Testing the tools for revealing and characterizing the iodine–iodine halogen bond in crystals

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To understand what tools are really suitable to identify and classify the iodine–iodine non-covalent interactions in solid organic polyiodides, we have examined the anisotropy of the electron density within the iodine atomic basin along and across the iodine–iodine halogen bond using the Laplacian of electron density, one-electron potential and electron localization function produced by Kohn–Sham calculations with periodic boundary conditions. The Laplacian of electron density exhibits the smallest anisotropy and yields a vague picture of the outermost electronic shells. The one-electron potential does not show such a deficiency and reveals that the valence electron shell for the halogen-bond acceptor iodine is always wider than that for the halogen-bond donor iodine along its σ-hole direction. We have concluded that the one-electron potential is the most suitable for classification of the iodine–iodine bonds and interactions in complicated cases, while the electron localization function allows to distinguish the diiodine molecule bonded with the monoiodide anion from the typical triiodide anion.

1. Introduction

Challenges related to characterization of the halogen-bonding diversity (Desiraju et al., 2013) and iodine–iodine non-covalent interactions in crystals are the focus of attention of many researchers working in crystal engineering. The crystalline organic polyiodides reported in works (Walsh et al., 2001; Kloo et al., 2002; Küpper et al., 2011; Groenewald et al., 2012; Terraneo et al., 2014; Cavallo et al., 2016) show the chains and multidimensional nets formed by highly polarizable iodine atoms. Such netted structural organization is usually supported by iodine–iodine halogen bonds and promotes an easy transition to the ionic liquid state (Fei et al., 2006). Such structures also show the conductivity (Jentzsch et al., 2015) and nonlinear optical properties in acentric crystals (Yanagida et al., 2015; Yin et al., 2012).

The establishment of the structural features of iodine-containing crystalline compounds necessarily includes halogen-bond identification. The well known geometric criteria allow the most common Type I and Type II halogen–halogen interactions (Abola & Sundaralingam, 1973; Desiraju & Parthasarathy, 1989) to be distinguished. Nevertheless, more reliable criteria of halogen bonding are needed for intermediate-type mutual halogen–halogen arrangements. In addition, in complicated cases of multiple iodine interactions, as they take place in crystals, it may be necessary to identify which iodine atoms can be considered to be the halogen-bond donor.
Characterizing the iodine–iodine halogen bond

Comprehensive identification and characterization of the halogen bonds in crystals demands the subatomic level description of non-covalent interactions, i.e. locating the intraatomic electron concentration and depletion regions for bounded halogen atoms. These features are clearly observed in the outermost (valence) electron-density shells of bonded atoms (Tsirelson et al., 1995), and they define the mutual arrangement of halogens in complexes or crystals of compounds under consideration. Therefore, the study of non-covalent interactions of I atoms first has to focus on the features of the valence shells.

The above-mentioned charge-density features within iodine atomic basins anisotropically shield the nuclei influence on the crystalline surroundings. As a result, the electron donor/acceptor role of halogen atoms is mainly determined by the specific picture of electrostatic interactions between a pair of bounded I atoms. This is described by means of the $\sigma$-hole concept based on features of the electrostatic potential mapped on the molecular electron-density surface (Politzer et al., 2010). This concept yields quite a reliable criterion for the halogen-bond formation for isolated molecules: the $\sigma$-hole (Politzer et al., 2015) appears bright, and it is an illustrative tool to show the direction of the interaction. Moreover, in certain cases the quantitative characteristics of a $\sigma$-hole allow the comparative estimation of the halogen-bond energy in complexes (Bartashevich & Tsirelson, 2013). At the same time, the identification of iodine halogen bonds in crystals is not straightforward. Firstly, traces of the $\sigma$-hole for certain molecules can be hidden by contributions from the crystalline surroundings (Bartashevich, Yushina, Stash & Tsirelson, 2014), especially for the relatively weak interactions. Secondly, the quantitative estimation of electrostatic potential extremes has to take into account the volume-dependent integration constant (Tsirelson et al., 2001), making a comparison of the bond strength in different crystals impossible.

