Pressure-induced Polymerization and Electrical Conductivity of a Polyiodide

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Abstract: We report the high-pressure structural characterization of an organic polyiodide salt in which a progressive addition of iodine to triiodide groups occurs. Compression leads to the initial formation of discrete hepta-iodide units, followed by polymerization to a 3D anionic network. Although the structural changes appear to be continuous, the insulating salt becomes a semiconducting polymer above 10 GPa. The features of the pre-reactive state and the polymerized state are revealed by analysis of the computed electron and energy densities. The unusually high electrical conductivity can be explained with the formation of new bonds.

Polyiodides (PI) in crystal form were discovered over 190 years ago.^[1] Their structural diversity, due to the bonding flexibility of iodine, remains the subject of constant interest.^[2–4] Nowadays, various PI are known, ranging from I_3^- to I_{29}^{3-} , with the general formula: I^{n-}_{2m+n} , up to $n = 4$. Their building blocks consist of I_3^- as a donor and I_2 as an acceptor forming a charge transfer (CT) complex. CT complexes can interact further to form extended structures with topologies up to cubic. Because the aggregation of iodine units is somewhat unpredictable, the design of PIs is not easy. Moreover, the classification of higher units is, so far, pragmatically based on the distance between iodine atoms, but universal criteria are still lacking.

Different theoretical approaches to study bonds in PI exist, e.g. calculations of the potential energy surface and bond order^[5], the energy decomposition analysis (EDA)^[6], the analysis of the electron density and its Laplacian at bond critical points (BCP)^[7], the electron localization function, and the one-electron potential^[8]. Furthermore, the energy density at BCP^[9] and the interacting quantum atom (IQA) method^[10] were used to analyze halogen bonds^[11].

Depending on the forces exerted by the organic counter ions (*chemical pressure*), PI exhibit useful electrochemical properties, like charge-carrier transportation, high electrolyte energy density,

high redox reaction reversibility^[12,13], and a wide range of electrical conductivity, from insulator to metallic behavior^[14,15]. Hence, PI found technical applications in electronic and electrochemical devices such as flow batteries, fuel cells, dye-sensitized solar cells and optical devices.^[12,16,17]

Compared with the chemical pressure, an external *mechanical pressure* more substantially affects the crystal inter- and intramolecular landscape. In fact, a huge lattice strain may induce phase transformations and even chemical reactions. The achievable static high pressure (HP) in standard diamond anvil cells (DACs) is tens of gigapascals. Such a pressure changes significantly the Gibbs energy, increasing the internal energy and making the PV term dominant. Similarly large energy changes are, instead, not accessible in solids by temperature alteration which induces instead sublimation or melting due to the dominant entropic term. The volume contraction is the main driving force for the addition reaction to atoms linked by unsaturated bonds and formation of extended assemblies, otherwise unstable at ambient pressure. One can apply this concept also to polyvalent iodine, typically able to expand its coordination in hepta-iodides or organic iodonanes^[18]. Although compression may produce exotic chemical bonding and properties, only few spectroscopic studies focused on PI at HP. Raman spectroscopy demonstrated that solid organic PI under HP can catenate. Penta-iodides form I_3^- chains in iodine-doped poly(vinyl alcohol) films at as low as 0.2 GPa^[19], while a pressure between 0 and 3.4 GPa is needed for bond formation in PI confined into carbon nanotubes^[20]. Such a catenation does not occur in aqueous solution, advocating solid phase as a preferred matrix for a reaction between iodine units.

Figure 1: The iodine units around the tetraethylammonium cation in TEAI at ambient pressure. The shortest ($d_1 = 3.479(4)$ Å) iodine-iodine intermolecular distances are marked in orange and the second shortest ($d_2 = 3.494(4)$ Å) in green.

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Figure 2: a) Unit cell axes and volume of TEAI as a function of pressure. Lines represent 3rd order Vinet equation of state^[21] (fitted using EoSfit7c^[22]). The calculated Bulk Modulus is 7.7(5) GPa, which coincides with that of pure I₂^[23]. b) Evolution of d_1 and d_2 (see Fig. 1) with pressure. c) Electric resistance (measured on two different samples) and calculated band gap.

