

Environmental Issue

There are several environmental problems for which computational chemistry can offer either a solution or insights that will enable us as environmental chemists to provide methods that will help alleviate these issues. Three examples include:

- Negative ion chemical ionization mass spectrometry (NICI MS) has the potential to be a very useful technique in identifying various polycyclic aromatic hydrocarbons (PAHs) in soil and sediment samples, at the same time being transparent to aliphatic hydrocarbons, which may contribute to chemical noise from a typical sample matrix. The tendency of these compounds to give a significant signal under NICI MS conditions depends on the individual compound's ability to capture an electron. Therefore, the electron affinity (EA) of a compound should be a measure of the negative ion sensitivity under chemical ionization MS conditions.
- Another issue that can be clarified by computational chemistry is the structure of ions under electron capture processes. Much of the work on chlorinated compounds (e.g., pesticides) is performed by GC-Electron Capture Detector (ECD). However, NICI MS gives much the same performance at an enhanced specificity. Many of the ions that then show a response are Cl^- , which is of little structural confirmation. Structural optimizations may help identify the ions, which could help in molecular determination under the electron capture process.
- A third area of research is the matter of phototoxicity. Many compounds show increased toxicity, when introduced into the outdoor environment. This occurs for drugs, as well as common pollutants, such as the PAHs. To understand what compounds may be a threat for increased phototoxicity, and, therefore, what compounds to target for screening, predictive methods based on computational methods were proposed.

Research Goals

The major objective of this work is to apply the methods of computational chemistry to the problems of environmental analytical chemistry. We hope that the successful application of computational methods to environmental analytical chemistry will complement instrumental methods. The specific goals are as follows:

- Calculate the EAs of a group of PAHs for which there is experimental information and correlate with the experimental EAs.
- Identify outliers from this correlation curve.
- Compare gas-phase free energies with solution-phase reduction potentials to estimate unknown or questionable EAs.
- Recalibrate the data to obtain a consistent set of EAs.
- Use calibration curve to determine EAs of high-molecular weight PAHs for which the EAs have not been measured.
- Determine the relationship between EAs and sensitivity under NICI MS.
- Run electronic structure calculations on chlorinated cations of environmental significance. Correlate this data with the experimental results for the major ion.
- Calculate excited states of PAHs and compare to their experimental phototoxicity results. Use this model to estimate phototoxicity of other pollutants.

These specific goals will permit a more intelligent interpretation of analytical data obtained by current methodology and will also permit the design of new analytical procedures that could improve the quality of the data gathered in the future.

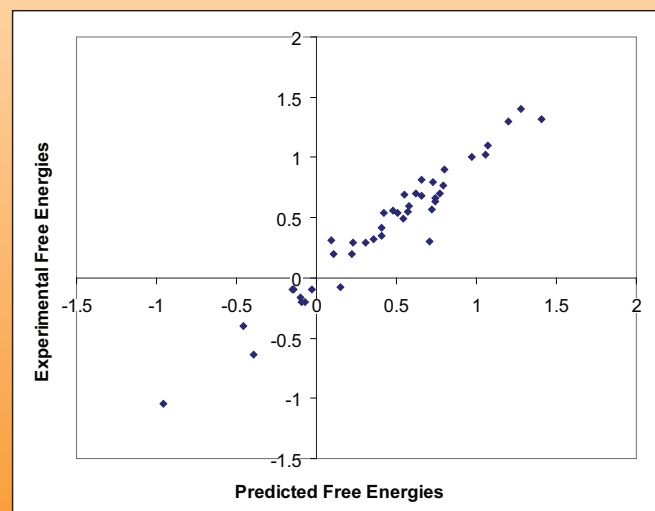
Methods/Results

Theoretical Methods

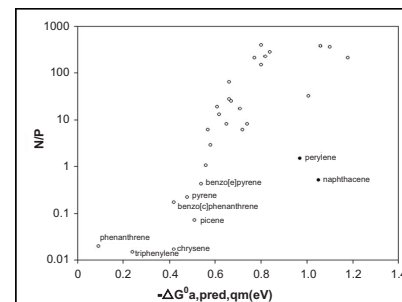
- Energies of both the neutral and anionic forms of the PAHs at their respective optimized geometries were calculated to give a direct EA.
- Complete geometry optimizations for the neutral and anionic forms of all molecules were first carried out by the Hartree-Fock (HF) method with the 6-311G(d,p) basis set. These geometry optimizations were followed by frequency calculations.
- All geometries were reoptimized using density functional theory (DFT) methods using the B3LYP/6-311G(d,p) and B3LYP/6-31+G(d,p) levels, and frequency calculations were carried out in order to verify that the stationary points thus obtained were true minima and to determine thermodynamic parameters for the determination of reaction energetics.
- For the open-shell radical anions, all calculations were done with spin-unrestricted methods, where spin contamination from quartet and higher spin states is a potential problem. Remarkably smaller values were found with the UB3LYP method than with the HF and MP methods, with values (from 0.7523 to 0.7709) close to the expected 0.75 value for a pure doublet spin state.
- Thermochemical data were calculated with zero-point and thermal energy corrections from scaled B3LYP/6-311G(d,p) frequencies using a scaling factor of 0.96 for DFT frequencies for the thermal and entropy terms derived from linear regressions on experimental frequencies of organic molecules and PAHs.
- For the phototoxicity work singlet and triplet excited state calculations were performed with a 6-311G(d,p) basis set, using the configuration interaction approach, modeling excited states as combinations of single substitutions out of the Hartree-Fock ground state (CI-Singles or CIS).

