proposed for alkali cation complexes with 12-crown-5, is discussed. It assumes that the experiment measures dissociation from higher-lying metal/ether complexes, rather than the global minimum, which serves as the reference point for the theoretical values. However, a limited search for a much higher-energy Rb^+(15-crown-5) structure proved unsuccessful.

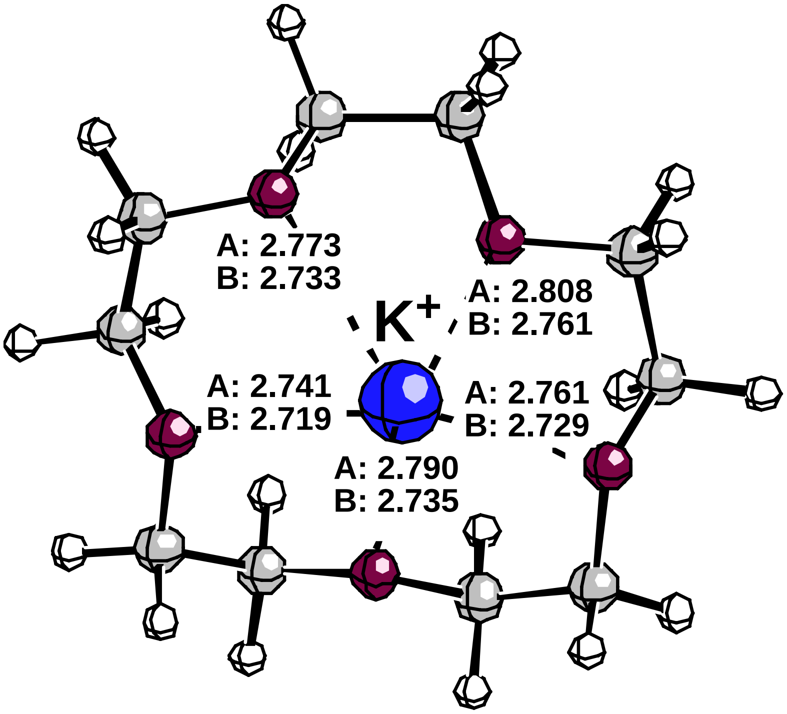
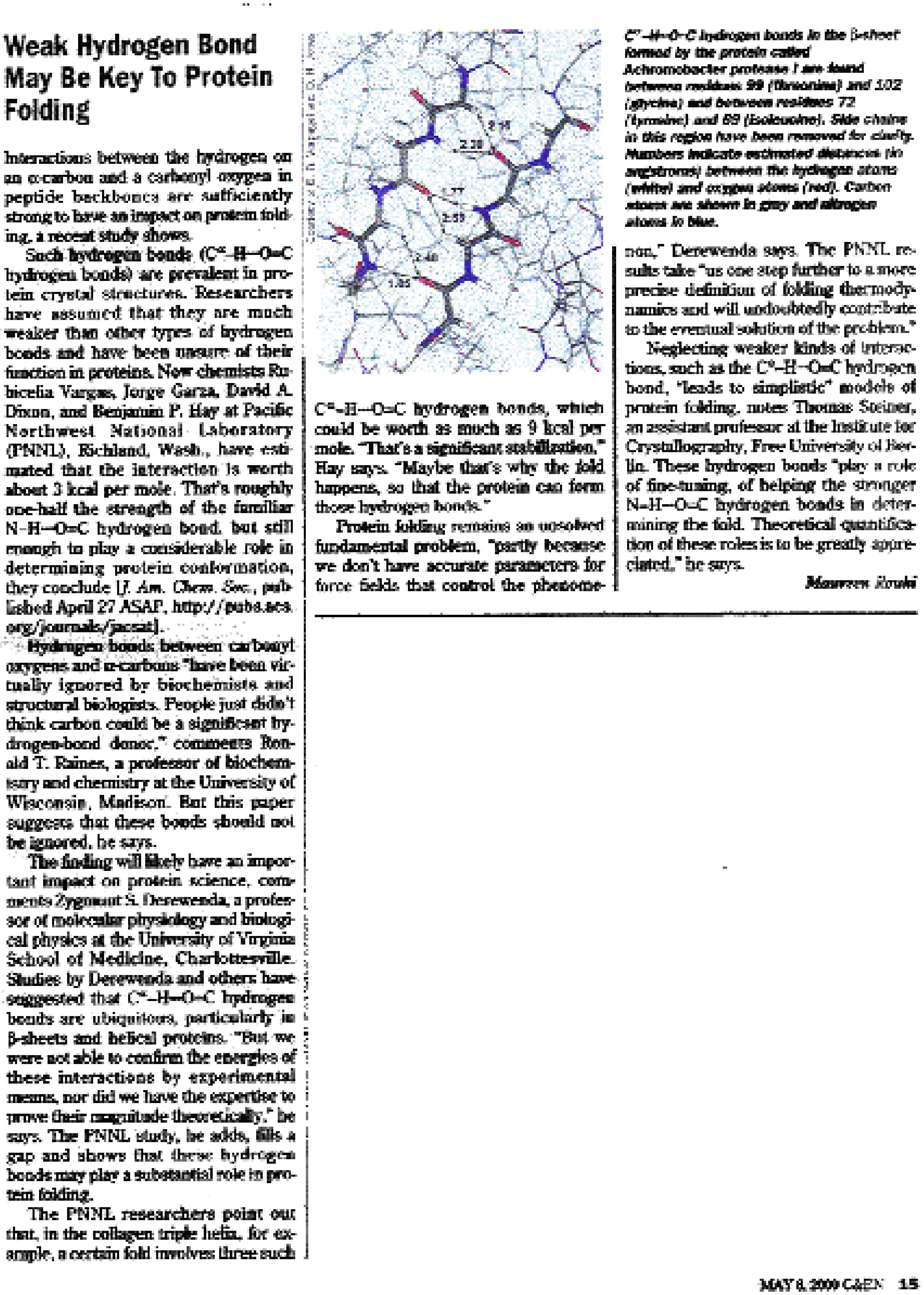


