Carbonyl Hypoiodites as Extremely Strong Halogen Bond Donors

Shilin Yu, Jas S. Ward, Khai-Nghi Truong, and Kari Rissanen*

Abstract: Neutral halogen-bonded O–I–N complexes were prepared from in situ formed carbonyl hypoiodites and aromatic organic bases. The carbonyl hypoiodites have a strongly polarized iodine atom with larger σ-holes than any known uncharged halogen bond donor. Modulating the Lewis basicity of the selected pyridine derivatives and carboxylates leads to halogen-bonded complexes where the classical O–I···N halogen bond transforms more into a halogen-bonded COO⁻···I–N⁺ ion-pair (salt) with an asymmetric O–I–N moiety. X-ray analyses, NMR studies, and calculations reveal the halogen bonding geometries of the carbonyl hypoiodite-based O–I–N complexes, confirming that in the solid-state the iodine atom is much closer to the N-atom of the pyridine derivatives than its original position at the carboxylate O-atom.

Halogen bonding (XB) has become one of the most studied non-covalent interactions, more specifically electrophile-nucleophile interactions, as demonstrated by the rapid increase of publications since 2007.[1–8] Halogen bonding has recently been defined to occur between halogens being electrophilic and neutral or anionic nucleophiles.[9]

Despite ongoing debate about the true nature of the halogen bonding,[10–13] it is frequently used as a non-covalent interaction to construct supramolecular complexes. Owing to the similarity of the bonding geometries and directionality its kinship with hydrogen bonding is more than evident. Halogen bonding has been successfully applied to control the self-assembly of a multitude of host–guest systems (ion-pair recognition, biomolecular/chemical separations), as well as the synthesis of functional materials (porous, magnetic, phosphorescent, liquid crystals).[1,2] Crystal engineering,[1–4,14] the origin of halogen bonding, established the directionality, and specificity resulting in complex structures with appealing architectures. Owing to the demand of very precise design principles, hollow capsular molecular assemblies solely based on halogen bonding have only very recently been prepared.[15,16] Owing to its nature, halogen bonding is more directional than hydrogen bonding,[17] yet it is much more difficult to study in solution and has therefore been demonstrated mostly in the solid-state.[18–21]

When an electron is removed from the halogen atom, it becomes a positively charged free ion, a halenium ion X⁺ (X = I, Br or Cl). These cations can be regarded as very strong *bis*-functional XB donors, though the reactivity of the free halenium ion effectively prevents their use as such. However, by applying suitable Lewis bases in the synthesis, the halenium ions can be trapped into a [L–X–L]⁺ complex exhibiting a three-center-four-electron (3c-4e) bond. First of these, namely the iodonium bis(pyridine) complexes with a [N–I–N]⁺ 3c-4e bond, were reported in the 1960's by Hassel et al.,[22] Crichton et al.,[23] and Hague et al.[24] They have attracted a lot of attention, especially within the halogen bonding community and have recently been reviewed.[25,26] The iconic example, *bis*(pyridine)iodonium(I) tetrafluoroborate, Barluenga's reagent,[27] is a mild iodination reagent and an oxidant. Barluenga's reagent is a relatively stable white solid and is soluble in both organic and aqueous solutions, and its applicability in organic synthesis has been widely demonstrated.[28] Erdélyi[29–34] has demonstrated that the [N–I–N]⁺ halogen bond by very precise and comprehensive studies in solution, supplemented with computational calculations confirming that the [N–I–N]⁺ halogen bond is symmetric with the iodine atom located in the center between the N-atoms. The anionic analogue [O–I–O]⁻, *viz.* dioxoiodane compounds, have recently applied as reagents in organic synthesis.[35]

The most studied of the Barluenga-type halonium ion complexes[36–39] are the symmetrical [N–X–N]⁺ (X = Br or I) complexes.[24,27] Asymmetric heteroleptic halonium complexes have been prepared by Erdélyi and co-workers,[30] with the help of molecular clefts. Only very recently the first unrestrained heteroleptic [N₁–I–N₂]⁺ complexes have been reported in the solid-state[40] and solution.[41]

