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Mass Spectrometric and Theoretical Study of Polyiodides: The Connection between Solid State, Solution, and Gas Phases

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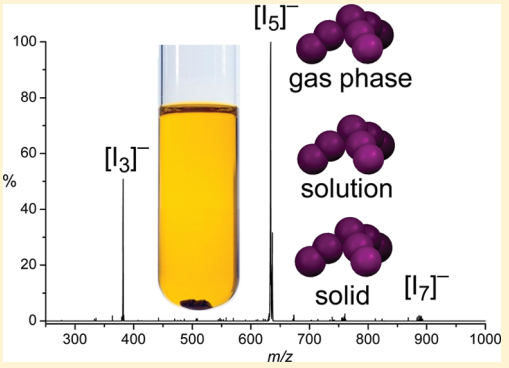
Supporting Information

ABSTRACT: Polyiodides have been transferred intact from acetonitrile solution to the gas phase and analyzed by mass spectrometry. A range of ions were observed, including $[I_{11}]^-$, $[I_{13}]^-$, and $[I_{15}]^-$, which have higher iodine/iodide ratios than any previously characterized ions. Theoretical calculations show that branched structures are strongly favored, a result which is in excellent agreement with with gas phase fragmentation studies (MS/MS) and also previous solid state studies. This study demonstrates the utility of mass spectrometry to provide structural information in the absence of other spectroscopic handles.



INTRODUCTION

Polyiodide salts are a structurally diverse and highly complex class of compounds.[1] Their extraordinary properties, especially those related to their conductivity, have led to widespread applications in electronics,[2] batteries,[3] optical devices,[4] and dye-sensitized solar cells.[5] Despite their complexity, polyiodides are simple to make by mixing elemental iodine with iodide salts in appropriate ratios.[6] The structure of the polyiodide depends on both the I_2/I^- ratio and the countercation,[7] and in the solid state large cations and/or those with multiple charge result in the largest and most structurally diverse polyiodide anions. Structures often contain multiple polyiodides, a classic case being $[Lu(dibenzo\text{-}18\text{-}crown\text{-}6)(H_2O)_3(thf)_6]^{3+}$, which crystallizes with 2 equiv of $[I_3]^-$, 6 of $[I_5]^-$, and 1 each of $[I_8]^{2-}$ and $[I_{12}]^{2-}$.[8] The most iodine-rich polyiodide corresponds to the ferrocenium salt of $[I_{29}]^{3-}$,[9] which comprises a three-dimensional (3D) network made up of $[I_5]^-$, $[I_{12}]^{2-}$, and I_2 units. Polyiodides can alternatively be thought of as comprising I_2 and I^- and/or $[I_3]^-$ units linked through donor−acceptor interactions.[10]

Despite the manifest richness of the solid-state structures of polyiodides, much less is known about their existence in solution or in the gas phase. Polyiodides in solution are dominated by $[I_3]^-$, but contain a complex mixture of higher polyiodides in low concentration, and lacking a diagnostic spectroscopic handle, they are not easily studied. It has even been stated that there is *no* experimental evidence for the formation of higher polyiodides in aqueous solution.[11] Electrospray ionization mass spectrometry (ESI-MS)[12] is a technique capable of analyzing solution speciation in detail,[13] including very labile species (provided conditions are carefully selected).[14] Consequently, polyiodides are ideal analytes for the technique, as most of the likely species differ in m/z and ESI-MS is well-suited to the study of complex mixtures (fragmentation is minimal and all separation is carried out in the gas phase). Consistent with other spectroscopic techniques, previous studies of polyiodides by ESI-MS have not detected any iodides higher than $[I_3]^-$ regardless of the overall composition,[15] although ESI-MS was not the principal focus of these investigations. We set out with the higher polyiodides as our principal focus, and based on the importance of polyiodides in solar cells, selected the benchmark system 1-propyl-3-methylimidazolium (pmim) iodide/iodine,[16] and remarkably, excellent correlations between these gas phase studies and previous studies on polyiodides in the solid state were obtained.

