# **Inorganic Chemistry**

pubs.acs.org/IC



# Remote Substituents as Potential Control Elements for the Solid-State Structures of Hypervalent Iodine(III) Compounds

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**ABSTRACT:** Hypervalent iodine (HVI) compounds are very important selective oxidants often employed in organic syntheses. Most HVI compounds are strongly associated in the solid state involving interactions between the electropositive iodine centers and nearby electron lone pairs of electronegative atoms. This study examines the impact of remote substituents on select families of HVI compounds as means to achieve predictable two-dimensional extended solid-state materials. Crystallographic analyses of 10 HVI compounds from several related classes of  $\lambda^3$  organoiodine(III) compounds, (diacetoxyiodo)benzenes, (dibenzoatoiodo)benzenes, [bis(trifluoroacetoxy)iodo]benzenes, and  $\mu$ -oxo-[(carboxylateiodo)benzenes], provide insights into how remote substituents and the choice of carboxylate groups can impact intermolecular interactions in the solid state.



# ■ INTRODUCTION

Hypervalent iodine (HVI) compounds have often been employed as mild and highly selective oxidants in organic syntheses.<sup>1-4</sup> HVI compounds have also recently found new applications as versatile catalysts and reagents for oxidative addition, reductive elimination, ligand exchange, and coupling reactions.<sup>5-10</sup> HVI compounds thus offer promise as metalfree alternatives to traditional transition metal compounds in catalytic applications. Compared with transition metal compounds, HVI compounds offer several advantageous characteristics, which include the facts that they are more environmentally benign, less toxic, and earth abundant.<sup>11-14</sup>

While advantages for HVI compounds are apparent, challenges for using some HVI compounds remain due to limited solubility, which is often caused by extensive aggregation in the solid state.<sup>15,16</sup> HVI compounds feature electropositive iodine centers, and these sites of positive charge interact with electronegative atoms much in the same way hydrogen atoms form hydrogen bonds that dictate the solid-state structures of many materials.<sup>17-20</sup> In a 1972 review, Alcock described intermolecular contacts involving nonmetallic elements that are closer than the sum of the van der Waals radii and are approximately linear as secondary bonds.<sup>21</sup> The analogy between secondary bonds and hydrogen bonds was explored by Hoffmann, noting the interplay between electrostatic and donor-acceptor interactions.<sup>22,23</sup> The important acceptor functionality was identified as a  $\sigma^*$  orbital. Crabtree has reviewed the connections among hypervalency, secondary bonding, halogen bonding, and hydrogen bonding.<sup>24</sup> Orpen recognized early on the potential to utilize secondary bonding as a design element for crystal engineering of the heavier p-block compounds.  $^{\rm 25}$ 

While the term secondary bonding was originally introduced for intermolecular interactions between heavier main group compounds, the term halogen bonding has evolved to describe similar intermolecular interactions between halogens and neighboring sites of electron density  $(R-X\cdots B)$ .<sup>26</sup> Specifically, IUPAC defines halogen bonding as follows. "A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity".<sup>27</sup> Common in many halogen bonding interactions involving organoiodine species are a number of notable physical attributes, which include (a) roughly linear arrays of  $R-I\cdots D$  (D = donor atom) and (b)  $I\cdots D$  distances that are smaller than the sum of van der Waals radii.

Halogen bonding involving organoiodine compounds has been attributed to the presence of regions of positive electrostatic potential at the iodine center, known as  $\sigma$  holes, that can favorably interact with negatively charged atoms.<sup>28–31</sup> A number of reports have examined the theoretical basis for these I···E interactions,<sup>32</sup> and Justik has

Received: February 5, 2021 Published: May 10, 2021



recently discussed the history and connections between secondary bonding and halogen bonds, in the context of reviewing structural HVI chemistry.<sup>33</sup> Kiprof has shown *ab initio* molecular orbital calculations focusing on iodine oxygen bonds in hypervalent 10-I-3 iodine compounds.<sup>34</sup>