Figure 5. The optimized geometry of K^+(15-crown-5).

Study of C-H···O hydrogen bonds in N,N'-dimethylformamide dimers

Although the existence of C^{α}-H···O hydrogen bonds in protein structures recently has been suggested, little is known about their strength and, therefore, the relative importance of these interactions. We have found that similar interactions occur in N, N-dimethylformamide dimers. High-level *ab initio* calculations (MP2/aug-cc-pVTZ) yield electronic association energies (D_e) and association enthalpies (ΔH^{298}) for four dimer geometries. These data provide a lower limit of D_e=2.1 kcal/mol for the C^{α}-H···O=C hydrogen bond. A linear correlation between C-H···O bond energies and gas-phase proton affinities was found. The gas-phase anion proton affinity of a peptide C^{α}-H hydrogen was calculated (355 kcal/mol) and used to estimate values of D_e=-4.0±0.5 kcal/mol and ΔH^{298}=-3.0±0.5 kcal/mol for the C^{α}-H···O=C hydrogen bond. The magnitude of this interaction, roughly one-half the strength of the N-H···O=C hydrogen bond, suggests the C^{α}-H···O hydrogen bonding interactions represents a hitherto unrecognized, significant contribution to the determination of protein conformation. The results of this study were published in the paper "How Strong is the C^{α}-H···O=C Hydrogen Bond?" which was published in the *Journal of the American Chemical Society* (Vargas *et al*. 2000a). In addition, the relevance of our paper to protein-folding was recognized in the May 2000 (Rouhi 2000) edition of *Chemical & Engineering News* (Figure 6.).



Weak Hydrogen Bond May Be Key To Protein Folding

Interactions between the hydrogen on an α-carbon and a carbonyl oxygen in peptide backbones are sufficiently strong to have an impact on protein folding, a recent study shows.

Such hydrogen bonds (C^{α}–H--O=C hydrogen bonds) are prevalent in protein crystal structures. Researchers have assumed that they are much weaker than other types of hydrogen bonds and have been unsure of their function in proteins. Now chemists Rubicelia Vargas, Jorge Garza, David A. Dixon, and Benjamin P. Hay at Pacific Northwest National Laboratory (PNNL), Richland, Wash., have estimated that the interaction is worth about 3 kcal per mole. That's roughly one-half the strength of the familiar N–H--O=C hydrogen bond, but still enough to play a considerable role in determining protein conformation, they conclude [*J. Am. Chem. Soc.*, published April 27 ASAP, http://pubs.acs.org/journals/jacsat].