EA Results

The DFT regressions show remarkably good fits with experiment, with both the B3LYP/6-311G(d,p) and B3LYP/6-31+G(d,p) methods giving similar regression statistics and identical standard errors of 0.09 eV. Between our estimated EAs from reduction potentials and Born theory and those from the *ab initio* and DFT methods, we propose reassignments or a resolution of conflicting experimental EAs for nearly half (18 of 37) of the PAH molecules for which experimental EAs have been reported.



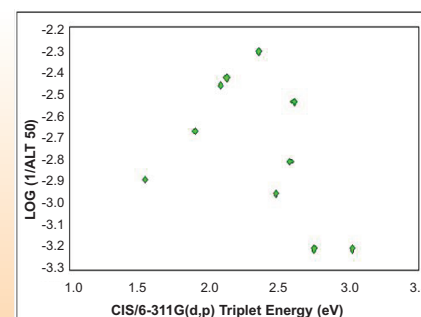
Negative ion sensitivity as a function of EA



Log plot of the negative ion to positive ion ratio versus free energy for electron attachment predicted from the B3LYP/6-31+G(d,p) calculations. The solid points are outliers.

There appears to be a threshold effect; below 0.5 eV there is no signal enhancement. Enhancement continues until about 1 eV when it plateaus.

Phototoxicity Model

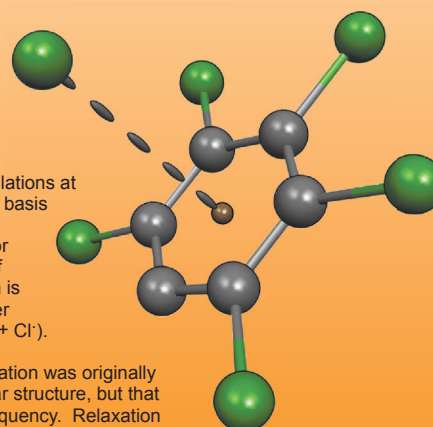


The correlation of calculated excited triplet state energies with the experimental phototoxicity for ten PAHs.

The Electron Capture Structures of Chlorinated Hydrocarbons

Thermodynamic calculations at a variety of levels and basis sets indicated that the most stable product for the electron capture of C_6Cl_6 is C_6Cl_6^- (which is more stable than either $\text{C}_6\text{Cl}_5^- + \text{Cl}^-$ or $\text{C}_6\text{Cl}_5 + \text{Cl}^-$).

The geometry optimization was originally constrained to a planar structure, but that gave an imaginary frequency. Relaxation of this constraint and with a HF/6-311+G(d) calculation, an unusual geometry of Cs symmetry was obtained in which one Cl atom is located above the approximate center of the ring.

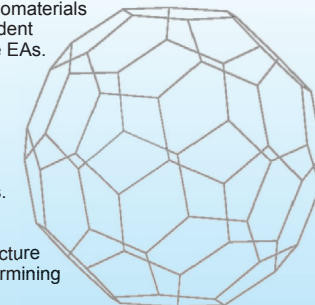


Conclusions

- We have found that a combination of theoretical calculations and experimental data for electron affinity and solution reduction potential data can be used to reinterpret the experimental data for PAHs to find a self-consistent set of all the results.
- This extensive set of re-evaluated experimental electron affinities (EAs), or free energies of electron attachment, is now available, as well as reliable predicted electron affinities from quantum theoretical calculations or from solution reduction potentials and theoretically predicted solvation energies.
- Comparisons between the negative-ion to positive-ion sensitivities (*N/P* ratios) and these new electron affinities show a rough correlation between the two. By calculating the EA for a PAH, one can predict whether a sensitivity enhancement under NICI MS conditions is to be expected. Since aliphatic hydrocarbons and many other substances have negative or very low EAs, NICI MS is expected to be a good technique for detecting PAHs in samples contaminated with other hydrocarbons or compounds with low EAs.
- Phototoxicity versus triplet excited state energy shows promise to predict phototoxicity in other compounds, based on the PAH model. Knowing the phototoxicity potential of compounds gives risk assessors a reason to prioritize certain pollutants.

Future Directions

- Future calculations on EAs will be directed at high-molecular-weight PAHs and especially those which are carcinogenic.
- These calculations direct our work on NICI MS to apply this technique to certain high-molecular-weight PAHs with a goal of developing a method for the more toxic PAHs in complex matrices (contaminated with aliphatic hydrocarbons and other low EA materials).
- Additionally, solvation models will be applied to these high-molecular-weight PAHs in various solvents to simulate PAHs in the aquatic environment.
- Ultimately, calculations will be performed for carbon-based nanomaterials. As part of our work on PAHs, the EA of fullerene was calculated. Models for fate and transport of nanomaterials through the environment are dependent upon knowing basic parameters like EAs. The solvent work mentioned above will be extended to fullerenes and single-walled nanotubes.
- Traditional quantitative structure-activity relationships (QSARs) do not work for fullerene-type materials. Therefore, calculating fundamental properties for fullerenes by computational chemistry will aid in the structure activity relationships that aid in determining toxicity.



Impact

- The use of computational chemistry has helped us in our methods development program. The use of a self-consistent set of data of EAs of PAHs has enabled us to determine the individual PAHs that show enhanced sensitivity under NICI MS methods. This has potential use for exposure and risk assessments.
- The determination of EAs will impact the models that relate to the movement of carbon-based nanoparticles through the environment.
- Structure determination has allowed us to better understand the electron capture process that is important for GC-ECD and NICI MS of chlorinated compounds.
- Finally, simple approximations using excited state CIS calculations may be able to help us determine phototoxicity of compounds found in the environment.