Apart from the above mentioned charged XB complexes, also neutral N–I···N and N–I···O–N XB complexes are easily prepared from suitable haloimides and halosulfonimides as the XB donors and pyridine derivatives or pyridine-*N*-oxides as the XB acceptors, extensively studied by Fourmigué[42,43] and Rissanen.[19–21,44]

Inspired by the above-mentioned work, we sought to probe the R–COO–I molecules, namely carbonyl hypoiodites, as a potential new motif of halogen bond donors. To the best of our knowledge, carbonyl hypoiodites which were stabilized by pyridine were first studied by Carlsohn in his habilitation in 1932.[45] In 1940s, Kleinberg, Zingaro and co-workers reported the preparation of a series of iodine(I) salts by the reaction of different silver carboxylates and iodine in the presence of pyridine, 2-picoline or 4-picoline as the stabilizing ligand.[46–49] Some of these salts were effectively utilized as iodination reagents with interesting antibacterial properties.[43] Furthermore, the two known single crystal

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structures manifesting pyridine benzoyl hypoiodite **1b** [named as benzoato-pyridine-iodine(I)] and bis-pyridine phthaloyl hypoiodite [phthalato-bis(pyridine-iodine(I)], were reported 40 years ago by Hartl.[50] In addition to their synthesis,[27] use of structurally related anionic complexes [R—COO—I—OOC—R]⁻, which should be considered as the anionic-type 3c-4e XB complexes with two oxygen atoms as XB acceptors,[25] have been utilized as dynamic axles in the construction of rotaxanes.[51]

Herein, we report the investigations on neutral O—I—N complexes, treated as new examples of halogen-bonded complexes, where the carbonyl hypoiodites act as XB donors. The results clearly show that carbonyl hypoiodites are very promising as strong halogen bond donors, giving unambiguous NMR spectra and manifesting very strong salt-like character (at least in the solid-state) where the iodine has jumped from the carboxyl oxygen to the N-atom of the pyridine derivative forming a very strongly halogen-bonded [RCOO⁻][⁺I—N(py)] ion-pair.

The synthesis route to the neutral hypoiodite O—I—N complexes is illustrated in Scheme 1.[47,49] Characterization and details of the synthesis and the NMR studies of all twelve hypoiodite complexes (**1b**, **1d**, **2a–2d**, **3a**, **3b**, **3d**, **4a**, **4b** and **4d**) from pyridine and its selected derivatives, silver carboxylates, and elemental iodine are presented in the Supporting Information (SI).

The ^{15}N NMR chemical shift values based on the ^{1}H-^{15}N HMBC measurements (SI) of the pyridinic nitrogen of **2a–2d** and free ligand **2** are summarized in the Table 1. The complexation-induced chemical shift change, $\Delta\delta_N$, defined as $\delta(^{15}N_{O-I-N}) - \delta(^{15}N_L)$, with O—I—N as the halogen-bonded complexes and **L** as free **1–4**, is very large and manifests a dramatic change in the chemical environment of the pyridinic *N*-atom during the complexation. With increasing Lewis basicity of the carboxylates the $\Delta\delta_N$ increases. The stable *N*-methyl-DMAP cation $[2-CH_3]^+$, as the PF_6^- salt, has
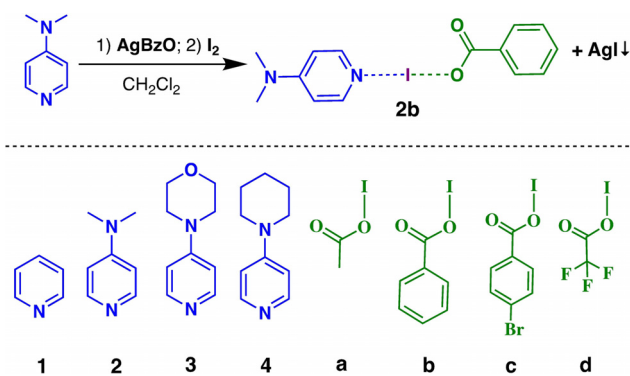
Table 1: The O—I and I—N distances from SCXRD and DFT studies and the ^{15}N NMR chemical shifts for **1b**, **2**, **2a–2d**, **3b**, [2CH₃]PF₆, [2—I—2]PF₆, and 2-NISac.