In addition to the molecular electrostatic potential, the Laplacian of electron density, $\nabla^2 \rho(r)$, is a suitable tool for identification of halogen bonding: these functions reflect the electron-density inhomogeneity in the outermost electron shells of bounded halogens in crystals (Tsirelson et al., 1995; Savin et al., 1997; Gatti, 2005; Bartashevich & Tsirelson, 2014). The one-electron potential

$$P(r) = \frac{1}{4} \frac{\nabla^2 \rho(r)}{\rho(r)} - \frac{1}{8} \frac{|\nabla \rho(r)|^2}{\rho(r)},$$  

(1)

where $\rho(r)$ is the electron density, consists of two terms: the first term alternates while the second is always negative. The $P(r) < 0$ regions correspond to the positive local electron kinetic energy, while regions $P(r) > 0$ determine the potential barriers, within which the electron is classically forbidden. It has been accepted (Sagar et al., 1988) that the odd zeros of the $P(r)$ function are suitable for the determination of atomic shell boundaries as the regions not allowing the electron concentration. Kohout (2001) has taken the maxima of the $P(r) > 0$ function as the positions to demarcate the radii for electron shell boundaries. The shells radii for an isolated I atom obtained according to this criterion are as follows: 0.210, 0.280, 0.241, 0.699 Å. Recently, Kohout (2016) proposed to use so-called Position Uncertainty Curvature, $PUC = -\nabla^2 \log \rho(r)$, to represent the electronic shell structure. The minima of the PUC is located opposite the maxima of the $P(r)$ function. For $^{131}$I(1$S$) the shell radii given by the PUC minima (Kohout, 2016) and calculated using the wavefunctions of Clementi & Roetti (1974) are as follows: 0.023, 0.085, 0.255, 0.776 Å.

The ELF for closed-shell systems is defined as

$$\eta(r) = \left[ 1 + \left( \frac{D_p(r)}{D_0(r)} \right)^2 \right]^{-1/2},$$  

(2)

where

$$D_p(r) = r(r) - \frac{1}{8} \frac{||\nabla \rho(r)||^2}{\rho(r)}$$  

(3)

is Pauli’s kinetic energy density (March, 1986; Levy & Hui, 1988), $\rho(r)$ is the electron density, $\eta(r)$ is the positively defined electronic kinetic energy density and

$$D_0(r) = \frac{3}{10} (3\pi^2)^{2/3} r^{5/3}$$  

(4)

is the kinetic energy density of a homogeneous electron gas with density locally equal to $\rho(r)$. The electron localization function has already been used in the study of halogen bonding (Triguero et al., 2008; Li et al., 2012; Cheng et al., 2015).

The application of the Laplacian of electron density for heavy atoms meets some restrictions. Commonly, the regions with $\nabla^2 \rho(r) < 0$ are treated as the electron concentrations in atomic shells (Bader et al., 1987; Bader, 1990). However, it is well known (Shi & Boyd, 1988; Kohout et al., 1991; Eickerling & Reiher, 2008) that for the atoms with $Z \geq 29$ (Z is the atomic number) the areas with $\nabla^2 \rho(r) < 0$ are not observed for the outermost electron shells. This fact limits the applications of the Laplacian of electron density to describe the iodine halogen bonds.

The questions arise: what methods and functions based on electron density and its derivations are suitable to sort out the observed iodine bonding diversity in crystals? What mechanism holds the neighbouring I atoms together? This work aims to answer these questions. We will consider the various ways to express the anisotropy of the charge distribution within the halogen basin for iodine–iodine halogen bonds in the crystalline organic polyiodides. For this purpose we will compare the advantages and deficiencies of the functions $L(r) = -\nabla^2 \rho(r)$, $\eta(r)$ and $P(r)$ applied to crystalline organic polyiodides with 1⋯1 halogen bonds. The series of organic polyiodides: NUTSOL (Abate et al., 2010), NUTSUR (Abate et al., 2010), DULZOZ01 (Filgueiras et al., 2001), YUSYUH (Nelyubina et al., 2010), the crystalline $\text{I}_2$ (Bertolotti et al., 2014) and the electrically neutral crystalline complexes with $\text{I}_2$: HAFLAC (Antoniadis et al., 2003),...
NULBUR (Bailey et al., 1997), TIJLUU (Skabara et al., 2007) from the Cambridge Structural Database (Groom et al., 2016) have been examined and are listed in Table S1 of the supporting information. We have also taken advantage of our observations of chalcogenazolo(ino)quinolinium polyiodides with I-·I halogen bonds, which have been synthesized and analysed in our group: QIRZEY (Batalov et al., 2013), ZOJPAR (Batalov et al., 2014), DOWMAF (Bartashevich, Yushina, Vershinina et al., 2014), DOWMEJ (Bartashevich, Yushina, Vershinina et al., 2014), SUFLUC (Bartashevich, Nasibullina et al., 2016; Slepukhin, 2015), EJUPOQ (Bartashevich, Batalov et al., 2016) and IVOVOG (Bartashevich, Stash et al., 2016).

