Halogen Bonding and Other Iodine Interactions in Crystals of Dihydrothiazolo(oxazino)quinolinium Oligoiodides from the Electron-Density Viewpoint

Published as part of the Crystal Growth & Design virtual special issue IYCr 2014 - Celebrating the International Year of Crystallography

Ekaterina V. Bartashevich,*† Irina D. Yushina,‡ Adam I. Stash,§ and Vladimir G. Tsirelson§

†South Ural State University, Lenin Ave., 76, 454080 Chelyabinsk, Russia
‡L.Ya. Karpov Institute of Physical Chemistry, ul. Vorontsovo Pole 10, 103064 Moscow, Russia
§D.I. Mendeleev University of Chemical Technology, Miusskaya Square 9, 125047 Moscow, Russia

Supporting Information

ABSTRACT: The spatial organization of electron density in dihydrothiazolo(oxazino)quinolinium crystals with oligoiodide anions of various structures has been studied on the basis of 3D periodic Kohn–Sham calculations. The combination of QTAIMC and the analysis of one-electron potential and electrostatic potential has revealed the significant differences between halogen bonds (Type II interactions) and van der Waals (Type I) interactions for iodine atoms in crystalline environment. The traces of σ-holes in electrostatic potential on the zero-flux interatomic surfaces of iodine moieties are the distinctive feature of halogen bonding; they do not appear in the weak van der Waals I⋯I interactions at all. The analysis of superposition of the gradient fields of the electron density and electrostatic potential has allowed detection of the strong electron redistribution along the oligoiodide chain [I3⋯I−⋯I−⋯I3]; the electron density is shifted from I3− moiety to the cation via iodine molecule I2 as a mediator. The quantitative relationship between the experimentally measured dissociation energy Dc(I−⋯I−⋯I−) and the kinetic energy density at the bond critical point in the whole range of observed iodine interactions has been established.

INTRODUCTION

Development of crystallography has led to characterization of the crystalline substances on the level of electron-density features responsible for 3D architecture of crystals.1−4 It has become possible owing to new X-ray diffraction instrumentation and an increasing number of tools suitable for description and treatment of the tiny details of electron density.5,6 The new level of detailed elaboration of the crystal organization has opened the avenue to working many fundamental problems of crystal engineering out, especially identification and characterization of structure-forming halogen bonding interactions in solids.

The recent work dealing with noncovalent interactions of halogens in crystals7−10 shows that the characterization of halogen bonds is based on the extensive experience and modern methods of charge density analysis.11−13 Understanding the halogen bonds as essential features of significant supramolecular synthons appears to be the important problem of crystal design technology, which is now being solved from crystallographic, spectroscopic, and computational positions. In this work we focus on the electronic structure features of quinolinium oligoiodides14−16 C12H11INS+I3− (1), 2-(C12H11INS+I3−)-I3 (2), and C12H4INO+I3−I3 (3). The ability of these compounds to form the different crystalline structures of oligoiodides with varying composition makes them interesting objects in solid state design. On one hand, the variety of crystals packaging allows us to highlight the specific patterns of iodine aggregation. On the other hand, the halogen bond characterization in terms of the electron density leads to development of new effective tools in crystal engineering. The above-mentioned crystals (1), (2), and (3) exhibit various interactions with iodine participation that differ in strength and nature. They can be divided into four main groups: (1) covalent I−I bonds in molecular iodine interacting with crystalline environment; (2) strong intramolecular bonds in triiodide anion I−I−I−I; (3) charge-assisted halogen bonds I−I−I−I−I (Type II); (4) weak van der Waals interactions I⋯I− (Type I). For the first time, we have used for this analysis a consistent combination of approaches, such as Quantum Theory of Atoms in Molecules and Crystals (QTAIMC),17 the Green (or

Received: June 30, 2014
Revised: September 3, 2014

dx.doi.org/10.1021/cg500958q | Cryst. Growth Des. XXXX, XXX, XXX−XXX
influence) function for the electron density, one-electron potential, the electrostatic potential (ESP) mapped onto the molecular electron-density surfaces, and superposition of the gradient fields of electron density and electrostatic potential. Crystalline 1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-a].quinolinium and (iodomethylene)-2,3-dihydro-[1,4]oxazino[2,3,4-ff]quinolin-4-ium salts can be obtained as oligoiiodides with various iodine ratios in an anion. In crystallographic database CSD v 5.35 (2014) there are few analogs for such co-crystals, in which a C, N, S, H-containing heterocyclic anion forms crystalline salts with two or more oligoiiodides of different structures (without taking into account any other molecules: water, solvents, etc.) in a crystal cell. Organic cations containing only C-, N-, H or C-, S-, H atoms and forming the crystals with various oligoiiodides occur more frequently. For example, N,N'-diethyl-4,4'-bipyrillidium cation can form either the simple triiodide salt or the complicated structures containing a combination of tri- and pentaiiodide anions. At that, the distinctions in crystal packing result in distortion of cation structure; it is planar in one case, while it goes slightly out of plane in the other one. Similar examples are also widespread among thiofulvalene derivatives. Such cation-radical salts reveal low-temperature conductivity, so this fact has led to continued interest in these compounds over the past decades.

