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Computational study of halogen-halogen interactions in polyhalide ionic liquids

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Abstract

Recent years have seen many specific applications of polyhalide ionic liquids (ILs) such as oxidizing solvents for metals and alloys, immersion fluids for optical mineralogy, and electrolyte components for dye-sensitized solar cells. In this work, interhalogen interactions in a set of polyhalide ILs composed of polyhalide anions, $[X_3]^-$, $[X_5]^-$ and $[X_7]^-$ ($X = \text{I}$ or Br), with two typical cations, tetramethylammonium $[\text{NMe}_4]^+$ and 1,3-dimethylimidazolium $[\text{DMIM}]^+$, were thoroughly studied from a computational point of view. In addition, a halogen-bonded supramolecular anion, $[\text{C}_6\text{F}_{13}\text{-I}\cdots\text{I}\cdots\text{I-C}_6\text{F}_{13}]^-$, was also taken into account for comparison. Unlike those in bare polyhalide ions, halogen-halogen interactions in ionic pairs for the investigated ILs are somewhat asymmetric caused by the interactions between the cations and the anions. Most interhalogen contacts in ionic pairs have some covalent content, while $\text{I}\cdots\text{I}$ interactions in the complexes of the supramolecular anion are purely noncovalent. In general, there are two classes of interhalogen bonds in ionic pairs: one class with longer $\text{X}\cdots\text{X}$ distances shows primarily ionic character, while the other with shorter distances has a larger degree of covalency, i.e. intermediate ionic/covalent nature.

Keywords Polyhalide ionic liquids · Interhalogen interactions · Covalency · Computational

Introduction

Room temperature ionic liquids (ILs) are completely composed of ions with melting points below 100°C [1–3]. These non-volatile liquids have several unique properties, such as excellent thermal stability, high ionic conductivity, and low combustibility, which are being explored as environmentally benign solvents [4–7]. In addition, ILs have also been described as “designer solvents” with characteristics that can be tuned to meet specific requirements for a particular application [8, 9].

ILs can be roughly divided into three categories: (i) aprotic ILs, the most frequently used ILs so far; (ii) protic ILs that are formed by the simple proton transfer from a Brønsted acid to a Brønsted base [10–12]; (iii) solvate ILs, the equimolar mixtures of alkali metal salts and oligoethers [13]. Over the past few years, polyhalide ILs consisting of polyhalide anions in their structure have attracted increasing research interest and can be recognized as an important subclass of ILs [14, 15]. A common synthesis route of these ILs is the addition of elemental chlorine, bromine or iodine to halide IL precursors.

Polyhalide ILs have been used as selective halogenation reagents in organic synthesis for a long time. Bortolini et al. previously studied several trihalide ILs composed of trihalide anions ($[I_3]^-$, $[IBr_2]^-$, $[ICl_2]^-$) and imidazolium cations with different alkyl chain lengths as reagent-solvents for stereoselective iodination of alkenes and alkynes. High yields and stereoselectivities of the reactions were observed when using these “green” alternative media [16]. Of particular attention is that many other specific applications of such ILs were also reported in recent years. For example, a series of polyhalide ILs, which are comprised of trihalides (like $[I_3]^-$, $[Br_3]^-$, $[IBr_2]^-$) and higher polyhalides ($[I_5]^-$, $[I_7]^-$, $[I_9]^-$) with imidazolium cations, have been developed as immersion fluids for optical mineralogy [17]. These environmentally benign fluids not only have high refractive indices but also reduce health risk. Subsequently, the group of Kloo prepared some trihalide ILs containing trihalide ions ($[Br_3]^-$, $[IBr_2]^-$, $[I_2Br]^-$) and imidazolium cations with different lengths of alkyl chains, which were used as electrolyte components for dye-sensitized solar cells [18]. They found high efficiency and long-term stability achieved by these ILs-based electrolytes. More recently, a number of trihalide ILs consisting of trihalides (like $[I_3]^-$, $[Br_3]^-$, $[IBr_2]^-$, $[I_2Br]^-$) and a variety of cations, e.g. imidazolium, ammonium, phosphonium and pyridinium, were synthesized and applied as oxidizing agents for dissolving various metals and alloys under mild conditions [19, 20]. These trihalide ILs provided a safe dissolution method for

metals and alloys, because the whole dissolution process can proceed without the production of any gases.

Polyhalide ions have been extensively investigated during the last decades due to their interesting structures and vast applications. The most well-studied polyhalides are the simplest trihalide anions ($[X_3]^-$, $X = \text{Cl}, \text{Br}, \text{I}$), in which the bonding was characterized as a three-center, four-electron ($3c-4e$) σ bond through topological analysis of either experimental or theoretical electron density [21]. Furthermore, recent X-ray adsorption spectroscopy (XAS) experiments have unraveled that the degree of charge transfer in solid-state I_2Cl^- and I_2Br^- materials is comparable to that detected in coordination complexes, and $X\cdots X$ contacts in these systems thus should have substantial covalent contributions [22]. However, halogen-halogen interactions in polyhalide ILs, especially those in higher polyhalide ILs, have received far less attention to date. Given that polyhalide ILs have shown great potential in diverse fields of chemistry, it is certainly necessary to study the properties of interhalogen interactions in these ILs from a computational viewpoint.

Scheme 1 Chemical structures of polyhalide anions under study ($X = \text{I}$ or Br).