The solubility and extended aggregation of HVI compounds can be modulated greatly by introduction of suitable intramolecular substituents to occupy coordination sites about the iodine center that might otherwise be involved in intermolecular interactions.<sup>15–17</sup> Understanding of how these species are arranged in the solid state would allow access to evaluate the impact of substituents on structures and crystal design. For example, our group has found that introduction of an ortho tert-butyl-sulfonyl group in iodosylbenzene transforms the polymeric and insoluble iodosylbenzene into a pseudocyclic soluble compound.<sup>35</sup> The Zhdankin group reported a series of HVI (III) compounds bearing intramolecular I…O (IntraI…O) with an array of substituents, such as an ester of 2-iodoxybenzoic acid, acetoxy of benziodoxole, and benziodazoles.<sup>36-38</sup> Amino acid-derived benziodazoles can use I...E interactions to self-assemble into macrocyles.<sup>39</sup> Togni has shown that perfluoroorganyl benziodoxolones can undergo aggregation to yield polymeric supramolecular structures.<sup>40</sup> Wirth and colleagues also explored intramolecular I...E interactions using furan and thiophene moieties in the vicinity of the iodine(III) center and found new applications.<sup>41,42</sup> The Huber group showed the intermolecular I…O (InterI…O) of iodonium salts to coordinate with diester and diamide.43 Other functional groups have also been employed to modify the properties of HVI species.<sup>44–51</sup>

Though intentionally designed intramolecular I…E interactions are prominent in HVI chemistry, studies of intentionally designed intermolecular I…E interactions using remote substituents have been a limited area of research. By contrast, crystal engineering using substituted organoiodine-(I) compounds has been well developed over recent years.<sup>26,29,52,53</sup> Interestingly, these interactions in the solid state can even lead to different photophysical properties, including new types of organic phosphorescent materials.<sup>54–56</sup>

This study reports on a systematic investigation of the impact of remote substituents (Z) on halogen bonding involving organoiodine(III) compounds in the solid state. Our specific approach focused on *para-Z*-substituted common (and stable)  $\lambda^3$  HVI species, represented by the general structure in Figure 1. A simple design goal was to ascertain if



**Figure 1.** Potential oligomeric solid-state structure driven by intermolecular I…E interactions.

oligomeric or polymeric arrays would be established in the crystalline state driven by these novel intermolecular interactions. Evidence that this approach may be general is provided by several *para*-Z- $\lambda^3$ -iodanes. Of particular note are *p*-NO<sub>2</sub>-PhICl<sub>2</sub> and the diaryliodonium salt [(*p*-NO<sub>2</sub>-PhI)Ph]-BF<sub>4</sub> that form extended coordination polymers in the solid state linked by I···O<sub>2</sub>N secondary bonds with a range of 3.00–3.56 Å.<sup>47,57</sup>

Among well-studied  $\lambda^3$  HVI compounds, organoiodine-(III)-carboxylates represent prototypical examples of HVI compounds and versatile platforms for ready variations at the carboxylate and iodoarene sites. Notably, (dicarboxalatoiodo)benzenes have even been used as crosslinkers to produce functional polymers.<sup>58,59</sup> Many HVIs of the form ArI(O<sub>2</sub>CR)<sub>2</sub> have already been reported as their synthesis from appropriate ArI is usually straightforward.<sup>11,60,61</sup> Those that have been structurally characterized display significant I···O interactions between the carboxylate oxygen atoms and the iodine centers. In most of these structures, both carboxylate oxygen atoms coordinate to the iodine center via I···O interactions yielding a local "bow tie" type of structure (Figure 2A) with the CO<sub>2</sub>, I, and C<sub>ippo</sub>



**Figure 2.** Commonly observed I···O interactions in (dicarboxylatoiodo)arenes. Intramolecular and intermolecular I···O interactions are colored red and blue, respectively.

