

Structural Consequences of Halogen Bonding in Dialkylimidazolium: A New Design Strategy for Ionic Liquids Illustrated with the I₂ Co-Crystal and Acetonitrile Solvate of 1,3-Dimethylimidazolium Iodide

Steven P. Kelley,^{‡,#} Hanwen Pei,[§] Volodymyr Smetana,[§] Anja-Verena Mudring,^{§,*} and Robin D. Rogers^{‡,§,*}

[‡]College of Arts & Sciences, The University of Alabama, Tuscaloosa, AL, 35487

[§]Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius väg 16 C, 106 91 Stockholm, Sweden

*E-mail: anja-verena.mudring@mmk.su.se; rdrogers@ua.edu

Abstract: The reaction of 1,3-dimethylimidazolium-2-carboxylate with elemental iodine in acetonitrile rapidly affords crystalline iodide salts of the 1,3-dimethyl-2-iodoimidazolium cation ([C₁mim-2-I]⁺), [C₁mim-2-I]·0.5I₂ and [C₁mim-2-I]·0.5CH₃CN, depending on the temperature. Analysis of the two structures shows the significant role of halogen bonding interactions between the cation and anion in the [C₁mim-2-I]I salts which reduces the ionicity of the compounds. This observation is backed by theoretical calculations revealing the importance of halogen bonding as a design strategy for ionic liquids (ILs), which, so far, has been underestimated. The halogen bonding is also analyzed in terms of this new design concept for ILs.

Introduction

Ionic liquids (ILs) are molten salts characterized by their unusually low melting points (regularly defined as less than 100 °C).¹ ILs are used in applied research, often as replacements for more typical molecular liquids,²⁻⁵ as well as fundamental research aimed at understanding how the behavior of a molten salt differs from that of a molecular liquid near the same temperature.⁶⁻⁹ A very big difference, and one which is conceptually easy to understand, is that ILs are composed of at least two discrete ions, so their properties can be tuned by changing one ion while preserving the other(s). However, as the field advances there is growing awareness of the importance of

[#]Current address: Department of Chemistry, University of Missouri, 601, S. College Avenue, Columbia, Missouri 65211, United States

interionic interactions themselves on both the properties of the ions and the macroscopic properties of the compound itself. Interionic interactions control charge transfer between ions and aggregation, in turn affecting many of the most important materials properties of ILs such as melting point,¹⁰ viscosity,¹¹ conductivity,¹² solubility,¹³ solvating ability,¹⁴ and chemical reactivity.¹⁵

Approaches have been devised for enhancing or weakening the interactions between ions in an IL by taking advantage of specific interactions. For instance, the strong interactions between a metal cation and anion can be used to direct the formation of complex anions,⁹ or a neutral Lewis base can be used to make a metal complex cation which interacts weakly with the anion.¹⁶ Similarly, hydrogen bonding between Brønsted acidic cations and basic anions can be used to promote charge transfer and aggregation between the cation and anion,¹⁷ while neutral hydrogen bond donors can be used to weaken cation-anion interactions.¹⁸ Coulombic interactions can also be controlled by, for instance, adding a long alkyl chain to the cation to promote segregation of charged and uncharged zones, which can lead to liquid crystalline phases.¹⁹

It is no coincidence that the phenomena on which these approaches are based – metal coordination, hydrogen bonding, and cation-anion interactions – are the same as those used in crystal engineering to control the assembly of non-covalently bound moieties into a crystal lattice.²⁰ However, there is one tool used in crystal engineering which has gone virtually unused in the design of ionic liquids – the halogen bond. Halogen bonding occurs between a Lewis base and the partial positive charge (called a σ -hole) on a polarizable atom (usually a halogen, although σ -hole interactions are known for group 5a and 6a elements as well) bonded to an electron withdrawing group.²¹ This interaction is strong and directional, making it useful for predictable assembly of molecules in crystal engineering.²² It is not a commonly observed phenomenon in ILs, however. Halogenated cations are not commonly used in ILs; they are synthetically more difficult to access and do not normally offer advantages except for a few uses, such as high-density ILs²³ or fluorinated cations for increased hydrophobicity.²⁴ Anions are not likely to be electron-withdrawing enough to act as halogen bond donors, although trihalide ions offer a rare example of IL-forming anions which engage in anion-anion interactions.²⁵⁻²⁷

The most systematic study of ILs actually designed to incorporate halogen bonding comes from series of reports on the synthesis and crystal structures of halogenated dialkylimidazolium salts by Mukai and Nishikawa.²⁸⁻³² These studies have shown that IL melting points correlate

directly with both cation molecular weights and halogen bond donor strength, and halogen bonding is an important influence in the crystal packing (similar to hydrogen bonding in hydrogenated dialkylimidazolium cations).³³ The importance of halogen bonding has also been evaluated in ionic liquid crystals.³⁴ The strength of halogen bonding iodinated dialkylimidazolium cations and their counterions has been studied by density functional theory calculations which predict that the counterion is more likely to interact Coulombically with the imidazolium ring, and that the partial positive charge on the ring is larger than the partial charge in the σ -hole.³⁵

The scarcity of studies dedicated to the halogen bonding in ILs means that until it is shown to be effective for a particular purpose, little progress is likely to be made in understanding it. We therefore decided to contribute as well to its investigation, beginning with the obstacle of synthesizing halogenated cations. Here we report a novel approach for the synthesis of the 1,3-dialkyl-2-iodoimidazolium cation by reacting air stable 1,3-dimethylimidazolium-2-carboxylate ($C_{1mimCOO}$) with iodine. 1,3-Dimethyl-2-iodoimidazolium ($[C_{1mim-2-I}]^+$) was chosen as our cation due to the prevalence of dialkylimidazolium cations in ILs, as well as the recent demonstration of 2-haloimidazolium groups as potent halogen bond donors in anion receptors.^{36,37}

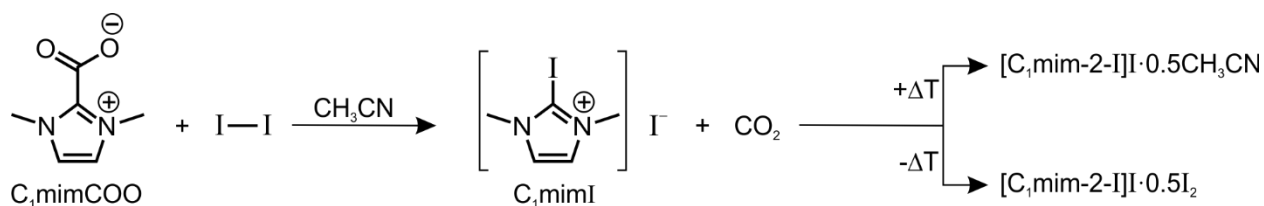
This particular cation was not expected to give a low melting salt but was chosen to promote the formation of a crystalline material which could be studied by single crystal X-ray diffraction (SCXRD). Cation-anion interactions and the degree of ionicity have observable effects on the crystal structure, which can in turn be used to make predictions and help understand experimental studies of the liquid state.³⁸ Our synthesis resulted in the isolation of two halogen bonded crystalline compounds, one a $[C_{1mim-2-I}]I \cdot 0.5I_2$ co-crystal and the other a $[C_{1mim-2-I}]I \cdot 0.5CH_3CN$ solvate, which allowed the comparison of this salt in the presence of a competing extra halogen bond donor (I_2) vs. a competing base (CH_3CN).

