Anomalous Electronic Properties of Iodous Materials: Application to High-Spin Reactive Intermediates and Conjugated Polymers

Yunfan Qiu
Iowa State University, yunfan@iastate.edu

Arthur Winter
Iowa State University, winter@iastate.edu

Follow this and additional works at: https://lib.dr.iastate.edu/chem_pubs

Part of the Organic Chemistry Commons

The complete bibliographic information for this item can be found at https://lib.dr.iastate.edu/chem_pubs/1214. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Anomalous Electronic Properties of Iodous Materials: Application to High-Spin Reactive Intermediates and Conjugated Polymers

Abstract
Manipulating frontier orbital energies of aromatic molecules with substituents is key to a variety of chemical and material applications. Here, we investigate a simple strategy for achieving high-energy in-plane orbitals for aromatics simply by positioning iodine atoms next to each other. The lone pair orbitals on the iodines mix to give a high-energy in-plane σ-antibonding orbital as the highest occupied molecular orbital (HOMO). We show that this effect can be used to manipulate orbital gaps, the symmetry of the highest occupied orbital, and the adopted electronic state for reactive intermediates. This electronic effect is not limited to reactive intermediates, and we demonstrate that this iodine buttressing strategy also can be used to achieve small HOMO–lowest unoccupied molecular orbital (HOMO–LUMO) gaps in organic electronic materials. Iodinated oligomers of several of the most popular conducting polymers are computed to have smaller HOMO–LUMO gaps than the unsubstituted materials. This iodine buttressing approach for generating high-energy in-plane HOMOs is anticipated to be highly general. While the unusual properties of fluorous materials are well established, at the other extreme on the periodic table novel properties of iodous materials may await discovery.

Disciplines
Organic Chemistry

Comments
This document is the unedited Author’s version of a Submitted Work that was subsequently accepted for publication in The Journal of Organic Chemistry, copyright © American Chemical Society after peer review. To access the final edited and published work see DOI: 10.1021/acs.joc.9b03289. Posted with permission.
Anomalous Electronic Properties of Iodous Materials: Application to High-Spin Reactive Intermediates and Conjugated Polymers

Yunfan Qiu and Arthur H. Winter*
Department of Chemistry, Iowa State University, 2101 Hach Hall, Ames, Iowa 50010, United States

ABSTRACT: Manipulating frontier orbital energies of aromatic molecules with substituents is key to a variety of chemical and material applications. Here, we investigate a simple strategy for achieving high-energy in-plane orbitals for aromatics simply by positioning iodine atoms next to each other. The lone pair orbitals on the iodines mix to give a high-energy in-plane $\sigma$-antibonding orbital as the HOMO. We show that this effect can be used to manipulate orbital gaps, the symmetry of the highest occupied orbital, and the adopted electronic state for reactive intermediates. This electronic effect is not limited to reactive intermediates, and we demonstrate that this iodine buttressing strategy also can be used to achieve small HOMO-LUMO gaps in organic electronic materials. Iodinated oligomers of several of the most popular conducting polymers are computed to have smaller HOMO-LUMO gaps than the unsubstituted materials. This iodine buttressing approach for generating high-energy in-plane HOMOs is anticipated to be highly general. While the unusual properties of fluorous materials are well established, at the other extreme on the periodic table novel properties of iodous materials may await discovery.

INTRODUCTION

The ability to manipulate frontier orbitals$^1$ is critical to numerous chemical phenomena, including controlling the ground state spin configurations of reactive intermediates$^{2-4}$ and organometallics complexes,$^5$ tuning the optical properties of molecules and polymers, and altering photochemical pathways and photophysical processes. It is also fundamentally important to the design of magnetic and electronic materials, as well as conducting and semiconducting conjugated polymers.$^6-9$

Here, we demonstrate that adjacent iodines appended to aromatic rings results in the generation of a very high-energy occupied orbital that result from the antibonding mixing of the in-plane iodine lone pair orbitals, and this electronic effect can be used to drastically alter the properties of reactive intermediates and conjugated polymers containing multiple iodines. We show that this property is unique to iodine, as bromo or other halo-substituted materials do not show this electronic effect, and hints at novel properties for iodous materials that invite experimental exploration.

