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Halogen-Bonded [N−I−N]⁻ Complexes with Symmetric or Asymmetric Three-Center−Four-Electron Bonds

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ABSTRACT: A series of **LH[Z−I−Z]** halogen(I) complexes, where **Z** = saccharinato or phthalimido anions and **LH** = pyridinium, pyrazinium, tetrabutyl (TBA)- or tetramethylammonium (TMA) cations, were prepared, structurally characterized, and discussed as complexes consisting of a [N−I−N]⁻ anion with a three-center−four-electron (3c-4e) halogen bond, and a hydrogen-bonding (pyridinium or pyrazinium) or inert (TBA or TMA) cation. The symmetric [N−I−N]⁻ anion, reminiscent of the triiodide [I−I−I]⁻ anion, is found to be structurally equivalent to its cationic analogue [N−I−N]⁺ with N−I bond lengths of 2.26 Å. In contrast to the homoleptic [N−I−N]⁺ complexes, asymmetry of the N−I bond lengths (2.21 and 2.28 Å) was observed for those [N−I−N]⁻ complexes which manifested a hydrogen bond to only one saccharinato moiety, thus being structurally analogous to the asymmetric heteroleptic [N−I−N]⁺ complexes. The results show that the 3c-4e [N−I−N] halogen bond, being either positively or negatively charged, can be asymmetrized by an external hydrogen bond ([N−I−N]⁻) or by using two different ligands (heteroleptic [N−I−N]⁺).
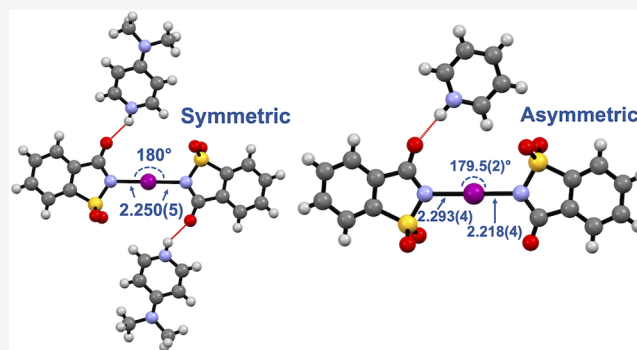
Over the last 20 years the study of the interactions of polarized halogen atoms with nucleophilic counterparts, i.e., halogen bonding[1−5] (XB) R−X···Nu (R = any atom, X = halogen, and Nu = a nucleophile), has matured to be an important research area in the domain of noncovalent interactions and has recently been defined to occur between the electrophilic region of a halogen atom and neutral or anionic nucleophiles.[6] There has been a recent boom of halogen bonding and other electrophile−nucleophile interactions, such as chalcogen[7] and pnictogen[8] bonding, as demonstrated by the rapid increase of publications over the past decade.[9−11]

Halogen bonding has found utility as a noncovalent interaction to construct supramolecular systems, and due to the similarity of the bonding geometries and directionality, comparisons with hydrogen bonding can be drawn. 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 materials with versatile functionalities such as porosity, magnetism, phosphorescence, and liquid crystallinity.[1−5] Crystal engineering[1−4,12] has established the directionality and specificity of halogen bonding, resulting in complex

structures with appealing architectures, with hollow capsular molecular assemblies solely based on classical halogen bonding having been reported recently.[13,14] Due to its electronic origin as a σ-hole interaction, halogen bonding is more directional than hydrogen bonding,[15] though the classical R−X···Nu halogen bonding has been more difficult to study in solution and has therefore been studied mostly in the solid state.[16−19]