Results and Discussion

2-Iodoimidazolium cations are typically synthesized by reacting a hydrogenated imidazolium salt with a strong base to generate the carbene, which can then react with an iodinating agent to become iodinated at the 2-position.³⁹ This is an air-sensitive procedure. However, there are numerous reports of dialkylimidazolium ILs forming carbene adducts in which the counterion is the only base; these include catalytic metal complexes,¹⁵ complexes with the counterion itself,⁴⁰ chalcogens,⁴¹ and CO_2 adducts.⁴² Of these, the zwitterionic CO_2 adduct, 1,3-dialkylimidazolium-

2-carboxylate, is also known to be isolable, air stable, and synthetically versatile precursor to other imidazolium salts and to carbene complexes.⁴³ We investigated whether 1,3-dimethylimidazolium-2-carboxylate ($C_1\text{mimCOO}$), a carbene precursor that can readily be synthesized in bulk from methylimidazole and dimethyl carbonate,⁴³ could react with iodine in the absence of any base.

Solid $C_1\text{mimCOO}$ obtained as reported previously⁴⁴ was ground together with one molar equivalent of I_2 with a mortar and pestle at ambient conditions. Acetonitrile was added as a solvent and reaction medium to the resulting mixture, and a dark brown solution formed immediately. The solvent was evaporated with heat, and within one hour large, colorless plates were observed to have formed. The brown solution remained liquid but was greatly reduced in volume. The reaction mixture was removed from heat, and brown needles appeared from the liquid within hours of standing at room temperature (Scheme 1).



Scheme 1: Reaction of $C_1\text{mimCOO}$ with I_2 dissolved in acetonitrile and crystallization of $[\text{C}_1\text{mim-2-I}]\text{I} \cdot 0.5\text{CH}_3\text{CN}$ upon heating and $[\text{C}_1\text{mim-2-I}]\text{I} \cdot 0.5\text{I}_2$ upon cooling.

Examination of the solids under optical polarizing microscopy revealed that both the colorless plates and the brown needles were large single crystals (greater than 1 mm in length). SCXRD was used to determine the structure of both. The brown crystals formed at room temperature were found to be the iodine co-crystal, $[\text{C}_1\text{mim-2-I}]\text{I} \cdot 0.5\text{I}_2$, and the colorless crystals formed at higher temperature were found to be the acetonitrile solvate, $[\text{C}_1\text{mim-2-I}]\text{I} \cdot 0.5\text{CH}_3\text{CN}$, confirming in both cases the heterolytic cleavage of the I_2 molecule to give the expected $[\text{C}_1\text{mim-2-I}]\text{I}$ salt.

$[\text{C}_1\text{mim-2-I}]\text{I} \cdot 0.5\text{I}_2$ (Figure 1 left) crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$. There is a single unique cation-anion pair and half of a unique I_2 molecule, which resides on a crystallographic center of inversion. Assignment of the structure as a co-crystal of the iodide salt with I_2 rather than a salt of the I_3^- anion is supported by the fact that the iodide ion is closer to the cationic iodine than the I_2 molecule ($\text{I}2 \cdots \text{I}1$ 3.4056(3) Å vs. $\text{I}2 \cdots \text{I}3$ 3.4619(4) Å); for triiodide the I-I distances would be expected to be much shorter (2.9-3.1 Å).⁴⁵

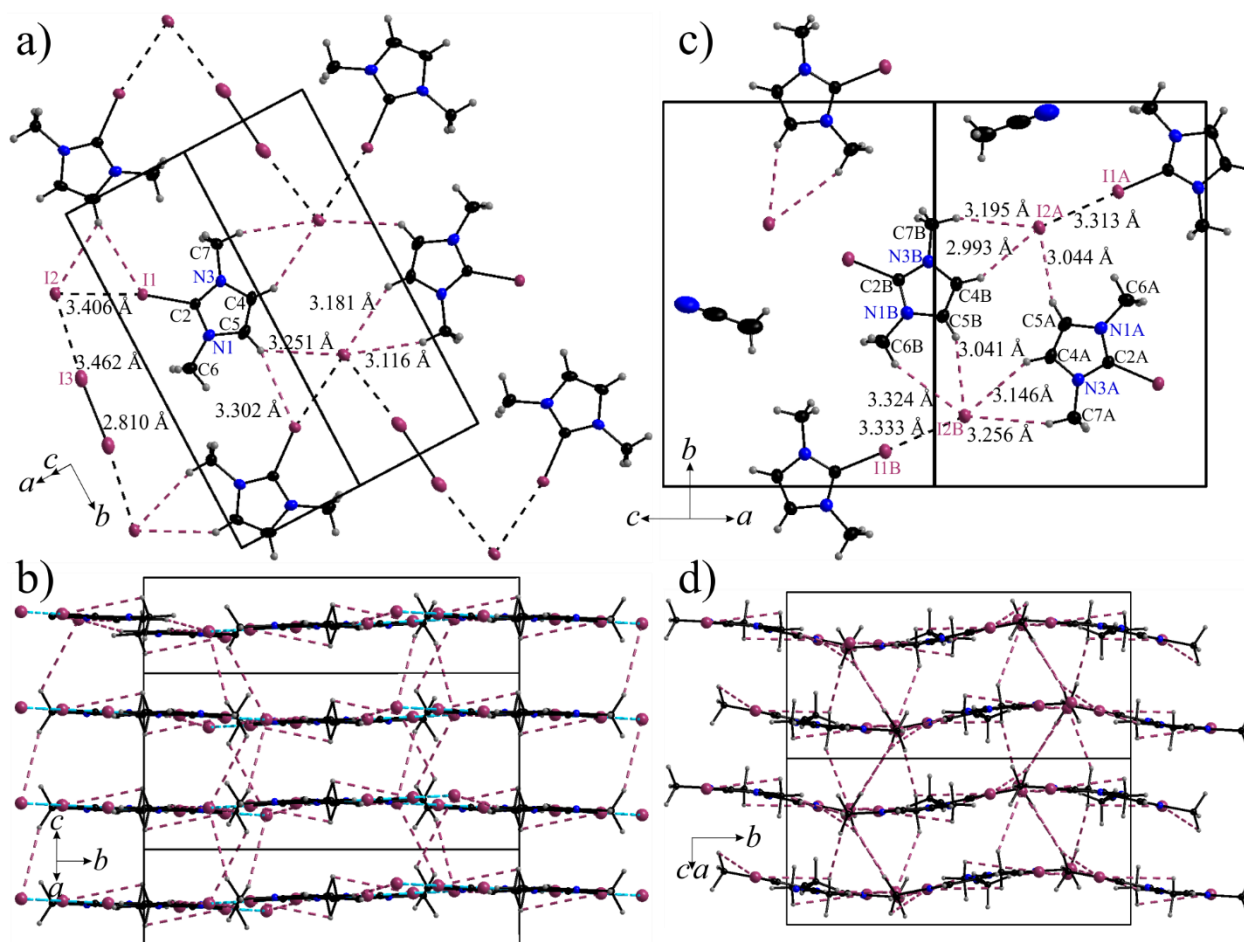


Figure 1. 50% probability ellipsoid plots of single layers in the crystal structures of $[\text{C}_1\text{mim-2-I}]\text{I}$ (a) and $[\text{C}_1\text{mim-2-I}]\text{I}\cdot 0.5\text{CH}_3\text{CN}$ (c), and the packings of the corresponding layers (b and d, respectively). Dashed lines indicate closest intermolecular contacts.