atoms in the same plane. Rotation about the  $I\!-\!C_{\textit{ipso}}$  bond in this form (i.e., the plane of the iodoaryl ring) occurs to varying extents. Less common are examples in which only one of the two carboxylate oxygen atoms coordinates and allows the iodine engage in external I…E interactions (Figure 2B). Given the high propensity of the iodine center to engage in intramolecular I...O interactions with one or more of the carboxylate groups, Z units are capable of offering donor atoms that might compete with the chelated carboxylate groups. Specifically, Z groups having lone pairs of electrons such as fluorine (F), nitro (NO<sub>2</sub>), cyano (CN), and methoxycarbonyl [CO(O)Me] were thus chosen to promote intermolecular I···E interactions over intramolecular I···O interactions and form extended structures. The resulting structures were analyzed and compared to previously reported structures of related (dicarboxylatoiodo)arenes.

# RESULTS AND DISCUSSION

**Synthesis of (Dicarboxylatoiodo)arenes.** A series of p-Z-PhI [Z = F, CN, C(O)OMe, or NO<sub>2</sub>] were oxidized in acetic acid to afford the previously reported corresponding p-Z-PhI(OAc)<sub>2</sub> (1a-1d).<sup>60-65</sup> A variety of specific conditions have been reported for the synthesis of ArI(OAc)<sub>2</sub>. Three synthetic methodologies, differing in oxidants, were examined to optimize the yield for each compound (Scheme 1). Method I used sodium perborate.<sup>60</sup> Method II employed m-CPBA.<sup>61</sup> Method III utilized solid sodium hypochlorite pentahydrate.<sup>62</sup> In our hands, method I proved to be optimal for 1a, while method III gave the best results for 1b-1d. Nuclear magnetic resonance (NMR) spectra for 1a-1d were consistent with reported data (see the Supporting Information). The synthesis and handling of HVI compounds in general should be done carefully and on small scales, owing Scheme 1. Synthesis of  $1-3^a$ 



<sup>*a*</sup>Method I: 10 equiv of  $NaBO_4$ ·4H<sub>2</sub>O in AcOH for 6 h at 40-45 °C. Method II: 1.1 equiv of *m*-CPBA in AcOH for 9–48 h at 55 °C. Method III: 1.0 equiv of NaClO·5H<sub>2</sub>O in AcOH at room temperature for 10 min. Asterisks indicate compounds structurally characterized in this study. TFA is trifluoroacetic acid, BZA is benzoic acid.

to reports of explosive decomposition under heating and/or extensive drying.<sup>1,66,67</sup>

Compounds 1a-1d provided access, via carboxylate exchange reactions, to related (dibenzoateiodo)arenes 2a-2d and [bis(trifluoroacetoxy)iodo]arenes 3a-3c. The two types of crystals of  $\mu$ -oxo- $\lambda^3$ -iodanes 4c (OAc) and 5d (O<sub>2</sub>CCF<sub>3</sub>) were obtained from the slow evaporation of 1c from glacial acetic acid and the slow evaporation of 1d from trifluoroacetic acid, respectively. (Dibenzoateiodo)arenes 2a-2d, 3c, and  $\mu$ -oxo- $\lambda^3$ -iodanes 4c and 5d are new, while the other (dicarboxylatoiodo)arene synthesis has been reported. All compounds were authenticated by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}NMR spectroscopy.