Hydrogen bonds between carbonyl oxygens and α-carbons "have been virtually ignored by biochemists and structural biologists. People just didn't think carbon could be a significant hydrogen-bond donor," comments Ronald T. Raines, a professor of biochemistry and chemistry at the University of Wisconsin, Madison. But this paper suggests that these bonds should not be ignored, he says.

The finding will likely have an important impact on protein science, comments Zygmunt S. Derewenda, a professor of molecular physiology and biological physics at the University of Virginia School of Medicine, Charlottesville. Studies by Derewenda and others have suggested that C^{α}–H--O=C hydrogen bonds are ubiquitous, particularly in β-sheets and helical proteins. "But we were not able to confirm the energies of these interactions by experimental means, nor did we have the expertise to prove their magnitude theoretically," he says. The PNNL study, he adds, fills a gap and shows that these hydrogen bonds may play a substantial role in protein folding.

The PNNL researchers point out that, in the collagen triple helix, for example, a certain fold involves three such C^{α}–H--O=C hydrogen bonds, which could be worth as much as 9 kcal per mole. "That's a significant stabilization," Hay says. "Maybe that's why the fold happens, so that the protein can form those hydrogen bonds."

Protein folding remains an unsolved fundamental problem, "partly because we don't have accurate parameters for force fields that control the phenomenon," Derewenda says. The PNNL results take "us one step further to a more precise definition of folding thermodynamics and will undoubtedly contribute to the eventual solution of the problem."

C^{α}–H--O=C hydrogen bonds in the β-sheet formed by the protein called Achromobacter protease I are found between residues 99 (threonine) and 102 (glycine) and between residues 72 (tyrosine) and 89 (isoleucine). Side chains in this region have been removed for clarity. Numbers indicate estimated distances (in angstroms) between the hydrogen atoms (white) and oxygen atoms (red). Carbon atoms are shown in gray and nitrogen atoms in blue.

Neglecting weaker kinds of interactions, such as the C^{α}–H--O=C hydrogen bond, "leads to simplistic" models of protein folding, notes Thomas Steiner, an assistant professor at the Institute for Crystallography, Free University of Berlin. These hydrogen bonds "play a role of fine-tuning, of helping the stronger N–H--O=C hydrogen bonds in determining the fold. Theoretical quantification of these roles is to be greatly appreciated," he says.

Maureen Rouhi

MAY 8, 2000 C&EN 15

Figure 6. Article on hydrogen-bonding that appeared in *Chemical & Engineering News.*

Conformational Analysis of N, N, N', N'-tetramethylsuccinamide

A conformational analysis of N,N,N',N'-tetramethylsuccinamide was performed. An initial set of 22 geometries was obtained through an exhaustive conformer search using molecular mechanics. The structures were further optimized using DFT with the generalized gradient approximation. Single-point energies on DFT were performed at MP2 levels using double-*zeta* plus polarization (DZP) functions and aug-cc-pVTZ. The lower-energy conformations were further optimized at the MP2 level. The geometries were rationalized in terms of rotational potential energy surfaces in simple compounds, intramolecular C-H···O hydrogen bonding, and dipole-dipole repulsion. The results of this study were reported in the paper "Conformational Analysis of N, N,N',N'-tetramethylsuccinamide: The role of C-H···O Hydrogen bond," which was published in the *Journal of Physical Chemistry* (Vargas *et al*. 2000b).

References

Vargas, R, J Garza, DA Dixon, and BP Hay. 2000a. "How Strong is the C^{α}-H...O=C Hydrogen Bond?" *Journal of the American Chemical Society* 122(19):4750-4755, DOI: 10.1021/ja993600a.

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Ab initio study of rotational barriers in N-methylbenzamide and benzylamide systems

High-level *ab initio* calculations for the torsional potential energy surface (PES) of N-methylbenzamide and benzylamide were performed. In order to obtain the torsional PES, we optimized a constrained DFT geometry using the local density approximation (LDA) and the gradient-corrected approximation (*i.e.*, Becke-Lee-Yang-Parr; BLYP) by freezing the torsional angle and optimizing the remaining geometry parameters. MP2/DZP geometry optimizations for some points were done for N-methylbenzamide; for N-benzylamide only single points with this basis set were carried out. For both systems, single-point energy calculations at the BLYP/DFT geometries were computed at the MP2 level using the aug-cc-pVTZ basis set. The rotational barrier for N-methylbenzamide, in contrast to the result found for simple amides, shows that DFT can properly describe the rotational barrier for this kind of amide. The barrier height for the benzene ring torsion is not very large in both cases, ≤3 kcal/mol. The amide group is more difficult to rotate in the benzyl amide than in the N-methylbenzamide since the rotation in the former molecule involves the passing of the oxygen atom over the benzene ring. Both molecules studied are stabilized by C-H···O contacts in the optimized geometries and present pyrimidalization of the nitrogen in the amide group.