2. Calculations

Periodic three-dimensional calculations of crystals possessing a set of tri- and polyiodide chains have been performed by the Kohn–Sham method with B3LYP an exchange-correlation functional. The CRYSTAL14 (Dovesi et al., 2005) program package has been used. The modified (Towler, 1995) DZVP basis set for I atoms and adapted 6-31G** basis set for C, H, N, O and S atoms (Gatti et al., 1994) have been used. Eleven electron shells instead of 14 in the original DZVP basis set due to merging s- and p-shells into hybrid sp-shells have been applied.

Experimental space group and crystal structure parameters have been taken as the starting point in the calculations; the optimization of the atomic positions has been carried out with the fixed experimental unit cell. The shrinking factor according to Monkhorst & Pack (1976) has been set to 8 in all unit-cell directions. Truncation criteria for two-electronic integrals have been set as follows: overlap threshold for Coloumb integrals and Hartree–Fock exchange integrals equals $10^{-8}$ a.u.; the penetration threshold for Coloumb integrals is $10^{-8}$ a.u.; the first and second criteria for pseudo-overlap are $10^{-8}$ and $10^{-16}$ a.u., respectively. The absence of the imaginary vibration modes has been checked, thus the equilibrium structures have definitely achieved the position of minima. The harmonic frequency calculations have been performed at the centre of the Brillouin zone via the coupled perturbed Kohn–Sham analytical approach (Pascale et al., 2004). Raman active vibrations have been selected on the basis of intensity calculations (Maschio et al., 2013), characteristic modes have been assigned to I–I vibrations from the analysis of atomic displacements (Hanson, 2010). For the series of considered compounds, the calculated and experimental wavenumbers (Abate et al., 2010; Antoniadis et al., 2003; Bailey et al., 1997; Bartashevich, Stash et al., 2016; Congeduti et al., 2000; Nour et al., 1986; Skabara et al., 2007; Yushina et al., 2015; Yushina et al., 2016) are listed in Table S2.

The computed crystalline electron densities have been expressed in terms of the crystallographic space-extended multipole model (Hansen & Coppens, 1978), enabling calculation of a wide range of modern descriptors, characterizing the chemical bonds and intermolecular interactions (Stash & Tsirelson, 2002, 2005, 2014). The X-ray diffraction structure factors have been calculated to $\sin (\theta)/\lambda \leq 1.25 \text{ Å}^{-1}$ and used to reconstruct the electron density within the multipole model using the MOLDOS2003 program (Protas, 1997; Stash, 2003). The adjustable model parameters are as follows: the electronic occupations of the spherical parts of the valence shells and the space-extended higher multipoles (up to hexadecapoles for non-H atoms and up to quadrupoles for H atoms), as well as the radial expansion/contraction coefficients of valence parts of the atoms. Unit weights have been assigned to the structure factors during the refinement. Disagreement factors (Table S3) and the residual electron-density maps (Fig. S1) with average error $\sim 0.02 \text{ e Å}^{-2}$ are listed in the supporting information.

The relativistic effects, important for heavy atoms, are accounted for in our work using the proper basis sets (Su & Coppens, 1997; Macchi & Coppens, 2001). Because of the scarceness of iodine basis sets suitable for calculations with periodic boundary conditions, we have to rely on the comparison of our data with those obtained with a more comprehensive relativity consideration for simple iodine-containing substances (Pilmé et al., 2012).

Calculations of the distributions of the electron localization function, ELF, have been carried out with the TOPOND14 program (Gatti & Casassa, 2016). Quantum topological analysis of electron density have been performed using the WinXPRO program package, Version 3.1.15 (Stash & Tsirelson, 2002, 2014).