In this work, a series of polyhalide ILs composed of trihalide ($[I_3]^-$, $[Br_3]^-$, $[IBr_2]^-$), pentahalide ($[I_5]^-$, $[Br_5]^-$, $[I_2Br_3]^-$) and heptahalide anions ($[I_7]^-$, $[Br_7]^-$, $[I_3Br_4]^-$) with two typical cations, tetramethylammonium $[NMe_4]^+$ and 1,3-dimethylimidazolium $[DMIM]^+$, were systematically investigated by using DFT calculations. In addition, a halogen-bonded supramolecular anion, $[C_6F_{13}-I\cdots I\cdots I-C_6F_{13}]^-$ (abbreviated as $[SI_3]^-$), was also considered for comparison, as displayed in Scheme 1. Very recently, Bruce and co-workers have firstly reported unconventional halogen-bonded ionic liquid crystals based on such supramolecular anions and imidazolium cations [23]. To gain a deeper understanding of halogen-halogen interactions in these ILs, many computational approaches, such as quantum theory of atom in molecules (QTAIM) [24], electron localization function (ELF) [25], mayer bond order (MBO) [26, 27], intrinsic bond strength index (IBSI) [28], and independent gradient model (IGM) [29, 30], were also employed. For the first time the features of interhalogen interactions in polyhalide ILs and their discrepancies versus classical halogen bonds were examined.

Computational methods

All the geometries of isolated ions and ionic pairs for the investigated ILs were fully optimized without any symmetry constraints via the hybrid functional B3LYP including empirical dispersion correction term (DFT-D3) [31–33], which has been widely used for studying molecular interactions in a large number of ILs [34, 35]. The aug-cc-pvdz-PP basis set [36], which uses pseudopotentials to describe the core electrons, was employed for the heaviest I atom (28 core electrons), while for the remaining atoms Dunning's correlation-consistent basis set, aug-cc-pvdz [37], was applied. Frequency calculations were carried out at the same level of theory for all the optimized geometries to affirm that they are real minima on the potential energy surface. All of these calculations were performed by means of the Gaussian 09/16 suite of programs [38, 39].

Many possible binding sites for polyhalide anions around the cations were initially taken into consideration, and the most stable configurations of ionic pairs were then employed for the following analyses. The interaction energy was computed as the difference between the energy of ionic pair and the sum of the energies of optimized cation and anion with considering the basis set superposition error (BSSE) correction [40].

To obtain interhalogen bonding characteristics, the QTAIM, ELF and IGM analyses were

Table 1 Geometric data for bare polyiodide ions and ionic pairs containing these anions^a

Complexes	r_1	r_2	θ									
I ₃ ⁻	3.020	3.020	180.0									
[DMIM][I ₃]	3.031	2.991	169.3									
[NMe ₄][I ₃]	3.037	2.986	168.8									
Complexes	r_1	r_2	r_3	r_4	θ_1	θ_2	θ_3					
I ₅ ⁻	3.128	3.128	2.911	2.910	177.8	177.8	107.6					
[DMIM][I ₅]	3.182	3.134	2.868	2.894	169.8	172.9	88.0					
[NMe ₄][I ₅]	3.098	3.071	2.913	2.929	176.5	174.5	90.6					
Complexes	r_1	r_2	r_3	r_4	r_5	r_6	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6
I ₇ ⁻ -P	3.211	3.211	3.211	2.855	2.855	2.855	178.6	178.6	178.6	101.8	101.8	101.8
[DMIM][I ₇]-P	3.166	3.210	3.238	2.869	2.847	2.836	175.6	175.9	173.0	86.5	92.4	86.9
[NMe ₄][I ₇]-P	3.231	3.231	3.231	2.847	2.846	2.846	170.9	170.9	170.9	84.3	84.4	84.4
Complexes	r_1	r_2	r_3	r_4	r_5	r_6	θ_1	θ_2	θ_3	θ_4	θ_5	
I ₇ ⁻ -L	3.191	3.191	2.994	2.994	2.868	2.868	178.1	103.1	180.0	103.1	178.1	
[DMIM][I ₇]-L	3.201	3.197	3.006	2.983	2.857	2.859	176.4	90.6	176.6	99.5	172.2	
[NMe ₄][I ₇]-L	3.160	3.160	2.990	2.990	2.876	2.876	177.9	99.6	177.5	99.6	177.5	
Complexes	r_1	r_2	θ									
SI ₃ ⁻	3.329	3.328	87.0									

[DMIM][SI ₃]	3.407	3.469	75.9
[NMe ₄][SI ₃]	3.430	3.430	100.9

^aDistances in angstroms, angles in degrees. The definitions of r and θ are shown in Scheme 1.

Results

Geometrical properties of polyhalide ions in ionic pairs for the investigated ILs

The optimized structures of ionic pairs containing polyiodide anions ($[I_3]^-$, $[I_5]^-$, $[I_7]^-$) are displayed in Figures 1 and S1, and the geometrical data of these complexes and isolated polyiodides are summarized in Table 1. Unless otherwise noted, we only concentrate on the results of these systems, since ionic pairs involving polybromide anions ($[Br_3]^-$, $[Br_5]^-$, $[Br_7]^-$) and mixed ones ($[IBr_2]^-$, $[I_2Br_3]^-$, $[I_3Br_4]^-$) generally exhibit similar geometrical features.