$[\text{C}_1\text{mim-2-I}]\text{I}\cdot 0.5\text{CH}_3\text{CN}$ (Figure 1 right) also crystallized in $P2_1/c$ ($Z = 4$) with 2 moles of the salt per mole of included solvent, but there are two symmetry inequivalent pairs of ions and one full-occupancy CH_3CN molecule in the asymmetric unit. We note that during manuscript preparation this solvate was reported in the supplementary material for a very recent study of noble metal corrosion⁴⁶ (CCDC 1894840). However, the details of how it was obtained were not reported in the experimental section and in the main text of that paper confusingly appears to refer rather to $[\text{C}_1\text{mim-2-I}]\text{I}$ than its solvate. Therefore, here we will focus more on the role of halogen and to a lesser extent hydrogen bonding in the isolation of a specific product and the structural consequences.

In crystalline $[\text{C}_1\text{mim-2-I}]\text{I}\cdot 0.5\text{I}_2$, the cation makes short contacts (intermolecular distances shorter than or comparable to the sum of the van der Waals radii of the two atoms) to 5 anions, one through a $\text{C2-I}\cdots\text{I}^-$ halogen bond, 1.5 through the aromatic $\text{CH}\cdots\text{I}^-$ and the other 2.5 through hydrogen bonds to the methyl groups (Figure 2a). In addition to 6 cation-anion contacts, the anion makes a short contact to the I_2 molecule (Figure 2b) which is at a $175.16(1)^\circ$ angle to the I-I bond, indicating that it is a halogen bond as well. As the I_2 molecule is on a crystallographic center of symmetry, both iodine atoms make identical halogen bonds to two separate iodide ions with no other short contacts (Figure 2c). It is worth noting that short intercationic methyl–methyl contacts are also observed as an indirect consequence of the halogen bonding interactions densifying the structure.

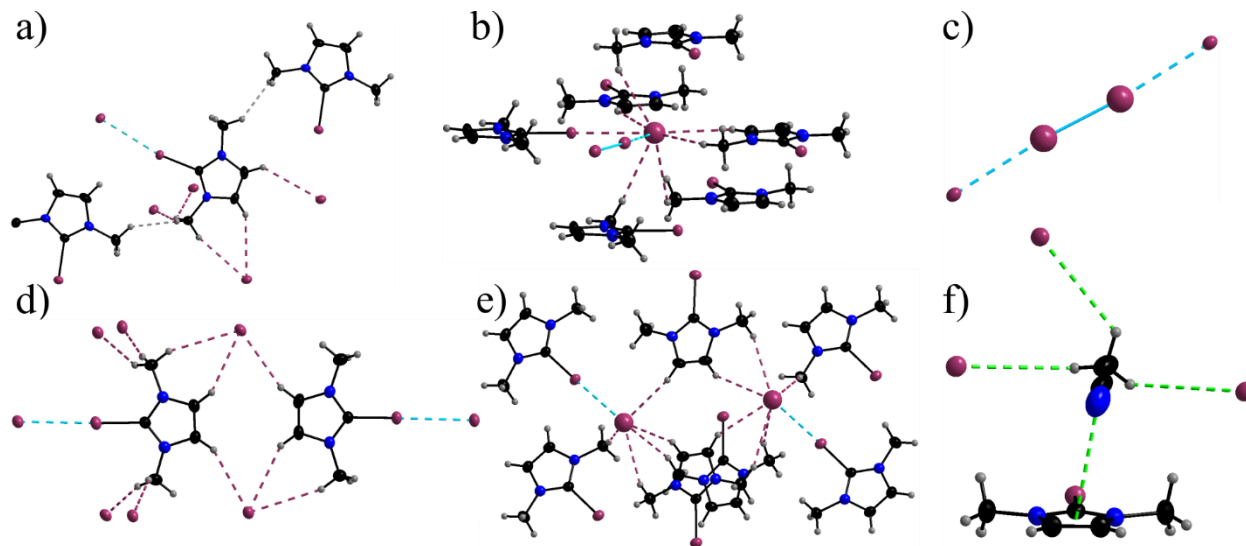


Figure 2. Intermolecular environments of individual species in $[\text{C}_1\text{mim-2-I}]\text{I}\cdot 0.5\text{I}_2$ (*top*) and $[\text{C}_1\text{mim-2-I}]\text{I}\cdot 0.5\text{CH}_3\text{CN}$ (*bottom*). From left to right: Environments around cation(s), anion(s), and neutral molecules. Plum lines indicate less than the sum of the van der Waals radii contacts. Blue lines indicate halogen–halogen bonds. In the case of CH_3CN (*bottom right*) with no short contacts, green lines are used to represent the shortest intermolecular contacts.

One of the unique cations in $[\text{C}_1\text{mim-2-I}]\text{I}\cdot 0.5\text{CH}_3\text{CN}$ makes short contacts to 7 anions, one through a $\text{C2B-I1B}\cdots\text{I2B}^-$ halogen bond, 1.5 through hydrogen bonds to the imidazolium ring carbon atoms C4A and C5A, and the rest through hydrogen bonds to the methyl groups (Figure 2d). The other unique cation makes short contacts just to 3 anions, two of which are common with the first cation and the last one is $\text{C2A-I1A}\cdots\text{I2A}^-$ halogen bond. Both anion I2A and I2B make short contacts to 5 cations (Figure 2e) three of which are common and one in each case through

direct halogen-halogen bonds mentioned above for the cations. There are no significant, *i.e.* less than the sum of the van der Waals radii, contacts between the cation and the CH₃CN molecule, but interestingly the solvent molecule resides above the C2 position of one of the crystallographically unique cations, which is where commonly in structures of similar ILs, the anion would be found (Figure 2f). The existing CH \cdots I–C/I $^-$ and CN \cdots C_g (lp– π) contacts range between 3.346(4) and 3.460(1) Å, while a potential CN \cdots I–C halogen bond exceeds 4 Å, all of them being comparably weak.

In dialkylimidazolium ILs, the electrostatic interaction is typically the strongest between the anion and the C2 of the cation, where the greatest concentration of positive charge resides.⁴⁷⁻⁴⁹ Short contacts between anions and C2 that are approximately perpendicular to the imidazolium ring plane are extremely common features in the crystal structures of these salts, including those of comparatively weakly basic anions such as I $^-$.⁵⁰ It is therefore noteworthy that this short contact is completely absent from the crystal structure of [C₁mim-2-I]I·0.5I₂, and for half of the cations in [C₁mim-2-I]I·0.5CH₃CN, an electrically neutral CH₃CN occupies this position instead of an anion (see above). The surprising absence of the typically dominant cation-anion stacking interaction in both structures could indicate that the strong halogen bond weakens the electrostatic interaction between [C₁mim-2-I]⁺ and I $^-$ by reducing the charge density of the already charge-diffuse iodide anion. Our experimental results also deviate from the DFT study of interactions between iodinated dialkylimidazolium cations and CF₃SO₃⁻ anions, which predicted the out-of-plane contact to be the most favorable ion pair.³⁵ While this is no doubt partially due to the difference in the anions, it also indicates the effect that additional cations may have on the electrostatic interaction strength. *While the electrostatic interaction may be much stronger than the halogen bond for a gas phase ion pair, these crystal structures suggest that the presence of hydrogen and halogen bonding may weaken the electrostatic interaction to the point where it is no longer the dominating influence in packing.*