A special niche of halogen-bonding research has emerged from those studies where an electron has been removed from the halogen atom, resulting in a positively charged *halenium* ion, X⁺ (X = I, Br, or Cl), yet more appropriately named as halogen(I) cations. According to the definition of the halogen bond,[6] these cations can be regarded as very strong bisfunctional XB donors; however, the free halogen(I) cation is highly reactive and cannot be isolated or used as such. Nevertheless, the halogen(I) cations can be stabilized by
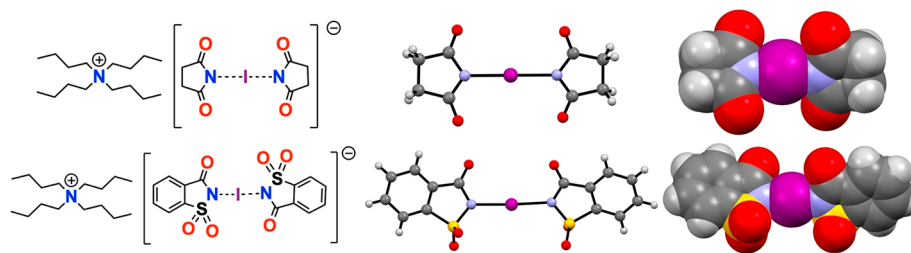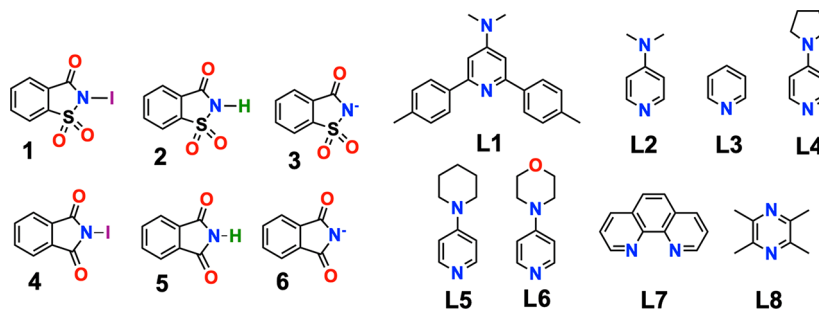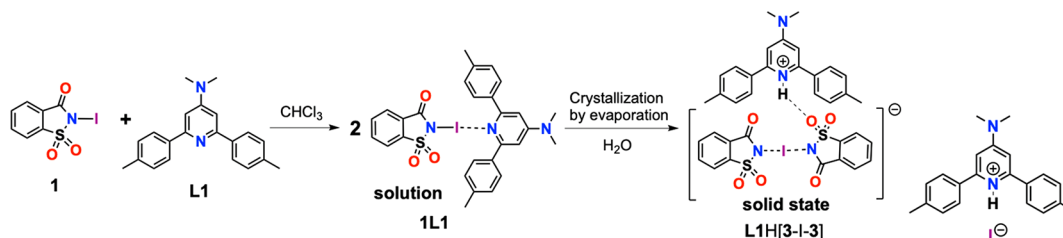
Figure 1. X-ray structures of [N···I···N]⁻ complexes YUNPUV[54] and DIQWIM.[55]

Scheme 1. List of Components Used in This Work: 1 and 4 as the XB Donors and 3, 6 and L1−L8 as the XB Acceptors

**Scheme 2. Synthesis of 1L1 and the Serendipitous Formation of L1H[3−I−3]**

complexation with two suitable Lewis bases (L), trapping them as a [L−X−L]⁺ complex exhibiting a three-center−four-electron (3c-4e) bond. Combining an iodine(I) cation with two pyridine ligands leads to the bis(pyridine)iodine(I) cation with a [N−I−N]⁺ 3c-4e bond, reported already in the 1960s by Hassel et al.,[20] Creighton et al.,[21] and Haque et al.[22] Such stabilized halogen(I) complexes have attracted a lot of attention, especially within the halogen bonding community, and have recently been reviewed.[23,24] The iconic example, bis(pyridine)iodine(I) tetrafluoroborate (Barluenga's re-agent),[25] 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 demon-strated.[26] Erdélyi[27−32] has demonstrated with very precise and comprehensive studies in solution, supplemented with computational calculations, that the [N−I−N]⁺ halogen bond has a very strong interaction ratio R_{XB} < 0.65 (R_{XB} defined as the sum of the vdW radii of the interacting atoms divided by their contact distance), as well as being linear and symmetric with the iodine atom located in the center between the N atoms with a very small N−I distance variation. Over the last 5 years the field of halogen(I) chemistry has expanded greatly, with recent developments including the first iodine(I)-based capsules,[33−36] helicates,[37] asymmetric complexes,[38,39] halogen-bonded organic frameworks (XOF),[40] halogen-bonded hierarchical materials,[41] and solid-state nucleophilic I⁺···Ag⁺ interactions.[42−44]