As expected, bare triiodide ion displays a linear and symmetrical structure with two equivalent $I\cdots I$ distances, hence indicating the delocalized 3c-4e bond. However, this anion becomes asymmetric in [DMIM][I₃] and [NMe₄][I₃] with the difference between the two $I\cdots I$ distances being of about 0.04 Å. Furthermore, this anion tends to bent in ionic pairs ($\theta \approx 169^\circ$), which can be ascribed to the interactions between this anion and the cations. Notably, upon the formation of ionic pair complexes one $I\cdots I$ distance elongates and simultaneously the other shortens, leading to a comparable overall length to isolated I_3^- (ca. 6.04 Å). Therefore, in IL environment trihalide anions have a less linear and asymmetric structure caused by the cation-anion interactions.

Bare pentaiodide ion can be considered as the adduct of two Lewis acidic I_2 molecules with a Lewis basic iodide anion. As a matter of fact, the two interacting $I\cdots I$ distances (r_1 and r_2) are computed much longer than other two distances (r_3 and r_4) in this anion that has a V-shaped structure. Similarly, when complexed with the cations, the pentaiodide anion becomes asymmetric, in view of the two I_3 units exhibiting different $I\cdots I$ distances and interaction angles. Furthermore, owing to the I atoms in I_5^- involved into HB interactions with the cations, this anion undergoes an obvious bent, producing two almost perpendicular I_3 units ($\theta_3 \approx 90^\circ$). Overall, iodine-iodine bonds in [DMIM][I₅] and [NMe₄][I₅] can be divided into two catalogues: the shorter ones showing the $I\cdots I$ distances approaching that of molecular I_2 (2.732 Å) and the longer ones with the distances moving towards those in the complexes of SI_3^- (ca. 3.43 Å).

Two configurations, pyramid (P) and long chain (L), were constructed for bare heptaiodide ion, as displayed in Scheme 1. In P configuration, r_1 , r_2 and r_3 are identical (about 3.21 Å)

accompanied by equivalent r_4 , r_5 and r_6 (ca. 2.86 Å), and θ_1 , θ_2 and θ_3 are close to 180° while θ_4 , θ_5 and θ_6 amount to 101.8°. Evidently, this configuration can be seen as the adduct of three I₂ molecules with a single iodide anion. As a result of three I₂ molecules establishing iodine-iodine contacts with I[−], the interacting I⋯I distances in I₇[−] (r_1 , r_2 , r_3) appear to be approximately 0.03 Å longer than those in I₅[−] (r_1 and r_2). In contrast, in the L configuration three kinds of interatomic distances (r_1/r_2 , r_3/r_4 , r_5/r_6) and two different triiodide angles ($\theta_1/\theta_3/\theta_5$, θ_2/θ_4) were detected, which can be viewed as the I₂⋯I₃[−]⋯I₂ motif. The central I₃ unit remains essentially linear with the distances close to those in triiodide ion. In general, these geometrical features of isolated hepta-iodide ion are reproduced in [DMIM][I₇] and [NMe₄][I₇]. However, all the triiodide angles in ionic pairs become smaller, thus suggesting less linear interactions and more bent structures, as also observed in the cases of I₅[−] and I₃[−]. Furthermore, in the L configuration of ionic pairs, the two I₂ molecules are located at the same side of the central I₃ unit, unlike that in isolated I₇[−]-L, because the anion is able to establish more HBs with the cations in such geometry. Similarly, I⋯I bonds in [DMIM][I₇] and [NMe₄][I₇] can be classified into two groups: the shorter ones with the interatomic distances less than 3.0 Å and the longer ones having the distances within the 3.160-3.238 Å range.

As can be deduced from Table 2, polybromide ions and mixed ones exhibit similar geometric properties as those of polyiodides, with the exception of shorter Br⋯Br and Br⋯I distances. This can be attributed to the smaller atomic radius of the Br atom with respect to the I atom. Here it is worth mentioning that different polyhalide anions affect the interaction energies of ionic pair complexes to a less degree with the largest gap amounting to only about 4 kcal/mol. Although higher polyhalides have a more diffuse charge, more HB interactions can be formed between these larger anions and the cations.

Table 2 Geometric data for bare polybromide ions and mixed ones and ionic pairs containing these anions^a

Complexes	r_1	r_2	θ				
Br ₃ [−]	2.641	2.641	180.0				
[DMIM][Br ₃]	2.661	2.599	172.2				
[NMe ₄][Br ₃]	2.652	2.605	171.9				
IBr ₂ [−]	2.798	2.798	180.0				
[DMIM][IBr ₂]	2.803	2.767	168.2				
[NMe ₄][IBr ₂]	2.807	2.755	168.2				
Complexes	r_1	r_2	r_3	r_4	θ_1	θ_2	θ_3
Br ₅ [−]	2.764	2.764	2.513	2.513	177.8	177.8	109.4