Stretching and torsional potential energy surfaces of [Fe(III)(cathecolate)3]$^{3-}$

The geometries for the ground and transition states of $[Fe(III)(cathecolate)_3]^{3-}$ were optimized using DFT within the LDA and gradient-corrected and hybrid approximations. The Slater-Vosko-Wilk-Nusair (SVWN), BLYP, and B3LYP functionals for local, gradient-corrected, and hybrid approximations, respectively, were used to approximate the exchange-correlation energy. All exchange-correlation functionals were tested with a double-*zeta* basis set. In order to obtain the stretching and bending for the bond, Fe-O, and the dihedral angle, Fe-O-C-C, respectively, constrained optimizations were carried out using the same basis set and the exchange-correlation functionals SVWN and B3LYP (see Figure 7). Performing the calculations required significant care in order to obtain the PES.

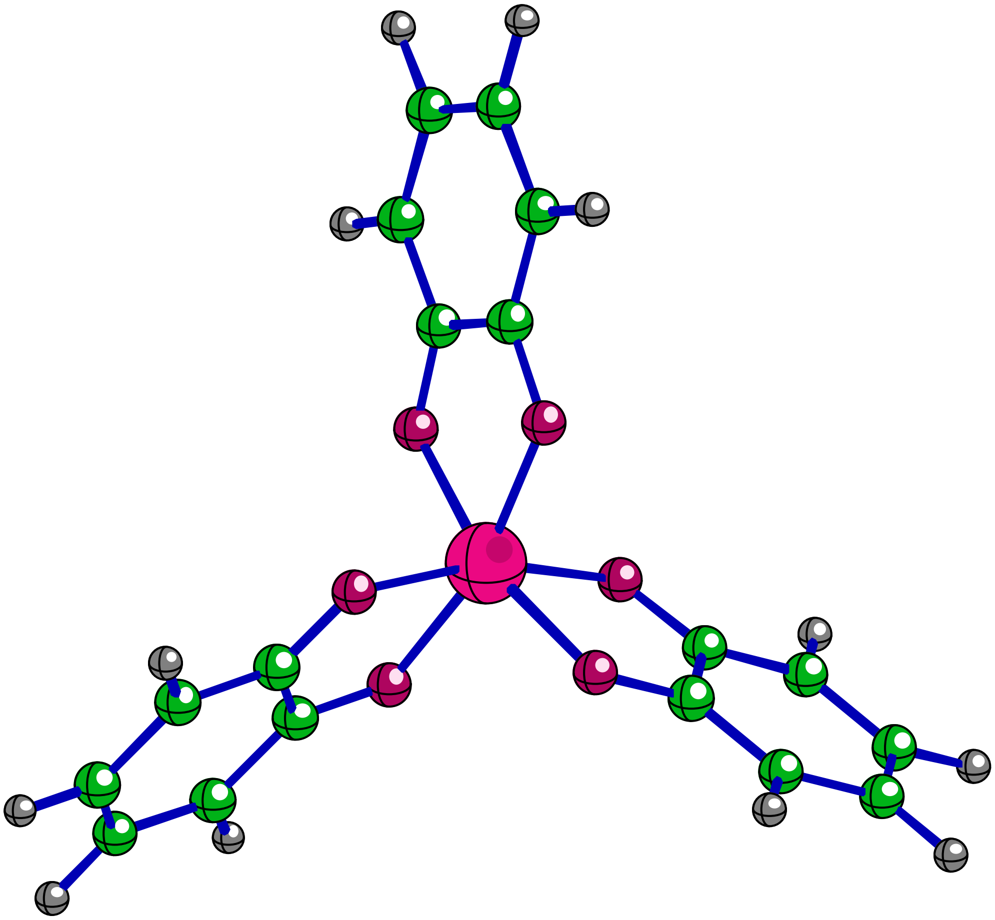

Figure 7. DFT/B3LYP structure of the [Fe(III)(cathecolate)3]$^{3-}$ ion.