RESULTS AND DISCUSSION

A series of polyiodide ionic liquids $[pmim][I]\cdot nI_2$ ($n = 1-5$) were prepared by addition of the appropriate amount of iodine to [pmim][I] (Scheme 1), diluted in acetonitrile and analyzed by

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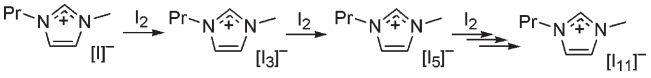
Scheme 1. Preparation of Polyiodides under Solvent-Free Conditions



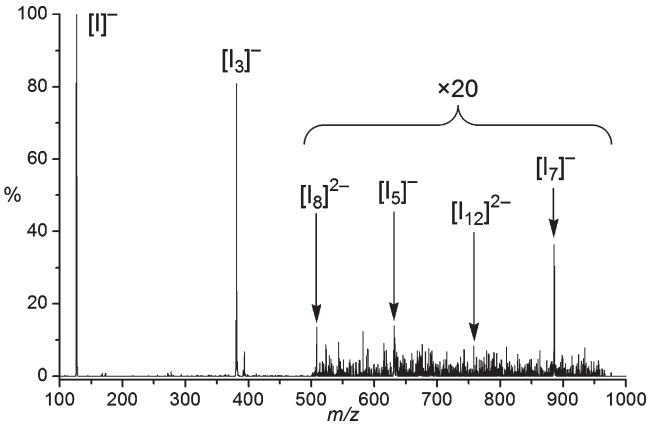


Figure 1. Negative-ion ESI-MS of [pmim] [I]·4I_2 (10 μmol L^{-1}) in acetonitrile. The spectral region above m/z 500 is shown at an intensity 20× that recorded, to reveal the higher polyiodides.

ESI-MS (see Experimental Section). Solutions of 10 μM based on iodide were used since it was found that at higher concentrations the spectra were complicated by the appearance of aggregates containing the cation,[17] namely, $[(pmim)_n(I_3)_{(n+1)}]^-$, $[(pmim)_n(I)_{(n+1)}]^-$, and combinations of the two. The solutions were stable; speciation did not change over several days of analysis, and no special precautions were taken.

At first glance the negative-ion ESI-MS of [pmim][I]·4I_2 appears to contain only $[I]^-$ and $[I_3]^-$. The higher polyiodides are present in very low abundance as the spectra are recorded near the sensitivity limit of the instrument to avoid the appearance of aggregate ions (see above). Nonetheless, close inspection at higher m/z reveals a variety of characteristically monoisotopic ions (Figure 1).

The m/z value gives a good indication of the likely identity of each ion with unambiguous confirmation provided by tandem MS. The anions $[X_3]^-$ (X = Cl, Br, I) fragment predominantly by loss of X_2, although via a minor fragmentation mechanism X• can also be lost to leave a detectable radical anion.[18] All of the polyiodides $[I_{2n+1}]^-$ (n = 1−7) were found to fragment by I_2 loss (Figure 2) through collision-induced dissociation (CID) in the ion trap, and in each case the base peak in the MS/MS is $[I_{2n-1}]^-$.

There are different pathways by which the fragmentation of the monoanionic polyiodides $[I_{2n+1}]^-$ (n = 1−7) might proceed. In principle, cleavage may occur at any bond, although most likely where two even-electron fragments are generated rather than two radicals. Such bonds are found to be longest in the solid-state structures. For example, assuming $[I_{15}]^-$ has a linear structure, fragmentation might be expected to occur with equal efficiency at any point in the chain and the fragments $[I_{2n+1}]^-$ (n = 1−7) would appear with roughly the same abundance. However, such a pattern is not observed, and instead, the dominant fragmentation involves loss of iodine. This observation is consistent not only with the polyiodides observed in solid state