Iodine is highly polarizable, and its bond distances vary widely, so the presence of molecular iodine in [C₁mim-2-I]I·0.5I₂ is also useful as sort of *in situ* probe of the cation's halogen bonding strength. The CSD⁵¹ contains examples of 2-iodoimidazolium salts of polyiodide anions but only one (moreover, a very recent) example of a co-crystals containing both I and I₂ – [C₁mim-2-Br]I·0.5I₂.⁵² The linear but dissymmetric I \cdots I₂ \cdots I $^-$ complex observed in [C₁mim-2-I]I·0.5I₂ which has been previously described as the I₄²⁻ superanion, is very rare, and is reportedly unstable

unless stabilized by noncovalent interactions.⁵²⁻⁵⁵ All of this indicates that the structure of the cation is controlling the speciation of the anion as well through its effect on the strength of the halogen bond. This observation is further confirmed by the distances comparison in [C₁mim-2-I]·0.5I₂ and its isostructural Br analogue [C₁mim-2-Br]I·0.5I₂.⁵² Despite the smaller sum of the van der Waals radii C-Br···I⁻ contacts are longer 3.499(1) vs 3.4056(3) Å, while I⁻···I₂ contacts become shorter 3.426(1) vs 3.4623(4) Å. Of course enhanced I⁻···I₂ interactions lead to a larger polarization within the I₂ molecule and consequently longer I-I bonds – 2.826(1) vs 2.8095(4) Å.

The crystal structures of imidazolium-2-iodide salts of polyiodide anions include [1,3-bis(2,6-diisopropylbenzene)imidazolium]I₃,⁵⁶ [1,3-di(mesityl)imidazolium]I₃,⁵⁷ and [1,3-di(adamantly)imidazolium]I₃.³⁹ While the difference between I⁻···I₂···I⁻ and I₃⁻ is quite clear from comparison of the I-I distances in these structures, the C2-I and C2-I···I distances are quite similar in all cases (Figure 3). This indicates that the formation of the I⁻···I₂···I⁻ moiety is strictly controlled by the electrostatics of the cation. Since [C₁mim-2-I]⁺ is the smallest dialkylimidazolium cation, it has the most concentrated positive charge, is the most electron poor, and should therefore be the strongest halogen bond donor of these. This effect alone appears to be enough to cause the change in speciation among solid dialkylimidazolium iodides, particularly affect polyiodide formation.

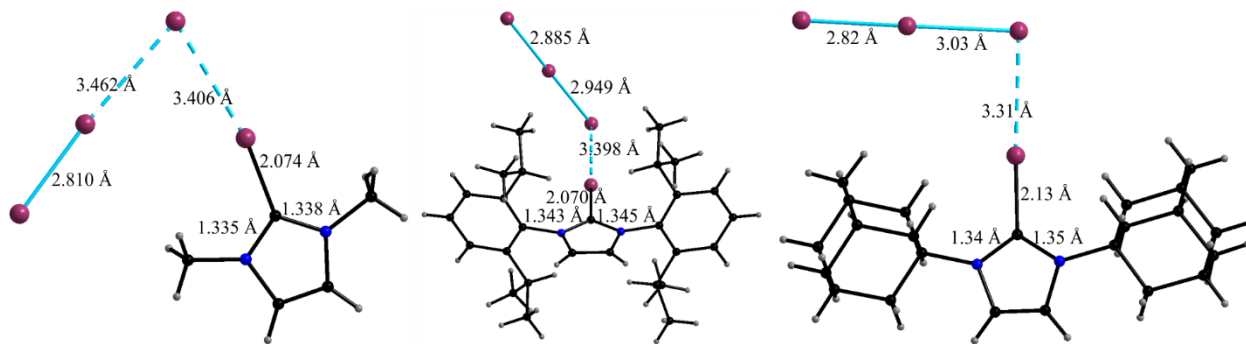


Figure 3. Packing diagrams of [C₁mim-2-I]·0.5I₂ vs. bis(diisopropylbenzene) and di(adamantly) analogs with I₃⁻, redrawn using coordinates from refs. ⁵⁶ and ³⁹.

Comparison of the crystal structures of [C₁mim-2-I]·0.5I₂ and [C₁mim-2-I]·0.5CH₃CN with similar compounds from the literature indicates that the [C₁mim-2-I]⁺ has especially strong halogen bonding. Strong *hydrogen* bonding has been used previously to design ILs with long-lived ion pairs which show reduced ionicity in certain situations, such as membrane transport.⁵⁸ In these

crystalline compounds, evidence for a decrease in ionicity due to ion pairing can be observed through the dominance of the halogen bond and other interactions over the electrostatic anion-ring interaction. Speciation is also shown to be affected by halogen bonding. While hydrogen bonding has been used to control properties such as these, the strongest hydrogen bonds involve small, electronegative atoms. Halogen bonding may play a stronger role in controlling the properties of Γ^- and I_3^- ILs used as electrolytes and redox couples in dye sensitized solar cells, for instance.⁵⁹⁻⁶¹

To provide better insight into the relevance of halogen bonding in $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{I}_2$ and $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{CH}_3\text{CN}$, theoretical calculations have been performed. In these, the individual electrostatic potential maps for $[\text{C}_1\text{mim-2-I}]^+$, Γ^- , I_2 as the relevant constituents of $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{I}_2$ and $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{CH}_3\text{CN}$ have been calculated, as well as the for the units as observed in the crystal structures, i.e. $[\text{C}_1\text{mim-2-I}]\Gamma^-$ for $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{CH}_3\text{CN}$ and $\{[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{I}_2\}_2$ for $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{I}_2$ (Figure 4).

The electrostatic potential map for the $[\text{C}_1\text{mim-2-I}]$ cation, Figure 4a (right) reveals a strongly electron deficient site on the terminal iodine atom, also known as a σ -hole (dark blue regions). Similarly, for the I_2 unit, (Figure 4a left), σ -holes are observed at the end of the terminal sites of the iodine atoms. These electron-deficient areas of the $[\text{C}_1\text{mim-2-I}]$ cation and the I_2 unit interact with Γ^- resulting in the formation of a $[\text{C}_1\text{mim-2-I}]\Gamma^-$ ion pair for $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{CH}_3\text{CN}$ and $\{[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{I}_2\}_2$ ion pairs in $[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{I}_2$, where the $[\text{C}_1\text{mim-2-I}]$ cation and the additional I_2 molecule interact with the negative Γ^- ion (Figure 4c). Comparison with the electrostatic potential map calculated for the $[\text{C}_1\text{mim-2-I}]\Gamma^-$ ion pair (Figure 4b) and a $\{[\text{C}_1\text{mim-2-I}]\cdot 0.5\text{I}_2\}_2$ unit (which corresponds to a metastable configuration in the gas phase, Figure 4d), confirms that it is the energetically favorable interaction between the negative region and the positive region of the constituents that drives the primary assembly of the ions in the solid.