In addition, the Kohn–Sham calculations accomplished by the geometry optimization for molecular complexes of pyridine with diiodine have been carried out and the quantum topological analysis has been performed by the AIMAll professional program package (Keith, 2015).

Figure 1

(a) Two-dimensional map of the $L(r)$ function superimposed with critical points of $L(r)$ retained in the I–N–C plane of the pyridine-I$_2$ molecular complex. (b) Distribution of $L(r)$ along the halogen bond I···N (Direction X) and across it (Direction Y).
3. Results and discussion

3.1. The iodine halogen bond in terms of the Laplacian of electron density

Let us follow the features of the $L(r)$ function in the molecular complex pyridine-I$_2$ with I⋯N halogen bonds (Fig. 1). The profiles of $L(r)$ characterize the differences in curvature of the electron density for the I atom along and across the halogen bond. Along the I⋯N halogen bond, the critical points (CPs) of the $L(r)$ function are as follows: CP (3, -3) at 0.357 Å from the iodine nucleus; CP (3, +3) at a distance of 0.526 Å; CP (3, +1) at a distance of 1.371 Å. The latter CP is very close to the bond critical point (BCP) in the electron density, and it has the value of $L(r) = -0.079$ a.u.

Thus, the values of the $L(r)$ function in the outermost electron shell of the I atom remain negative. Such an observation is in good agreement with the observation about the electron density depletion in the α-hole area or in the region of relatively low shielding of the halogen nucleus, if we look along the halogen bond. The next CPs (3, -1) and (3, -3) are at the distances of 1.910 Å and 2.278 Å from the iodine nucleus, and they belong to the atomic basin of nitrogen, which is the acceptor of the halogen bond. The CP (3, -3) with the value $L(r) = 2.519$ a.u. corresponds to the charge concentration in the outermost electron shell of nitrogen.

On the contrary, the one-dimensional profile of $L(r)$ perpendicular to the halogen bond shows the positive maximum at a distance of 0.355 Å; it corresponds to CP (3, -3). Then the negative minimum occurs at a distance of 0.524 Å, corresponding to CP (3, +3). After the negative one-dimensional maximum placed at 1.197 Å from the iodine nucleus, the negative one-dimensional minimum at the distance of 1.374 Å is detected, corresponding to CP (3, -1). The values of $L(r)$ in the last two points are $-0.032$ and $-0.037$ a.u., respectively. Therefore, in an orthogonal direction to the line of the halogen bond, in the outermost electron shell of the I atom, the negative $L(r)$ maximum is present and it only slightly differs from the previous negative minimum of $L(r)$. The differences in the topology of $L(r)$ along the I⋯N halogen bond and in a transverse direction reflect the anisotropy of electron density features around iodine bonded with pyridine by the halogen bond. Thus, for a typical halogen bond in the diiodine molecular complex, the $L(r)$ function identifies anisotropic charge distribution. Note that this $L(r)$ anisotropy is weakly pronounced for the outermost electron shell of the iodine. The differences in the two orthogonal directions can be unnoticeable without careful topological analysis. Moreover, to provide detail on the $L(r)$ curvature in the valence shell, the special scaling in the range from $-0.08$ to 0.08 a.u. may be required, as in Fig. 1(b).

The molecular crystals often contain chains and nets formed by one type of halogen atom interacting with each other. Such homoatomic halogen bonds in the polyiodides of organic crystals are based on the mutually agreed anisotropy in the charge density (according to the ‘key-lock’ or ‘lump-to-hole’ principle) in the electron shells for the interacting I atoms.

3.2. Charge concentration and depletion features of the iodine–iodine halogen bond in crystals

For the iodide anion I$^{-}$, artificially extracted from the crystalline environment of thiazoloquinolinium monoiiodide SUFLUC (Slepukhin, 2015) using multipole model parameters, the distributions of $L(r)$ and $P(r)$, calculated along the halogen bond I$^{-}⋯C–I$, have been examined (Fig. 2). At 1.10–1.20 Å from the iodine nucleus, the $L(r)$ function does not cross zero (or the abscissa axis), and the last (the fifth) bend of $L(r)$ is negative. In other words, the function $L(r)$ does not detect the concentration of the electron density in the valence shell of iodine. This deficiency is eliminated by using the one-electron potential $P(r)$ (Tsirelson & Stash, 2004). As we have established previously (Bartashevich, Yushina, Stash & Tsirelson, 2014) for the iodine-derived heterocyclic cations and polyiodide anions, the anisotropy of the $P(r)$ function justifies the predisposition of the bounded iodine to the halogen bonding, and it clearly illustrates the ‘key-lock’ principle for iodine–iodine halogen bonds in crystals.