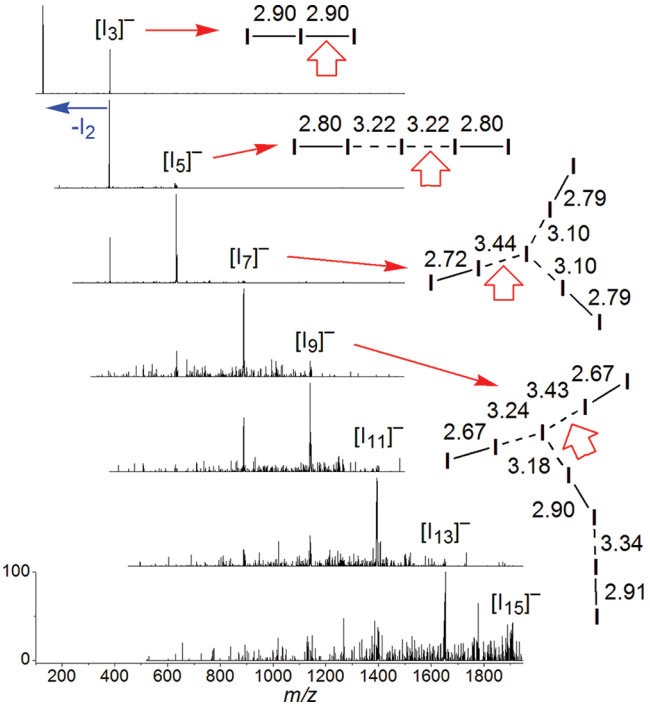


Figure 2. Negative-ion ESI-MS/MS of the ions $[I_{2n+1}]^-$ (n = 1−7). The precursor ion in each case is labeled. Fragmentation proceeds through sequential loss of I_2. The base product ion peak in all MS/MS spectra is the loss of one I_2, but loss of two and even three I_2 units can be observed. To the right of the spectra, crystallographically determined connectivity and bond lengths (Å) for $[I_9]^-$, $[I_7]^-$, $[I_5]^-$, and $[I_3]^-$ are shown.[1] Note that breaking the longest bond leads to I_2 loss in all cases, consistent with the MS/MS results.

Table 1. Calculated Bond Lengths (r/Å) and Vibrational Frequencies (ν/cm^{-1}) of I_2, I_2^-, I_3^-, and I_5^- from This Work and Selected Literature Values

ion	method	r1	r2	ν_1	ν_2	ν_3
I_2	CCSD(T)/ECP-TZ(2df)[a]	2.709		210.2		
I_2	B3LYP/SC-ECP[b]	2.703		213.2		
$[I_2]^-$	CCSD(T)/ECP-TZ(2df)[a]	3.299		105.5		
$[I_2]^-$	B3LYP/SC-ECP[b]	3.331		89.5		
$[I_3]^-$	CCSD(T)/ECP-TZ(2df)[a]	2.982		107.8	58.2	129.3
$[I_3]^-$	B3LYP/SC-ECP[b]	2.994		105.3	53.8	133.2
$[I_5]^-$	B3PW91/ECP-TZ(2df)[a]	2.857	3.065	157.4[c]	143.5[c]	109.9[c]
$[I_5]^-$	B3LYP/SC-ECP[b]	2.884	3.103	152.5[c]	138.7[c]	96.6[c]

[a] Ref 20a. [b] This work. [c] ν_1, ν_2, ν_3 here correspond to ω_9, ω_8, and ω_7, respectively, in ref 20a.

structures,[1] but also with a theoretical study on the solid-state polybromides $[Br_{2n+1}]^-$ (n = 1−4) which found that the most stable structures are those that are heavily branched.[19] The MS/MS data suggests that branched structures are also likely for these higher polyiodides.