Unusual properties of iodine-containing molecules have previously been suggested. For example, the $\sigma$ orbital mixing pattern of iodine lone pair orbitals (shown in Figure 1) has previously been used$^{10-12}$ to develop a system that may feature $\sigma$-aromaticity, the term first used by Dewar$^{13}$ for describing the bond properties in cyclopropane. As shown in Figure 2, the $5p$ orbitals of the iodines produce an in-plane $\sigma$-antibonding HOMO for the neutral hexaiodobenzene C$_6$I$_6$. After two-electron oxidation, the cyclic I$_6$ portion of its dication meets the Hückel (4n+2) criteria. As a result, the $\sigma$-$\pi$ double aromaticity, suggested by Schleyer$^{14-15}$ is argued to exist in the C$_6$I$_6$ dication. Iodine can also engage in halogen bonding and features strong dispersion interactions as a result of its high polarizability.$^{16-18}$

Beyond such studies, however, relatively little work has been performed on iodine-containing materials, as they are synthetically more challenging to make than bromo or chloro compounds, and have many more electrons than the other halogens, making them more computationally expensive to model. Indeed, basis sets for iodine are not even included in popular computational programs such as Gaussian.$^{19}$ Thus, there has been relatively little exploration of the properties of iodous materials, either by experimental or computational means, and so unique properties
may have been overlooked by the common assumption that iodine behaves similarly to other halogens.

Nevertheless, elements at the extremes on the periodic table often feature unique properties. In this paper, we show computationally that iodine buttressing can achieve unprecedented predicted spin states for cationic reactive intermediates. Among the high-spin manifolds, benzylic cationic reactive intermediates, including phenyloxenium, nitrenium, and carbenium ions have drawn broad attention because of their critical role in many important industrially and synthetically useful reactions, as well as in biological processes.

These benzylic cationic reactive intermediates exhibit contrasting reactivities and accordingly produce distinct reaction products depending on their electronic configurations (Figure 3). In general, reactive intermediates adopting closed-shell singlet ground states react as typical electrophiles and thus undergo nucleophilic additions (e.g., hydrogen atom abstraction or radical additions). Switching the ground states of these reactive intermediates can consequently switch the reactivity patterns of these intermediates between electrophilic and diradical reactions. Furthermore, triplet ions, if appropriately stabilized, may find use as building blocks for magnetic organic materials.

Both experimental and theoretical studies have shown that the parent phenyloxenium ion (Ph-O⁺), phenylnitrenium ion (Ph-NH⁺), and benzyl cation (Ph-CH₂⁺) have closed-shell singlet ground states. The spin configurations are depicted in Figure 3, along with their lowest energy triplet states. In all three cases, it is energetically unfavorable to populate an electron into the empty p-orbital on the centered atom to achieve a triplet state because the p orbital energy is elevated by the antibonding conjugation with the benzene ring. Thus, the singlet states of benzylic cations are favored, with large singlet-triplet energy gaps for these species. As a result, almost all benzylic cationic reactive intermediates are ground state singlet species, with a few exceptions.

However, substituting the reactive intermediate can alter the energies of the frontier orbitals and lead to triplet ground states being adopted. Here, we find that iodine atoms substituted on the aromatic rings lower the singlet-triplet energy gaps for these species. As a result, almost all benzylic cationic reactive intermediates are ground state singlet species, with a few exceptions.

We also demonstrate that this iodine buttressing strategy is applicable to other chemical processes where small HOMO-LUMO gap are desirable, such as optical and electronic materials. Here, we show that the HOMO-LUMO gap...
LUMO gaps decrease when multiple iodine atoms are substituted to the oligomers of several common organic conducting/semiconducting polymers (see Figure 4), including poly(p-phenylene)(PPP), poly(p-phenylene sulfide)(PPS), poly(p-phenylenevinylene)(PPV), which are among the most common classes of conjugated polymers.\textsuperscript{45-47} The HOMO-LUMO gaps of the oligomers can be used to estimate the band gap of their corresponding conducting polymers.\textsuperscript{48} In the same manner as demonstrated for the reactive intermediates, the HOMO orbitals of these iodinated oligomers are generated from the $\sigma$-antibonding combination of the iodine lone pair orbitals, leading to smaller HOMO-LUMO gaps and a change in the electronic character of the material. In addition, given that the HOMO orbitals change from $\pi$ character to $\sigma$-antibonding orbitals, these conducting materials are anticipated to have different conducting behavior, and may feature the possibility for conductivity through the $\sigma$ framework. While in general iodination reactions are less well developed than other halogenations, recent developments in organo-iodine synthesis\textsuperscript{49-52} may allow the synthesis of such new iodinated materials featuring novel properties.