[DMIM][Br ₅]	2.828	2.776	2.468	2.495	171.9	174.0	90.4					
[NMe ₄][Br ₅]	2.711	2.710	2.530	2.530	176.3	176.3	93.2					
I ₂ Br ₃ [−]	2.911	2.911	2.688	2.688	178.2	178.2	106.6					
[DMIM][I ₂ Br ₃]	2.962	2.920	2.650	2.673	169.4	172.5	91.5					
[NMe ₄][I ₂ Br ₃]	2.982	2.982	2.641	2.641	172.9	172.9	105.9					
Complexes	<i>r</i> ₁	<i>r</i> ₂	<i>r</i> ₃	<i>r</i> ₄	<i>r</i> ₅	<i>r</i> ₆	θ ₁	θ ₂	θ ₃	θ ₄	θ ₅	θ ₆
Br ₇ [−] -P	2.859	2.859	2.859	2.455	2.455	2.455	178.6	178.6	178.6	104.0	104.0	104.0
[DMIM][Br ₇]-P	2.796	2.855	2.882	2.477	2.449	2.436	176.9	177.2	174.7	90.1	98.1	89.9
[NMe ₄][Br ₇]-P	2.867	2.867	2.867	2.448	2.448	2.448	172.7	172.7	172.7	87.1	87.1	87.1
I ₃ Br ₄ [−] -P	3.002	3.002	3.001	2.637	2.637	2.637	178.8	178.8	178.8	101.9	101.9	101.9
[DMIM][I ₃ Br ₄]-P	2.973	3.019	3.031	2.645	2.627	2.623	174.6	173.9	172.2	90.6	92.1	89.8
[NMe ₄][I ₃ Br ₄]-P	3.042	3.041	3.041	2.627	2.628	2.628	168.9	168.9	168.9	86.9	86.9	86.9
Complexes	<i>r</i> ₁	<i>r</i> ₂	<i>r</i> ₃	<i>r</i> ₄	<i>r</i> ₅	<i>r</i> ₆	θ ₁	θ ₂	θ ₃	θ ₄	θ ₅	
Br ₇ [−] -L	2.850	2.850	2.611	2.611	2.461	2.461	177.9	105.5	180.0	105.5	177.9	
[DMIM][Br ₇]-L	2.861	2.874	2.642	2.580	2.448	2.445	176.0	91.5	176.0	99.1	172.8	
[NMe ₄][Br ₇]-L	2.816	2.816	2.607	2.607	2.470	2.470	177.1	103.5	178.8	103.5	178.8	
I ₃ Br ₄ [−] -L	2.981	2.981	2.778	2.778	2.648	2.648	178.3	104.5	180.0	104.5	178.3	
[DMIM][I ₃ Br ₄]-L	2.979	2.985	2.789	2.764	2.640	2.639	177.6	94.1	175.5	100.5	175.5	
[NMe ₄][I ₃ Br ₄]-L	2.939	2.940	2.775	2.775	2.657	2.656	178.5	101.9	176.7	101.9	176.7	

^aDistances in angstroms, and angles in degrees. The structures of ionic pairs of mixed polyhalide anions with [NMe₄]⁺ are given in Figure S2. The definitions of *r* and θ are shown in Scheme 1.

Fig. 2 AIM graphs of ionic pairs of polyiodide anions with [NMe₄]⁺. The orange points correspond to BCPs, and bond paths are shown as yellow lines.

Table 3 AIM results for ionic pairs containing polyiodide anions^a

Complexes	Contacts	$10^2\rho(r)$	$10^2\nabla^2\rho(r)$	$10^2G(r)$	$10^2V(r)$	$ V(r) /G(r)$	$10^2H(r)$
[DMIM][I ₃]	r_1	3.896	4.462	1.585	-2.010	1.268	-0.425
	r_2	4.023	4.492	1.672	-2.221	1.328	-0.549
[NMe ₄][I ₃]	r_1	3.890	4.579	1.573	-2.001	1.272	-0.428
	r_2	4.241	4.480	1.681	-2.242	1.333	-0.561
[DMIM][I ₅]	r_1	2.935	4.726	1.296	-1.411	1.089	-0.115
	r_2	3.209	4.795	1.392	-1.585	1.139	-0.193
	r_3	5.225	3.670	1.949	-2.981	1.530	-1.032
	r_4	4.998	3.872	1.887	-2.807	1.488	-0.919
[NMe ₄][I ₅]	r_1	3.408	4.868	1.460	-1.702	1.166	-0.243
	r_2	3.572	4.895	1.521	-1.818	1.195	-0.297
	r_3	4.800	4.120	1.847	-2.664	1.442	-0.817
	r_4	4.668	4.231	1.815	-2.572	1.417	-0.757
[DMIM][I ₇]-P	r_1	2.988	4.855	1.335	-1.457	1.091	-0.121
	r_2	2.738	4.746	1.246	-1.306	1.048	-0.060
	r_3	2.600	4.654	1.193	-1.222	1.024	-0.029
	r_4	5.212	3.674	1.947	-2.976	1.528	-1.029
	r_5	5.424	3.406	1.996	-3.141	1.574	-1.145
	r_6	5.526	3.304	2.026	-3.227	1.593	-1.200
[NMe ₄][I ₇]-P	r_1	2.656	4.623	1.199	-1.241	1.035	-0.042
	r_2	2.652	4.623	1.197	-1.239	1.035	-0.042
	r_3	2.653	4.623	1.197	-1.239	1.035	-0.042
	r_4	5.415	3.441	1.996	-3.132	1.569	-1.136
	r_5	5.420	3.441	1.998	-3.136	1.570	-1.138
	r_6	5.420	3.441	1.998	-3.136	1.570	-1.138
[DMIM][I ₇]-L	r_1	2.817	4.714	1.265	-1.352	1.069	-0.086
	r_2	2.830	4.741	1.267	-1.348	1.064	-0.082
	r_3	4.055	4.725	1.664	-2.147	1.290	-0.483
	r_4	4.240	4.583	1.700	-2.255	1.326	-0.555
	r_5	5.353	3.426	1.965	-3.074	1.564	-1.109
	r_6	5.323	3.498	1.968	-3.061	1.555	-1.093
[NMe ₄][I ₇]-L	r_1	3.032	4.842	1.343	-1.477	1.100	-0.133
	r_2	3.033	4.840	1.344	-1.478	1.100	-0.134
	r_3	4.153	4.734	1.702	-2.220	1.304	-0.518
	r_4	4.151	4.758	1.701	-2.218	1.304	-0.517
	r_5	5.174	3.649	1.923	-2.935	1.526	-1.011
	r_6	5.173	3.650	1.923	-2.934	1.526	-1.011
[DMIM][SI ₃]	r_1	1.773	3.436	0.797	-0.735	0.922	0.062
	r_2	2.019	3.688	0.892	-0.861	0.965	0.030
[NMe ₄][SI ₃]	r_1	1.927	3.631	0.863	-0.818	0.948	0.045
	r_2	1.928	3.633	0.863	-0.819	0.948	0.045