In addition to the aforementioned positively charged XB complexes, the almost nearly as strong (R_{XB} = 0.65−0.67) but neutral N−I···N and N−I···O−N XB complexes, which are easily prepared from suitable haloimides and halosulfonimides as the XB donors and pyridine derivatives or pyridine N-oxides as the XB acceptors, have been extensively studied by Fourmigué[45,46] and us.[17−19,47,48] Until very recently it was believed that other uncharged XB complexes cannot exhibit halogen bonds (R_{XB} < 0.65) similarly strong as those of aforementioned complexes, yet our recent work on stabilized carbonyl hypoiodites[49−51] has shown that R_{XB} values below 0.62 are possible.

The compositionally similar but negatively charged [O−I−O][52,53] or [N−I−N][54−57] systems have been much less studied, and not at all in the context of halogen bonding. The few X-ray structures of the [N−I−N]⁻ systems[54−57] as their tetrabutylammonium (TBA) salts (Figure 1) manifest structures analogous to their [N−I−N]⁺ counterparts. Corresponding [N−Br−N]⁻ X-ray structures have been also reported (from phthalimide, CSD codes[58] JUBNEZ,[56] XITPEY,[56] and JEJZED[57]).

Based on the scarcity of the [N−I−N]⁻ systems, we became interested in systematically studying (Scheme 1) specific [N−I−N]⁻ systems in the context of halogen bonding and comparing them to their cationic [N−I−N]⁺ counterparts, as well as to the neutral haloimide and hypoiodite XB systems.

Inspired by the previous work on halogen-bonded complexes of haloimides and pyridine-based ligands,[17−19,45−48]

Scheme 3. Other Synthetic Routes to [N−I−N]⁻ Complexes

a)

2 + L2 → L2H   3 → **1** → L2H[3-I-3]

b)

2 → (NaOMe, MeOH) → Na3 → (TBABr) → TBA3 → **1** → TBA[3-I-3]
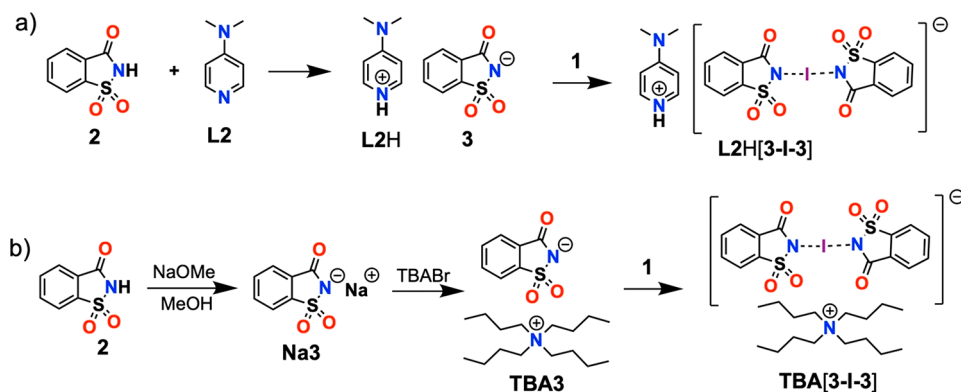
Table 1. Geometrical Parameters of the [N−I−N]⁻ Complexes