Structural Analyses of (Dicarboxylatoiodo)arenes. Crystals suitable for single-crystal X-ray diffraction analyses for 1a were grown by layering a solution of 1a in CH<sub>2</sub>Cl<sub>2</sub> with hexanes. Crystals for X-ray studies of 1b-1d were grown by slow evaporation of the solvent from concentrated solutions (1b and 1c, ClCH<sub>2</sub>CH<sub>2</sub>Cl; 1d, acetic acid). The four crystal structures, displayed in Figure 3, conform to the generic structure shown in Figure 2A. The <sup>Intra</sup>I…O distances in 1a-1d varied within the range of 2.74-2.85 Å (Table 1). No significant intermolecular interactions with para-Z substituents were noted, with the exception that a potential weak interaction between a p-NO2 oxygen atom might be ascribed to a long I···O contact distance of 3.48(1) Å, just below the sum of the I-O van der Waal radii of 3.50 Å [compared to an I1...O4 distance of 2.82(6) Å].<sup>68</sup> The I-O bond lengths span the range of 2.11-2.18 Å and are consistent with the mean I-O bond length of 2.14 Å and in the range of 1.84–2.47 Å.<sup>34</sup> A large number of  $ArI(O_2CR)_2$ have been structurally characterized; eight of these structures are of the form p-Z-PhI(OAc)<sub>2</sub>, and these are listed in Table 1 for comparison. 48,49,69–73

It thus appears that it is rather challenging for <sup>Inter</sup>I···O bonds to compete with the internal I···O bonds provided by the vicinal carboxylates. Recognizing that I···O interactions are driven in large part by electrostatic attractions, we investigated carboxylates that have less electron rich oxygens  $(CF_3CO_2^- \text{ and } PhCO_2^-)$  and hence presumably weaker IntraI···O interactions. Crystals suitable for X-ray analysis were grown either by layering a solution of (dicarboxylatoiodo)-arenes in CH<sub>2</sub>Cl<sub>2</sub> with hexanes (**2a**, **2e**, and **3a**) or by slow



Figure 3. ORTEP representations of 1a-1d. Ellipsoids drawn at the 50% probability level. Violet atoms are iodine, red atoms oxygen, green atoms fluorine, and blue atoms nitrogen. Hydrogens have been omitted for the sake of clarity.

Table 1. Comparison of Key Distances of 1a-1d and Related Compounds

| Z                      | <sup>Intra</sup> I…O (Å)/I–О (Å) | Refcode                |
|------------------------|----------------------------------|------------------------|
| <i>p</i> -F (1a)       | [2.826/2.140]; [2.846/2.172]     | this work              |
| <i>p</i> -CN (1b)      | [2.765/2.166]; [2.850/2.117]     | this work              |
| <i>p</i> -C(O)OMe (1c) | [2.803/2.138]; [2.844/2.143]     | this work              |
| p-NO <sub>2</sub> (1d) | [2.740/2.137]; [2.826/2.161]     | this work              |
| p-C(O)OEt              | [2.819/2.147]; [2.864/2.139]     | TUKPAT <sup>69</sup>   |
| $p-S(=O_2)OCH_2^{i}Pr$ | [2.780/2.133]; [2.801/2.141]     | NIVHUW <sup>49</sup>   |
| p-Cl                   | [2.779/2.149]; [2.820/2.160]     | NEZTET <sup>48</sup>   |
| p-CH <sub>3</sub>      | [2.825/2.139]; [2.847/2.164]     | NEZTAP <sup>48</sup>   |
| Н                      | [2.776/2.134]; [2.857/2.172]     | IBZDAC <sup>70</sup>   |
| Н                      | [2.817/2.158]; [2.851/2.153]     | IBZDAC11 <sup>71</sup> |
| Н                      | [2.805/2.144]; [2.867/2.163]     | IBZDAC12 <sup>72</sup> |
| Н                      | [2.818/2.153]; [2.850/2.161]     | IBZDAC13 <sup>73</sup> |

evaporation from trifluoroacetic acid solutions (3c). Not all derivatives produced crystals of sufficient quality for single X-ray diffraction experiments, and in some cases, excess handling led to hydrolysis and formation of crystalline  $\mu$ -oxo- $\lambda^3$ -iodanes (4c and 5d).

Structurally characterizations of ArI(ArCO<sub>2</sub>)<sub>2</sub> have been limited to two examples, PhI(*o*-MePhCO<sub>2</sub>)<sub>2</sub> and PhI-(C<sub>6</sub>F<sub>5</sub>CO<sub>2</sub>)<sub>2</sub>. To complement these data, crystals of *p*-F-PhI(PhCO<sub>2</sub>)<sub>2</sub> (**2a**) and PhI(PhCO<sub>2</sub>)<sub>2</sub> (**2e**) were successfully grown, and the resulting structures are shown in Figure 4. Summary data for all four structures are listed in Table 2.<sup>74,75</sup> Both PhI(*o*-MePhCO<sub>2</sub>)<sub>2</sub> and **2a** conform to the generalized structure **A** in Figure 2. Structural analysis shows compound **2e** is in the solid state; however, one of the two benzoate arms is rotated by 61.8° (as calculated by planes of two CO<sub>2</sub> subunits). This rotation leads to significant asymmetry to the IntraI···O bonds [2.88(0) and 3.04(8) Å]. The weakened IntraI···O interaction, however, is compensated by formation of



Figure 4. ORTEP representations of 2a, 2e, 3a, 3c, and 4c. Ellipsoids drawn at the 50% probability level. Violet atoms are iodine, red atoms oxygen, green atoms fluorine, and blue atoms nitrogen. Hydrogens have been omitted for the sake of clarity.

| Table 2 | . Comparison | of | Key | Distances | of | 2a, | 2e, | and |
|---------|--------------|----|-----|-----------|----|-----|-----|-----|
| Related | Compounds    |    |     |           |    |     |     |     |

| Z                  | Ar       | $\stackrel{Intra}{I} \cdots O  (\mathring{A})/I - O  (\mathring{A})//\stackrel{Inter}{I} \cdots O  (\mathring{A})$ | Refcode              |
|--------------------|----------|--|----------------------|
| <i>p</i> -F (2a)   | Ph       | [2.751/2.173]; [2.879/2.138]   | this work            |
| Н (2е)             | Ph       | [2.880/2.159//3.065];<br>[3.048/2.122//3.065]  | this work            |
| Н                  | o-tolyl  | [2.934/2.136]; [2.934/2.136]   | RBIHOZ <sup>74</sup> |
| $F_5(Ar = C_6F_5)$ | $C_6F_5$ | [3.120/2.101//2.957];<br>[3.132/2.135//2.957]  | CAJMAB <sup>75</sup> |

an <sup>Inter</sup>I···O bond [3.06(5) Å] that affords a dimeric array of structure type **B** for **2e** (Figure 4). Interestingly, in the reported structure of  $C_6F_5I(O_2CC_6F_5)_2$ , both carboxylate entities have moved away from that as depicted in structure **A** to increase the accessibility of the iodine center across from the phenyl ring.<sup>79</sup> In the solid state, this compound exists as a loosely associated dimer with a single <sup>Inter</sup>I···O bond at 2.95(7) Å, while the <sup>Intra</sup>I···O bond is around 3.13 Å.

Upon comparison of the (diarylcarboxylateiodo)arenes to the (diacetoxyiodo)arenes, it seems that the likelihood of departing from structure **A** is increased by the decreased basicity of the carboxylate unit. Upon further extension of this argument, it would portend that trifluoroacetoxycontaining iodoarenes would have even greater propensity for structural flexibility, as is seen in **3a** and **3c** (Figure 4). All four previously structurally characterized  $ArI(CF_3CO_2)_2$ species (data listed in Table 3) indeed show a marked

| Table 3 | . Comparison | of | Key | Distances | of | 3a, | 3c, | and |
|---------|--------------|----|-----|-----------|----|-----|-----|-----|
| Related | Compounds    |    |     |           |    |     |     |     |

| Z                         | $^{Intra}I{\cdots}O$ (Å)/I–O (Å)// $^{Inter}I{\cdots}O$ (Å) | Refcode              |
|---------------------------|---|----------------------|
| <i>p</i> -F (3a)          | [2.970/2.156//3.049]; [3.151/2.132//<br>3.049]              | this work            |
| <i>p</i> -C(O)ОМе<br>(3с) | [2.962/2.175//3.019]; [3.159/2.126//<br>3.019]              | this work            |
| т-СООН                    | $[3.083/2.182//3.042]$ ; $[3.144/2.141//3.042]^a$           | YIVHER <sup>76</sup> |
| p-CH <sub>3</sub>         | [3.001/2.169//2.987]; [3.137/2.137//<br>2.987]              | BIHFUW <sup>45</sup> |
| Н                         | [3.001/2.171//3.057]; [3.153/2.133//<br>3.057]              | CEZBEO <sup>77</sup> |
| Н                         | [3.000/2.186//3.038]; [3.133/2.139//<br>3.038]              | CEZBEO0178           |
| $F_5(Ar = C_6F_5)$        | [3.075/2.147//3.190]; [3.121/2.128//<br>3.190]              | KELBUY <sup>79</sup> |
|                           |   |                      |

<sup>a</sup>Average of five independent molecules in unit cell.

preference for structure type **B**, having one of the carboxylate groups shifted away to allow intermolecular I···O interactions and dimeric associations.<sup>45,76–79</sup> The dimers within the structure of  $ArI(CF_3CO_2)_2$  where Ar = 3-COOH are also aggregated by bifurcated hydrogen bonding, leading to interesting polymer arrays.<sup>76</sup>

During the search for conditions to grow X-ray quality crystal types of 1 and 3, crystals of the hydrolysis products  $\mu$ -oxo- $\lambda^3$ -iodanes 4c and 5d were obtained (Scheme 2 and

#### Scheme 2. Formation of 4c and 5d



Figure 5). This led to the opportunity to expand this study to analogues of (dicarboxylatoiodo)arenes having an oxo-iodane group replacing one of the carboxylates. Previously characterized  $\mu$ -oxo- $\lambda^3$ -iodanes fall into two main classes, compounds that arise by hydrolysis of two independent (dicarboxylatoiodo)arenes, and heterocyclic compounds based on diaryl and dinaphthyl backbones. The former are more relevant for structural comparisons here. Structural details for 4c and 5d in Table 4.<sup>80–83</sup> The four reported  $\mu$ oxo- $\lambda^3$ -iodanes and 4c all feature extensive intermolecular bonding I···O interactions of varying degrees [structures C, D, and D' (Figure 6)]. In structure type C, there are a pair of [I–O–I]···O=C interactions that hold together a dimeric assembly of two molecules.<sup>80</sup> In structure types D and D', one of the [I–O–I]···O=C interactions involves a third molecule, thus forming a polymeric assembly in the solid

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Figure 5. ORTEP representations of 5d showed two crystallographically independent molecules and their independent polymer chains formed via <sup>InterI…O</sup> interactions (highlighted in blue dashed lines). Select bond lengths (angstroms) and angles (degrees): 12...O6, 3.15(8); 12...O7, 3.20(6); 11...O8, 2.99(1); 11...O9, 3.44(4); 11'...O6', 3.32(1); 11'...O7', 3.07(4); 12'...O8', 2.96(9); 11'...O1', 2.98(7); 11...O6, 3.03(9). Ellipsoids drawn at the 50% probability level. Violet atoms are iodine, green atoms fluorine, red atoms oxygen, and blue atoms nitrogen. Hydrogens have been omitted for the sake of clarity.