A database of alkane structural information-based on DFT

A database of alkane isomers ($C_nH_{(2n+2)}$) for n=1-6 has been developed within the framework of the Extensible Computational Chemistry Environment (ECCE). These calculations were performed with the DZVP2 orbital basis set, the SVWN LDA functional, and the B3LYP hybrid functional. The B3LYP functional was used to explore non-local effects on geometries, energies, and frequencies. In general, the geometries changed only slightly between the two functionals (less than 0.01 D for bond distances and 0.5 degree for angles and torsions). However, some systems, such as 2,3-dimethylbutane, had larger changes (0.03 D for bond distances and 1.0 degree for some angles and torsions). The energetics show that the LDA energy differences between isomers can be up to three times larger than those for the B3LYP energy differences; in particular, there were changes in the ordering of some of the isomers. In general, B3LYP frequencies increased from the LDA values.

Isodesmic reactions for thermochemistry

Isodesmic reactions are basically bond-separation reactions where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing those same kinds of bonds. The method used to examine the reactions is similar to the G2 theory, with the exception that coupled-cluster (CC) methods are used instead of quadratic configuration interaction (QCI) and the aug-cc-pVnZ basis sets are used instead of the 6-31G(d) family (Merrill and Gordon 1999). This method also eliminates the "higher-level correction" for the isodesmic reactions. Energetics of isodesmic reactions were calculated at the MP2(FC)/aug-cc-pVDZ, MP2(FC)/aug-cc-pVTZ, and CCSD(T)(FC)/aug-cc-pVDZ levels on MSCF resources. The geometries and frequencies at the MP2/aug-cc-pVDZ level were calculated with local resources at Ames Laboratory. The test molecules that were examined are those of Raghavachari et al. (1997). Some of the geometries, frequencies, and energetics were obtained from the EMSL Computational Results Database (<http://www.emsl.pnl.gov/proj/crdb/>). While the calculations have been completed, the results are still being examined. A paper is in preparation with the results of this work.

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Raghavachari, K, BB Stefanov, and LA Curtiss. 1997. "Accurate Thermochemistry for Larger Molecules: Gaussian-2 Theory with Bond Separation Energies." *Journal of Chemical Physics* 106(16): 6764-6767.

Accurate determination of the binding energies of the first few water clusters

We have obtained accurate binding energies for the first few (n=3-6) water clusters using the family of correlation consistent basis sets. Estimates of the MP2 complete basis set limits are: -15.8 kcal/mol (cyclic trimer), -27.6 kcal/mol (cyclic tetramer), -36.3 kcal/mol (cyclic pentamer), -44.8 kcal/mol (cyclic hexamer), -45.8 kcal/mol (cage hexamer) and -45.9 kcal/mol (prism hexamer). The effects of additional correlation estimated at the CCSD(T) level of theory indicate that the MP2/CBS values are accurate to within 0.2 kcal/mol.

The parameterization of interaction potentials for water is commonly performed using available data from a variety of environments ranging from clusters to liquid water and ice. The results for water clusters offer the advantage of probing the fundamental interactions at the molecular level and, therefore, systematically identifying the physical terms necessary to describe hydrogen bonding. However, no direct experimental measurements have been performed to date for the interaction energies of even small clusters, such as the water dimer, let alone of liquid water and/or ice. Most energetic information used in the parameterization of interaction potentials comes either directly from calculations or indirectly from measurements of thermodynamic quantities such as the heat of vaporization/sublimation for the various water/ice phases.

First-principles electronic calculations offer the advantage of providing this much-needed energetic information, which is the cornerstone in the benchmarking and parameterization of interaction potentials for water. The issue of accuracy is of outmost importance since, for instance, numbers within "chemical accuracy" (1 kcal/mol) for the binding energies of small water clusters are needed in order to ensure transferability for larger systems, such as bulk water and ice, and thus produce meaningful results. This scale typically represents a small (~1-2%) percentage of the cluster binding energies. However, the computational cost, theoretically, crosses from N^3 to N^5, with N being proportional to the size of the system. For example, in order to tighten the accuracy of the computed binding energies of a water hexamer from 10 to 1% requires a 10,000 times increase in the computational cost. These calculations are currently impossible on conventional computers, which use serial architectures.