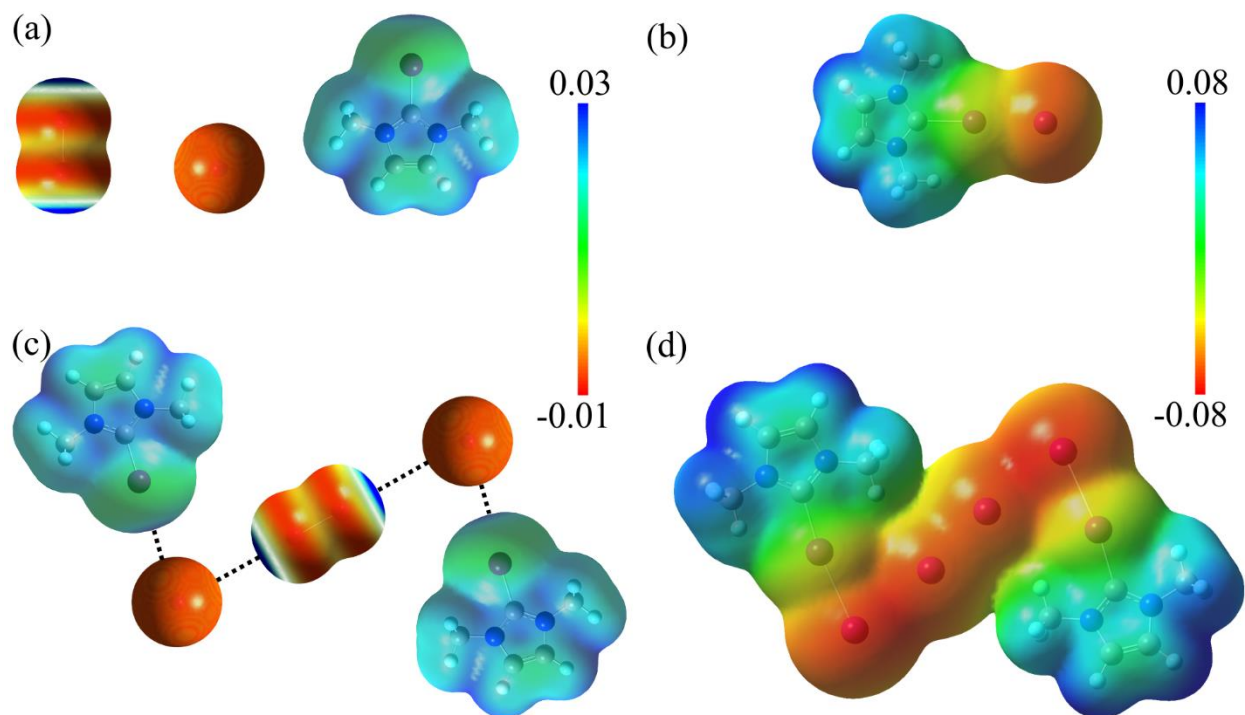


Figure 4. Electrostatic potential (0.001 density isosurface) (a) I₂, I⁻, and [C₁mim-2-I]⁺; (b) for a geometry optimized [C₁mim-2-I] unit; (c) calculated individually for [C₁mim-2-I]⁺, I⁻ and I₂ mapped onto the {[C₁mim-2-I]·0.5I₂}₂ ion assembly as found in the crystal structure of [C₁mim-2-I]·0.5I₂ (d) for a geometry optimized {[C₁mim-2-I]·0.5I₂}₂ fragment.

Summary.

Halogen bonding has not gone unnoticed by the IL community, but the need for halogenated cations has hindered the application of this phenomenon. A niche for halogen bonding is needed to drive further research forward. In this study, we have shown that halogen bonding can play a primary influence on the ionicity and speciation in iodide and polyiodide salts. Moreover halogen bonding has been found useful for the control of certain structural features, particularly formation of the layered structures through reduction of the 3D cation-anion interactions. The new method developed here allows direct access to the halogen bonding functionality and high purity, since 1,3-dimethylimidazolium-2-carboxylate and iodine can be obtained as pure crystalline solids and the by-product, CO₂, is spontaneously evolved.

While future investigations will no doubt unearth halogen bond donors beyond dialkylimidazolium cations, we believe that these cations will continue to play an important role in fundamental studies for several important reasons. While they do readily form ILs depending on how they are substituted, the charged imidazolium core undergoes a number of strong

interactions and are easily modified not only through the side chains but also through derivatization of the core through carbene-facilitated substitutions. The salt we have investigated here can be used to prepare other $[\text{C}_1\text{mim-2-I}]^+$ salts through anion metathesis. It is known that dialkylimidazolium ILs with more basic anions such as acetate can also act as carbene reservoirs.^{41,62,63} This reactivity may allow imidazolium ILs to be functionalized with halogen bond donors in a single step and can particularly be useful for the future development of imidazolium polyhalides and related ILs as battery-type electrolytes⁶⁴⁻⁶⁶ and redox mediators in dye sensitized solar cells.⁶⁷⁻⁶⁹

Experimental:

Materials and methods: Iodine (ACS Reagent, >99.8%, Sigma-Aldrich, St. Louis, MO) and acetonitrile (99.8%, EMD Chemicals, Darmstadt, Germany) were used as received. The synthesis of 1,3-dimethylimidazolium-2-carboxylate was previously reported.⁴⁴ The reaction of iodine and $\text{C}_1\text{mim-2-COO}$ to give the crystalline products $[\text{C}_1\text{mim}]\text{I}\cdot 0.5\text{I}_2$ and $[\text{C}_1\text{mim}]\text{I}\cdot \text{CH}_3\text{CN}$ was performed as follows: Solid $\text{C}_1\text{mim-2-COO}$ (87.5 mg) and I_2 (79.0 mg, 0.345 mol. eq.) were weighed onto tared weighing paper and transferred to an empty borosilicate glass culture tube at room temperature and briefly homogenized by hand grinding with a glass stirring rod. Acetonitrile (2 mL) was added to the reaction vessel using a Pasteur pipette. The mixture was swirled, and the resulting dark brown solution was decanted from the undissolved solids into a 20 mL glass scintillation vial. The solution was placed in a heated sand bath (85 °C), allowing the acetonitrile to boil off. As the volume of the solution decreased, colorless plate-like crystals were visible growing on the side of the reaction vessel, and the reaction mixture was removed from heat and allowed to stand at room temperature. Brown needles appeared from the liquid within hours of standing. Single crystals of both products were, thus isolated directly from this reaction mixture, but at different temperatures.

Crystal structure determination: Data were collected on a Bruker diffractometer equipped with a PLATFORM 3-circle goniometer and an APEX II CCD area detector (Bruker AXS, Madison, WI, USA). For structure solution, a hemisphere of unique data was collected with Mo-K α radiation ($\lambda = 0.71054 \text{ \AA}$) using strategies of scans about the omega and phi axes with 0.5° frame widths. Crystals were cooled to $-100 \text{ }^\circ\text{C}$ during collection under a cold stream of N_2 gas using an N-Helix cryostat (Oxford Cryosystems, Oxford, UK). Data collection, unit cell determination, data

reduction, scaling, and absorption correction were performed using the Apex3 software suite.⁷⁰ Both crystal structures were solved by direct methods using SHELXT⁷¹ and refined by full matrix least squares refinement against $|F^2|$ using SHELXL.⁷² Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms were placed in calculated positions and allowed to ride on the carrier atom; hydrogen atoms on methyl groups were refined using a riding-rotating model.