^aAll values are given in a.u.

QTAIM analysis

The QTAIM method, based on the critical points of the electron density $\rho(r)$, has been widely used to visualize and quantify noncovalent interactions [24]. Popelier and Koch proposed some basic topological criteria to characterize weak interactions: the existence of bond critical point (BCP) between the donor and acceptor atoms; $\rho(r)$ at BCP for closed-shell interactions varying from 0.002 a.u. to 0.04 a.u. [43, 44].

All interhalogen bonds in ionic pairs under investigation were identified by the QTAIM method, i.e. the presence of a BCP between the two halogen atoms involved, as displayed in Figure 2. The AIM parameters at the BCPs for these complexes are summarized in Tables 3 and S1. It is clear that the values of $\rho(r)$ fall beyond the proposed range of noncovalent interactions (> 0.04 a.u.) for a number of $X\cdots X$ bonds. Furthermore, these bonds always have shorter interatomic distances, while those within the range commonly possess longer distances. For example, in [DMIM][I₅] and [NMe₄][I₅], the two interacting I $\cdots$ I contacts (r_1 and r_2) with longer distances have smaller $\rho(r)$, ranging from 2.935 a.u. to 3.572 a.u., whereas $\rho(r)$ for other two shorter contacts (r_3 and r_4) is predicted to be out of the range (4.668 a.u. $\sim$ 5.225 a.u.). As a matter of fact, the values of $\rho(r)$ correlate well with the distances for all interhalogen interactions in the complexes of polyiodide ions, as displayed in Figure S3.

Tables 3 and S1 also lists the energetic properties at the BCPs, i.e. local kinetic energy density $G(r)$, local potential energy density $V(r)$, and electronic energy density $H(r)$. The relationships of these AIM parameters are given as follows

$$1/4\nabla^2\rho(r)=2G(r)+V(r) \quad (1)$$

$$H(r)=G(r)+V(r) \quad (2)$$

$G(r)$ is usually positive while $V(r)$ is always negative [45, 46]. It has been proposed that the interactions are purely noncovalent if $H(r) > 0$ or $|V(r)|/G(r) < 1$, whereas the interactions have some covalent content when $H(r) < 0$ or the ratio > 1 [47]. As can be seen from Tables 3 and S1, negative values of $H(r)$ are predicted for most interhalogen interactions in ionic pairs under study, thereby implying some degree of covalency. Furthermore, $X\cdots X$ contacts with shorter interatomic distances always possess higher ratio and vice versa. For instance, in [DMIM][I₅] and [NMe₄][I₅], the two interacting I $\cdots$ I contacts (r_1 and r_2) have the ratio values smaller than 1.2, while the ratio of other two shorter contacts (r_3 and r_4) increases, approaching the magnitude of molecular I₂

(about 1.8). Consequently, the former interhalogen interactions can be recognized as strong ionic halogen bonds, while the latter ones show a larger degree of covalency, that is, intermediate ionic/covalent nature.

It is noteworthy that some $\text{Br}\cdots\text{Br}$ contacts in ionic pairs including heptabromide anion exhibit positive $H(r)$ with the ratio < 1 (cf. Table S1), in line with longer interatomic distances and smaller values of $\rho(r)$. Clearly, these interhalogen interactions are entirely noncovalent and can be considered as conventional weak halogen bonds, as those in the complexes of SI_3^- .

Fig. 3 Contour line map of $\nabla^2\rho(r)$ for polyiodide anions in representative ionic pairs. Bond CPs are shown in blue, nuclear CPs in brown, and bond paths are shown as brown lines.

The contour line maps of Laplacian of electron density $\nabla^2\rho(r)$ for polyiodide anions in representative ionic pairs are depicted in Figure 3. The blue and brown points denote bond and nuclear CPs, respectively. Evidently, in $[\text{NMe}_4][\text{I}_5]$ a stronger polarization along the terminal bond paths (r_3 and r_4) is observed compared with other two paths (r_1 and r_2), which indicates a higher covalent content for the former two $\text{I}\cdots\text{I}$ bonds, consistent with the above findings. Similarly, in the two configurations of $[\text{NMe}_4][\text{I}_7]$, the polarization along the terminal bond paths appears to be stronger than other paths. Furthermore, the central I_3 unit in $[\text{NMe}_4][\text{I}_7]\text{-L}$ shows a similar contour plot as that in $[\text{NMe}_4][\text{I}_3]$.