Complex	d(O—I) [Å] (**XRD**/DFT)	d(I—N) [Å] (**XRD**/DFT)	δ_{15N}[b] [ppm]	$\Delta\delta$[c] [ppm]
1b	**2.159(5)**/2.133	**2.299(7)**/2.301	−148.7	−81.0
2	–	–	−108.6	–
2a	**2.203(11)**/2.15	**2.234(14)**/2.27	−204.7	−96.1
2b	**2.210(3)**/2.171	**2.241(3)**/2.247	−209.5	−100.9
2c	**2.21(1)**[a]/2.18	**2.22(1)**[a]/2.24	−212.2	−103.6
2d	**2.312(4)**/2.248	**2.173(4)**/2.189	−238.0	−129.4
[**2—CH₃**]PF₆	–	–	−224.0	−115.4
[**2—I—2**]PF₆	–	–	−216.1	−107.5
2-NISac[42]	**2.292(2)**[d]/2.314	**2.218(2)**/2.247	−200.8	−92.2
3b	**2.230(4)**/2.164	**2.232(4)**/2.2.257	−202.1	−102.5

[a] Average of four crystallographically independent complexes in the asymmetric unit. [b] The ^{1}H-^{15}N HMBC NMR chemical shift of pyridinic nitrogen in [O—I—N] complexes or free ligands in CD_2Cl_2. [c] The ^{15}N NMR chemical shift change upon complexation. [d] (Sac)N—I bond length.

a $\Delta\delta_N$ between **2c** and **2d** (Table 1). Compared with the corresponding trifluoroacetate salt of DMAP ([2H]TFAc), the hypoiodite complex **2d** has a much larger $\Delta\delta_N$ (−129.4 vs. −85.6 ppm, Table S1), which indicates a bigger increase of the electron density around pyridinic nitrogen in **2d**.[52,53]

The $\Delta\delta_N$ of three benzoate-based O—I—N complexes (**1b**, **2b** and **3b**) was also compared, as shown in Table 1. When the nucleophilicity of the used base increases, the larger the ^{15}N NMR chemical shift change. The complex **1b** has the smallest ^{15}N NMR chemical shift change value, which is still bigger than that for pyridinium trifluoroacetate ([1H]TFAc) (−81.0 vs. −70.0 ppm, Table S1).

The single crystals of the complexes **1b**, **2a**, **2b**, **2c**, **2d**, **3b**, **3d**, **4a** and **4d** were grown either from dichloromethane or chloroform upon slow evaporation or by vapor diffusion of pentane, diethyl ether or petroleum ether into dichloromethane, chloroform or acetonitrile. The crystallographic details are presented in the SI (Table S1). The DMAP- (**2a**, **2b**, **2c**, and **2d**) and benzoate-based (**1b**, **2b**, and **3b**) O—I—N complexes will be discussed as two directly comparable series of complexes. The O—I bonds for **2a**, **2b** and **2c** (Table 1, Figure 1) are very similar to each other (ca. 2.21 Å) and identical for the O—I—O bonds (cf. 2.20 Å) in the anionic dioxoiodane complexes.[35] The I—N bond distances (Table 1) for **2a**, **2b**, and **2c** are all equal (ca. 2.23 Å) and very much resemble those observed for previously reported 3c-4e [N—I—N]⁺ halogen-bonded iodonium complexes.[22,37,40,54,55] A notable exception is the **2d** where the I—N bond length of 2.173(4) Å is much too short to be a conventional 3c-4e halogen bond. The iodine is about 0.08 Å closer to the pyridinic nitrogen in **2d** than in a typical halonium ion [N—I—N]⁺ complex and 0.04 Å closer than in the NISac-DMAP (**2-NISac**) (inner)-salt complex reported by Fourmigué (cf. 2.218(2) Å).[34]