Because no crystallographic data is available for the anions $[I_{11}]^-$, $[I_{13}]^-$, or $[I_{15}]^-$, and only $[I_2]^-$, $[I_3]^-$, and $[I_5]^-$ gas-phase structures of polyiodides have been studied quantum-chemically, we addressed this limitation and performed calculations on all of the species observed by ESI-MS.[20] Computations for these systems, as well as for the benchmark I_2, are in reasonable

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agreement with the previously published theoretical studies (Table 1).

For larger $[I_{(2n+1)}]^-$ anions (n = 3, 4), as well as for $[I_{2n}]^{2-}$ (n = 4) dianions, neither quantum-chemical nor experimental gas phase data are available, so the optimized geometry parameters of the hepta-, octa-, and nona-iodides were compared with the corresponding crystallographic data (Figures 3−5, respectively). Reasonable agreement of the computations for the isolated anions with the experimental data obtained for the solids suggests that the influence of the counterions and lattice surrounding the structure of the polyiodides is not crucial, with the anions adopting similar topologies in the gas, solution, and solid phases.

Attempts were made to find stable forms of the polyiodides that have not been characterized in crystals. These computations, indeed, revealed a "tetrahedral" structure for $[I_9]^-$ (Figure 4), being more heavily branched than typical "pyramidal" structure shown in Figure 3, the former being less energetically stable than the latter by about 2 kcal·mol^{-1}. The more stable "pyramidal" $[I_9]^-$ configuration was used as a basis to build up hypothetical, arbitrary structures of undecaiodide $[I_{11}]^-$, tridecaiodide $[I_{13}]^-$, and pentadecaiodide $[I_{15}]^-$. Optimization of these starting geometries resulted in the stable structures shown in Figure 5.

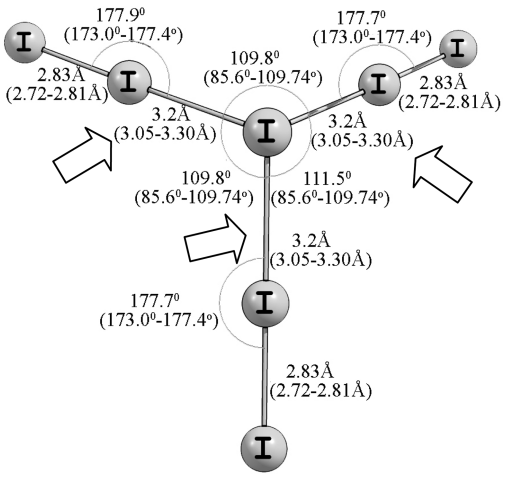

Figure 3. Optimized structure of $[I_7]^-$. The computed geometry parameters are given with the corresponding crystallographically determined values (in parentheses) from ref 1. Arrows indicate the longest bonds.

In all cases, the longest bonds in the computationally determined structures involve a bond to a terminal I_2 moiety, and breaking this fragment would give rise to a loss of −254 Da as the primary fragmentation process in the MS/MS investigations, which is in fact what is observed. In principle, doubly charged polyiodides could also be fragmented by I_2 loss, and might also cleave in an asymmetrical fashion, to produce two monoanionic (poly)iodides (homolytic cleavage seems less likely, as two radical anions would be obtained). The only two dianionic polyiodides observed in the ESI-MS that do not overlap with monoanions are $[I_8]^{2-}$ and $[I_{12}]^{2-}$, both of which have been characterized in the solid state.[8] We have assigned these as dianions rather than the monoanions $[I_4]^-$ and $[I_6]^-$, simply because the monoanions would not be even-electron species. $[I_8]^{2-}$ provided an MS/MS dominated by a product ion at m/z 381, which could correspond to $[I_3]^-$, $[I_6]^{2-}$, or quite likely, both (Figure 6). $[I_6]^{2-}$ has a high charge density, and as polyanions have a limited lifetime in the gas phase, it is likely to separate into 2 × $[I_3]^-$ in the gas phase, an example of an ion fragmenting into a product ion with the same m/z ratio. The two ions are indistinguishable as iodine is monoisotopic. $[I_{12}]^{2-}$ exhibited analogous behavior to $[I_8]^{2-}$, and there is evidence for $[I_8]^{2-}$ and $[I_{12}]^{2-}$ as product ions in the spectra of $[I_5]^-$ and $[I_7]^-$ (see Supporting Information), suggested that there is some $[I_{10}]^{2-}$ and $[I_{14}]^{2-}$ present in solution.