complex	N−I (Å)	I−N (Å)	N···N (Å)	N−I−N (deg)	C−N···N−C (deg)	N···O=C (Å)	N−H···O=C (deg)
L1H[3−I−3]	2.250(4)	2.250(4)	4.479(6)	180	180	2.854(6)[a] (×2)	141.8[a] (×2)
	2.239(4)	2.239(4)	4.497(6)	180	180		
L1H[3−I−3]H₂O	2.265(4)	2.275(4)	4.541(7)	178.8(2)	−128.9(2)	2.944(7)[a]	157.0[a]
						2.910(7)[b]	148.1[b]
L2H[3−I−3]	2.250(5)	2.250(5)	4.500(8)	180	−180	2.708(8) (×2)	146.2 (×2)
	2.261(5)	2.261(5)	4.521(8)	180	−180		
L3H[3−I−3][c]	2.218(4)	2.293(4)	4.512(6)	179.5(2)	174.3(2)	2.733(6)	175.3
L3H[3−I−3] DFT (in DCM)	2.210	2.275	4.484	178.2	165.9	2.746	162.8
L4H[3−I−3]	2.252(8)	2.252(8)	4.502(14)	180	180	2.681(14) (×2)	162.0(×2)
	2.262(9)	2.262(9)	4.526(15)	180	180		
L5H[3−I−3][c]	2.225(5)	2.262(5)	4.487(7)	177.6(2)	31.8(2)	2.821(7)	163.8
L6H[3−I−3] (C-monoclinic)	2.247(5)	2.253(5)	4.499(9)	179.6(2)	−176.8(2)		
L6H[3−I−3] (P-monoclinic)	2.250(5)	2.250(5)	4.499(8)	180	180		
	2.240(6)	2.240(6)	4.446(8)	180	180		
L7H[3−I−3][c]	2.217(5)	2.281(5)	4.496(8)	176.3(2)	150.0(2)	2.671(8)	141.8
L8H[3−I−3][d]	2.191(7)	2.299(6)	4.486(9)	174.8(2)	±72.2(2)	2.732(9)	178.1
TMA[**6−I−6**]	2.293(11)	2.293(11)	4.587(14)	180	0.5(4)		
TMA[**6−I−6**] DFT (in DCM)	2.235	2.246	4.481	179.2	7.6		
average (XRD)	2.255(6)	2.258(6)	4.505(9)	179.1(2)			
average[c] (XRD) (asym)	2.214(5)	2.284(5)	4.495(8)	176.1(2)			
DIQWIM[S4]	2.247	2.250	4.495	176.8	36.2		
[N−I−N]⁺ (CSD)[e]	**2.260**	**2.262**	**4.520**	**178.5**	ca. −140 to +180[f]		
					ca. 0		
					ca. +140 to +180		

[a]N−H···O=S. [b]HO-H···O=C. [c]Asymmetric [N−I−N], excluded from the average N−I calculation. [d]N−H···O hydrogen bond between the morpholinopyridinium moieties. [e]The average bond geometries from CSD. Data analyzed from 58 (97 data points) X-ray structures containing a [N−I−N]⁺ halogen bond of pyridine-based ligands/bases as XB acceptors. [f]The torsion angles form three groups 1st −140 to −180°, 2nd +140 +180° and the 3rd around zero. The large majority of the torsion angles are close to zero.

a cleft-containing diorthosubstituted pyridine, 2,6-ditolyl-4-(dimethylamino)pyridine (**L1**; Scheme 1) was synthesized through a known procedure (see the Supporting Information) to obtain the expected halogen-bonded complex **1L1**. The complexation of **1** (NISac) with **L1** in CHCl₃ proceeded smoothly, and the ¹H NMR spectrum (Figure S3) indicated the formation of the 1:1 halogen-bonded complex **1L1** (Scheme 2). The evidence that only the halogen-bonded complex **1L1** forms in solution is clearly visible in the ¹H NMR spectra (Figure S3), where the gradual addition of the ligand **L1** (Figure S2) into the solution of *N*-iodosaccharin (**1**) saturates with a 1:1 **1**:**L1** ratio, while **L1H**[3-I-3] would have presented itself with a 0.5:1 ratio.