Apart from the short I—N bond in **2d**, the O—I bond is elongated by 0.323 Å from the 1.989 Å obtained from the DFT calculations of the hypoiodite **d** (SI, Table S1) versus 2.312(4) Å from the SCXRD. This value is analogous to the strongest I⋯O halogen bonds observed in *N*-iodosaccharin-pyridine-*N′*-oxide halogen-bonded complexes,[19–21,44] and thus the O—I bond in **2d** is better described as an I⋯O halogen

Scheme 1. Synthesis of the O—I—N complexes, with DMAP (**2**) and Ag-benzoate given as an example (**2b**).
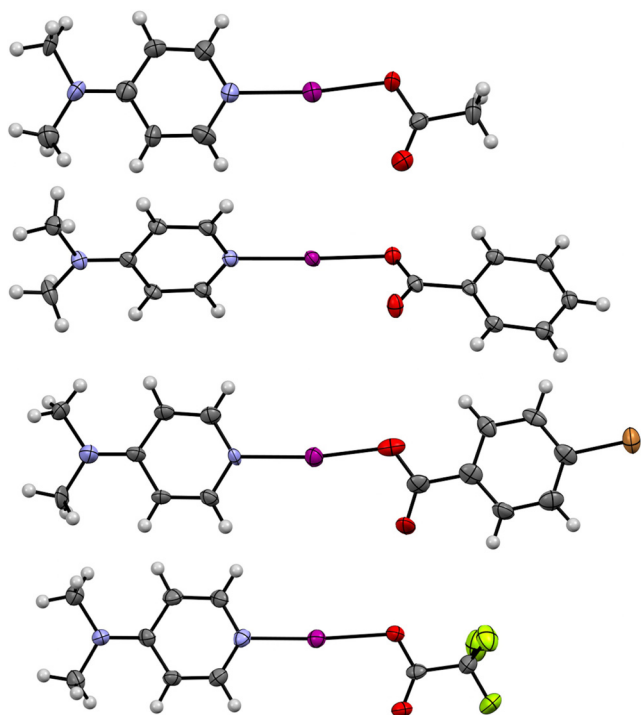
Figure 1. The X-ray crystal structures of **2a**, **2b**, **2c** and **2d** (top to bottom; thermal ellipsoids at 50% probability).[59]

bond. The O−I−N bond lengths in the solid-state for **2d** support its description as an ion-pair of the *N*-iodo-*N′*,*N′*-dimethylaminopyridinium cation, and a trifluoroacetate anion, stabilized by a very strong N$^+$−I···⁻O−C halogen bond. The shortest I−N bond of 2.167(4) Å was observed for complex **4d**, and similarly, the longest I−O bond length was for **2d** as previously stated, though virtually the same as in **4d** (cf. 2.308(4) Å).

Consistent with the general linearity of halogen bonds, the angles of the O−I−N moieties in all hypoiodite complexes fall within the range of 172.9(5)–178.1(1)° and are closer to the halogen bond angles observed for the *N*-iodosaccharin-pyridine-*N′*-oxide halogen-bonded complexes[19–21,44] than to the strictly linear 3c-4e [N−I−N]$^+$ halogen bonds.[22,37,40,54,55] The SCXRD data for **2a**–**2d** demonstrates the dynamic bonding situation for the O−I−N moiety, with shorter I−N bond lengths reflecting an increase in the *N*-iodopyridinium character of the pyridine derivative, concomitantly with an elongation of the O−I bond length reflecting an increase in the anionic character of the carboxylate component. As expected, substituted pyridines such as DMAP (**2**) and 4-piperidinopyridine (**4**), that are stronger nucleophiles, are better able to induce this increased *N*-iodopyridinium character in the O−I−N complexes described herein. Estimation of the *N*-iodopyridinium character is difficult as no *N*-iodopyridinium cation X-ray structure is known (only the *N*-fluoropyridinium cation is known).[56] In the 3c-4e [N−I−N]$^+$ halogen-bonded symmetric halonium complex [**2**−I−**2**]PF$_6$, the relative *N*-iodopyridinium character can be considered to be 50% (N−I: 2.250 Å, N−N: 4.500 Å),[36,40,57] while for the [**2**−I]$^+$ cation the I−N bond distance can only be