| Table 4. | Comparison | of Key | Distances | of 4c, | 5d, a | and Rel | lated Com | pounds |
|----------|------------|--------|-----------|--------|-------|---------|-----------|--------|
|----------|------------|--------|-----------|--------|-------|---------|-----------|--------|

| Z                         | R               | structure<br>type | <sup>Intra</sup> I…O (Å)/I–OAc (Å)// <sup>Inter</sup> I…O (Å)   | Refcode              |
|---------------------------|-----------------|-------------------|---|----------------------|
| <i>p</i> -C(O)OMe<br>(4c) | CH <sub>3</sub> | С                 | [2.894/2.235//3.704]; [2.991/2.215//3.303]  | this work            |
| p-NO <sub>2</sub> (5d)    | CF <sub>3</sub> | E/E'              | [2.987/2.287//3.074/3.321]; [3.039/2.279//3.158/3.206]; [3.150/2.257//3.444/2.991];<br>[3.175/2.261//2.969] | this work            |
| Н                         | CH <sub>3</sub> | С                 | [2.856/2.214//3.381]; [3.020/2.245//3.096]  | AHORIZ <sup>80</sup> |
| Н                         | $CF_3$          | $\mathbf{D}'$     | [2.938/2.258//3.497/3.389 (I…F)]; [3.273/2.287//3.083]  | DAJTUD <sup>81</sup> |
| m-CH <sub>3</sub>         | CF <sub>3</sub> | $\mathbf{D}'$     | [3.128/2.295//3.364/3.381 (I…F)]; [3.188/2.297//3.315]  | FAVBEJ <sup>82</sup> |
| p-CH <sub>3</sub>         | $CF_3$          | D                 | [3.060/2.248//3.216]; [3.452/2.288//3.080]  | RIMXEQ <sup>83</sup> |

state.<sup>81–83</sup> A weak I····FCF<sub>2</sub> interaction [3.38(9) Å] approximately *trans* to the I– $C_{ipso}$  bond in DAJTUD is present.<sup>83</sup>

Compound **5b**, however, presents a completely new type of structure format. First, the crystals of **5b** contain two independent molecules that differ mainly in the projection of the aryl units with respect to one another (highlighted in green in Figure 6). Second, each iodine center engages in halogen bonding between the *p*-nitro groups of neighboring molecules to assemble two parallel infinite coordination polymer chains **E** and **E**'. It thus appears that by combination of using the highly electron withdrawing  $CF_3$  carboxylate, in conjunction with replacement of one of the hindering carboxylates by an oxo unit, the HVI center can finally take advantage of the opportunity to engage in intermolecular interactions with the remote nitro substituent.

# SUMMARY AND FURTHER ANALYSIS

As mentioned above, (diacetoxyiodo)arenes predominantly exhibit "bow tie" structures having two intramolecular short I…O contacts in the solid state. This structural feature has often been reproduced in a number of theoretical studies.<sup>32</sup> While these structures are largely consistent in the solid state, in solution the acetoxy groups are actually dynamic and exchange oxygen atoms connected to the iodine atoms.<sup>84,85</sup> The fluxional process was proposed to involve intramolecular [1,3] sigmatropic shift of iodine as supported by density functional theory calculations. The barrier to exchange of these oxygens for PhI(OAc)<sub>2</sub>, as estimated by <sup>17</sup>O DNMR spectroscopy, is a  $\Delta G^{\#}$  of 45.5 kJ/mol with negligible entropy or solvent dependency. The same study showed nearly identical barriers for the *p*-OMe and *p*-NO<sub>2</sub> compounds. Interestingly, it was found that the <sup>17</sup>O and <sup>13</sup>C NMR resonances were insensitive to variation of *para* substituents. Similarly, the <sup>13</sup>C NMR shifts for C<sub>ipso</sub> carbons across the series were very narrow.