However, when the reaction mixture (1 equiv. of **L1** with a slight excess of **1**) was left to slowly evaporate, single crystals of

the completely unprecedented anionic [N−I−N]⁻ complex **L1H**[3−I−3] were obtained (Scheme 2). The composition of **L1H**[3−I−3] consisted of the protonated **L1** ligand (**L1H⁺**) and the *in situ* formed [3−I−3]⁻ complex anion. The structure of the complex anion, which can be regarded as two negatively charged saccharinato anions and an iodine(I) cation forming a three-center−four-electron (3c-4e) halogen bond between the saccharinato anion nitrogen atoms and the iodine(I) cation, was revealed by SCXRD analysis. We postulate that, upon concentration of the reaction mixture, the presence of small amounts of water in the CHCl₃ solvent likely led to the reaction where **1** (*N*-iodosaccharin), halogen-bonded to the sterically demanding XB acceptor **L1**, underwent a reversible protonation reaction[59] to afford **2** (saccharin) and HOI (hypoiodous acid), which is very unstable and rapidly
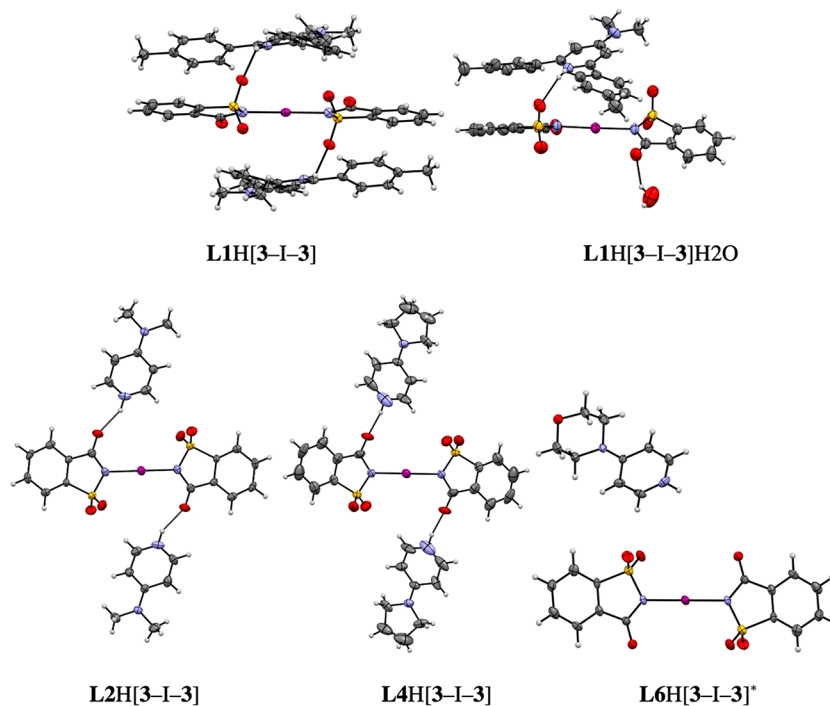
Figure 2. X-ray structures of the symmetric [N−I−N]⁻ complexes **L1**H[3−I−3], **L1**H[3−I−3]·H₂O, **L2**H[3−I−3], **L4**H[3−I−3] and **L6**H[3−I−3] (thermal displacement parameters at the 50% probability level). The asterisk refers to category C, from the C-monoclinic polymorph (Table 1).
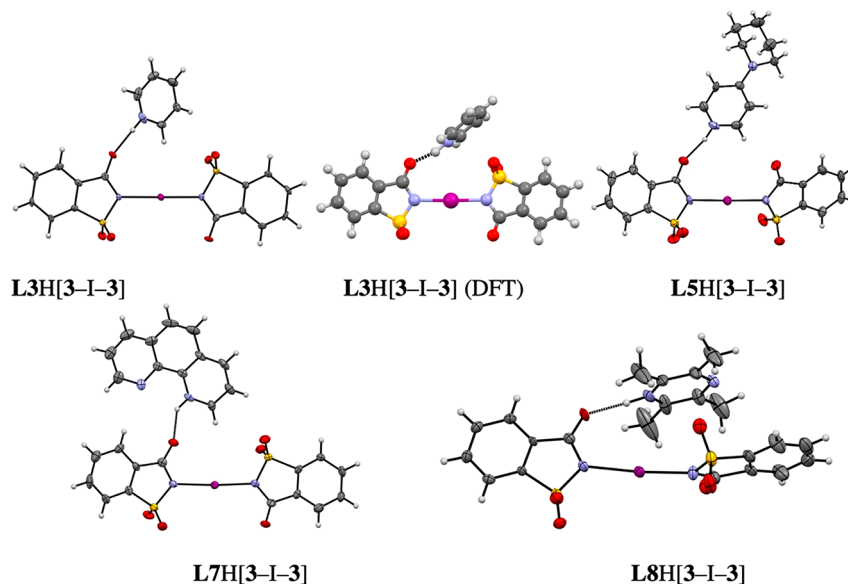