Fig. 4 ELF maps of polyiodide anions in representative ionic pairs.

Table 4 ELF, MBO and IBSI values for ionic pairs containing polyiodide anions

Complexes	Contacts	ELF	MBO	IBSI	Complexes	Contacts	ELF	MBO	IBSI
[DMIM][I ₃]	<i>r</i> ₁	0.396	0.590	0.166	[NMe ₄][I ₃]	<i>r</i> ₁	0.399	0.567	0.166
	<i>r</i> ₂	0.432	0.633	0.180		<i>r</i> ₂	0.437	0.599	0.176
[DMIM][I ₅]	<i>r</i> ₁	0.276	0.402	0.105	[NMe ₄][I ₅]	<i>r</i> ₁	0.331	0.467	0.123
	<i>r</i> ₂	0.308	0.461	0.114		<i>r</i> ₂	0.348	0.429	0.129
	<i>r</i> ₃	0.536	0.775	0.194		<i>r</i> ₃	0.492	0.697	0.175
	<i>r</i> ₄	0.515	0.772	0.183		<i>r</i> ₄	0.478	0.716	0.171
[DMIM][I ₇]-P	<i>r</i> ₁	0.276	0.356	0.096	[NMe ₄][I ₇]-P	<i>r</i> ₁	0.243	0.310	0.094
	<i>r</i> ₂	0.247	0.309	0.097		<i>r</i> ₂	0.242	0.310	0.093
	<i>r</i> ₃	0.232	0.288	0.093		<i>r</i> ₃	0.242	0.309	0.085
	<i>r</i> ₄	0.535	0.799	0.169		<i>r</i> ₄	0.554	0.826	0.195
	<i>r</i> ₅	0.555	0.840	0.194		<i>r</i> ₅	0.554	0.826	0.193
	<i>r</i> ₆	0.563	0.856	0.196		<i>r</i> ₆	0.554	0.826	0.182
[DMIM][I ₇]-L	<i>r</i> ₁	0.259	0.379	0.099	[NMe ₄][I ₇]-L	<i>r</i> ₁	0.284	0.366	0.127
	<i>r</i> ₂	0.262	0.346	0.114		<i>r</i> ₂	0.284	0.366	0.127
	<i>r</i> ₃	0.405	0.591	0.159		<i>r</i> ₃	0.414	0.575	0.183
	<i>r</i> ₄	0.431	0.599	0.165		<i>r</i> ₄	0.413	0.575	0.183
	<i>r</i> ₅	0.552	0.846	0.193		<i>r</i> ₅	0.535	0.787	0.222
	<i>r</i> ₆	0.547	0.866	0.210		<i>r</i> ₆	0.535	0.786	0.222
[DMIM][SI ₃]	<i>r</i> ₁	0.158	0.241	0.069	[NMe ₄][SI ₃]	<i>r</i> ₁	0.175	0.233	0.063
	<i>r</i> ₂	0.188	0.176	0.064		<i>r</i> ₂	0.175	0.233	0.063

ELF, MBO and IBSI results

The ELF approach is capable of showing the degree of electronic localization at different positions in three-dimensional real space, which has been extensively used for a wide variety of systems, such as organic molecules, atomic crystals, coordination compounds and clusters, as well as for different issues, e.g. examining aromaticity, portraying favorable electronic delocalization path and exploring variation of electronic structure during chemical reaction [48–51]. ELF is essentially an indicator for determining electron localization degree in local region.

The ELF graphs of polyiodide ions in representative ionic pairs are displayed in Figure 4, and the ELF values of X··X bonds in all studied complexes are summarized in Tables 4 and S2. As can be seen, in [NMe₄][I₅] the terminal two I··I bonds (r_3 and r_4) have larger ELF values, moving towards the magnitude of molecular I₂ (about 0.65), thus suggesting a greater degree of covalency. In contrast, the ELF values of the two interacting I··I contacts (r_1 and r_2) decrease, that is, a more delocalized character of the electrons of these bonds. Similarly, in the two configuration of [NMe₄][I₇], the shorter iodine-iodine bonds always have larger ELF values and vice versa. Furthermore, the ELF plot of the central I₃ unit in [NMe₄][I₇]-L is similar to that in [NMe₄][I₃], in good agreement with the above QTAIM outcomes. Notably, the smallest ELF values (< 0.2) are predicted for I··I interactions in the complexes of SI₃[−], which indicates the greatest degree of electronic delocalization. Therefore, a disappearing covalent contribution occurs and these interactions are purely noncovalent, as also unveiled by the QTAIM method.

The MBO is an index for the definition of bond strength, which has been proved very effective in chemical reaction analysis and description of bonding mechanism of complex molecules [52]. The MBO between atom A and B is defined as

$$I_{AB} = I_{AB}^{\alpha} + I_{AB}^{\beta} = 2 \sum_{a \in A} \sum_{b \in B} \left[\left(P^{\alpha} S \right)_{ba} \left(P^{\alpha} S \right)_{ab} + \left(P^{\beta} S \right)_{ba} \left(P^{\beta} S \right)_{ab} \right] \quad (3)$$

where P^{α} and P^{β} are alpha and beta density matrix, respectively, and S is overlap matrix.