Theoretical calculations: DFT (density functional theory) calculations were performed using the Gaussian 16 package⁷³ at BP86/ def2-TZVPP level of theory with Grimme's-D3 dispersion correction.⁷⁴ This dispersion correction is appropriate over medium ($\approx 2\text{-}5$ Å) and long ranges (>5 Å), and is an effective method to obtain binding structures of complexes with reduced computational cost. We considered the generalized gradient approximation (GGA) because of its low computational cost. The GGA functional in the present work was BP86, which is composed of the Becke exchange functional and the Perdew correlation functional.^{75,76} The Karlsruhe “def2” of the doubled polarized triple- ζ -basis set (TZVPP) was adopted here.^{77,78} The geometries of each individual molecule and ion and thereafter their pair aggregations as observed in the respective crystal structures were optimized. Electron densities were obtained from the periodic DFT calculations and analyzed and visualized using the GaussView5 program.⁷⁹

Acknowledgements

This research was supported in part through the Göran Gustafsson prize by the Royal Swedish Academy of Science to A.-V. M. and by the Swedish Research Council (Vetenskapsrådet, VR) through grant 2016-05405 (V. S. and A.-V. M.), a Tage Erlander professorship to R. D. R. (VR grant 2018-00233) and the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Heavy Elements program under Award Number DE-SC0019220 (R. D. R.).

Data availability. Related crystallographic information has been deposited with the Cambridge Structural Database and can be downloaded free of charge from <https://www.ccdc.cam.ac.uk/>. Accession codes: CCDC 1961533, 1961534.

Notes

The authors declare no competing financial or non-financial interest

ORCID

Steven P. Kelley: 0000-0001-6755-4495

Hanwen Pei: 0000-0002-2743-8550

Volodymyr Smetana: 0000-0003-0763-1457

Anja-Verena Mudring: 0000-0002-2800-1684

Robin D. Rogers: 0000-0001-9843-7494

Corresponding Authors

*E-mail: anja-verena.mudring@mmk.su.se; rdrogers@ua.edu

References

- (1) Rogers, R. D.; Seddon, K. R. Ionic Liquids--Solvents of the Future? *Science* **2003**, *302*, 792.
- (2) Hallett, J. P.; Welton, T. Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508-3576.
- (3) Smiglak, M.; Pringle, J. M.; Lu, X.; Han, L.; Zhang, S.; Gao, H.; MacFarlane, D. R.; Rogers, R. D. Ionic liquids for energy, materials, and medicine. *Chem. Commun.* **2014**, *50*, 9228-9250.
- (4) Wang, H.; Gurau, G.; Rogers, R. D. Ionic liquid processing of cellulose. *Chem. Soc. Rev.* **2012**, *41*, 1519-1537.
- (5) Billard, I.; Ouadi, A.; Gaillard, C. Liquid-liquid extraction of actinides, lanthanides, and fission products by use of ionic liquids: from discovery to understanding. *Anal. Bioanal. Chem.* **2011**, *400*, 1555-1566.
- (6) Fayer, M. D. Dynamics and structure of room temperature ionic liquids. *Chem. Phys. Lett.* **2014**, *616-617*, 259-274.
- (7) Hollóczki, O.; Malberg, F.; Welton, T.; Kirchner, B. On the origin of ionicity in ionic liquids. Ion pairing versus charge transfer. *PCCP* **2014**, *16*, 16880-16890.
- (8) Schmeisser, M.; van Eldik, R. Elucidation of inorganic reaction mechanisms in ionic liquids: the important role of solvent donor and acceptor properties. *Dalton Trans.* **2014**, *43*, 15675-15692.
- (9) Estager, J.; Holbrey, J. D.; Swadźba-Kwaśny, M. Halometallate ionic liquids – revisited. *Chem. Soc. Rev.* **2014**, *43*, 847-886.
- (10) Reichert, W. M.; Holbrey, J. D.; Swatloski, R. P.; Gutowski, K. E.; Visser, A. E.; Nieuwenhuyzen, M.; Seddon, K. R.; Rogers, R. D. Solid-State Analysis of Low-Melting 1,3-Dialkylimidazolium Hexafluorophosphate Salts (Ionic Liquids) by Combined X-ray Crystallographic and Computational Analyses. *Cryst. Growth Des.* **2007**, *7*, 1106-1114.
- (11) García, G.; Atilhan, M.; Aparicio, S. Viscous origin of ionic liquids at the molecular level: A quantum chemical insight. *Chem. Phys. Lett.* **2014**, *610-611*, 267-272.
- (12) Xu, W.; Angell, C. A. Solvent-Free Electrolytes with Aqueous Solution-Like Conductivities. *Science* **2003**, *302*, 422.

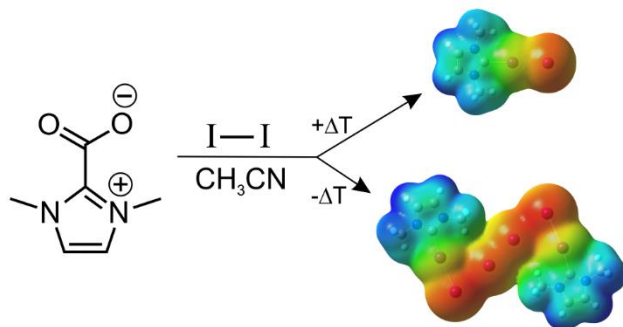
- (13) Pereira, J. F. B.; Flores, L. A.; Wang, H.; Rogers, R. D. Benzene Solubility in Ionic Liquids: Working Toward an Understanding of Liquid Clathrate Formation. *Chem. Eur. J* **2014**, *20*, 15482-15492.
- (14) Pereiro, A. B.; Araújo, J. M. M.; Oliveira, F. S.; Esperança, J. M. S. S.; Canongia Lopes, J. N.; Marrucho, I. M.; Rebelo, L. P. N. Solubility of inorganic salts in pure ionic liquids. *J. Chem. Thermodyn.* **2012**, *55*, 29-36.
- (15) Leadbeater, N. E. Opening an Aladdin's cave: the Suzuki coupling in a room-temperature ionic liquid. *Chem. Commun.* **2014**, *50*, 1515-1518.
- (16) Mandai, T.; Yoshida, K.; Ueno, K.; Dokko, K.; Watanabe, M. Criteria for solvate ionic liquids. *PCCP* **2014**, *16*, 8761-8772.
- (17) Bica, K.; Rogers, R. D. Confused ionic liquid ions—a “liquification” and dosage strategy for pharmaceutically active salts. *Chem. Commun.* **2010**, *46*, 1215-1217.
- (18) Johansson, K. M.; Izgorodina, E. I.; Forsyth, M.; MacFarlane, D. R.; Seddon, K. R. Protic ionic liquids based on the dimeric and oligomeric anions: $[(\text{AcO})_x\text{H}_{x-1}]^-$. *PCCP* **2008**, *10*, 2972-2978.
- (19) Holbrey, J. D.; Seddon, K. R. The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals. *J. Chem. Soc., Dalton Trans.* **1999**, 2133-2140.
- (20) Desiraju, G. R. Crystal Engineering: From Molecule to Crystal. *J. Am. Chem. Soc.* **2013**, *135*, 9952-9967.
- (21) Politzer, P.; Murray, J. S.; Clark, T. Halogen bonding and other σ -hole interactions: a perspective. *PCCP* **2013**, *15*, 11178-11189.
- (22) Mukherjee, A.; Tothadi, S.; Desiraju, G. R. Halogen Bonds in Crystal Engineering: Like Hydrogen Bonds yet Different. *Acc. Chem. Res.* **2014**, *47*, 2514-2524.
- (23) Ye, C.; Shreeve, J. n. M. Syntheses of Very Dense Halogenated Liquids. *J. Org. Chem.* **2004**, *69*, 6511-6513.
- (24) Niedzicki, L.; Żukowska, G. Z.; Bukowska, M.; Szczeciński, P.; Grugeon, S.; Laruelle, S.; Armand, M.; Panero, S.; Scrosati, B.; Marcinek, M.; Wieczorek, W. New type of imidazole based salts designed specifically for lithium ion batteries. *Electrochim. Acta* **2010**, *55*, 1450-1454.
- (25) Dean, P. M.; Clare, B. R.; Armel, V.; Pringle, J. M.; Forsyth, C. M.; Forsyth, M.; MacFarlane, D. R. Structural characterization of novel ionic salts incorporating trihalide anions. *Aust. J. Chem.* **2009**, *62*, 334-340.
- (26) Van den Bossche, A.; De Witte, E.; Dehaen, W.; Binnemans, K. Trihalide ionic liquids as non-volatile oxidizing solvents for metals. *Green Chem.* **2018**, *20*, 3327-3338.
- (27) Li, X.; Van den Bossche, A.; Vander Hoogerstraete, T.; Binnemans, K. Ionic liquids with trichloride anions for oxidative dissolution of metals and alloys. *Chem. Commun.* **2018**, *54*, 475-478.
- (28) Mukai, T.; Nishikawa, K. 4,5-Dihaloimidazolium-based ionic liquids: effects of halogen-bonding on crystal structures and ionic conductivity. *RSC Advances* **2013**, *3*, 19952-19955.
- (29) Mukai, T.; Nishikawa, K. Zigzag Sheet Crystal Packing in a Halogen-bonding Imidazolium Salt: 1-Butyl-4,5-dibromo-3-methylimidazolium Iodide. *X-ray Structure Analysis Online* **2010**, *26*, 31-32.
- (30) Mukai, T.; Nishikawa, K. Halogen Bonding and Hydrogen Bonding in 4,5-Diiodo-3-methyl-1-propylimidazolium Hexafluorophosphate. *X-ray Structure Analysis Online* **2010**, *26*, 39-40.

- (31) Mukai, T.; Nishikawa, K. Syntheses and crystal structures of two ionic liquids with halogen-bonding groups: 4,5-dibromo- and 4,5-diiodo-1-butyl-3-methylimidazolium trifluoromethanesulfonates. *Solid State Sci.* **2010**, *12*, 783-788.
- (32) Mukai, T.; Nishikawa, K. Halogen-bonded and Hydrogen-bonded Network Structures in Crystals of 1-Propyl- and 1-Butyl-4,5-dibromo-3-methylimidazolium Bromides. *Chem. Lett.* **2009**, *38*, 402-403.
- (33) Fuller, J.; Carlin, R. T.; De Long, H. C.; Haworth, D. Structure of 1-ethyl-3-methylimidazolium hexafluorophosphate: model for room temperature molten salts. *J. Chem. Soc., Chem. Commun.* **1994**, 299-300.
- (34) Cavallo, G.; Terraneo, G.; Monfredini, A.; Saccone, M.; Priimagi, A.; Pilati, T.; Resnati, G.; Metrangolo, P.; Bruce, D. W. Superfluorinated Ionic Liquid Crystals Based on Supramolecular, Halogen-Bonded Anions. *Angew. Chem. Int. Ed.* **2016**, *55*, 6300-6304.
- (35) Li, H.; Lu, Y.; Wu, W.; Liu, Y.; Peng, C.; Liu, H.; Zhu, W. Noncovalent interactions in halogenated ionic liquids: theoretical study and crystallographic implications. *PCCP* **2013**, *15*, 4405-4414.
- (36) Walter, S. M.; Kniep, F.; Herdtweck, E.; Huber, S. M. Halogen-Bond-Induced Activation of a Carbon-Heteroatom Bond. *Angew. Chem. Int. Ed.* **2011**, *50*, 7187-7191.
- (37) Raatikainen, K.; Cavallo, G.; Metrangolo, P.; Resnati, G.; Rissanen, K.; Terraneo, G. In the Pursuit of Efficient Anion-Binding Organic Ligands Based on Halogen Bonding. *Cryst. Growth Des.* **2013**, *13*, 871-877.
- (38) Kelley, S. P.; Narita, A.; Holbrey, J. D.; Green, K. D.; Reichert, W. M.; Rogers, R. D. Understanding the Effects of Ionicity in Salts, Solvates, Co-Crystals, Ionic Co-Crystals, and Ionic Liquids, Rather than Nomenclature, Is Critical to Understanding Their Behavior. *Cryst. Growth Des.* **2013**, *13*, 965-975.
- (39) Arduengo, A. J.; Kline, M.; Calabrese, J. C.; Davidson, F. Synthesis of a reverse ylide from a nucleophilic carbene. *J. Am. Chem. Soc.* **1991**, *113*, 9704-9705.
- (40) Tian, C.; Nie, W.; Borzov, M. V.; Su, P. High-Yield Thermolytic Conversion of Imidazolium Salts into Arduengo Carbene Adducts with BF₃ and PF₅. *Organometallics* **2012**, *31*, 1751-1760.
- (41) Rodríguez, H.; Gurau, G.; Holbrey, J. D.; Rogers, R. D. Reaction of elemental chalcogens with imidazolium acetates to yield imidazole-2-chalcogenones: direct evidence for ionic liquids as proto-carbenes. *Chem. Commun.* **2011**, *47*, 3222-3224.
- (42) Gurau, G.; Rodríguez, H.; Kelley, S. P.; Janiczek, P.; Kalb, R. S.; Rogers, R. D. Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids. *Angew. Chem. Int. Ed.* **2011**, *50*, 12024-12026.
- (43) Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. 1,3-Dimethylimidazolium-2-carboxylate: the unexpected synthesis of an ionic liquid precursor and carbene-CO₂ adduct. *Chem. Commun.* **2003**, 28-29.
- (44) Smiglak, M.; Hines, C. C.; Reichert, W. M.; Shamshina, J. L.; Beasley, P. A.; McCrary, P. D.; Kelley, S. P.; Rogers, R. D. Azolium azolates from reactions of neutral azoles with 1,3-dimethyl-imidazolium-2-carboxylate, 1,2,3-trimethyl-imidazolium hydrogen carbonate, and N,N-dimethyl-pyrrolidinium hydrogen carbonate. *New J. Chem.* **2013**, *37*, 1461-1469.
- (45) Slater, R. The triiodide ion in tetraphenyl arsonium triiodide. *Acta Crystallogr.* **1959**, *12*, 187-196.