No stable branched forms were found computationally for $[I_8]^{2-}$, instead the linear form seen in Figure 7 was found to be stable. These results are in agreement with the observation that though a lot of branched forms of $[I_{(2n+1)}]^-$ anions are present in crystals,[1] whereas only one branched structure of $[I_8]^{2-}$, with an

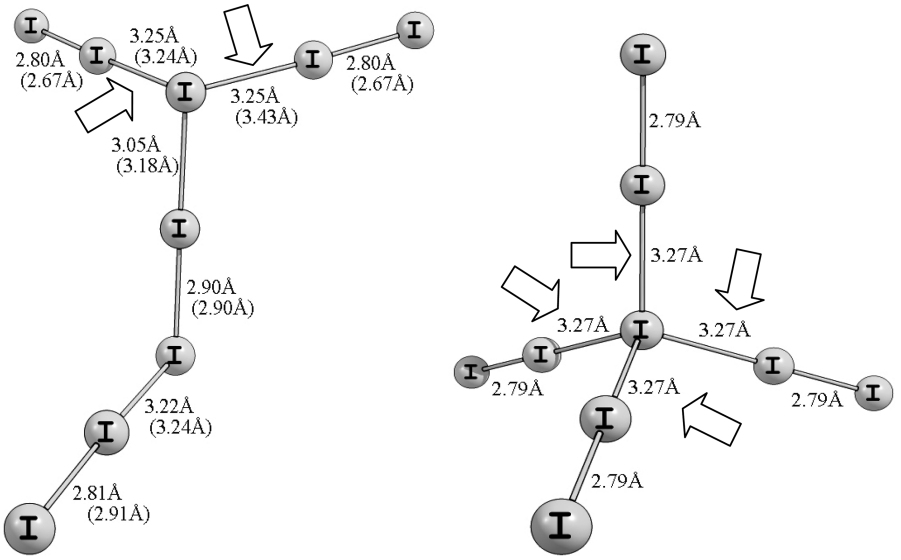

Figure 4. Optimized structure of $[I_9]^-$ (left) with the computed bond lengths and the corresponding crystallographically determined values (in parentheses) from ref 1. E = −2662.5367015 au (−1670741.8 kcal/mol); sum of electronic and zero-point energies = −2662.533522 a.u (−1670739.8 kcal/mol). Optimized "tetrahedral" structure of $[I_9]^-$ (right) and the computed bond lengths. E = −2662.533585 au (−1670739.8 kcal/mol); sum of electronic and zero-point energies = −2662.530574 au (−1670737.9 kcal/mol) Arrows indicate the longest bonds.