Figure 3. X-ray structures of the asymmetric [N−I−N]⁻ complexes **L3**H[3−I−3], **L5**H[3−I−3], **L7**H[3−I−3], and **L8**H[3−I−3] (thermal displacement parameters at the 50% probability level).

undergoes a disproportionation reaction to form elemental iodine. This was also supported by the observation of a deep pinkish color. Saccharin **2** can react with **L1**, which acts as a strong Lewis base, leading to formation of **L1**H⁺ and the saccharinato anion **3**. The newly formed **3** then coordinates with **1** (*N*-iodosaccharin), affording the anionic [N−I−N]⁻ complex anion [3−I−3]⁻, which is more stable than a mixture of **1** and **3** (Scheme 3a).

The serendipitous discovery of the formation of the **L1**H[3−I−3] led us to develop two different synthetic routes (Scheme 3) to obtain similar complexes. The staring materials

in route a) are solids; thus, to test if mechanochemistry could be used as well, the complex **L3**H[3−I−3] was prepared mechanochemically under solvent-free conditions (see section 2.3 in the Supporting Information). Subsequent crystallization of the complexes in a suitable solvent (dichloromethane, slow evaporation, or vapor diffusion of *n*-pentane or ethyl acetate into a dichloromethane solution of the complex) or directly from the reaction mixture (route b) led to the formation of the new [N−I−N]⁻ complexes **L1**H[3−I−3]H₂O, **L2**H[3−I−3], **L3**H[3−I−3], **L4**H[3−I−3], **L5**H[3−I−3], **L6**H[3−I−3], **L7**H[3−I−3], and **L8**H[3−I−3]. Besides the saccharinato-
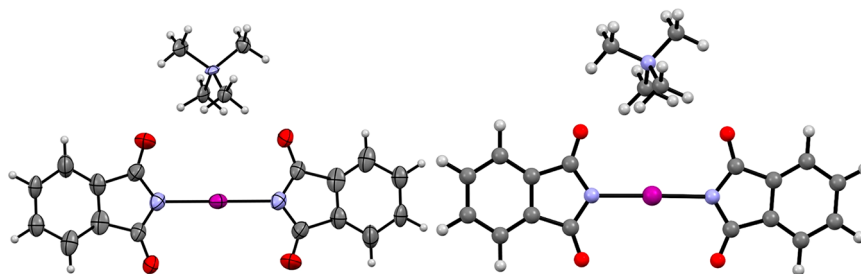
Figure 4. X-ray structure of TMA[**6**−I−**6**] (thermal displacement parameters at the 50% probability level; left) and the DFT structure (M06-2X/def2-TZVP with C-PCM DCM solvent model; right).

based [**3**−I−**3**]⁻ anions, the tetramethylammonium (TMA) salt of the phthalimido-based complex TMA[**6**−I−**6**] was also prepared using route b) (Scheme 3) starting from TMA **6** (tetramethyl phthaloimidato salt) and **4** (*N*-iodophthalimide). The complex TMA[**6**−I−**6**] was prepared to compare the effect of a cation incapable of hydrogen bonding (TMA) to the hydrogen-bond donating cations, **L1**H⁺−**L8**H⁺.

