

Evaluating Computational and Structural Approaches to Predict Transformation Products of Atmospheric Polycyclic Aromatic Hydrocarbons

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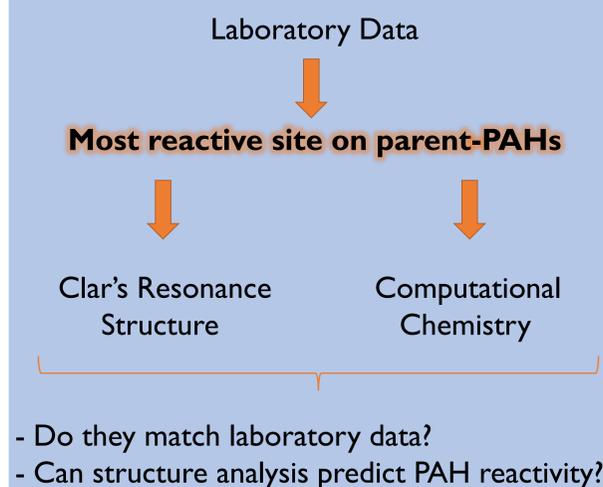
Introduction

- Atmospheric parent polycyclic aromatic hydrocarbons (PAHs) react with atmospheric oxidants (e.g., OH•, NO_x, O₃) (Jariyasopit, et al., *Environ. Sci. Technol.*, 2014)
- The reactions result in the formation of PAH-transformation products (PAH-TPs) such as nitrated-PAHs (NPAHs), oxygenated-PAHs (OPAHs), and hydroxylated-PAHs (OHPAHs) (Yu, et al., *J. Environ. Sci. Health C. Environ. Carcinog. Ecotoxicol. Rev.*, 2002)
- Some PAH-TPs are known to be more toxic than their parent structures (Wang, et al., *Environ. Sci. Technol.*, 2011)
- The formation of these PAH-TPs can be predicted computationally (Jariyasopit, et al., *Environ. Sci. Technol.*, 2014)

Research Question

Can PAH-TPs that are most likely to form in the atmosphere be predicted from the structure of parent-PAHs?

Approach

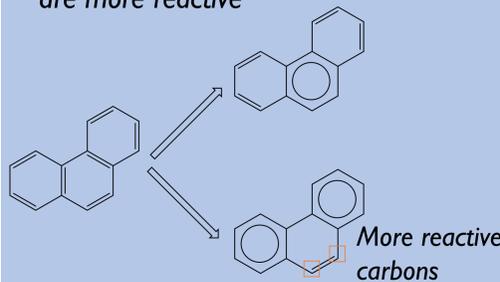


Laboratory Data

- 59 published works
- Gas and particle phase laboratory experiments
- 15 tested parent-PAHs (13 PAHs in the U.S. Environmental Protection Agency priority list of pollutants and 2 molecular weight 302 amu PAHs)
- Collected data are limited to exposure to three atmospheric oxidants: OH•, NO_x, and O₃
- PAH-TPs are limited to just primary NPAH, OPAH, and OHPAH products—and not on further degradation products

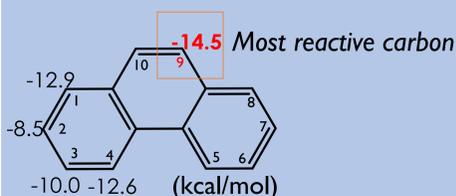
Structure Analysis

- Clar's resonance structure analyzes the stability of parent-PAH resonance structures based on the number of aromatic π-sextets
- The higher the number of aromatic π-sextets for a resonance structure, the more stable that resonance is
- This results in a ring with carbons that are more reactive



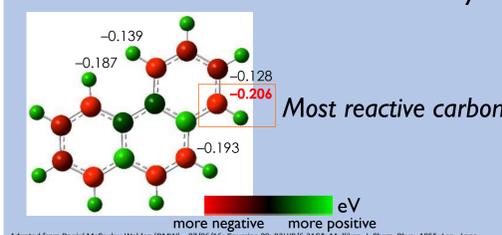
Computational Chemistry: ΔG_{rxn}

- Parent-PAHs react with OH•, resulting in OH-PAH adducts
- The change in Gibbs free energy of the reaction (ΔG_{rxn}) resulting in the formation of OH-PAH adducts can predict the likeliest substitution site on a parent-PAH
- Computational chemistry calculates the most negative ΔG_{rxn} (i.e., the most favorable site for reaction)



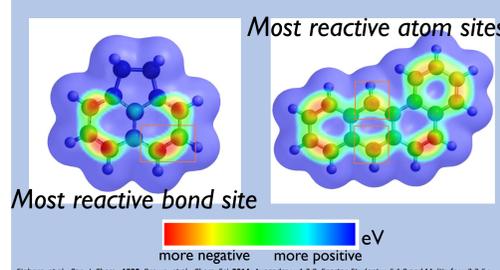
Computational Chemistry: Mulliken

- The electron density of a parent-PAH can be determined based on partial charge calculation
- Carbon with the most negative partial charge is predicted to have the most electron density, indicating carbon that is most susceptible to be attacked by atmospheric oxidants
- Computational chemistry calculates carbon with the most electron density



Computational Chemistry: ALIE

- Average local ionization energy (ALIE) is a molecular surface parameter that determines the average energy required to remove an electron from a certain position on a molecule
- The reactivity can occur on atom or bond sites
- Lower ALIE = more reactive site



PAH	Major NPAH Products Substitution Sites	OPAHs and OHPAHs Substitution Sites	Clar's Reactive Ring	Lowest OHPAH Adduct Stability (kcal/mol)	Highest Electron Density (eV)	Lowest ALIE (eV)
NAP	C1	C1+2, C1+4, C1, C2	C1-C2*	C1	C1	C1-C2
ACY	C4	C1+2, C1, C1	C3-C5*	C1	C3	C1-C2, C4-C5*
ACE	C4	C1+2, C1, C1	C3-C5*	C5	C1	C4-C5
FLO	C3	-	C1-C4*	C2, C4	C9	C4
PHE	C9	C1+4, C9+10, C1, C2, C3, C4, C9	C9-C10	C9/C10	C1	C9-C10
ANT	C9	C9+10, C9	C9-C10	C9/C10	C9	C9
FLT	C2/C3	-	C1-C3/ C4-C6	C3	C1	C2-C3
PYR	C1/C4	C1	C4-C5/ C9-C10	C1	C1	C1 and C4-C5
BaA	C7	C7+12	C5-C6	C7	C7	C7
CHR	C6	-	C5-C6	C6	C6	C5-C6
BkF	C7	-	C1-C3/ C4-6	C3	C7	C7
BaP	C6	C1+6, C3+6, C6+12, C4+5	C4-C5	C6	C6	C6
BghiP	C5	-	C3-4/ C11-12	C5	C7	C5
DBaIP	C5	-	C5-C8	C5	C5	C5
DbaIP	C6	-	C4-C5	C6	C6	C6

Table 1. Tabulated data indicating the substitution sites of the 15 parent-PAHs based on laboratory data and the predictive models. *Indicates Clar's aromatic π-sextet predict equal reactive rings due to symmetrical parent-PAH structures, indicates that the lowest ALIE bond site is on C1-C2, but since nitration is not expected to occur on this bond, the next lowest ALIE bond site (C4-C5) is used. 2-NFLT and 4-NPYR are major particle-phase products, while 3-NFLT and 1-NPYR are major gas-phase products.

Results

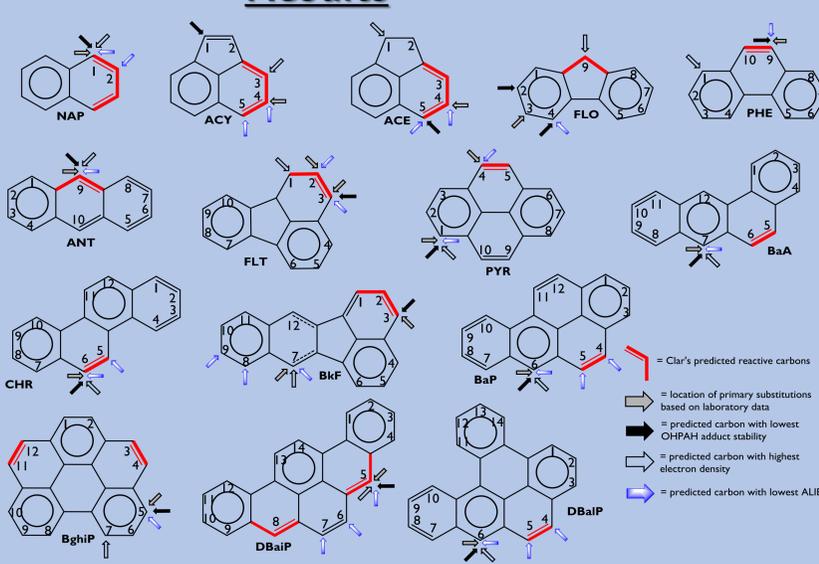


Figure 1. All approaches to predict PAH reactivity prediction and laboratory results.

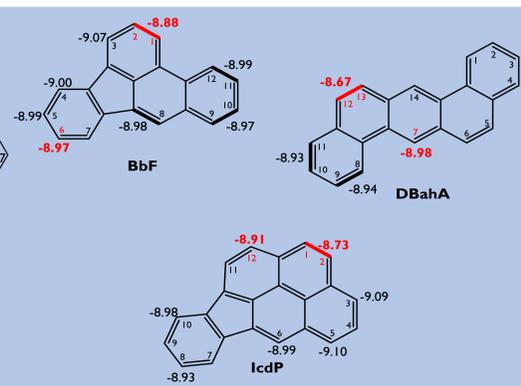


Figure 2. The results of predicted average local ionization energy (ALIE) (eV) for all 13 PAHs that were not studied in the laboratory (B3LYP/6-31G(d)). Reactive bond sites are highlighted in black, with most reactive atom or bond sites are highlighted in red.

Conclusions

- Structural analysis alone cannot predict the formation of atmospheric PAH-TPs
- ALIE is a robust computational model that predicts the formation of atmospheric PAH-TPs
- Computational approach can help predict a list of PAH-TPs that are previously unstudied