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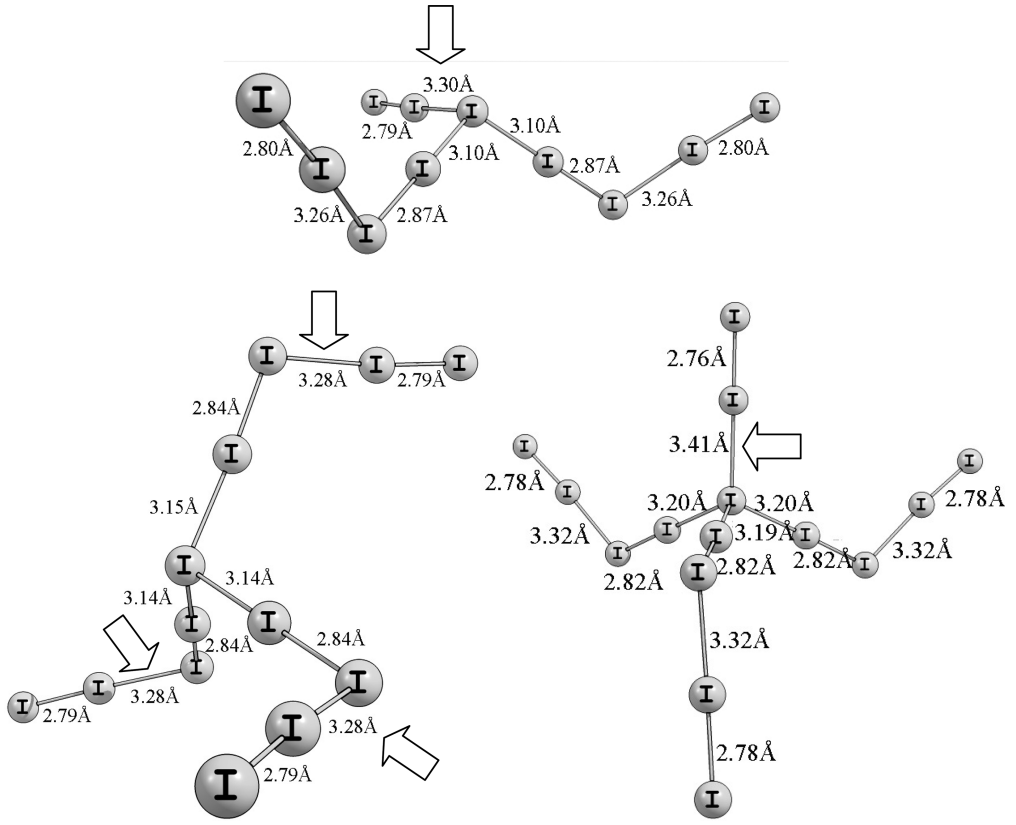

Figure 5. Optimized structures and the computed bond lengths of $[I_{11}]^-$ (E = −3254.179579 au = −2041997.7 kcal/mol); sum of electronic and zero-point energies = −3254.175643 au = −2041995.2 kcal/mol)); $[I_{13}]^-$ (E = −3845.820434 au = −2413252.3 kcal/mol); sum of electronic and zero-point energies = −3845.815815 au = −24113249.4 kcal/mol)); $[I_{15}]^-$ (E = −4437.457103 au = −2784504.3 kcal/mol); sum of electronic and zero-point energies = −4437.451642 au = −2784504.3 kcal/mol)). Arrows indicate the longest bonds.

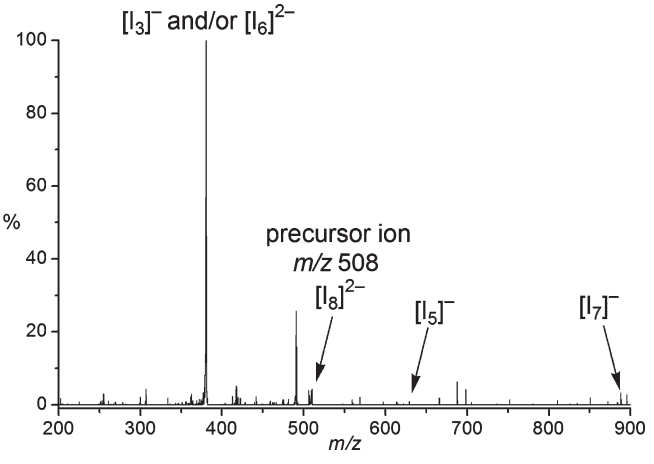

Figure 6. ESI-MS/MS of $[I_8]^{2-}$.The identity of the peak at m/z 490 is unknown, but is likely to be a fragment from an ion coincident with the precursor ion at m/z 508. The loss of 18 Da is consistent with elimination of water, a common fragmentation pathway for polar molecules, and confirms that the ion is not related to the polyiodide species.