Based on geometrical parameters (Table 1) from the single-crystal X-ray diffraction (SCXRD) analysis, the prepared [N−I−N]⁻ complexes can be divided into three categories: (A) symmetric, HB (**L1**H[**3**−I−**3**], **L1**H[**3**−I−**3**]H₂O, **L2**H[**3**−I−**3**], and **L4**H[**3**−I−**3**]), (B) asymmetric, HB (**L3**H[**3**−I−**3**], **L5**H[**3**−I−**3**], **L7**H[**3**−I−**3**], and **L8**H[**3**−I−**3**]), and (C) symmetric, non-HB (**L6**H[**3**−I−**3**] (C-monoclinic), **L6**H[**3**−I−**3**] (P-monoclinic), and TMA[**6**−I−**6**]). As there is a small variation of the N−I bond distances in the known [N−I−N]⁺ complexes, the definition of asymmetry of the [N−I−N]⁻ moiety is based on the statistically significant deviation from the symmetric situation. This has been done by taking into account the estimated standard deviations (esds) of the N−I bond distances at the 3σ level. The N−I bond distance averages (Table 1) in category A fall with 99.5% probability between 2.237 and 2.273 Å and between 2.240 and 2.276 Å and between 2.199 and 2.229 Å and between 2.267 and 2.299 Å in category B.

The non-HB category C has only two examples, with the phthalimidato anion [**6**−I−**6**]⁻ exhibiting clearly longer, symmetric N−I bond distances [2.293(11) Å], while both polymorphs of **L6**H[**3**−I−**3**] show N−I distances analogous to those of category A. Similar systematic and statistically significant differences have been observed only in the heteroleptic [N−I−N]⁺ complexes[60] but have not been observed for the homoleptic [N−I−N]⁺ complexes,[23,24,58,59] where the average N−I bond length is 2.26 Å (Table 1). The N−I bond lengths for all the symmetric species (Figure 2) are remarkably within the exceptionally narrow range of 2.239(4) Å for **L1**H[**3**−I−**3**] and 2.262(9) Å for **L4**H[**3**−I−**3**], which are all crystallographically indistinguishable from one another with respect to their esd values, with the values themselves all lying within the reported range for the analogous [N−I−N]⁺ complexes.[58,59]

The largest variation was observed for the asymmetric (Figure 3) **L8**H[**3**−I−**3**] with N−I bond lengths of 2.191(7) and 2.299(6) Å, with the former bond length being shorter than any reported for the analogous [N−I−N]⁺ complexes. There are only two reported unrestrained asymmetric [N−I−N]⁺ solid-state structures, both by the authors,[38,60] which possess heteroleptic ligands: [I(pyridine)(DMAP)]PF₆ and [I(mtz)(DMAP)]PF₆ (DMAP = 4-dimethylaminopyridine; mtz = 1-methyl-1,2,3-triazole). These complexes exhibited

N−I bond length differences of 0.020 and 0.148/0.177 Å (as two independent molecules were present in the asymmetric unit cell), respectively, which makes the N−I bond length difference induced by hydrogen bonding in **L8**H[**3**−I−**3**] (0.108 Å) a viable strategy toward instigating asymmetry in 3c-4e halogen-bonded complexes (whether neutral or positively/negatively charged), and apparently one that can quantitatively rival the methodology of utilizing heteroleptic pairs of nucleophiles which suffers from disadvantages like ligand scrambling.[38,44]

The N−I−N angles (Table 1) are predominantly symmetry-restrained and therefore perfectly linear (180°), with only minor deviations from linearity observed for the asymmetric complexes (maximum of 174.8(2)° for **L8**H[**3**−I−**3**]). As noted previously for [N−I−N]⁺ and neutral O−I−N complexes,[23,24,27−32,49−51] the N···N intramolecular distances within the complexes are dictated by the electronic considerations of the iodine(I) cations which tightly restricts this distance as it satisfies its own electronic needs. This is reflected in the negligible deviation from the average values of 4.505(9) Å (symmetric) and 4.495(8) Å (asymmetric) for all complexes (Table 1), which is at most 0.049 Å for the asymmetric complex **L6**H[**3**−I−**3**]. However, this is not including TMA[**6**−I−**6**] (Figure 4) that exhibits a slightly larger deviation of 0.082 Å, which contains a much more sterically bulky cation that cannot be directly compared to the other examples.

Due to the known inaccuracy of the hydrogen atom positions (calculated to their idealized positions and refined as riding atoms), the heavier element (N and O) distances are instead given for the NH hydrogen-bond donors to the (C=)O hydrogen-bond acceptor groups. These intermolecular distances range from 2.67(1) to 2.94(1) Å (Table 1) and can all be considered hydrogen bond contacts of reasonable strength.

To provide insight into whether the packing interactions in the asymmetric complexes (category B) play a larger role than the hydrogen bonding, a DFT calculation in solution was performed (SPARTAN20,[61] M06-2X/def2-TZVP with C-PCM DCM solvent model; see the Supporting Information for details) for **L3**H[**3**−I−**3**]. The computationally obtained geometry (Table 1 and Figure 3) for **L3**H[**3**−I−**3**] agrees surprisingly well with the crystallographically determined structure, with a deviations of only +0.008 and −0.018 Å for the N−I bond distances, −0.028 Å for the N···N distances, and −1.3° for the N−I−N angle. This clearly indicates that the packing forces in category B are not the cause of the asymmetric [N−I−N]⁻ moiety but that it is caused by the hydrogen bonding from the HB-donor cation to only one of the saccharinato ligands (Figure 3). In the DFT-calculated

model of **L3**H[**3−I−3**] S=O···centroid(py) is 2.969 Å with an orthogonal orientation (torsion S−O−N−C = 89.4°, Figure 3) toward the S=O bond, indicating a O···π interaction. In the X-ray structure of **L3**H[**3−I−3**] the same torsion angle is −8.6° (Figure 3), not manifesting the same pyridinium cation O···π interaction due to the weak H-bonds to the S=O groups of the adjacent [**3−I−3**]$^-$ anions. As the phthalimidato-based complex TMA[**6−I−6**] (Figure 4) shows symmetric but longer N−I bond distances (Table 1), its structure was also computationally studied as with **L3**H[**3−I−3**] (Figure 4). The computed geometry differs in all geometrical parameters from the SCXRD-obtained structure, except for the N−I−N angle (Table 1). The DFT-obtained N−I bond distances are not symmetrical (2.235 vs 2.246 Å) and deviate −0.058 and −0.047 Å from the SCXRD values. The N···N length also deviates −0.106 Å from the SCXRD value (Table 1). This small, but marked, deviation between the DFT and SCXRD values results from the packing interactions between the TMA cation and the [**6−I−6**]$^-$ anion, as they form a 1-D polymer, [···TMA$^+$···[**6−I−6**]$^-$···TMA$^+$···[**6−I−6**]$^-$···TMA$^+$···[**6−I−6**]$^-$···]$_n$, in the solid state (Figure S6 in the Supporting Information).

In conclusion, a series of anionic [N−I−N]$^-$ complexes containing hydrogen-bond acceptors on the N-based ligands were synthesized and charge-balanced with a variety of different hydrogen-bond donors. The resulting complexes could be sorted into three groups based on SCXRD studies: symmetric HB (hydrogen-bonded), asymmetric HB, and asymmetric non-HB. The X-ray studies revealed two important outcomes; the anionic halogen-bonded [N−I−N]$^-$ complexes were structurally similar to their cationic [N−I−N]$^+$ analogues, with a near-identical range of N−I bond lengths being observed, and asymmetry in the N−I bond lengths of the [N−I−N]$^-$ complexes could be introduced via hydrogen bonding to one of their nitrogen-based ligands, with metrics comparable to or surpassing those of the asymmetry resulting from the strategy of creating heteroleptic [N1−I−N2]$^+$ systems, which suffer from the disadvantage of ligand scrambling, and which is not an issue for the homoleptic complexes reported herein.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.2c01162.

Experimental details, synthesis and single crystal preparation, and single-crystal diffraction data (PDF)

Accession Codes

CCDC 2212725−2212735 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.

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