## CALCULATIONS

Periodic 3D calculations of crystals (1), (2), and (3) have been performed by the Kohn–Sham method with B3LYP exchange-correlation functional. The CRYSTAL09 program package has been used. The modified DZVP basis set for iodine atoms (11 electron shells instead of 14 in original DZVP basis set due to merging s- and p-shells into hybrid sp-shells) and basis sets for C, H, N, O, S atoms from ref 36 have been used. Crystal geometries from X-ray diffraction experiments were taken as a starting point. Then, optimization of atomic positions has been carried out for all atoms of the irreducible part of the crystallographic cell with fixed space group and unit cell parameters. The Monkhorst-Pack 8 × 8 × 8 grid has been used. Truncation criteria for bielectric integrals have been set as follows: overlap threshold for Coloumb integrals and HF exchange integrals equals 10⁻⁸ au, penetration threshold for Coloumb integrals is 10⁻⁸ au; the first and second criteria for pseudo-overlap are 10⁻⁶ and 10⁻¹⁶ au, respectively.

Modern scientific software allows determination of only a limited number of properties directly from the crystalline many-electron wave functions. At the same time, representation of crystalline ED in terms of a crystallographic space-extended multipole model enables calculation of a wide range of modern descriptors characterizing chemical bonds and intermolecular interactions using the WinXPRO program. The multipole model has some deficiencies in the description of the shared atomic interactions; it performs well for the closed-shell interactions, such as I—I and I—I. Therefore, the X-ray diffraction structure factors with sin(θ)/λ ≤ 1.25 Å⁻¹ for (1) and (3), and sin(θ)/λ ≤ 1.11 Å⁻¹ for (2), have been calculated. They have been used to reconstruct ED within the framework of Hansen-Coppens multipole model; the MOLDOS2003 program has been used. The adjustable model parameters are as follows: the electronic occupations of spherical parts of valence shells and of the space-extended multipoles (up to hexadecapoles for non-hydrogen atoms and up to quadrupoles for H atoms), as well as the expansion/contraction coefficients of radial parts of the atoms. Unit weights have been assigned to the structure factors during the refinement. The refinement indices do not exceed R = 0.0014 for (1), R = 0.0012 for (2), R = 0.0010 for (3).

To check how the multipole model represents the quantities derived from the crystalline wave function, we have computed ED for the plane illustrating I₂—I₂ interaction in crystal 2 using both methods (see Supporting Information, Figure 1S; also see Table 1S, 2S). Comparison shows that the values of corresponding contour lines, characterizing the ED features derived by both methods, are in good agreement with each other. This justifies our methodology.

The relativistic effects, which are proportional to Z², may be significant for electronic structure of iodine (Z = 53). However, it is difficult to take them into account in the periodical solid-state computation. Fortunately these effects mainly influence the inner electronic shells leading to contraction of s- and p-shells and to some expansion of the d-shells. The overall effect leads to the shift of the radial electron-density shell maxima of ~0.02 au toward the nuclei. The account for relativity in calculations negligibly effects one-electron potential, aside from small shifts of OEP maxima and minima. Its influence on the electrostatic potential is also small. Therefore, we used in our periodic calculations all-electron nonrelativistic CRYSTAL09 methodology.

Quantum topological analysis of electron density including calculation of the bond critical point (BCP) characteristics, atomic basin boundaries, and electron populations of atomic basins, has been performed by WinXPRO program package, v 3.0.13. The accuracy of the atomic basin boundary determination has been controlled by calculation of the integral \( \int_V \rho(r) \, dV \) for each atomic basin, \( \Omega_z \); the integral values do not exceed 10⁻³ au. Gradient fields of electrostatic potential (ESP) and electron density and 3D colored ESP images mapped on the ED surfaces of molecules or ions have been visualized using TrajPlot and 3DPlot programs.

## ATOMIC CHARGES AND BOND CRITICAL POINTS OF OLIGOIIOIDIDE MOIETIES

The Bader’s atomic charges \( q(A) = Z(A) - Q(A) \), where Z(A) is the atomic number, and Q(A) is the electron population calculated by integrating the electron density over corresponding atomic zero-flux basins A, are given for triiodide anions in crystals (1), (2), and (3) in Table 1. They show that the total charge of triiodide anion is relatively high (~0.94 e) in (1) where the I⁻ moiety does not form an oligojromeric complex in a crystal. In (2) or (3), the triiodide anion, being a member of a

<table>
<thead>
<tr>
<th>Table 1. Atomic Charges (e) of Iodine Mieities</th>
</tr>
</thead>
<tbody>
<tr>
<td>fragment</td>
</tr>
<tr>
<td>Terminal atoms I in a triiodide anion</td>
</tr>
<tr>
<td>Central atom I in a triiodide anion</td>
</tr>
<tr>
<td>Atom I in a diiodide molecule</td>
</tr>
<tr>
<td>Atom I in a cation</td>
</tr>
<tr>
<td>Full charge of a triiodide anion</td>
</tr>
</tbody>
</table>
To a lesser extent, it is typical for the ellipsoid to be transformed into a discoid, which is perpendicular to the negative charge on $I_3^-$. Eigenvalues of the Hessian of electron density, $\lambda$, are given for example, the ellipsoid of a typical covalent bond ($I_3^- \cdot I$). The highest anisotropy of the ellipsoid and $\lambda_3$ show small variations of negative charge values.