\textbf{RESULTS AND DISCUSSION}

Iodine buttressing lowers HOMO-LUMO energy gaps for hypovalent reactive intermediates and leads to predicted triplet ground state benzylic cations. Table 1 shows the computed singlet-triplet gaps along with the HOMO-LUMO gaps of the lowest energy singlet state for aryl oxenium ions, aryl nitrenium ions, and benzylic cations. As is well known from both experiment and theory, the parent phenyloxenium ion (Ph-O\textsuperscript{+}, 1), phenylnitrenium ion (Ph-NH\textsuperscript{+}, 5), and benzylic cation (Ph-CH\textsubscript{2}\textsuperscript{+}, 8) have closed-shell singlet ground states with large singlet-triplet energy gaps, which are also reflected by large HOMO-LUMO gaps.\textsuperscript{36-37} Thus, these ions react like typical closed-shell electrophiles by undergoing nucleophilic additions. It is also worth noting that phenyloxenium and phenylnitrenium ions have $n,\pi^*$ triplets as their lowest triplet energy states as illustrated in Figure 3. These triplet states can be arrived at conceptually by starting with the singlet state and transferring one electron from the in-plane lone pair to the out-of-plane empty $p$ orbital on the heteroatom, with an accompanying change in the electron spin. In contrast, benzylic cations lack a lone pair and have $\pi,\pi^*$ triplet states.\textsuperscript{38}
Table 1. Singlet-triplet state energy gaps ($\Delta E_{ST}$ in kcal/mol) and the HOMO-LUMO gaps ($E_{\text{HOMO-LUMO}}$ in eV) of the singlet state for benzylic cationic reactive intermediates (B3LYP/6-311G(d,p)). A negative $\Delta E_{ST}$ indicates a singlet ground state.

<table>
<thead>
<tr>
<th>Structure</th>
<th>X</th>
<th>Y</th>
<th>R_1</th>
<th>R_2</th>
<th>R_3</th>
<th>R_4</th>
<th>R_5</th>
<th>$\Delta E_{ST}$ (kcal/mol)</th>
<th>$E_{\text{HOMO-LUMO}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>-13.2</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td></td>
<td>-1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>Mes</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>Mes</td>
<td></td>
<td>+3.9</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>Mes</td>
<td>I</td>
<td>I</td>
<td>Mes</td>
<td></td>
<td></td>
<td>+2.9</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>N</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>-18.4</td>
<td>3.4</td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td>Mes</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>Mes</td>
<td></td>
<td>-0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>7</td>
<td>CF_3</td>
<td>Mes</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>Mes</td>
<td></td>
<td>+5.1</td>
<td>1.1</td>
</tr>
<tr>
<td>8</td>
<td>C</td>
<td>H_2</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>-39.4</td>
<td>3.6</td>
</tr>
<tr>
<td>9</td>
<td>H_2</td>
<td>Mes</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>Mes</td>
<td></td>
<td>-11.5</td>
<td>1.4</td>
</tr>
<tr>
<td>10</td>
<td>(CF_3)_2</td>
<td>Mes</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>Mes</td>
<td></td>
<td>+2.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

However, a large change is observed when iodines are substituted on the phenyl rings. For the phenyloxenium ion, 1, when all five hydrogen atoms on the benzene ring of 1 are replaced with iodine atoms (pentaiodo phenyloxenium ion, 2), the singlet-triplet gap changes from -13.2 kcal/mol to -1.3 kcal/mol (a negative value indicates a singlet ground state), making the computed singlet and triplet states nearly degenerate. To understand the basis behind the lowered singlet-triplet gap, visualized Kohn-Sham orbitals of the HOMO and LUMO for the closed-shell singlet ground states are shown in Figure 5. As expected, the LUMO of 1 is derived from the orbital mixing involving the filled $p$ orbitals on the benzene ring and the out-of-plane empty $p$ orbital, while the majority of the HOMO consists of the nonbonding orbital on the oxygen atom. For ion 2, however, the planar delocalized molecular orbital shape of the nature of the LUMO is largely unperturbed, while the HOMO switches from an oxygen centered orbital to a through-space iodine-centered $\sigma$ antibonding orbital. The absolute energy values of the frontier orbitals in Figure 5 also indicate that, despite both absolute energies of HOMO and LUMO being elevated, the high energetic nature of an antibonding orbital still results in a much lower HOMO-LUMO gap for ion 2.