The external $P(r)$ minimum for the free iodine atom appears at a distance of 1.135 Å from the nucleus (Fig. 2b). Fig. 2 shows that it coincides with the external negative-valued inflection of the $L(r)$ function. We emphasize that the external negative $P(r)$ minimum corresponds to the positive values of the local electron kinetic energy (Tsirelson & Stash, 2004). It is an important advantage of the $P(r)$ function, which can be

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**Figure 2**

Calculated functions for the I atom, extracted from the crystalline continuum of SUFLUC: (a) $L(r)$, (b) $P(r)$. A decimal logarithmic scale is used for the distance (Å).
used as an indicator of the electron concentration in the outer-shell region, especially for I atoms and anions.

Taking the boundaries of the electronic shells at the maxima of the \( P(\mathbf{r}) \) function, we analyzed these boundaries for the iodide atom, artificially extracted from the diiodine molecule in a crystal. We have found four maxima of \( P(\mathbf{r}) \) at distances of 0.022, 0.082, 0.241 and 0.700 Å. For the monoiodide anion extracted from a crystal, the similar values are as follows: 0.018, 0.078, 0.239 and 0.694 Å. Thus, the radii for electronic shell boundaries of the deformed iodine atom ‘removed’ from a crystal are fairly close to the shell radii found by Kohout for the isolated iodine atom \(^{53}\text{I}(1S)\).

To elucidate how to change the shell structure features for the iodine involved in non-covalent interactions with crystalline environment, we analyzed the positions of \( P(\mathbf{r}) \) maxima in the number of organic polyiodide crystals in which iodine atoms participate in halogen bonds as donors or as acceptors. The first example of the \( I_2 \cdots \cdot I(1) \) halogen bond between the triiodide anion and the diiodine molecule in the polyiodide with the complex structure \( I^3 \cdots \cdot I_2 \) in the crystal DOWMEJ (Bartashevich, Yushina, Vershinina et al., 2014) is shown in Fig. 3(a). We have passed along the halogen bond \( I_2 \cdots \cdot I_1 \), starting in one case from the atom \( I_2 \) that is the halogen-bond acceptor, as well as in the opposite direction, starting in the other case from the atom \( I_1 \) that is the halogen-bond donor.

Considering the interacting I atom, we have to accept that the position of the fourth positive maximum of the \( P(\mathbf{r}) \) function represents the boundary between the fourth and fifth electronic shells, and the position of the fifth negative minimum corresponds to the peak of electron concentration in the outer-shell region. Compared with the isolated I atom, the inner boundary of the fifth shell is further from the nucleus for the halogen-bond acceptor and closer to the nucleus for the halogen-bond donor (Tables S4 and S5).

The second example which has drawn our attention is the halogen bond in the crystal fragment of EJUPOQ (Bartashevich, Batalov et al., 2016; Fig. 3b). Let us compare two different non-covalent interactions of one I atom, following along the halogen bond and along the weak van der Waals interaction, namely, the Type I interaction. In the direction of the halogen bond \( I^1 \cdots \cdot I^2 \) the inner boundary of the fifth electronic shell of \( I^1' \) is located 0.010 Å further from its nucleus than in the direction of the van der Waals interaction \( I^1 \cdots \cdot I^3' \). At the same time, the peak corresponding to the electron density accumulation in the fifth shell is 0.012 Å closer to its nucleus along the halogen bond than that along the van der Waals interaction. Thus, for the \( I^1' \) atom the distance from the inner boundary to the peak in the outermost shell is 0.435 Å, where iodine as the halogen-bond donor is an electron acceptor. Nevertheless, the considered distance equals 0.457 Å in an orthogonal direction, in which the \( I^1' \) is involved in the van der Waals interaction. Thus, the inner part of the outermost shell is compressed more strongly in the direction in which the iodine atom is an electron acceptor.

For participants of the halogen bond \( I^1 \cdots \cdot I^1 \), the differences in boundary or peak positions are usually small and do not exceed 0.05 Å. The full radial width of the outermost valence shell is another matter. The positions of the one-electron potential extremes for the outermost electron shells along the iodine–iodine interactions are presented in Table 1. The average width of the valence shell for the halogen-bond acceptor is 1.20 Å, and for the halogen-bond donor it is 1.07 Å. As a result, we concluded that for the pair of interacting iodine atoms, the outermost shell for a halogen-bond acceptor is always wider than that for a halogen-bond donor. In other words, the outermost shell of the atom providing a lone pair for the halogen bond is slightly wider in \( P(\mathbf{r}) \) than the outermost shell of the atom accepting this electron pair. We note that the relativistic analytical wave-functions of Macchi & Coppens (2001) always give positions of boundaries and peaks closer to the nucleus (Table S3) than the Hartree–Fock wavefunctions (Clementi & Roetti, 1974; Table S4).

Now we are in a position to discuss the behaviour of the abovementioned functions \( L(\mathbf{r}) \) and \( P(\mathbf{r}) \) for various pairs of neighbouring I atoms in crystals. Let us compare three different cases of iodine–iodine interactions in the crystal DOWMEJ (Bartashevich, Yushina, Vershinina et al., 2014): the covalent bond \( I^1 \cdots I^1 \); the typical charge-assisted halogen bond \( I^1 \cdots I^3 \); and the weak van der Waals interaction \( I^1 \cdots I \) (Type I). For all of them the bond paths in the electron density
are observed. We have focused on the relative positions of one-dimensional maxima and minima of \( L(r) \) and \( P(r) \) functions along the lines between selected pairs of I atoms (Fig. 4).

At the centre of the homoatomic covalent bond I1—I1 (Fig. 4a), the symmetrical maximum of the \( L(r) \) function is detected. In the position of the central peak at the equal distances 1.435 Å from I atoms, the maximum of the \( P(r) \) function is also observed (Fig. 4d). The two nearest minima of the \( P(r) \) function are located at a distance of 0.365 Å; they are positive and equal in magnitude, \( P(r) = 0.097 \text{ a.u.} \)

For the halogen bond I2···I1 with the interatomic distance 3.431 Å (Fig. 4b), the \( L(r) \) function has a distinct inflection from the side of the I2 atom, which is acting as an electron donor in this pair of atoms. This inflection coincides with the negative minimum of the \( P(r) \) function (−0.092 a.u.) located at the 1.114 Å from I2 (Fig. 4e). On the contrary, from the side of the I1 atom acting as an electron acceptor, the slowing of the decrease in \( L(r) \) function is not observed, and the minimum \( P(r) = 0.112 \text{ a.u.} \) lies in positive values at 1.100 Å from the atom I1. Comparing the characteristics of extremes of the one-dimensional \( L(r) \) and \( P(r) \) functions in the region of valence shells, it is possible to elucidate the role of each I atom in a typical halogen bond. In other words, we can establish whether each specific iodine atom is the donor or the acceptor of a halogen bond. For iodine, which is the halogen-bond acceptor, the negative minimum of \( P(r) \) is expected in the outermost electronic shell, but for the iodine, which is the halogen-bond donor, the positive minimum of \( P(r) \) manifested. Thus, the sign of the \( P(r) \) extreme in a valence shell is important for iodine–iodine halogen-bond identification in crystals with nets and chains formed by complex polyiodide anions.

**Figure 4**

Calculated (B3LYP/DZVP) \( L(r) \) function (top) and \( P(r) \) function (bottom) for (a) covalent bond I1—I1, (b) typical halogen bond I2···I1, (c) weak (Type I) van der Waals interaction I2···I(4) in the crystal structure of DOWMEJ (Bartashevich, Yushina, Vershinina et al., 2014).
For the van der Waals interaction I₂···I₄ (3.850 Å) between two I atoms of the neighbouring triiodide anions, the two negative minima of the \( P(r) \) function are observed. The first of them with the value \( P(r) = -0.068 \) a.u. is 1.127 Å from I₂; the second minimum of \( P(r) = -0.029 \) a.u. is 1.126 Å from I₄ (Fig. 4f). The \( L(r) \) function has two weakly expressed inflections from both I₂ and I₄ (Fig. 4c). The positions of these inflections coincide with the minima of the \( P(r) \) function. According to the geometric criterion, the non-covalent interaction I₂···I₄ is not a halogen bond and it belongs to the Type I halogen–halogen interactions. According to the behaviour of the \( L(r) \) and \( P(r) \) functions for such a pair of I atoms, it is impossible to distinguish one atom from another: both atoms are similar. This means it is not a halogen bond.

