Cost Effective Methods to Estimate the Electronic and Physical Properties of Homo-Halogenated Benzenes

Presented By: Kylie Pearce, Major: Chemistry
Research Mentor: Bohdan Schatschneider
Kellogg Honors College Capstone Project

Introduction

- Organic materials are seen as promising replacements for inorganic semiconductors due their ability to be easily modified and their affordability.
- A high carrier mobility (μ_{mob}) is one of the most important properties to consider when identifying suitable organic semiconductors.
- Other properties that correlate with a high carrier mobility can be calculated using computational chemistry methods including band gap, valence and conduction band dispersion, and polarizability.
- Studying the properties of homo-halogenated benzene crystals and how they compare to molecules in the gas phase, provides insight as to how different halogens affect the electronic properties of an organic crystal and thus their semiconducting ability.

Computational Methods

- Structures were taken from the Cambridge Crystal Structure Database (CCSD) and were geometry optimized.
- Solid state calculations were performed with the CASTEP software package in Material Studios.
- Additional calculations were preformed in the CrystalExplorer software package.

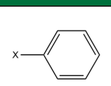
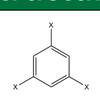
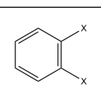
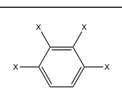
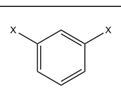
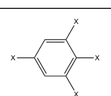
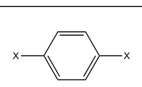
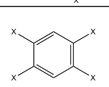
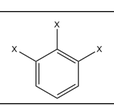
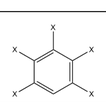
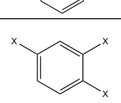
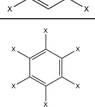
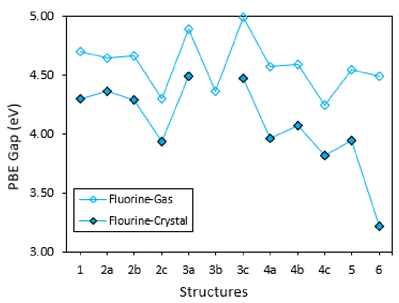
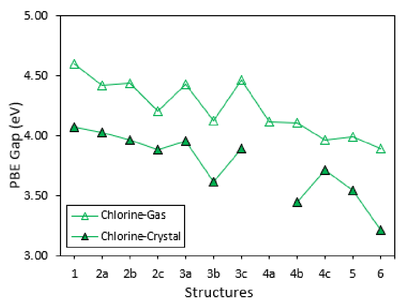
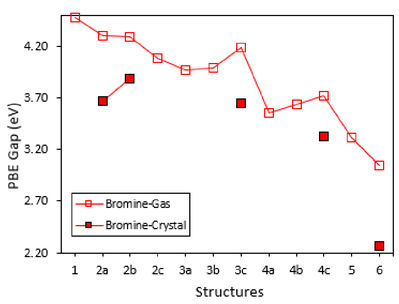
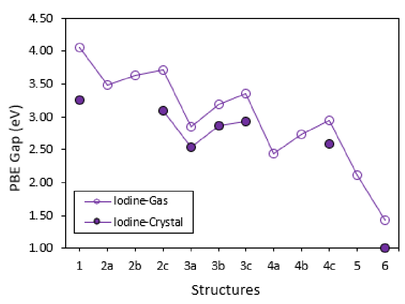
Structure Name	Structure	Structure Name	Structure
1		3c	
2a		4a	
2b		4b	
2c		4c	
3a		5	
3b		6	

Table 1 displays the various orientations of halogen atoms around a benzene ring. These orientations correspond with a specific structure name shown in the left-hand columns. The symmetrical structures include structures 2c, 3c, 4c, and 6 while the asymmetrical structures include structures 1, 2a, 2b, 3a, 3b, 4a, 4b, and 5.









Figures 1-4 show both the HOMO-LUMO gap and the band gap of the homo-halogenated benzene molecules used in this study. It is shown that as the number of halogens in the benzene ring increases both the HOMO-LUMO gap and the band gap decrease regardless of which halogen happens to be attached to the benzene ring.