unusual $[(I_5^-)\cdot(I_3^-)]$ configuration, has been reported.[21] Moreover, the linear structure is consistent with the MS/MS study, as cleavage of the longest bond (3.56 Å) would produce $[I_5]^-$ and $[I_3]^-$. The low abundance of $[I_5]^-$ suggests that it is prone to

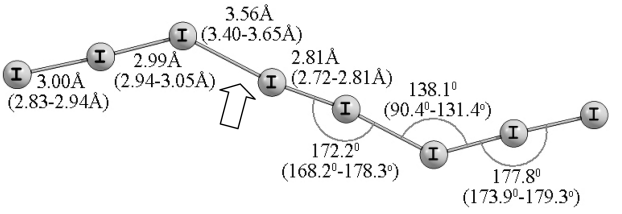

Figure 7. Optimized structure of $[I_8]^{2-}$. The computed geometry parameters and the corresponding crystallographic data (in parentheses) taken from ref 1. The arrow indicates the longest bond.

further fragmentation via I_2 loss, and the appearance of $[I_7]^-$ suggests that a small amount of the precursor ion fragments via the pathway $[I_8]^{2-} \rightarrow [I_7]^- + [I]^-$.

In summary, a large number of polyiodides including $[I_{2n+1}]^-$ (n = 1−7) and $[I_{2n}]^{2-}$ (n = 4−7) were transferred to the gas phase and identified by ESI-MS(/MS). $[I_{11}]^-$, $[I_{13}]^-$, and $[I_{15}]^-$ have higher iodine/iodide ratios than any previously characterized polyiodide. These species are present in solution, and it is likely that their abundance increases with concentration (as the solubility of free iodine decreases). Indeed, many of the polyiodides observed by MS have been observed in the solid state, which suggests that the exotic solid state structures characterized by crystallography may have their components prefabricated in solution. Stable structures were calculated for all $[I_{2n+1}]^-$ ions, and branched structures with the longest bond lengths to terminal

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I_2 units were predicted, hence confirming the observed fragmentation pattern in the MS/MS experiments. This study demonstrates the utility of ESI-MS(/MS) in the discovery of new polyiodides, and has shown that correlations between gas, solution, and solid phases are justified.

EXPERIMENTAL SECTION

The polyiodide salt [pmim][I]·$4I_2$, where [pmim] = the 1-propyl-3-methyl-imidazolium cation, was prepared by addition of 4 equiv of elemental iodine to the 1-propyl-3-methylimidazolium iodide salt at room temperature. For mass spectrometric analysis, a 10 μmol L^{-1} solution in acetonitrile (HPLC grade, Acros) was prepared. Mass spectra were collected in negative ion mode on a ThermoFinnigan LCQ DecaXP Plus quadrupole ion trap instrument (Thermo Fisher Scientific, Bremen, Germany) equipped with an orthogonal ESI ion source in the range from m/z 100−2000. Samples were infused directly into the source at a flow rate of 5 μL min^{-1} using a syringe pump. The spray voltage was set at 4 kV, the capillary temperature at 100 °C and the capillary voltage at −6 V. For CID experiments, an isolation width of 10 Da and a relative collision energy of 25% were used. Data acquisition and analysis were carried out using the Xcalibur software package (Thermo Fisher Scientific).

All quantum-chemical calculations were carried out using the Gaussian-03 suite of programs.[22] Becke's three-parameter exchange functional[23] was used in combination with the Lee−Yang−Parr correlation functional (B3LYP).[24] Following full geometry optimizations without any symmetry constraints, all stationary points were characterized as minima by analysis of the Hessian matrices. Calculations were carried out with the aug-cc-pVTZ basis set including small-core energy consistent relativistic pseudoptentials (MDF-28 SC-ECPs)[25] from the Stuttgart and Dresden (SDD) basis set library.[26]

ASSOCIATED CONTENT

Supporting Information. Further details are given in Figures SI1−SI8. This material is available free of charge via the Internet at http://pubs.acs.org.

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