One very recent computational effort particularly relevant to our study calculated the structures of a series of p-Z- $C_6H_4I(OAc)_2$  and predicted redox potentials.<sup>86</sup> This investigation determined that changes of p-Z from H to NO<sub>2</sub> increased the compound's oxidation potential by 0.05 V. Using their methodology, we have extended their calculations pubs.acs.org/IC





Figure 6. Structural representations for  $\mu$ -oxo- $\lambda^3$ -iodane compounds.

to include Bader's quantum theory of atoms in molecules (QTAIM) and noncovalent interactions on *p*-Z-C<sub>6</sub>H<sub>4</sub>I(OAc)<sub>2</sub> (Z = H, NO<sub>2</sub>, or OMe).<sup>87–89</sup> These results revealed very minor changes for Mulliken charges on iodine or the acetoxy oxygen atoms across the series, consistent with the NMR studies discussed above. The determined bond critical points and NCI plot for PhI(OAc)<sub>2</sub> are shown in Figure 7.

As one might anticipate, the values of  $\rho(\mathbf{r})$  for the two hypervalent I–O bonds (0.099) are much smaller than for the I–C bond (0.14). Notably, no bond critical points are found to indicate significant covalent bonding between iodine and remote oxygen atoms, in line with a previous study.<sup>90</sup> The NCI plot, however, suggests the presence of weak attractive interactions of a magnitude similar to that of van der Waals interactions. Analyses of the p-NO<sub>2</sub> and p-OMe analogues are very similar (see the Supporting Information). These intramolecular I···O interactions appear to be dominated by Coulombic attractions.

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Figure 7. Computed bond critical points and NCI plots of  $PhI(OAc)_2$ . The surface color red indicates repulsions, green van der Waals attractions and/or weak interactions, and blue stronger attractive interactions.

In a preliminary computational attempt to examine polymer **5b**, we carried out similar analyses for a subsection (a dimer based on X-ray coordinates) of one of the two coordination polymers within the crystal of **5b**. Figure 8 reveals several noteworthy points (full pictures available in the Supporting Information). First, the p-NO<sub>2</sub> oxygen atoms that are positioned approximately *trans* to the C–I bond and at a distance  $\leq$ 3.32 Å now yield bond critical points,



Figure 8. Computed bond critical points and NCI plots of 5b. The surface color red indicates repulsions, green van der Waals attractions and/ or weak interactions, and blue stronger attractive interactions.

suggesting the donation of electron density into  $\sigma^*$  orbitals in addition to the electrostatic attractions. Second, the *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> rings that lie above one another have attractive van der Waals surfaces between them, which might also be a stabilizing force to drive this type of coordination polymer formation.

# CONCLUSION

Carboxylate derivatives of  $\lambda^3$ -iodanes comprise a huge and important class of HVI compounds. A systematic effort to introduce remote *para* substituents to promote intermolecular I···O interactions and formation of extended structures was found to be challenging as intramolecular and intermolecular I···O interactions between the oxygen atoms of the carboxyl groups dominated the solid-state structures. By employing

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three synergistic strategies of (a) using a weakly basic carboxylate (CF<sub>3</sub>CO<sub>2</sub> vs CH<sub>3</sub>CO<sub>2</sub>) to decrease the oxygen atom donor ability, (b) the electron rich oxygen-centered lone pairs of nitro group as donors, and (c) the presence of fewer carboxylates at the iodine center (i.e., one vs two per iodine atom), an unusual coordination polymer structure for  $\mu$ -oxo- $\lambda^3$ -iodane **5b** was achieved. The results of this study thus can serve as basis for the rational design of further HVI compounds for crystal engineering.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00339.

Detailed information of synthetic and experimental procedures, NMR spectra ( ${}^{1}H$ ,  ${}^{13}C$ , and  ${}^{19}F$ ), X-ray crystallographic structures, and computational details (PDF)

#### **Accession Codes**

CCDC 2056489 and 2056498–2056506 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors appreciate the helpful advice of Dr. Kazunori Miyamoto from the University of Tokyo (Tokyo, Japan) for the synthesis of 1a-1d via a sodium hypochlorite method. The authors also thank Zakary Ekstrom from Case Western Reserve University and Maxim R. Radzhabov from the University of Illinois, Chicago (Chicago, IL), for helpful discussions.

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