Specifically, the HOMO-LUMO gap of 1 is computed to be 2.7 eV, while the other of 2 is lowered to 1.2 eV. Furthermore, the two SOMOs of 2 for its lowest triplet energy state are presented in Figure 5 as well, suggesting an $n, \pi^*$ triplet state where one electron initially from the lone pair of an iodine atom is populated into the delocalized $\pi$ orbital. The comparison between the molecular orbitals of 1 and 2 shows that the through-space antibonding orbital induced by iodine buttressing can alter the predicted ground state from closed-shell singlet to triplet. In addition, two through-space bonding orbitals of 2 are also pictured in Figure 5 as further confirmation of the spatial interaction between the nonbonding orbitals of iodine atoms.
We then anticipated that other groups, like mesityl groups (Mes), can also be incorporated to further increase the energy of the σ-delocalized antibonding iodine-centered HOMOs. Mes was selected because it adopts a geometry orthogonal to the core aromatic ring, potentially allowing the filled pi orbitals on the mesityl group to overlap with the iodine lone pair orbitals, which can further amplify the antibonding orbital mixing. Iodinated phenyl oxenium ion derivatives were examined with mesityl groups substituted. A striking feature from the intermediates substituted with both iodine and mesityl groups is that, for 3 and 4, the positive values for their singlet-triplet energy gaps in Table 1 indicate that these ions are predicted to adopt triplet ground states. The two SOMOs for the lowest triplet states of 3 and 4, visualized in Figure 6, strongly indicate that the frontier orbitals of 3 and 4 are involved in the same fashion as those in the purely iodinated oxenium ion 2, but also show that the filled \( \pi \) orbitals of the Mes group are engaged in the \( \sigma \)-antibonding combination. The two SOMO orbitals also suggest 3 and 4 adopt unprecedented \( n,\pi^* \) triplet spin configuration for these iodinated phenyloxenium ions. Thus, a combination of iodination and ring substitution can lead to substituted phenyloxenium ions with unprecedented high-spin ground states predicted.

In comparison to phenyloxenium 1, phenyl nitrenium ion 5 and benzyl cation 8 have larger singlet-triplet gaps of -18.4 kcal/mol and -39.4 kcal/mol respectively. The same pentaiodo-substitution pattern as that of 3 gives substituted phenyl nitrenium and carbenium ions, 6 and 9. Although the iodination does lead to a smaller HOMO-LUMO energy gap for nitrenium and carbenium ions, 6 and 9, it is still not sufficient enough to overcome the intrinsically large singlet–triplet energy in favor of the singlet. Ion 6 has a \( \Delta E_{ST} \) of -0.6 kcal/mol, a near-degenerate singlet-triplet energy, and the carbenium ion 9 has a -11.5 kcal/mol singlet-triplet energy difference in favor of the singlet. Hence, for benzylic cations featured with nitrogen and carbon centers, even though the through-space antibonding orbital exists and narrows the singlet-triplet energy gap, it does not switch the predicted ground state from singlet to triplet, but rather makes the two states closer to being degenerate.

However, additional substitutions allow the triplet to become the predicted ground state for benzyl cations and phenylnitrenium ions. Both phenyl nitrenium and carbenium ions have the availability to be further substituted on the hypovalent heteratom. In a recent computational work, the linear free-energy relationship (LFER) plots showed that the direct substitution, varying from electron-donating to –withdrawing, to the carbon center of the xanthlenyl cations can adjust the singlet-triplet gap.63 We attached common electron-withdrawing groups to the nitrogen or carbon centers of benzylic cations to determine if this method could result in triplet ground state species. This is in fact the case. Ions 7 and 10 both show positive \( \Delta E_{ST} \) values (ground state triplet) when a trifluoromethyl group is installed on the centered atom. (Other common electron-withdrawing groups were also evaluated, such as cyano and nitro groups. See Table S2 in the Supporting Information). Unlike the iodine-substitution, which raises the HOMO orbital, electron-withdrawing groups on the formally cationic atom lowers the LUMO, which narrows the HOMO-LUMO and leads to predicted triplet ground states (see Figure S1 in the Supporting Information).
Figure 7. Orbital representation for the two SOMOs of their lowest triplet states of 7 and 10.

The two SOMOs of the lowest triplet states for 7 and 10 are shown in Figure 7. Thus, a remarkable prediction from these computations is that reactive intermediates that have singlet ground states and large singlet-triplet gaps (up to ~40 kcal/mol) can become computed ground state triplet species when iodines are attached to the ring.

**Iodine buttressing generates smaller HOMO-LUMO energy gaps for organic electronic materials.** There is no reason to think this iodine—iodine orbital interaction is restricted to having an effect on the ground state of reactive intermediates. Thus, we examined other systems where tuning HOMO-LUMO gaps and altering the nature of the frontier orbitals is desirable. For instance, intrinsically conducting polymers (ICPs) have important applications in organic semiconductors and organic light emitting devices (OLEDs). Small band gaps of the conducting/semiconducting polymers usually indicate better conductivity properties, and the band gap can be extrapolated by evaluating the HOMO-LUMO gaps of the corresponding oligomers.