obtained with computational methods (SI, section 3). The DFT computed value for the I−N bond distance in [**2**−I]$^+$ is 2.042 Å. Using these two values and the SCXRD measured I−N distances, the relative *N*-iodopyridinium character can be estimated for the Fourmigué reported **2**-NISac complex[34] (56.5%), **2d** (67.6%), **3d** (62.4%) and **4d** (69.1%) in the solid-state. Due to the dynamic nature[51] of the O−I−N moiety in solution, no clear correlation about the *N*-iodopyridinium character in the solid-state and in solution can be given.

When keeping the trifluoroacetyl hypoiodite moiety constant but changing the pyridine moiety, namely complexes **2d**, **3d**, and **4d**, no apparent differences in the halogen bonding geometries were observed, as in all complexes the O−I (**2d**: 2.312(4) Å, **3d**: 2.282(5) Å, **4d**: 2.308(4)) Å, the I−N bond distances (**2d**: 2.173(4) Å, **3d**: 2.194(5) Å, **4d**: 2.167-(4) Å) and the O−I−N angles (**2d**: 175.5(2)°, **3d**: 172.1(2)°, **4d**: 175.0(1)°) are very similar. This is very likely due to the fact that all **2**, **3** and **4** are very strong Lewis bases and act as very strong XB donors enhancing the ion-pair formation in the solid-state.

For comparison of the halogen bonding geometries from the SCXRD and DFT calculations (SPARTAN′18,[58] M06-2X, def2-TZVP) with non-polar solvent model (DCM) were performed. The detailed experimental SCXRD and calculated DFT geometries are given in SI (Table S1). The DFT calculated bond geometries are extremely close to those experimentally determined by SCXRD. This is a convincing proof that the computational values obtained for the non-single crystalline complexes are feasible and can be used to discuss the dynamic bonding behavior of the O−I−N system.

The hypoiodites **a**–**d** showed no trend on the O−I bond distance as in all cases it is 1.99 Å (DFT, Table S1). Drastic elongation of the O−I bond occurs during the O−I−N complex formation as the O−I bond get longer by 0.17–0.34 Å, and correspondingly the I−N bonds shorten (Table S1). The N···O distance in all O−I−N complexes also remains virtually unchanged (4.43–4.48 Å).

The molecular electrostatic surface potential maps (MEPS, Figure 2) of the hypoiodites **a**–**d** reveal very large σ-holes, ranging from +170.41 kJ mol^{-1} (**a**) to +234.55 kJ mol^{-1} (**d**). Due to the strong polarizing power of the carboxylate moiety these values are large when compared to some common strong halogen bond donors like trifluoroiodomethane (+139.50 kJ mol^{-1}), iodoacetylene (+165.47 kJ mol^{-1}), ICl (+182.41 kJ mol^{-1}) and *N*-iodosaccharin (+226.36 kJ mol^{-1}) (SI, Figure S75).
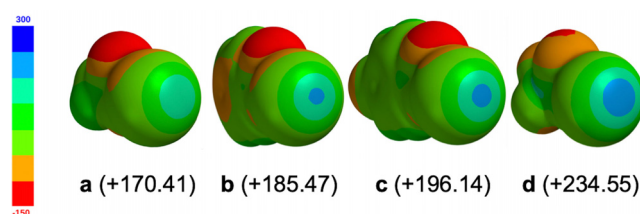

Figure 2. The electrostatic potential surfaces and the $V_{s,max}$ (kJ mol^{-1}) values calculated at the M06-2X/6–311+G(3df,2p) level on the 0.001 a.u. molecular surfaces for **a**–**d**.