The calculated MBO values of X··X bonds in ionic pairs under investigation are also listed in Tables 4 and S2. It is seen that in [DMIM][I₅] and [NMe₄][I₅] much larger MBO values are predicted for the terminal two iodine-iodine bonds (r_3 and r_4) with respect to other two ones (r_1 and r_2). As a consequence, the former bonds are much stronger than the latter ones, leading to a greater covalent content. Notably, the MBO values of the terminal three iodine-iodine bonds (r_4 , r_5 , r_6) in the P configuration of [DMIM][I₇] and [NMe₄][I₇] increase further, moving toward 1,

hence indicating intermediate covalent/ionic character. In contrast, the MBO values of the three interacting I...I contacts (r_1 , r_2 , r_3) further decrease, approaching those of the complexes of SI_3^- , which implies weaker strength and thus ionic nature. As expected, I...I bonds in the central I_3 unit of $[\text{DMIM}][\text{I}_7]\text{-L}$ and $[\text{NMe}_4][\text{I}_7]\text{-L}$ exhibit similar MBO values as those in the systems of I_3^- , consistent with the above QAIM and ELF findings. In fact, a good correlation was found between the MBO values and the interatomic distances for all interhalogen interactions in polyiodide ionic pairs (see Figure S3).

The IBSI, a powerful and robust tool for interpretation accessible to a wide community of chemists, was also recommended to quantify strength of chemical bonds. It has been demonstrated that magnitude of IBSI of transition metal coordination bond is markedly smaller than that of covalent bond, and magnitude of IBSI of weak interactions is even much lower [28]. This feature of IBSI may be used to distinguish types of interactions. The IBSI is expressed as

$$\text{IBSI} = \frac{(1/d^2) \int \delta g^{\text{pair}} dr}{(1/d_{\text{H}_2}^2) \int \delta g^{\text{H}_2} dr} \quad (4)$$

where d is the distance between the two atoms to be studied, and δg^{pair} represents atomic pair index. The denominator is the data for a reference system (H_2 in its equilibrium structure).

It is not surprising that all the trends found in ELF and MBO are reproduced in IBSI. For example, the terminal two iodine-iodine bonds (r_3 and r_4) in $[\text{DMIM}][\text{I}_5]$ and $[\text{NMe}_4][\text{I}_5]$ possess larger IBSI values compared with other two ones (r_1 and r_2). The lowest magnitude of IBSI is predicted for I...I interactions in the complexes of SI_3^- , thereby suggesting the weakest strength.

Fig. 5 IGM dyed isosurfaces of the interactions within anions for three representative ionic pairs.

Fig. 6 IGM dyed isosurfaces of the interactions within anions for other two representative ionic pairs.

IGM analysis

To gain deeper insight into the features of interhalogen interactions in polyhalide ILs, the IGM method, based on electron density gradient ($\nabla\rho$), was employed herein. This approach provides an intra/inter uncoupling scheme that automatically extracts the signature of intra- (δg^{intra}) and inter- (δg^{inter}) molecular interactions within and between two user-selected fragments. The δg function is defined as follows

$$g(r) = \left| \sum_A \nabla \rho_A(r) \right| \quad (5)$$

$$g^{\text{IGM}}(r) = \left| \sum_A \text{abs}[\nabla \rho_A(r)] \right| \quad (6)$$

$$\delta g(r) = g^{\text{IGM}}(r) - g(r) \quad (7)$$

where ρ_A stands for atomic density of atom A. The *abs* operator makes each of the three gradient

components to be its absolute value [53]. This method is remarkably attractive to assess the role of interactions that occur in an intramolecular mode between atoms or subfragments in one single molecule.

Figures 5 and 6 depict the color-coded δg isosurfaces of the interactions within the anions for representative ionic pairs, where strong attractive interactions are shown in blue and green region indicates weak interactions. Also given in these figures are the scatter plots of iodine-iodine bonds in these systems. The first observation from Figures 5 and 6 is the blue isosurfaces between the I atoms in polyiodide ionic pairs and the green isosurfaces between these atoms in the complexes of SI_3^- . Clearly, iodine-iodine interactions in ionic pairs are markedly stronger and thus have some covalent contributions, while $\text{I}\cdots\text{I}$ contacts in the latter complexes are much weaker and belong to conventional weak halogen bonds. Secondly, in $[\text{NMe}_4][\text{I}_5]$ the wider and darker blue isosurfaces between the terminal I atoms indicate somewhat stronger terminal $\text{I}\cdots\text{I}$ bonds (r_3 and r_4) with respect to other two ones (r_1 and r_2). Furthermore, the first spike peak in the scatter plot corresponds to the terminal $\text{I}\cdots\text{I}$ bonds, while the spike peak for other two ones is located at a less negative value. Therefore, the former interactions have a greater content of covalency, while the latter ones can be categorized as strong halogen bonds. Lastly, similar features of such interactions were also detected in the two configurations of $[\text{NMe}_4][\text{I}_7]$, and the central I_3 unit in $[\text{NMe}_4][\text{I}_7]\text{-L}$ shows similar IGM plots as those in $[\text{NMe}_4][\text{I}_3]$, in good accordance with the above QTAIM and ELF results.