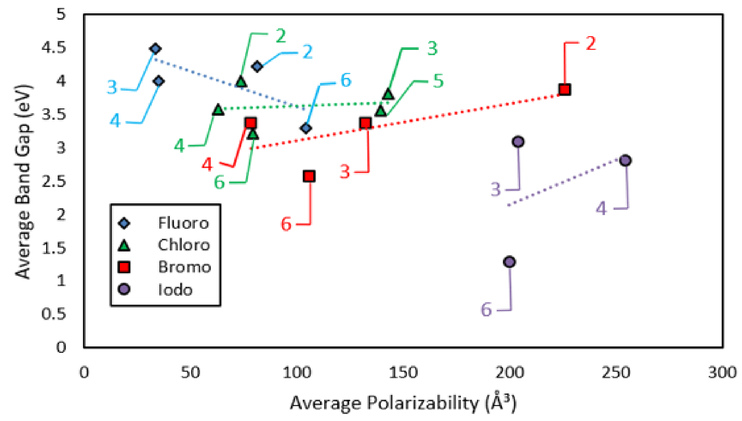
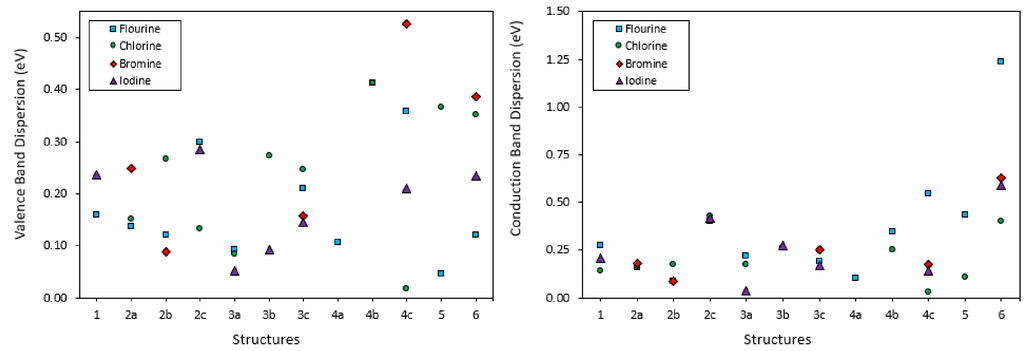


Figure 5 shows the relationship between the band gap and the polarizability of specific molecules. **Figure 5** on the left shows little correlation between these properties for any of the halogen groups. This is not in agreement with analysis between these two properties for gas-phase homo-halogenated benzenes that was preformed in previous a previous study.



Figures 6-7 show the relationship between the structure and either valence or conduction band dispersion. Both figures show that there is little correlation between band dispersion and structure and therefore implying that other factors may affect dispersion.

Conclusion

Gas phase homo-halogenated benzenes and their crystal counterparts show similar trends between the increased number of halogen substituents and a decrease in either the HOMO-LUMO gap or band gap. Due to the fact that these two properties are the ones most likely to contribute to a high carrier mobility like what is desired for most semiconductors, these results are very promising. This is because the HOMO-LUMO gap of a particular compound can be calculated much faster when compared to the band gap. Therefore, a large amount of molecules can be calculated quickly in order to help in the search for suitable organic semiconductors. Properties that were theorized to correlate with a low band gap did not show any relationship. For instance, a high polarizability should have resulted in a low band gap since the more halogens are attached to a benzene ring, the more polarizable it should become. In addition, dispersion values were unable to be predicted by structure alone meaning that it cannot be controlled at this time. Due to these unusual results, further research must be conducted in order to better explain why certain properties do or do not contribute to low band gaps in crystals.

References

1. Edwards, A. J.; Mackenzie, C. F.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A. Intermolecular Interactions in Molecular Crystals: What's in a Name? *Faraday Discuss.* **2017**, *203*, 93–112.
2. Jezowski, S. R.; Baer, R.; Monaco, S.; Mora-Perez, C. A.; Schatschneider, B. Unlocking the Electronic Genome of Halogenobenzenes. Phys. Chem. Chem. Phys. 2017, 19 (5), 4093–4103.
3. Bredas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. Charge-Transfer and Energy-Transfer Processes in π-Conjugated Oligomers and Polymers: A Molecular Picture. *Chem. Rev.* **2004**, *104*, 4971–5003.

Acknowledgements

This research was possible thanks to the National Science Foundation through the division of materials research grant. I would like to thank Cal Poly Pomona for providing opportunities for undergraduates to experience research. Additionally, I would like to thank the Schatschneider research group their contribution and support for this work.