To investigate whether the iodine buttressing effect is able to tune the band gap of these macromolecules, oligomers of some of the most common conducting polymers are examined. Figure 8 shows that these undoped iodinated oligomers have smaller HOMO-LUMO gap compared to the parent oligomers, and the σ-antibonding HOMO indicates the existence of the iodine buttressing orbital effect. Noticeably, the antibonding iodine-centered HOMO is retained in the cationic p-doped analogs (See Supporting Information). Importantly, this effect is restricted to iodine, as other halogens, such as bromines, do not show the same capability of changing the nature of the HOMO or the band gap (see Figure S2 and Figure S3 in the Supporting Information). The antibonding formation is attenuated and not observed when replacing iodine with bromine. More importantly, the singlet-triplet energy gap of pentabromo phenyloxenoum ion is computed to be -11.4 kcal/mol (see Table S2 in the Supporting Information), while the parent version, 1, has -13.2 kcal/mol energy difference. The comparison between these two energy values also demonstrates that bromine substituents have very limited potential to construct a high energy molecular orbital via antibonding formation.

**Figure 8.** Iodinated oligomers and their HOMO orbital visualization along with the HOMO-LUMO energy gaps (eV) for both the iodinated and non-iodinated oligomers.

Indeed, undoped conjugated polymers are in some cases preferred as the doping process produces radicals and the doped species may have the tendency to degrade. The inherent large band gaps, however, prohibit most of the conducting polymers from becoming excellent conductors. The iodine buttressing strategy provides an additional tuning factor for conjugated polymers to obtain a small band gap. More importantly, it radically changes the nature of the HOMO from a π orbital to the iodine-delocalized σ antibonding orbital, suggesting these materials may have unique photochemical and conducting properties.

**CONCLUSION**
In summary, adjacent iodine atoms can participate in through-space orbital mixing and lead to high-energy in-plane $\sigma$-antibonding HOMOs. When this iodine buttressing strategy is used to the benzyl cationic reactive intermediates, the generated through-space antibonding orbital acts as the HOMO and the high energy of the antibonding orbital lowers the HOMO-LUMO energy gap. Additional electron-withdrawing substitutions on the centered atom lower the LUMO. By narrowing the HOMO-LUMO gap, benzyl cationic reactive intermediates are predicted to adopt unprecedented $n,\pi^*$ triplet ground states, which should feature distinct magnetic properties and unique reactivity. This electronic effect of iodine-containing materials is anticipated to be highly general. For example, this iodine buttressing strategy can also be applied to other aromatic systems like organic electronic materials. Iodinated oligomers of some common conducting polymers show smaller HOMO-LUMO gaps than the unsubstituted materials, suggesting that they may feature altered conductivity properties. More importantly, these systems exhibit in-plane $\pi$-delocalized HOMOs, rather than the typical $\pi$ orbitals, which suggests these materials may feature unique conducting and photochemical/photophysical properties compared to the unsubstituted polymers with normal $\pi$–delocalized HOMOs.

Iodo-organics have seen use as substrates and reagents for cross-couplings, or as oxidants with hypervalent iodine reagents, but they have largely been ignored as potential end target materials with novel properties. Thus, one impact of these computational predictions is that they could spur the development of new methods for iodination to probe the unusual properties of iodous materials, much as we have recently seen developments in the ability to fluorinate organics to make fluororous materials. Such fluororous materials were once difficult to prepare, but new synthetic methodologies have enabled the use of polyfluorinated organics in a variety of applications, from separations science to pharmaceuticals to ultra-hydrophobic surfaces and materials. Extremes on the periodic table often lead to unique properties. These computational predictions invite experimental evaluation, and suggest that unique properties of iodous materials may await discovery.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Additional benzylic cations with their singlet-triplet gaps; molecular orbital analysis of selected structures; HOMOs of other oligomers and their $p$-doped analogues; computational coordinates and absolute energies (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: winter@iastate.edu

ACKNOWLEDGMENT

We thank the National Science Foundation (NSF CHE-1464956) and the Bailey Research Award for support of this work. This work used the HPC@ISU equipment at Iowa State University, some of which has been purchased through funding provided by NSF.

REFERENCES

10. Sagl, D. J.; Martin, J. C., The Stable Singlet Ground State Dication of Hexaiodobenzene: Possibly A $\sigma$–delocalized


28. McClelland, R. A., Flash Photolysis Generation and Reactivities of Carbenium Ions


47. Elsenbaumer, R. L.; Shacklette, L. W., Highly Conductive Meta Derivatives of


TOC Graphic: