Crystallographic characterization of NO$_2$C$_6$H$_4$-I(NTf)$_2$ (NTf = bistriflimide) is reported. Experimental results find that this compound can perform oxidation reactions that ArI(OTf)$_2$ is unable to and theoretical analysis indicates Ar-I(NTf)$_2$ is the most oxidizing in the ArI$_2$ class of compound known and may also be the most oxidizing compound in the class practically possible.

Iodine(III) reagents with the general structure ArI$_2$ are widely used oxidants in inorganic and organic chemistry. PhI$_2$ and PhF$_2$ are effective surrogates for difficult to handle Cl$_2$ and F$_2$ gas, and compounds such as PhI(OAc)$_2$ and PhI(OTFA)$_2$ are commercially available and effective a variety of oxidative processes.$^{1,2}$ A 2020 paper by Radzhabov and co-workers evaluated the oxidative capacities for a variety of ArI$_2$ compounds using theoretical methods, varying both the L ligand and the substituents on the aryl ring.$^{4}$ It was found that triflate ligands [ArI(OTf)$_2$] resulted in the highest oxidative capacity of the ligands considered. At the time of the publication of this report PhI(OTf)$_2$ was thought to be a useable, observable species and had been utilized in several reports in high profile journals, including as a starting point for reaction coordination calculations.$^{5,6}$ Later in 2020 we showed that PhI(OTf)$_2$ does in fact not exist and that PhI(OTf)(OAc) was the actual species effecting the transformations PhI(OTf)$_2$ was purportedly capable of.$^{7}$ This also meant that in calculations of reaction pathways in many cases where an -OTf is bound to iodine an -OAc is actually bound, a significant difference that could substantially change the relative energy for a given reaction intermediate.

Radzhabov found that of the aryl substituents considered a para nitro group confers the highest oxidative capacity onto ArI$_2$, although the effect is marginal compared to changing the ligand.$^{4}$ We hypothesized that despite making the entire molecule more electron poor, a nitro group might deactivate the ring enough to prevent decomposition of ArI(OTf)$_2$ via electrophilic aromatic substitution and enable isolation. This hypothesis proved correct and we were able to isolate NO$_2$C$_6$H$_4$-I(OTF)$_2$ via reaction of NO$_2$C$_6$H$_4$-F$_2$ and TMS-OTF.$^{12}$ NO$_2$C$_6$H$_4$-I(OTF)$_2$ proved to be highly reactive, capable of performing transformations that other ArI$_2$ species are incapable of, including the oxidation of cyclohexenes to aromatic rings and direct sp$^3$ C-H and C-F functionalization.$^{12}$ We hypothesized that use of an even more weakly coordinating ligand could further enhance the potential reactivity of the I(III) and targeted using bistriflimide (NTf) as the ligand as the next step. While we were undertaking this study Periana and co-workers isolated and spectroscopically characterized C$_6$F$_5$-I(NTf)$_2$ and showed that at elevated temperatures and pressures direct C-H activation of simple alkanes is possible.$^{13}$ They did not however confirm the structure by X-ray crystallography and in light of the previous misidentifications of PhI(OTF)$_2$, as well as other recent cases involving structural misassignment of I(III) complexes,$^{14,15}$ it is important that structural confirmation of ArI(NTf)$_2$ is obtained. In this report we structurally characterize NO$_2$C$_6$H$_4$-I(NTf)$_2$ and provide analysis that shows these NTf ligated species are significantly stronger oxidizing agents than NO$_2$C$_6$H$_4$-I(OTF)$_2$, representing the current frontier in the oxidative ability of ArI$_2$ and possibly the limit for this class of compound.

Periana and co-workers generated C$_6$F$_5$-I(NTf)$_2$ in situ from C$_6$F$_5$-I(OTFA)$_2$ and HNTf and were also able to isolate C$_6$F$_5$-I(OTFA)$_2$, in a 4-cycle exchange between C$_6$F$_5$I- (I(OTFA)$_2$) and HNTf.$^{12}$ We have previously found that TMS metathesis is an efficient one-step procedure for these types of transformations,$^{16}$ and examined if this would be effective for generation of NO$_2$C$_6$H$_4$I- (I(NTf)$_2$). Reactions of NO$_2$C$_6$H$_4$I-F$_2$ and NO$_2$C$_6$H$_4$I(OTFA)$_2$ were carried out with 2 equivalents of TMS-NTF in CDCl$_3$. In both cases conversion to a new I(III) compound was observed by $^1$H NMR spectroscopy, with the generation of TMS-F or TMS-OTFA, respectively.

The $^1$H NMR chemical shifts for the aryl ring were found at 8.71 and 8.92 ppm for NO$_2$C$_6$H$_4$I(NTf)$_2$, respectively.

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making up the asymmetric unit. For comparison, I(III) species containing I-N bonds with more nucleophilic [NR2]3 fragments have shorter I-N bonds, for example bonds between I(III) and carbazole at 206 pm,17 sulfoximine at 201 pm,18 and cyclohexylamide at 209 pm.19

With NO2-C6H4-I(OTf)2, we have demonstrated reactivity including rare hydride abstraction reactions by I(III) and C-F fluoride abstractions. The most remarkable observation thus far is the rapid, low temperature oxidation of cyclohexene rings into aryls.20 NO2-C6H4-I(OTf)2 can oxidize terpenes to p-cymene, a relatively facile oxidation, but also cyclohexene itself to benzene in a 4-electron oxidation using 2 equivalents of NO2-C6H4-I(OTf)2. While benzene is a trivial compound, this direct oxidation typically requires high temperatures, long reaction times and a Pd oxide catalyst using molecular O2 as the oxidant.20 NO2-C6H4-I(OTf)2 can perform this oxidation rapidly at -90 °C. Less reactive 3-methylcyclohexene was however unreactive to NO2-C6H4-I(OTf)2. Reaction of NO2-C6H4-I(NTf)2 with 3-methylcyclohexene in CDC13 resulted in the immediate generation of a brown solution. The 1H NMR spectrum showed total conversion to NO2-C6H4-I and the generation of toluene. Toluene is also a trivial product, but this result shows that NO2-C6H4-I(NTf)2 experimentally has an increased oxidative capacity over NO2-C6H4-I(OTf)2.

Given the observation that NO2-C6H4-I(NTf)2 can perform an oxidation that NO2-C6H4-I(OTf)2 performed poorly at we undertook theoretical studies to quantify how much more oxidizing NO2-C6H4-I(NTf)2 potentially is. We also included C6F5-I(NTf)2 reported by Periana and co-workers.21 To evaluate oxidative capability we undertook a similar model used by Radzhabov and co-workers,4 using the electronic energy change of the reaction ArI+2 e- → ArI+2L. We have previously found that the 3BLYP/6-311+G(d,p) method used in that study models the geometry of bound triflate species poorly. wPBE/def2TZVP models bound trflate well,21 so we have used that method to make comparisons between NTf and OTf bound species. For additional comparisons commercially available Ph(OAc)2, Ph(OTFA)2 and isoble Ph(OAc)(OTF) were also considered, as well as NO2-C6H4-I(OAc)2 and univale Ph(OTF)2, to give an effective of the nitro group. Ph(OAc)2, Ph(OTFA)2 and Ph(OTF)2 returned ΔE values of -372, -558 and -750 kJ/mol respectively for the model reduction. These values are in line with those obtained by Radzhabov and co-workers. Ph(OTF)2 decomposes via electrophilic aromatic substitution reactions with itself to give iodonium cations. Ph(OTF)(OAc), the compound that was misidentified for Ph(OTF)2 has a ΔE for the reaction at -543 kJ/mol, similar to Ph(OTFA)2. NO2-C6H4-I(OTF)2, which is isolable, returned a ΔE of -773 kJ/mol. In line with the Radzhabov results, substituents on the ring only have a modest effect on the oxidative capacity as compared with changing the ligand which has a large effect. NO2-C6H4-I(OTF)2 is more stable than Ph(OTF)2 despite the increased oxidative capacity due to the deactivating effect of the nitro group towards decomposition by electrophilic aromatic substitution. NO2-C6H4-I(NTf)2 is calculated to have a further increased oxidative capacity of -884 kJ/mol. In the C6F5-I(NTf)2, a further increase to -906 kJ/mol is calculated. The relative energy level of the LUMO also gives an indication of how susceptible to reduction and thus how oxidizing a given species is. For ArI2 compounds the LUMO generally has a contribution from the π system of the ring, as well as a σ symmetric component with antibonding character along the I-I-L axis. Population of this orbital results in the rupture of the I-I bonds and generation of I(II) as ArI. The method used for calculation of orbital energies was B3LYP/def2TZVP which Stephan and co-workers have previously used in the calculation of orbital energies for strongly Lewis acidic neutral boranes for the purpose of obtaining Global Electrophilicity Indices, which depend on relative orbital energies.33 The energy of the LUMO for NO2-C6H4-I(NTf)2, was calculated to be -4.02 eV, lower in energy than that of NO2-C6H4-I(OTf)2 at -3.75 eV (Figure 2). C6F5-I(NTf)2 has a calculated LUMO energy of -3.91 eV. For comparison commercially available Ph(OAc)2 and Ph(OTFA)2 have higher calculated LUMO energies at -1.61 and -2.51 eV, respectively. Ph(OTF)(OAc) again has a value very similar to Ph(OTFA)2 at -2.49 eV. This, coupled with the reduction energy data, suggests that in applications where Ph(OTF)(OAc) is generated and used in situ, Ph(OTFA)2 may also be potentially used.
For evaluating potential oxidative capacity in a model system using these more weakly coordinating anions a [C₆H₆]²⁺ fragment was used, in reality an aryl protective of EAS such as NO₂-C₆H₄- or -C₆F₅ would be needed. Attempts to optimize the geometry of C₆H₆(BF₄)²⁻ resulted in the iodine atom abstracting fluorides and then dissociation to form C₆H₆-I²⁺ and BF₃. This is consistent with reports on activating PhIF₂ with BF₃ as a catalytic Lewis acid, but no distinct reaction between them.\(^{23}\) We have observed experimentally that NO₂-C₆H₄-I(OTf)₂ is a powerful fluoride abstraction agent, capable of abstracting fluoride from fluoroadamantane.\(^{15}\) In-silico abstraction also occurs from PF₅, albeit less completely, but the fluoride becomes more strongly associated with the iodine, with an I-F bond of 201 pm and the geometry of the phosphorane becoming highly distorted (Figure 3). The I-F bond in PhIF₂ is calculated at 197 pm. The P-F contact shared with iodine is 220 pm and for comparison the axial P-F bonds are 158 pm. SbF₅ bound to iodine undergoes a similar distortion with an I-F bond of 206 pm, and the Sb-F to the same F being 214 pm. For comparison the axial Sb-F bonds in the calculated complex are 188 pm, essentially the same as free SbF₅ (189 pm). For both scenarios the best description of the resulting molecule is PhIF₂ interacting with SbF₅ or PF₅ Lewis acids. [B(C₆F₅)₃]⁻ was the least coordinating anion considered by Reed in the N-H---A IR study. As two [B(C₆F₅)₃]⁻ anions presented a system too large to study computationally we considered a model system using [B(C₆F₅)₃(C₆H₆)]⁻ with the [PhI]²⁺ fragment associated with a para and a meta C-F from the anion. Attempted geometry optimization resulted in dissociation and formation of PhI with iodine having been reduced to I(I) and the boron containing fragment becoming highly distorted, which indicates such a molecule is likely to be unviable.

![Figure 3. Schematics of optimized geometries of PhIF₂ and complexes with PF₅ and undecafluorocarborane with key bond distances indicated.](image)

The featured anions of Reed’s study are the extremely robust carborane anions,\(^{24}\) with the analogue featuring 11 B-F’s the least coordinating and only slightly less coordinating than [B(C₆F₅)₃]⁻ (N-H 3219 and 3233 cm⁻¹, respectively). Optimization of this anion bound to [PhI]²⁺ via meta carborane B-F results in a species with I-F contacts of 224 pm. The associated B-F has bonds of 146 pm. The uncomplexed meta B-F bonds are 136 pm, which indicates the anion is much less distorted than PF₅ or SbF₅. Overall the complex is the closest to a [PhI]²⁺ of the species considered. The model 2-electron reduction for this species returns a ΔE of -1221 kJ/mol, far beyond that of the [NTf]⁻ compounds. The LUMO has a calculated energy of -6.91 eV, much lower than any of the other analogues considered. These outlying values suggest that such a compound of [PhI]²⁺ paired with weakly coordinating carborane anions might be too strong of an oxidant to allow for observation or isolation in the condensed phase. The halogenated monocarborane anions also remain difficult to access and the TMS- or superacid species extremely challenging to handle.\(^{25}\) Given the predicted decomposition/abstraction reactions that arise from other weakly coordinating anions we hypothesize that ArI(NTf)₂ could represent the practical limit of oxidative capacity for ArI₂.

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**