While the asymmetric O−I−N halogen-bonded hypoiodite complexes are stable (with a few exceptions) under normal conditions, they can be prone to exchange reactions to the corresponding positively charged [L−I−L]$^+$ (L = Lewis base) halonium complex in the presence of excess Lewis base, depending on the strength of the Lewis base and the carboxylate used. This is unambiguously proven by a titration experiment monitored by ^{1}H NMR in d_2-DCM (Figure 3). The O−I−N hypoiodite complex **2d** (Figure 3a) was titrated with DMAP to probe the displacement of the TFAc anion. Given that DMAP is a strong nucleophile, it would be expected to replace the TFAc anion to form the [**2**−I−**2**]$^+$ halonium complex. This indeed happens as, with the increasing amount of DMAP, the signals of DMAP in **2d** (green color) gradually diminish, while new peaks (blue color) emerge for the symmetric [**2**−I−**2**]$^+$ halonium complex (Figure 3b–f). The ^{1}H NMR spectrum of a separately prepared [**2**−I−**2**]PF$_6$ halonium complex is shown in Figure 3h for reference. At two equivalents of **2** (Figure 3g), it was observed that the signals of **2d** had nearly completely disappeared.
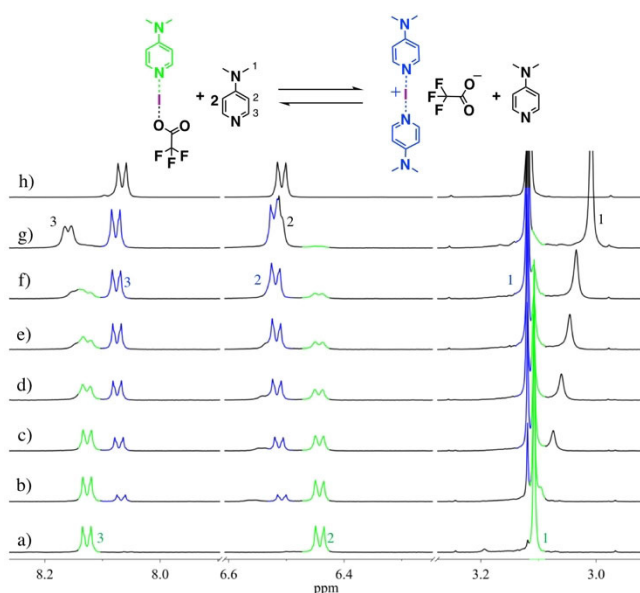

Figure 3. The ^{1}H NMR spectra (500 MHz, CD$_2$Cl$_2$, 25°C) of (a) pure **2d**, and **2d** in the presence of (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, (g) 2.0 equivalents of **2**, and (h) [**2**−I−**2**]PF$_6$.

In conclusion, a series of halogen-bonded O−I−N hypoiodite complexes have been synthesized, and their solid-state structures investigated, to probe the dependency between the O−I and I−N bond lengths and the Lewis basicity of the *N*-donor. The solid-state studies revealed that these O−I−N complexes can be described as a new class of halogen-bonded complexes, namely as a very strongly bound ion-pair comprised from an iodopyridinium cation and an anion derived from the respective acid used. The ^{1}H−^{15}N HMBC NMR studies reveal a drastic change in the chemical shift of the pyridinic nitrogen atom in the complexes, especially those from strong acids, resulting in a stable halogen-bonded

complex. The computational calculations support their characterization, revealing very large σ-holes of the parent hypoiodites. The $V_{s,max}$ value (+234.55 kJ mol^{-1}) of the trifluoroacetyl hypoiodite surpassed that of the previously strongest neutral halogen bond donor molecule, *N*-iodosaccharin (+226.36 kJ mol^{-1}). The exchange reactions of the hypoiodite complex **2d** (COO−I−N(**2**)) with excess of **2** results in the corresponding positively charged [**2**−I−**2**]$^+$ halonium complex, with COO$^-$ as the anion. Furthermore, the results provide useful knowledge for the development of XB based materials and O−I−N based antibacterial agents.

Conflict of Interest

The authors declare no conflict of interest.

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