Discussion

As stated above, polyhalide ions have been the target of a number of research works. The most well-studied polyhalides are the simplest trihalide anions, and the bonding in these anions can be described as a delocalized 3c-4e bond [54, 55]. Particularly, as revealed by previous K-edge XAS experiments, charge transfer is extremely large in some trihalide systems, comparable to that observed in coordination complexes. Consequently, $\text{X}\cdots\text{X}$ bonds in these systems should be partially covalent, analogous to coordination bonds [22]. However, interhalogen interactions in polyhalide ILs remain largely unexploited, although these ILs have shown potential applications in many scientific fields. Incorporating polyhalide ions into the IL structure could combine the properties of these ions (such as strong oxidizing power and high reactivity) and the advantages

of ILs (like negligible vapor pressure and highly tunable character).

Cation-anion interactions and intermolecular forces in ILs were intensively studied from both theoretical and experimental viewpoints, since these intrinsic interactions are directly related to the physicochemical properties of ILs. However, the interactions within anions or cations of ILs have drawn much less attention to date, possibly due to their absence in most cases. As a matter of fact, such intramolecular interactions play a fundamental role in certain specific characteristics of ILs. Wang et al. previously reported an interesting method for decreasing the viscosity variation in CO₂ capture process by amino-functionalized ILs through the formation of intramolecular HBs [56]. When it comes to polyhalide ILs, many of their applications are indeed based on the properties of polyhalide anions in which multiple halogen-halogen interactions are presented. For instance, trihalide ILs can be used as oxidizing solvents for metals and alloys, mainly arising from the strong oxidizing character of trihalides [19, 20, 57]. Therefore, a detailed understanding of interhalogen bonds in polyhalide ILs should be of particular importance for realizing the potential of these ILs.

According to our calculations on ionic pair complexes for a series of polyhalide ILs, all the defined angles become smaller in ionic pairs compared with those in isolated ions. Namely, the geometry of polyhalide anions tends to bent when complexed with the cations, on account of the formation of HBs between these anions and the cations. Furthermore, most interhalogen bonds in ionic pairs show some covalent content, and these bonds also have much larger ELF and MBO values than those in the complexes of SI_3^- with the presence of conventional weak halogen bonds. Notably, in higher polyhalide systems, halogen-halogen bonds can be divided into two catalogues according to interatomic distances: the longer ones belonging to strong ionic halogen bonds and the shorter ones having a larger degree of covalency.

The substantial covalent content of interhalogen interactions in ILs could be intriguing for systems where electronic transport is of significance. Furthermore, owing to the delocalized bonding in polyhalides, polyhalide ILs possess much lower viscosity with respect to traditional halide ILs, attractive as solvents or components of electrolytes. In addition, higher halogen concentrations in these ILs may also be beneficial for dye-sensitized solar cells, in which the iodide/triiodide redox couple was generally used [58]. All in all, polyhalide ILs not only show the properties of polyhalides but also have the favorable characteristics of ILs, and two different types of halogen-halogen interactions with some covalent contributions were characterized in higher

polyhalide ILs, which will inspire the applications of these ILs in a wider chemical community.

Conclusions

In the present work, interhalogen bonds in a series of polyhalide ILs, which are comprised of trihalides ($[\text{I}_3]^-$, $[\text{Br}_3]^-$, $[\text{IBr}_2]^-$), pentahalides ($[\text{I}_5]^-$, $[\text{Br}_5]^-$, $[\text{I}_2\text{Br}_3]^-$) and heptahalides ($[\text{I}_7]^-$, $[\text{Br}_7]^-$, $[\text{I}_3\text{Br}_4]^-$) with two typical cations ($[\text{NMe}_4]^+$ and $[\text{DMIM}]^+$), were investigated in detail using DFT calculations. In addition, $\text{I}\cdots\text{I}$ interactions in the complexes of a supramolecular anion SI_3^- with the same cations were also examined for comparison. Several computational approaches, such as QTAIM, ELF, MBO and IGM, were employed, with the aim of understanding these bonds in depth.

Compared with those in bare polyhalide ions, halogen-halogen interactions in ionic pairs for the ILs under study become somewhat asymmetric induced by the cation-anion interactions. As disclosed by the QTAIM method, most $\text{X}\cdots\text{X}$ bonds in ionic pair complexes are partially covalent, as a result of negative $H(r)$ or the ratio $|V(r)|/G(r) > 1$. Furthermore, $\rho(r)$ at the BCPs correlates well with the interatomic distance for all interhalogen interactions in polyiodide ionic pairs. Therefore, $\text{X}\cdots\text{X}$ bonds having shorter interatomic distances are relatively stronger, while the longer ones show a weaker strength. Notably, the shorter $\text{X}\cdots\text{X}$ bonds always possess larger ELF, MBO and IBSI values, approaching the magnitudes of molecular X_2 , while smaller values are estimated for the longer ones, moving towards those of the complexes of SI_3^- . On the basis of these findings, interhalogen interactions in ionic pairs can be divided into two groups: one group with longer interatomic distances can be recognized as strong ionic halogen bonds, while the other with shorter distances has a greater covalent content, i.e. intermediate ionic/covalent character.

The results and conclusions reported in this work can provide helpful guidance for applying polyhalide ILs in diverse scientific fields.

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Declarations

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Data availability Data can be obtained from the corresponding authors through email.

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