- (46) Holthoff, J. M.; Engelage, E.; Kowsari, A. B.; Huber, S. M.; Weiss, R. Noble Metal Corrosion: Halogen Bonded Iodocarbenium Iodides Dissolve Elemental Gold—Direct Access to Gold–Carbene Complexes. *Chem. Eur. J* **2019**, *25*, 7480-7484.
- (47) Del Pópolo, M. G.; Lynden-Bell, R. M.; Kohanoff, J. Ab Initio Molecular Dynamics Simulation of a Room Temperature Ionic Liquid. *J. Phys. Chem. B* **2005**, *109*, 5895-5902.
- (48) Hardacre, C.; Holbrey, J. D.; McMath, S. E. J.; Bowron, D. T.; Soper, A. K. Structure of molten 1,3-dimethylimidazolium chloride using neutron diffraction. *J. Chem. Phys.* **2002**, *118*, 273-278.
- (49) Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen, M.; Padua, A. A. H.; Sheppard, O.; Soper, A. K. Liquid Structure of the Ionic Liquid 1,3-Dimethylimidazolium Bis{(trifluoromethyl)sulfonyl}amide. *J. Phys. Chem. B* **2006**, *110*, 12055-12061.
- (50) Elaiwi, A.; Hitchcock, P. B.; Seddon, K. R.; Srinivasan, N.; Tan, Y.-M.; Welton, T.; Zora, J. A. Hydrogen bonding in imidazolium salts and its implications for ambient-temperature halogenoaluminate(III) ionic liquids. *J. Chem. Soc., Dalton Trans.* **1995**, 3467-3472.
- (51) Allen, F. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr. B* **2002**, *58*, 380-388.
- (52) Lampl, M.; Laus, G.; Kahlenberg, V.; Wurst, K.; Huppertz, H.; Schottenberger, H. Synthesis and crystal structures of 2-bromo-1,3-dimethylimidazolium iodides. *Acta Crystallogr. E* **2018**, *74*, 497-501.
- (53) Herbstein, F. H.; Schwotzer, W. Crystal structures of polyiodide salts and molecular complexes. 7. Interaction of thiones with molecular diiodine. The crystal structures of dithizone-diiodine, ethylenethiourea-bis(diiodine), bis(ethylenethiourea)-tris(diiodine), bis(dithizone)-heptakis(diiodine), and 1-(1-imidazolin-2-yl)-2-thioxoimidazolidinium triiodide-(ethylenethiourea-diiodine). *J. Am. Chem. Soc.* **1984**, *106*, 2367-2373.
- (54) Abate, A.; Brischetto, M.; Cavallo, G.; Lahtinen, M.; Metrangolo, P.; Pilati, T.; Radice, S.; Resnati, G.; Rissanen, K.; Terraneo, G. Dimensional encapsulation of I⁻⋯I₂⋯I⁻ in an organic salt crystal matrix. *Chem. Commun.* **2010**, *46*, 2724-2726.
- (55) Węclawik, M.; Gağor, A.; Piecha, A.; Jakubas, R.; Medycki, W. Synthesis, crystal structure and phase transitions of a series of imidazolium iodides. *CrystEngComm* **2013**, *15*, 5633-5640.
- (56) Breitenfeld, J.; Vechorkin, O.; Corminboeuf, C.; Scopelliti, R.; Hu, X. Why Are (NN₂)Ni Pincer Complexes Active for Alkyl–Alkyl Coupling: β-H Elimination Is Kinetically Accessible but Thermodynamically Uphill. *Organometallics* **2010**, *29*, 3686-3689.
- (57) Maitlis, P. M.; Haynes, A.; James, B. R.; Catellani, M.; Chiusoli, G. P. Iodide effects in transition metal catalyzed reactions. *Dalton Trans.* **2004**, 3409-3419.
- (58) Wang, H.; Gurau, G.; Shamshina, J.; Cojocar, O. A.; Janikowski, J.; MacFarlane, D. R.; Davis, J. H.; Rogers, R. D. Simultaneous membrane transport of two active pharmaceutical ingredients by charge assisted hydrogen bond complex formation. *Chem. Sci.* **2014**, *5*, 3449-3456.
- (59) Thorsmølle, V. K.; Rothenberger, G.; Topgaard, D.; Brauer, J. C.; Kuang, D.-B.; Zakeeruddin, S. M.; Lindman, B.; Grätzel, M.; Moser, J.-E. Extraordinarily Efficient Conduction in a Redox-Active Ionic Liquid. *ChemPhysChem* **2011**, *12*, 145-149.
- (60) Simon, S. J. C.; Parlane, F. G. L.; Swords, W. B.; Kellett, C. W.; Du, C.; Lam, B.; Dean, R. K.; Hu, K.; Meyer, G. J.; Berlinguette, C. P. Halogen Bonding Promotes Higher Dye-Sensitized Solar Cell Photovoltages. *J. Am. Chem. Soc.* **2016**, *138*, 10406-10409.

- (61) Parlane, F. G. L.; Mustoe, C.; Kellett, C. W.; Simon, S. J.; Swords, W. B.; Meyer, G. J.; Kennepohl, P.; Berlinguette, C. P. Spectroscopic detection of halogen bonding resolves dye regeneration in the dye-sensitized solar cell. *Nat. Commun.* **2017**, *8*, 1761.
- (62) Chiarotto, I.; Feroci, M.; Inesi, A. First direct evidence of N-heterocyclic carbene in BMIm acetate ionic liquids. An electrochemical and chemical study on the role of temperature. *New J. Chem.* **2017**, *41*, 7840-7843.
- (63) Kar, B. P.; Sander, W. Reversible Carbene Formation in the Ionic Liquid 1-Ethyl-3-Methylimidazolium Acetate by Vaporization and Condensation. *ChemPhysChem* **2015**, *16*, 3603-3606.
- (64) Skyllas-Kazacos, M. Novel vanadium chloride/polyhalide redox flow battery. *J. Power Sources* **2003**, *124*, 299-302.
- (65) Gross, M. M.; Manthiram, A. Long-Life Polysulfide–Polyhalide Batteries with a Mediator-Ion Solid Electrolyte. *ACS Appl. Energy Mater.* **2019**, *2*, 3445-3451.
- (66) Zhang, L.; Lai, Q.; Zhang, J.; Zhang, H. A High-Energy-Density Redox Flow Battery based on Zinc/Polyhalide Chemistry. *ChemSusChem* **2012**, *5*, 867-869.
- (67) Zakeeruddin, S. M.; Grätzel, M. Solvent-Free Ionic Liquid Electrolytes for Mesoscopic Dye-Sensitized Solar Cells. *Adv. Funct. Mater.* **2009**, *19*, 2187-2202.
- (68) Lennert, A.; Sternberg, M.; Meyer, K.; Costa, R. D.; Guldi, D. M. Iodine-Pseudohalogen Ionic Liquid-Based Electrolytes for Quasi-Solid-State Dye-Sensitized Solar Cells. *ACS Appl. Mater. Inter.* **2017**, *9*, 33437-33445.
- (69) Denizalti, S.; Ali, A. K.; Ela, Ç.; Ekmekci, M.; Erten-Ela, S. Dye-sensitized solar cells using ionic liquids as redox mediator. *Chem. Phys. Lett.* **2018**, *691*, 373-378.
- (70) Bruker, APEX3 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA., 2015
- (71) Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A* **2015**, *71*, 3-8.
- (72) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C: Struct. Chem.* **2015**, *71*, 3-8.
- (73) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; J. A., M., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J., Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016,
- (74) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.
- (75) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
- (76) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A* **1988**, *38*, 3098-3100.

- (77) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *PCCP* **2005**, *7*, 3297-3305.
- (78) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829-5835.
- (79) Roy, D.; Todd, K.; John, M., Gauss view, version 5, 2009



For table of contents only. The reaction of 1,3-dimethylimidazolium-2-carboxylate with elemental iodine in acetonitrile allows rapid access to two crystalline iodide salts $[C_1mim-2-I] \cdot 0.5I_2$ and $[C_1mim-2-I] \cdot 0.5CH_3CN$, depending on the temperature. Both compounds reveal significant contribution of halogen bonding reducing their ionicity and affecting the crystal structures.