In this study, we investigated the response of tetraethylammonium di-iodine triiodide (TEAI) to compression, using powder and single-crystal X-ray diffraction, electrical conductivity, and first principle calculations. TEAI was chosen after extensive screening of the Cambridge Structural Database^[24] (entries HALTAP^[25] and HALTAP01^[26]) in order to find a moiety with appropriate packing, ready for catenation between donor (I₃⁻) and acceptor (I₂) upon compression. Quaternary ammonium salts are often used as model cations for

PI studies^[27–30]. At ambient conditions, TEAI crystallizes in the orthorhombic *Aba2* space-group. I₂ and apical iodine atoms of the I₃⁻ anion form, through contacts d_1 and d_2 (Fig. 1), zig-zag chains extending along the crystallographic c axis, while oscillating in a direction. The same contacts form another zig-zag motif propagating along a and oscillating mainly along the b axis. These supramolecular chains encapsulate the isolated cations. Parallel chains form bilayers normal to the b axis due to the linkage with I₃⁻ spacers (Fig. S2). The distances between one I₂ and its neighboring two I₃⁻ units are unequal (d_1 and d_2 , Fig. 1 and 2b). They approach the acceptor at angles (α and β , respectively) favorable for formation of higher units. This happens when the I₃⁻ and I₂ are close enough for their frontier molecular orbitals to overlap. In extended systems, this interplay gives rise to valence and conducting bands^[31]. When the interaction is stronger, the bands broaden and the band gap decreases, leading to a semiconducting behavior, observed in many species^[32–34].

Figure 3: The electronic energy of I₅⁻ calculated in vacuo, as a function of δ_1 and δ_2 . The colour indicates the destabilization from the symmetric I₅⁻. The white circles represent entries in the Cambridge Structural Database containing I₅⁻. The black triangles represent TEAI at different pressures (the triangle size is proportional to the pressure).

We performed X-ray diffraction experiments on TEAI in various pressure transmitting media (PTM). Herein, we report data obtained using nitrogen as PTM, known to be hydrostatic up to ca. 10 GPa^[35] and chemically inert. The effects of other, less hydrostatic PTM, will be discussed in a forthcoming full paper. Upon pressurization up to 12.8 GPa, the crystal volume of TEAI contracts by 35%. The b axis, normal to the corrugated iodine bilayers, shows the highest linear compressibility, due to a lack of strong intermolecular interactions in this direction. Molecular volume compression trends (Fig. 2a) do not show any discontinuity ruling out the occurrence of phase transitions. The length of the unit cell axes a and b are well predicted by periodic density functional theory (DFT) calculations over the entire pressure regime whereas c is slightly overestimated. The length of contact d_2 is well simulated whereas the underestimation of d_1 at low pressure is due to neglecting temperature effects in the

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simulations, whereas all high-pressure experiments have been carried out at ambient temperature. The temperature effects on the lattice parameters were estimated by an additional diffraction experiment at 110K and ambient P (Table S4). Moreover, in the vicinity of the equilibrium geometry, the calculated energy surface is very flat (see Fig. 3 for I_5^-), which is the reason why some DFT functionals or basis sets may fail in predicting the geometry of the adducts, especially when perturbed by the electric field inside a crystal.

Figure 4: Bonding contribution in I_5^- as a function of δ_1 : the delocalization index is in red; the non-classic contributions to the binding energy (IQA or EDA) are in blue. The ionic KI and the covalent I_2 are shown as benchmarks. The reference states for the decomposition calculations are: $I^- + K^+ \rightarrow KI$, $I \cdot + I \cdot \rightarrow I_2$, $I_2 + I_3^- \rightarrow I_5^-$. IQA and EDA decomposition for I_3^- is shown in Fig S6 of the SI.

Perpendicular to the iodine bilayers, the compression induces a continuous decrease of α and β (Fig. 1 and Fig. S3). The contact d_2 , subtending the β angle, is less compressible than d_1 , subtending α (Fig. S3). As the pressure increases, differences between the respective distances d_1 and d_2 as well as α and β broaden. This forces the iodine zig-zag motif to bend out of its initial shape. It is illustrated by a gradual increase of torsion between triiodides (Fig. S3). Compression of the intermolecular iodine bonds does not cause any notable distortion of the intramolecular geometry of the I_2 and I_3^- units.

In order to gain more insight into the nature of the bond in PI, we used theoretical tools for bonding analysis. In TEAI, various interactions of PI units occur among themselves and with the cation, which complicates the analysis. For simplification and abstraction, we take I_5^- calculated in vacuo as benchmark. The stable structure of I_5^- has C_{2v} symmetry, which can be seen as two I_2 molecules symmetrically interacting with a central I^- (at distances δ_1 and δ_2) in a bent structure. In the solid state, this symmetry is distorted, due to the cations and the interactions with other I_3^- and I_2 moieties. We explored the potential energy surface of the system (see Fig. 3) and analysed electron density indicators along the transformation path leading to I_5^- . Fig. 3 shows that there is a similarity between the in vacuo potential energy surface and the one retrieved from the experimental crystal structures within the framework of structure correlation,^[36] although, as expected, the distances in the solid are typically shorter than in vacuo. In fact, one can easily observe an ideal translation of the crystal potential energy surface along the diagonal of the diagram in Fig. 3.

The effect of the mechanical pressure is completely different: the compressed structures of TEAI significantly deviate from the transformation path of the in vacuo or crystal potential surface at ambient pressure. It seems that the HP structures would not converge towards a symmetric I_5^- . This reflects well the multiple $I_3^-I_2$ interactions in the crystals that significantly perturb the picture of a localized I_5^- moiety (when compressed) and anticipates the catenation.

If analyzing only atomic positions, the formation of a genuine covalent bond may not be identified. Even the electron density itself would provide only partial indication of the nature of the chemical bonding, especially under compression. Therefore, we used a decomposition of both the electron density (through Quantum Theory of Atoms in Molecules^[37]) and the energy (through EDA and IQA^[38]) to analyze the nature of this interaction as a function of δ_1 . EDA and IQA are different schemes to partition the bond energy into classic, exchange-correlation and kinetic terms. For I_5^- the two methods provide the same picture (cf. Fig. 4): the classic (electrostatic) contribution always dominates and increases with δ_1 , whereas the non-classic (exchange) never exceeds 25% even at short δ_1 distances. The exchange is larger than in KI, but substantially smaller than in I_2 . Thus, the I-I bond in CT complexes is simultaneously of ionic and covalent nature,^[39] although the ionic one always dominates.

Figure 5: Green and orange: Energy density at the bond critical point (BCP) of the intermolecular contacts d_1 and d_2 calculated using the experimental structures. Black: Energy density at the BCP for the contact between I_3^- and I_2 of I_5^- in vacuo calculated at different distances δ_1 .

Fig. 5 shows the behaviour of the total energy density at the $I_3^-I_2$ BCP, proposed as criterion to identify a covalent bond:^[40] a negative value implies that the potential energy locally dominates over the kinetic energy and thus that the electron density contributes to stabilization. Because of the homeomorphism between electron density and potential energy density^[37], a negative energy density at BCP implies that the energy density is negative along the whole path interconnecting the valence shells of the interacting atoms. As shown in Fig. 5, the energy density at the BCP turns positive for $\delta_1 > 3.4$ Å. For the experimental structures at different pressures, the trend mimics I_5^- in vacuo both for d_1 (forming I_7^-) and d_2 (forming the extended chain). Thus, as

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a weak I...I contact shrinks, the shared electron density increases, as also shown by the delocalization index in I_5^- (Fig. 4), and becomes more stabilizing. Noteworthy, while the delocalization approaches one electron pair for I-I distances close to that in I_2 , the energy decomposition assigns anyway the dominant role to the electrostatic term. Even in I_2 it exceeds 60% of the total bond energy, in keeping with calculations for other homopolar diatomic molecules^[41].

In TEAl, the pressure induced addition reactions occur apparently in a continuous way, without changing the electronic states of the constituting moieties. However, the formation of an extended polymer raises the question whether this may affect the transport properties of the compound. For this reason, we carried out measurements of the electric resistance in TEAl and observed a dramatic drop between measurements at 9.4 and 11.1 GPa. This semi-conductive state is established for $d_1 \sim 3.18$ Å and $d_2 \sim 3.32$ Å. In this range of distances, the percentage of covalency contribution to the bond has reached ca. 20% and upon further shortening the increase is small (Fig. 4).

At variance from X-ray diffraction experiments, the resistivity was measured in nano-alumina powder, a non-hydrostatic PTM. Nevertheless, powder diffraction measurements performed in the same conditions, show that TEAl behaves in nano-alumina as in a hydrostatic medium and therefore the structure-property correlation (although not in situ) is reliable. The van der Pauw method^[42] enables to estimate the sheet resistance of TEAl, which is 1.36 Ω·cm at the highest pressure. Temperature scans in the range 25 – 55 °C (see Figure S7) showed that the variation of the electrical conductivity (inversely proportional to the resistivity) in TEAl under high-pressure obeys the usual semiconductor equation: $\sigma = Ae^{-E_g/2kT}$, where E_g is the band gap and A is a constant. Calculations prove a continuous band gap closure upon compression, in accordance with the measured decrease of resistivity.

As reported above, the semiconducting behavior is triggered at I-I distances for which the calculated covalent contribution to the bond is 20% (Fig. 4), which does not grow significantly upon further compression. On the other hand, the electron sharing continuously grows as the I-I distance decreases, which causes the valence band broadening and consequent band gap reduction, which seems continuous along the compression path. Noteworthy, only the gradual changes induced by pressure enable us to appreciate the structure-property correlation in such detail.

Recently, it was shown that PI also exhibit photoconductive properties, characteristic for CT complexes.^[17] This phenomenon, however, was not detected in TEAl under high-pressure, neither upon irradiation with a 1mW 532nm laser, nor with a 250W tungsten lamp.

In this paper, we studied the effects of applying pressure on a solid state polyiodide. The compression stimulates the approach between complementary I_3^- and I_2 units, which are clearly separated and interacting mainly electrostatically at ambient pressure, whereas the covalent contribution increases upon compression, as revealed by theoretical calculations. Ultimately, this leads to the formation of CT chains, which explains the drastically increased conductivity.

These features make TEAl a tunable pressure-sensitive electric switch. Structural studies at high pressure can rationalize the synthesis and search for future organic and hybrid

semiconductors based on PI. This includes structures with soft I...I contacts, which are the most prone for charge transport across the crystal under increased pressure. The results of this study indicate that solid PI may be used as solid electrolytes in dye-sensitized solar cells, which eliminates the need for organic-based gelators^[43] and ionic liquids in general.

Experimental Section

TEAl was synthesized according to the literature procedures^[26].

Single-crystal diffraction measurements. A prismatic crystal of TEAl with approximately 200 x 100 x 30 μm dimension was loaded in a Merrill-Bassett DAC, equipped with 0.5 mm diamonds and steel gaskets. Nitrogen was used as pressure-transmitting medium, and the pressure was calibrated with ruby fluorescence^[44]. X-ray diffraction was measured at the Material Science Beamline at Swiss Light Source ($\lambda = 0.49471$ Å)^[45]. Structures were refined with ShelXL^[46] incorporated in OLEX2^[47]. All non-iodine atoms were refined isotropically. Hydrogen atoms attached to carbons were geometrically placed and refined using a riding model. CCDC 1890310-1890317 (HP structures) and CCDC 1890330 (low-temperature structure) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Electrical conductivity measurements. Two crystals of TEAl with 60 x 60 x 80 μm size were loaded subsequently in DAC. A mixture of α-nanoalumina and epoxy glue 4:1 was used as pressure transmitting medium. Pressure was calibrated using ruby fluorescence method. Four leads of golden wire were pressed against the sample (Fig. 1 SI) and the electrical resistivity was measured using the four-probe method with a Keithley 2450 multimeter.

CRYSTAL14^[48,49] was used for geometry optimizations and single point calculations in the crystal, using the B3LYP functional and Grimme dispersion correction^[50] (for all atoms except iodine). The basis sets used were of POB_TZVP quality^{[51],[52]}. No imaginary frequency was calculated. Properties in the crystal were obtained with TOPOND. Gaussian16^[53] was used for geometry optimizations and single point calculations in vacuo at B3LYP/6-311G* level of theory^[54].

AIMAll 14.11.23^[55] was used for analysis of the electron density descriptors and IQA.

ADF^[56] with B3LYP/TZP, without frozen core and including scalar relativity was used for EDA.

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