We have performed full geometry optimizations of the water trimer clusters through the various hexamer isomers (*e.g.*, cage, prism, book, cyclic) at the MP2 level of theory with the aug-cc-pVTZ basis set. Single-point energies were computed at these optimized geometries with the larger aug-cc-pVQZ and aug-cc-pV5Z sets at the MP2 level of theory. All calculations were performed using the NWChem software package. The largest calculation for the water hexamer (1722 total contractions) was run on 128 nodes of the IBM Scalable Power system at the Environment Molecular Sciences Laboratory at Pacific Northwest National Laboratory. Basis set superposition error corrections were estimated using the function counterpoise method. Even with the largest basis set used in this study (aug-cc-pV5Z), the corrections amounted to ~1.0 kcal/mol for the various hexamer isomers. Table 1 shows our estimated MP2 CBS limits from using the binding energies obtained with the double- through the quintuple-*zeta* basis sets.

Table 1. Estimated MP2 Complete Basis Set Limits

Isomer	**Estimated MP2 CBS Limit (kcal/mol)**
Cyclic trimer	-15.8
Cyclic tetramer	-27.6
Cyclic pentamer	-36.3
Cyclic hexamer	-44.8
Cage hexamer	-45.8
Prism hexamer	-45.9

The effect of additional correlation estimated at the CCSD(T) level of theory for the trimer and tetramer clusters suggests that the MP2 values are accurate to within 0.2 kcal/mol for the total binding energies (see Figure 8).

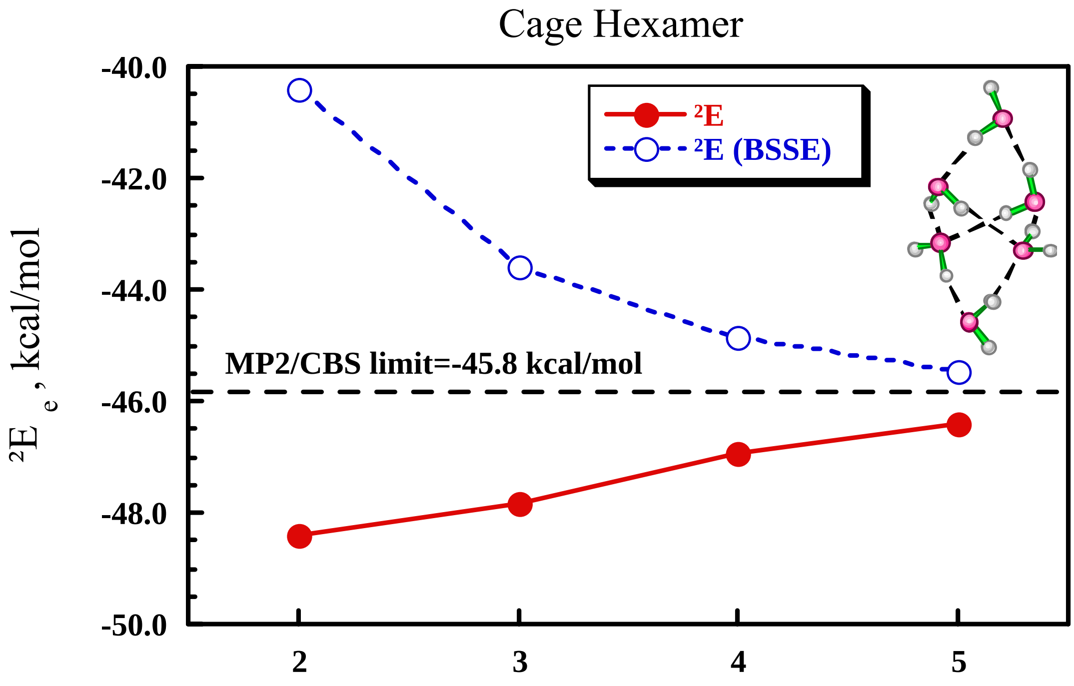

Figure 8. Convergence of the MP2 binding energy of the cage water hexamer with basis set.

List of all publications resulting from this work

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List of all presentations resulting from this work

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Dixon, DA. 2000. “Computational Thermochemistry and Kinetics.” Presented at *CCR NIChE Conference*, June 2000, Marco Island, FL.

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Xantheas, S. 1999. *American Chemical Society National Meeting*, Symposium on Water and Water Clusters, August 26, 1999, New Orleans, Louisiana.

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