The parameters of bond critical points in electron density for interactions involving iodine atoms are given in Table 2 and in the Supporting Information, Table 2S. They are visually represented in Figure 1 with bonding ellipsoids, principal semiaxes of which $a_1$, $a_2$, and $a_3$ are proportional to the eigenvalues of the Hessian of electron density, $\lambda_1$, $\lambda_2$, and $\lambda_3$. These ellipsoids are useful for direct visual comparison of different types of atomic interactions. For example, the ellipsoid of a typical covalent bond ($I_3^- \cdot I$) is slightly elongated along the bond path. For noncovalent interactions ($I_3^- \cdot I$), the ellipsoid is transformed into a discoid, which is perpendicular to the bond path. So, we observe discoid ellipsoids for iodine halogen bonds. To a lesser extent, it is typical for $I \cdot I$ bonds in $I_2$ molecule and $I_3^- \cdot I$ anion, which belong to the class of charge-shift bonds. The highest anisotropy of the ellipsoid principal axes is observed for van der Waals iodine interactions. These discoid ellipsoids remain perpendicular to the bond path, but additionally, they are stretched along the negative charge belts of iodine atoms (see below). For solid iodine similar results have recently been reported.

According to the values of the electron density at the BCPs, the strongest noncovalent interaction is the halogen bond $I_3^- \cdot I_2$ ($\rho(r_b) = 0.017$ au) in the crystal (3) (see Table 2). Such a situation occurs in spite of the difference between the atomic charges of iodine: for interaction $[I_3^- \cdot I_2]$ the difference is only $0.16$ e; for the case of [C—$I \cdot I$] it is twice as much: $-0.35$ e. This observation again confirms the conclusion of ref 56: the difference of the atomic charges is not a direct quantitative expression of halogen bonding strength in molecular complexes and crystals.

Crystal (1) yields a good example of relatively weak van der Waals $I \cdot I$ interactions (Figure 1a). The bond path in the electron density between two equivalent iodine atoms $I(1) \cdot I(1')$ belonging to cations has been found: $\rho(r_b) = 0.004$ au. In the common plane with them, the two pairs of cation—anion interactions are realized (see Figure 1A: I(2)·I(1'), $\rho(r_b) = 0.006$ au; and B: I(1)·I(2), $\rho(r_b) = 0.005$ au). In case B, both iodine atoms are oriented to each other by the “side” electrostatic interactions (toroidal belts of electron concentration values). In the case of I(1')·I(3) interaction, the orientation of electron concentration area in the triiodide anion into the charge-deficient region on the elongation of $C—I(1')$ covalent bond in the cation is similar to the orientation that could be attributed to halogen bonding. However, the angle

<table>
<thead>
<tr>
<th>crystal</th>
<th>interaction</th>
<th>main groups of interactions</th>
<th>$R$, Å</th>
<th>$\rho(r_b)$, au</th>
<th>$g(r_b)$, au</th>
<th>$v(r_b)$, au</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{12}$H$</em>{11}$INS$^+$I$_5^-$ (1)</td>
<td>I(2)·I(3)</td>
<td>$I^-·I^-·I^-$</td>
<td>2.988</td>
<td>0.040</td>
<td>0.024</td>
<td>$-0.032$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(4)</td>
<td>$I^-·I^-·I^-$</td>
<td>3.045</td>
<td>0.036</td>
<td>0.022</td>
<td>$-0.028$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>4.128</td>
<td>0.007</td>
<td>0.003</td>
<td>$-0.003$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>4.164</td>
<td>0.006</td>
<td>0.003</td>
<td>$-0.003$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>4.306</td>
<td>0.005</td>
<td>0.003</td>
<td>$-0.002$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>4.412</td>
<td>0.004</td>
<td>0.002</td>
<td>$-0.002$</td>
</tr>
<tr>
<td></td>
<td>I(1)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>4.433</td>
<td>0.004</td>
<td>0.002</td>
<td>$-0.001$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>2.863</td>
<td>0.048</td>
<td>0.030</td>
<td>$-0.042$</td>
</tr>
<tr>
<td></td>
<td>I(2)·I(3)</td>
<td>$I^-·I^-·I^-$</td>
<td>2.926</td>
<td>0.044</td>
<td>0.027</td>
<td>$-0.037$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>3.048</td>
<td>0.036</td>
<td>0.021</td>
<td>$-0.028$</td>
</tr>
<tr>
<td></td>
<td>I(4)·I(3)</td>
<td>$I^-·I^-·I^-$</td>
<td>3.431</td>
<td>0.020</td>
<td>0.011</td>
<td>$-0.011$</td>
</tr>
<tr>
<td></td>
<td>I(4)·I(3)</td>
<td>$I^-·I^-·I^-$</td>
<td>3.850</td>
<td>0.010</td>
<td>0.005</td>
<td>$-0.005$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>3.976</td>
<td>0.009</td>
<td>0.004</td>
<td>$-0.004$</td>
</tr>
<tr>
<td></td>
<td>I(3)·I(1)</td>
<td>$I^-·I^-·I^-$</td>
<td>4.614</td>
<td>0.003</td>
<td>0.002</td>
<td>$-0.001$</td>
</tr>
<tr>
<td></td>
<td>I(4)·I(3)</td>
<td>$I^-·I^-·I^-$</td>
<td>4.624</td>
<td>0.003</td>
<td>0.001</td>
<td>$-0.001$</td>
</tr>
</tbody>
</table>

| C$_{12}$H$_{11}$INOS$^+$I$_5^-$I$_2$ (2) | I(1)·I(1) | $I^-·I^-·I^-$ | 2.836 | 0.050 | 0.032 | $-0.046$ |
|                  | I(3)·I(4) | $I^-·I^-·I^-$ | 2.954 | 0.042 | 0.026 | $-0.034$ |
|                  | I(4)·I(3) | $I^-·I^-·I^-$ | 3.534 | 0.017 | 0.009 | $-0.009$ |
|                  | I(1)·I(2) | $I^-·I^-·I^-$ | 3.671 | 0.014 | 0.007 | $-0.007$ |
|                  | I(1)·I(2) | $I^-·I^-·I^-$ | 4.020 | 0.008 | 0.004 | $-0.004$ |
|                  | I(1)·I(3) | $I^-·I^-·I^-$ | 4.112 | 0.007 | 0.004 | $-0.003$ |
|                  | I(1)·I(3) | $I^-·I^-·I^-$ | 4.255 | 0.006 | 0.003 | $-0.002$ |
|                  | I(3)·I(3) | $I^-·I^-·I^-$ | 4.449 | 0.004 | 0.002 | $-0.002$ |
|                  | I(2)·I(4) | $I^-·I^-·I^-$ | 4.464 | 0.004 | 0.002 | $-0.001$ |
|                  | I(3)·I(4) | $I^-·I^-·I^-$ | 4.522 | 0.004 | 0.002 | $-0.001$ |
|                  | I(4)·I(3) | $I^-·I^-·I^-$ | 4.729 | 0.003 | 0.001 | $-0.001$ |
Resnati thesis\(^{50}\) that not every “halogen···halogen” interaction in crystals should be attributed to halogen bonds.

### ONE-ELECTRON POTENTIAL AND THE FEATURES OF I···I HALOGEN BONDS

Laplacian of electron density, \(\nabla^2\rho(r)\),\(^{18,61}\) and electron localization function (ELF)\(^{62,63}\) are widely used\(^{64,65}\) to illustrate the ability of molecules to form halogen bonds.\(^{66}\) However, it is known\(^{59}\) that values \(\nabla^2\rho(r) < 0\) indicating the electron concentration regions of outer electron shell do not appear for many atoms with atomic numbers \(Z \geq 20\). It results from the charge depletion of the d-orbital from the penultimate shell that compensates the charge concentration of the valence s- and p-orbitals. ELF has no such deficiency; however, there is another more physically grounded descriptor, which solves this problem for heavy atoms. For Br- and I-containing molecules the useful descriptor for localization of the bonding and lone electron pairs is the one-electron potential (OEP)\(^{21,22,65}\)

\[
P(r) = \frac{1}{4} \frac{\nabla^2\rho(r)}{\rho(r)} - \frac{1}{8} \left( \frac{\nabla \rho(r)}{\rho(r)} \right)^2
\]

The first term of this function alternates while the second is always negative. Negative regions of OEP correspond to the positive values of local electron kinetic energy (and approximately coincide with the outer-shell negative regions of \(\nabla^2\rho(r)\) of light atoms), i.e., they indicate the electron concentration regions. Positive OEP areas determine potential barriers, within which electron kinetic energy can be negative; thus, the OEP discovers the quantum behavior of electrons. Specific alternation of regions with positive and negative values of OEP depends on the distance from the nucleus and reveals the atomic shell structure.

We have used OEP function to reveal lone electron pairs of iodine atoms and to analyze the differences in its behavior for various oligoiiodide moieties. Figure 2 shows that both the triiodide as a component of the zigzag \([I_3\]···I−I−I−I3\)] in (2) and the single one in (1) exhibit very similar locations of lone electron pairs. OEP for the bounded iodine molecule as a part of the zigzag chain (Figure 2a) shows the orientation of electron deficiency regions behind the nuclei on the elongation

![Figure 1](image1.png)

**Figure 1.** (a) Fragment of dihydrothiazoloquinolinium \(C_{12}H_{11}INS^+I_3^-\) crystal (1) with bond paths formed by triiodide anions. The bond critical points of noncovalent interactions are presented by bonding ellipsoids (see text for explanations). (b) Fragment of dihydrothiazoloquinolinium \(2(C_{12}H_{11}INS^+I_3^-)I_2\) crystal (2) with bond paths formed by complex oligoiiodide anions. (c) Fragment of oxazinoquinolinium \(C_{12}H_{12}NO^+I_3^-\) crystal (3) with bond paths formed by complex oligoiiodide anions.

between the triiodide and covalent C—I(1′) bonds is slightly different from the right angle; the geometric criterion of the typical halogen bonding is not satisfied exactly. This fact allows us to mark the I(1′)···I(3) interaction as the *interaction with restricted signs* of halogen bonding.

According to refs 57 and 58, the range of geometric characteristics of halogen bonds can be significantly expanded by introduction of an intermediate Type of interactions, which span the range between pure Type I and Type II.\(^{59}\) Our results, (4.01 Å), angle between iodine atoms I(1′)···I(3)−I(2) (87°) and \(\rho(n)\) value (0.007 au), suggest that the above-mentioned I(1′)···I(3) interaction can be treated as such an Intermediate-Type interaction. This conclusion does not contradict the statement that the geometric definition (“Type II halogen···halogen contacts”\(^{60}\)) maintains a significant role in halogen bond identification. This agrees with the Metrangolo and

![Figure 2](image2.png)

**Figure 2.** One-electron potential: (a) the plane of oligoiiodide zigzag \([I_3\]···I−I−I\)]\(^-\) crystal (2); (b) the plane of triiodide anion and iodine in a cation, crystal (1). Solid lines correspond to the negative values of OEP and indicate electron concentration. Line intervals are \(\pm 2, 4, 8 \times 10^{-6}\) au \((-2 \leq n \leq 2\).

\[dx.doi.org/10.1021/cg500958q\] Cryst. Growth Des. XXXX, XXX, XXX–XXX
of the I—1 covalent bond to the electron concentration areas in the “side” part of terminal iodine atoms in the triiodide anion. Such mutual orientation of $I_3^−$ and $I_2$ moieties favors the formation of the halogen bonding of the key-and-lock type and enables the zigzag formation.

OEP along the interatomic lines for all considered I—1/1···1 interactions is shown in Figure 3. Independently of the type of interaction, the local maximum of $P(r)$ is located near BCP between iodine atoms. This maximum reveals the barrier which electrons must overcome when they are shared by the pair of interacting atoms. For the I(5)—I(5) covalent bond (Figure 3a), this barrier is lower, whereas for the I···1 bond (Figure 3c) it is relatively higher. The observed maximum for bonds in triiodide anions (Figure 3b) is in its turn lower than that for the I—1 van der Waals interactions (Figure 3c) and halogen bonds (Figure 3d). Also, $P(r)$ shows minima located at each interacting atom side.

It is worth noting that the depth of outer OEP minima shows clear differentiation between bonds with different polarity. Both minima are positively valued only for the covalent I—1 bond (Figure 3a). For this bond in iodine molecules (Figure 3a) and for van der Waals I···1 interactions (Figure 3c), the depths of the minima are almost equal. In the triiodide anion $I_3^−$ (Figure 3b) and in a typical I···1 halogen bond (Figure 3d) the minimum close to the electron-donor atom with a lower negative charge is significantly deeper than the one from the electron-acceptor atom side. The higher drop of OEP at the electron-donor atom side reveals the greater ability to concentrate electrons in the regions, which are close to the atomic basin boundaries. Such a feature of the OEP behavior deserves further exploration in a wider range of halogen bonds. Nevertheless, our results demonstrate that OEP detects significant differences for all four groups of the discussed I—1/1···1 interactions and allow us to categorize these interactions according to their polarity.

### SUPERPOSITION OF THE GRADIENT FIELDS OF ELECTRON DENSITY AND ELECTROSTATIC POTENTIAL

Zero-flux conditions $\nabla \rho(r) \cdot \mathbf{n}(r) = 0$, $r \mathbf{W}^{67}$ and $\nabla \varphi(r) \cdot \mathbf{n}(r) = 0$, $r \mathbf{V}^{66,69}$ where S and P are interatomic surfaces in electron density, $\rho$, and electrostatic potential, $\varphi$, respectively, allow us to identify the atomic $\rho$-basins and $\varphi$-basins in the corresponding gradient fields. The first of them defines chemically bonded atoms and the second one determines electrically neutral atomic fragments within a common electron–nuclear system. The analysis of superposition of these gradient fields provides information about the features of atomic interactions along the bond paths. $^{70,71}$ Figure 4a shows that the boundary of the $\varphi$-basin of I(5) (blue lines) penetrates into the region of the $\rho$-basin of I(4) (orange lines). This suggests that some fraction of the electrons belonging to I(4) in the triiodide anion is attracted to the nucleus of I(5) in the I$_2$ molecule. According to ref 66, this must be so in the case of typical halogen bonding. The $\rho$- and $\varphi$-basin boundaries of atoms are in close agreement within the bonds in I$_2$ and I$_3^−$.  

Figure 3. Distribution of one-electron potential along interatomic lines for four groups of observed I—I···1 interactions: (a) covalent I(5)—I(5) bond in molecular iodine; (b) intramolecular bond in triiodide anion [I(4)—I(3)—I(2)]$^−$; (c) van der Waals interactions I(5)···I(1); (d) halogen bond I(4)···I(5).
This agrees well with very weak variations of iodine atomic charges in the oligoiodide chains.

We have noted that the features of the ρ- and φ-basins superposition revealing the picture of electrostatic interactions in the crystals of organic oligoiodides substantiate the geometrical consideration of crystal packing of (1) and (2) given in ref 16. The laying of triiodides in (1) is realized along the longest axis of the heterocyclic cation. For those cases and when I₃⁻ is in the plane of quinoline rings, the interactions between the anion and the cation are executed due to I···H contacts. In the crystal (2) the entire zigzag of the complex anion [I₅⁻···I−···I] also tends to stay in the plane of neighboring quinoline rings.

Thus, consideration of mutual arrangement of the zero-flux boundaries of ρ- and φ-basins provides the specific information about the kind of I···I interactions. It has already been stated⁷² that no halogen interaction in alkenylthioquinoline–diiodine complexes can be defined as a halogen bond. Indeed, it looks like only if the part of ED of the electron-donor atom falls into the φ-basin of the halogen atom can we define the interaction as a halogen bond. This principle is useful for identification of the iodine halogen bonds in the studied crystals.

Note that one of the fragments of the oligoiodide chain in crystal (3) is locked to the cation (see Figure 1c, the bond path I(2)···I(1)). As a result, the typical halogen bond C—I···I₃⁻ is formed, and its type is identified by the geometrical characteristics. The covalent bonds C—I and I—I—I are situated at a right angle to each other. The σ-hole in electrostatic potential⁷³,⁷⁴ of the iodine atom belonging to the quinolinium cation is strictly oriented toward the belt of reduced ESP values, which encircles the triiodide anion. This is one of the strongest halogen bonds in a crystal with BCP electron density ρ(rₚ) = 0.014 au (see Table 2). The atomic charges of the iodine atom in the anion and in the cation significantly differ. Also, Figure 4b shows different sizes of ρ- and φ-basins for this interaction. The penetration of φ-basin I(2) into the ρ-basin of I(1) can be considered as the attraction of some portion of the electrons of atom I(2) in the anion to the nucleus I(1) in the cation.

Figure 4. Superposition of the electrostatic potential gradient field (blue) and electron density gradient field (orange): (a) the plane of the zigzag chain in 2(C₁₂H₁₁INS⁺I₃⁻)·I₂ (2); (b) the typical halogen bond between the atom I(1) in a cation and atom I(2) in triiodide anion, crystal C₁₂H₉INO⁺I₃⁻·I₂ (3).

Figure 5. Electrostatic potential imposed on the isosurfaces of ρ(r) = 0.012 au in the free triiodide anion (a) and on the zero-flux atomic surfaces of the cation and the triiodide fragment in (1) (b) and for triiodide anion in (2) (c). The black arrows indicate the traces of the σ-holes (enhanced ESP value); the blue arrows indicate the manifestations of van der Waals interactions (reduced ESP values).
**MAPPING OF ELECTROSTATIC POTENTIAL ON THE INTERATOMIC SURFACE OF IODINE MOIETIES**

The analysis of the electrostatic potential distributed on the isosurface of ED \( \rho(\mathbf{r}) \sim 0.001 \) au enveloping a free neutral molecule (“van der Waals surface”) is widely used to describe the ability of halogens to form halogen bonding.\(^{23-25,74}\) Such a picture for the free triiodide anion (B3LYP/6-311G **) at \( \rho(\mathbf{r}) \approx 0.012 \) au (see below) shows the \( \sigma \)-holes, the areas of enhanced ESP values on the elongation of the covalent bonds I—I behind the terminal iodine atoms (Figure 5a). Also, the “red belts” of reduced ESP values around each iodine atom are clearly visible. These belts correspond to the electron lone pairs distributed in the form of toroids in the planes perpendicular to the main axis of the triiodide molecule. Such a distribution of ESP on ED isosurfaces characterizes the potential ability of an atom to form complexes and chain structures by means of the halogen bonding, as for a donor of electron density.\(^{75,76}\)

A similar approach has been practiced for describing the interactions in crystals of different polymorphs using the Hirshfeld stockholder technique to define the molecular surface.\(^{77-81}\) However, corresponding ESP distributions on the ED isosurface around bounded molecules in a crystal may disappear under the influence of the crystalline environment.

We have somewhat modified this approach and considered the ESP on the interatomic surface, determined by the zero-flux condition for the gradient of electron density. It is worth noting that comparison of ESP around the triiodides in crystals (1) and (2), which differ by the additional iodine molecule in (2), is not straightforward. The fact is that ESP inside a finite cluster depends on the size of a system; more exactly, it depends on the surface term.\(^{**}\) Therefore, only relative ESP values within each cluster (not the ESP values themselves) have a physical meaning. Then, to retain the effect of the crystalline environment on ESP, the maximally symmetric electroneutral cluster should be selected. Hence the triiodide anion in each cluster was surrounded by eight cations and eight anions at a distance of 10 Å at least. Symmetrical arrangement provided the isotropic contribution to ESP from the surface term inside each cluster, while the chosen cluster size made sure that the contribution of more distant atoms to the inner-cluster electrostatic potential is negligible.

Figure 5b,c shows the ESP distribution on the interatomic surface between the bounded atoms in the triiodide anion and the iodine moieties with halogen bonds and van der Waals interactions. The important feature which follows from these pictures is a significant growth of the ESP values in the triiodide anion toward the bond paths. The enhanced ESP values, which can be treated as the traces of the \( \sigma \)-hole, encompass I—I bond paths in the triiodide anion (Figure 5b, black arrows). The total change in the ESP values on the interatomic surface for the central atom of the triiodide anion is about 0.6 au. In contrast, the change in ESP values on the interatomic surface between the iodine in the cation and the triiodide does not exceed 0.1 au; the traces of the \( \sigma \)-hole are negligibly weak here. Recall that this interaction C—I—I has been classified as the interaction with restricted signs of halogen bonding; it is in the intermediate range between the Type I and Type II interactions.

The enhancement of ESP on the interatomic surface, separating the basins I(4) in the triiodide anion and I(1) atom in diiodine molecule in (2), i.e., the trace of the \( \sigma \)-hole in ESP (see Figure 5c, black arrows), is not less than 0.4 au, and it is clearly expressed. This case corresponds to the typical halogen bond I—I.

Also, consideration of the whole crystalline environment has allowed us to reveal the regions of decreased ESP on the surface of iodine moieties induced by “side” van der Waals interactions (Type I) with sulfur and other iodine atoms (Figure 5b,c, blue arrows).

We conclude that the resulting pattern of the ESP distribution on the iodine interatomic surfaces in the considered crystals is in full compliance with the concept of relative strength and the nature of the bonding in the four classified groups of interactions. In the triiodide anion I—I and in typical halogen bonds I—I the strong enhancement of ESP toward the bond paths is observed on the interatomic surface.
For van der Waals interactions (Type I) the corresponding ESP change is reversed or not observed at all.

### ENERGIES OF I···I HALOGEN BONDS AND OTHER IODINE INTERACTIONS

Dependency $\rho(r_b) = f[R(I···I)]$ for halogen bonds and other iodine interactions is summarized in Figure 6a. Even a comparatively high negative charge of the electron-donor atom in triiodide anion and positive charge of the electron-acceptor atom in the cation do not move the halogen bonds in the $I^{-}$ anion closer to stronger interactions according to their characteristics. Typical halogen bonds occupy an intermediate position between strong bonds in triiodide anion and very weak van der Waals bonds and $I^{-}$ contacts (Type I) in crystals.

Estimations of the interaction energy $E_{int}$ between iodine atoms in triiodide anion based on different computational methods ranges from 113.9 kJ/mol for CCSD(T) ECP-TZ(2df) calculation\[^{82}\] to 174 kJ/mol for B3LYP/LACVP\[^{83}\]. The spread of values also depends on taking into account or ignoring the secondary interactions of the triiodide anion. Experimental mass-spectrometric estimation of the bond dissociation energy for triiodide anion $D_e(I_2 + I^-)$ has resulted in 126.4 kJ/mol.\[^{82}\] It is worth mentioning that the highest values of $\rho(r_b)$ are observed for the covalent bond in molecular iodine. Spectroscopic approximation of $D_e(I_2)$ in an iodine molecule has yielded values of 148.8 kJ/mol (0 K) and 151 kJ/mol (298 K).\[^{84}\]

Typical halogen bonds according to their $\rho(r_b)$ and $R(I···I)$ values appear to be closer to dispersion interactions with energies generally less than 20 kJ/mol. Nevertheless, the characteristics of charge-assisted halogen bonding differ from those for dispersion interactions. According to existing estimations, the energies of noncovalent interactions formed by $I$ anions lie within wide ranges. For example,\[^{85}\] the interaction energy $\Gamma···I_2$ obtained from the correlation $E_{int} = -0.5 \rho(r_b)$ (where $\rho(r_b)$ is electron potential energy at BCP estimated from the experimental ED)\[^{86}\] equals 20.1 kJ/mol. For interactions in pentaiodide anion $I_5$\[^{87}\] CCSD(T)/ECP-TZ(2df) calculation has resulted in $E_{int}(I^- = I_2 + I^-)$ of 55.1 kJ/mol for $r_1 = 2.857$ Å, $r_2 = 3.065$ Å.\[^{82}\] This result is in good agreement with the experimental dissociation energy $D_e(I_2 + I^-) = 49.2$ kJ/mol found from the mass spectrometry data\[^{82,87,88}\].

If we accept that dissociation energy $D_e$ (I−I) of van der Waals interaction (D···X) is proportional to interaction energies $E_{int} = E_{D,X} - E_D - E_X$ (where $E_D$ and $E_X$ are) in molecular complexes where iodine acts as an ED acceptor, then we can use the linear equation\[^{90}\]

$$E_{int} = -0.67 \pm 0.05\] \cdot g(r_b) \tag{1}$$

This correlation\[^{86}\] includes the local value of electron kinetic energy, $g(r_b)$, at BCP of I···X halogen bonds in neutral molecular complexes. The energy value of van der Waals interactions obtained according to eq 1 and averaged over the sampling of similar I···I interactions in crystals 1, 2, and 3 equals 4.7 kJ/mol. The range of these van der Waals interactions appears to be rather wide: from 2.2 to 9.1 kJ/mol. Equation 1 yields I···I halogen bond energies in oligoiodide crystals between 12.5 and 18.7 kJ/mol. These values are at least twice underestimated in comparison with literature data for $E_{int}$ (I−I) of isolated oligoiodide moieties. 

Thus, for estimation of halogen bonding energy in crystals, it is necessary to take into account the influence of the crystalline environment, in particular, the actual atomic charges, and the effect of ionization, when the bond is broken.

Nevertheless, comparison of the experimental dissociation energy $D_e$ for $I_2$, $I^-_2$, and our $E_{int}$ values from eq 1, averaged over each of four groups of observed interactions (see below), gives an opportunity to estimate their quantitative interrelations. Obtained values of $g(r_b)$ should be put into correspondence with the experimental dissociation energy $D_e$ (I···I) for three types of bonds: (1) 148.8 kJ/mol\[^{82}\] for covalent bonds in interacting $I_2$ molecule; (2) 126.4 kJ/mol\[^{82}\] for bonds in triiodide anion $I_2$; (3) 49.2 kJ/mol\[^{87,88}\] for charge-assisted halogen bonds $I^{-}···I$. For van der Waals I···I interactions we add an averaged energy value of 4.7 kJ/mol, according to eq 1. Dissociation energy $D_e$ (I···I) behavior

---

**Figure 7.** Correlation between the predicted interaction energies $E_{int}^{pred}$, eq 1, and predicted dissociation energy $D_e^{pred}$ (kJ/mol) of I−I/I···I bonds, eq 2: (a) full range of values, (b) van der Waals interactions and halogen bonds.
in two-factor space of averaged values of \(g(r_0)_{\text{mean}}\) and \(R(1-1/1-1)_{\text{mean}}\) is illustrated by Figure 6b. It shows that interrelation of \(D_e\) and averaged \(g(r_0)_{\text{mean}}\) values in BCP \(1-1/1-1\) bonds can be expressed as a power function. Variation of the parameters allowed us to obtain a quantitative dependency of dissociation energy for \(1-1/1-1\) bonds in a wider energy range. Thus, this equation can be suitable for approximate estimation of four groups of iodine interactions occurring in crystalline poly- and oligoiodides.

The following equation based on averaged values of kinetic energy density in BCP \(g(r)_{\text{mean}}\) and averaged interatomic distances \(R(1-1/1-1)_{\text{mean}}\) appears to be the best for observed interactions (correlation coefficient \(R = 0.990\), standard deviation for \(D_e^{\text{pred}}\) residual is 0.004 au):

\[
D_e^{\text{pred}}(\text{au}) = 1.50 \cdot [(g(r_0)_{\text{mean}})^2] \cdot \exp[R(1-1/1-1) - 1.56]
\]

(2)

In this equation, the values of \(g(r_0)_{\text{mean}}\) and \(R(1-1/1-1)\) are expressed in atomic units.

Therefore, for full sampling of \(1-1/1-1\) bonds in crystals 1, 2, and 3 (Table 2), a satisfactory linear correlation between \(E_{\text{dist}}^{\text{pred}}\) values, eq 1, and predicted dissociation energy values \(D_e^{\text{pred}}\), eq 2, can be clearly seen (correlation coefficient \(R = 0.990\), number of cases is 27, standard error of estimation is 1.0 kJ/mol). It is worth mentioning that the high correlation coefficient still remains even for low-energy weak \(1-1\) interactions (Figure 7b), and therefore this general relation (Figure 7a) features a linear character in the whole range of observed interactions from strong covalent bonds to weak van der Waals contacts.

## CONCLUSION

We have applied the combined approach including Quantum Topological Theory of Atoms in Molecules and Crystals, one-electron potential and electrostatic potential to carefully analyze and categorize the spatial electron-density features in crystalline quinolinium oligoiodides \(C_{12}H_{11}INS^+I_3^-\) (1) and 2-\((C_{12}H_{11}INS^+I_3^-)_{1-2}\) (2) and \(C_{12}H_{23}NO^+I_3^-\) (3). It has allowed us to establish the typical electron density and energy features responsible for formation of four main types of \(1-1/1-1\) iodine interactions in these crystals: intramolecular covalent bonds \(1-1\) in diiodine molecule; intramolecular covalent bonds in triiodine anions \(1-1-1\); charge-assisted halogen bonds \(1-1-1\); and van der Waals interactions \(1-1\). Comparison of atomic charges of the same triiodide anions in different crystals has shown that the full charge of \(I_3^-\) in crystal (1), which does not form an oligomeric chain, is relatively high, up to \(-0.94\) e. In crystals (2) or (3), the triiodide anion is involved in halogen bonding, and the electron density is delocalized along the oligoiodide chain \(\left(1-\cdots-1-1-1^{-}\right)\), which leads to diminishing the negative charge on \(I_3^-\) moiety.

It has been demonstrated that consideration of the one-electron potential minima, which are located close to interatomic boundaries, allows differentiating the iodine interactions of different polarity. Moreover, OEP also shows the significant distinctions between halogen bonds and van der Waals interactions of iodine atoms.

The analysis of \(\rho^{-}\) and \(\varphi\)-atomic basin superposition has revealed the structure-forming anisotropy of atomic electrostatic interactions of iodine in considered crystals. Halogen bonds \(1-1\) in complex anions favor electron redistribution along the oligoiodide chain and, as a result, enhance the significance of "side" electrostatic interactions between iodine moieties and atoms in heterocyclic cation. The electron density is shifted from the \(I_3^-\) moiety to a cation via iodine molecule \(I_2\) as a mediator.

The electrostatic potential imposed on the zero-flux interatomic electron density surfaces of iodine moieties in crystals explicitly illustrates the role of the "side" electrostatic interactions and reveals the significant distinctions in the different types of iodine binding in the crystalline continuum. In particular, the traces of the \(\sigma\)-holes, observed in the free \(I_2\) molecule or in the free anion \(I_3^-\), are exhibited only for relatively strong interactions, such as the typical halogen bond \(1-1\). The rapidly growing ESP values are seen toward the bond paths in these cases. For the weak van der Waals \(1-1\) interactions (Type 1), the traces of \(\sigma\)-holes on the interatomic surface do not appear at all.

The equation linking the experimentally measured dissociation energy \(D_e(1-1/1-1)\) and the averaged electronic kinetic energy density at the bond critical points, \(g(r_0)_{\text{mean}}\) with consideration for internuclear distances, \(1-1/1-1\), has been suggested. We have found that this equation remains valid in the wide interaction energy range and provides a simple and effective tool for prediction of the sublimation energy of iodine-containing crystals.

## ASSOCIATED CONTENT

3 Supporting Information

Comparison of obtained values for ED in the plane of polyiodide \(I_3^-\cdot I_2\) fragment for crystal 2 according to multipole-model approximation of ED and direct analysis of crystalline wave function and the parameters of bond critical points for iodine interactions derived using the multipole model are available for compounds 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

Crystallographic information files are available from the Cambridge Crystallographic Data Center (CCDC) upon request (http://www.ccdc.cam.ac.uk, CCDC deposition numbers are 815955 (crystal structure 1), 815956 (crystal structure 2), and 1005549 (crystal structure 3)).

## AUTHOR INFORMATION

### Corresponding Author

E-mail: kbartash@yandex.ru. Tel: +7 (351) 267-97-99; +7 (351) 267-95-64. Fax: +7 (351) 267-97-98.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, grant 13-03-00767a and grant 14-03-00961.

## REFERENCES


(35) Iodine Basis Set; http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets/1 basis.txt.


Esterhuysen, C. IUCr 2011 Satellite Workshop; Sigüenza, 2011; p 17.