Thus, the expressed inflection of the \( L(r) \) function, the relative location of \( P(r) \) extremes and the sign of the \( P(r) \) minimum in the region of the outermost shells allow us to identify a typical halogen bond between two I atoms in crystals. The availability of the above-mentioned qualities highlight the typical halogen bond among the other, non-specific iodine–iodine interactions. Negative values of the \( P(r) \) minimum closest to the centre of the halogen bond describe the I atom, which is an electron donor and a halogen-bond acceptor; the positive-valued \( P(r) \) minimum indicates an acceptor of electrons and a halogen-bond donor.

3.3. The electron localization function as a tool for identification of an iodine molecule inside the polyiodide anion in crystals

Let us now try to understand which criteria can be used to determine the limit of the I···I bond elongation, which can lead to another structural unit in the chains of three, four or five sequentially bonded I atoms. One such example is the case of the asymmetric triiodide anion in the 5-chloro-oxazinoquinolinium crystal EJUPOQ (Bartashevich, Batalov et al., 2016), in which motif I⁻·I is more typical than \( \text{I}_3^- \) (Svensson & Kloo, 2003).

We computed the ELF, \( \eta(r) \), for the systems with I···I halogen interactions in two different fragments including five I atoms as part of the polyiodide chains in DOWMEJ (Bartashevich, Yushina, Vershinina et al., 2016) and EJUPOQ (Bartashevich, Batalov et al., 2016; Fig. 5). The electron-concentration region of I₂ in the typical triiodide anion (I₂—I₃—I₄⁻) (Fig. 5a) is strictly oriented in the electron depletion region located on the extension of the I₁—I₁ covalent bond in the diiodine molecule. A more complicated task is the strongly asymmetric triiodide anion [I₂—I₃···I₄⁻] (Fig. 5b) with calculated and experimental (in brackets) bond lengths of 2.923 (2.871 Å) and 3.180 Å (3.005 Å; Fig. 5b). A number of \( \eta(r) \) characteristic features can be seen in the I₂—I₃⁻ fragment. Firstly, it is the absence of the domain limited by a value greater than 0.35 between I₃ and I₄ atoms. Secondly, the line \( \eta(r) = 0.50 \) goes between I₂ and I₃ atoms. Thirdly, the anisotropy of \( \eta(r) \) in the outer electron shell of atom I₄ is less evident, which makes this atom similar to the monoiodine anion. All the above-mentioned observations demonstrate the efficiency of \( \eta(r) \) in the identification of a bound diiodine molecule as part of the polyiodide anion. Thus, the fragment [I₂—I₃···I₄⁻] in EJUPOQ (Bartashevich, Batalov et al., 2016; Fig. 5b) can be clearly attributed to the structure of bound diiodine interacting with the monoiodide anion, I⁻·I⁻, rather than the typical and more symmetric triiodide anion.

In such cases, the analysis of the \( \eta(r) \) features is more reliable and illustrative than the analysis of two-dimensional maps of the Laplacian of electron density as it is impossible to clearly disclose the very small anisotropy of \( \nabla^2 \rho(r_0) \) in the outer shells of I atoms.

3.4. What descriptors of the electron density are suitable for the iodine interactions?

Let us follow the changes of the Laplacian of electron density, one-electron potential and electron localization...
function in the BCPs of the electron density for various types of iodine–iodine interactions in crystals. The considered set of iodine–iodine interactions includes 13 covalent bonds, seven bonds in triiodide anions, 39 halogen bonds and the weak van der Waals interactions. For all of them, QTAIMC reveals the bond paths with $\rho(\text{bcp}) \leq 0.002$ a.u., see Table 18.

As Fig. 6(a) shows, the relationship $\nabla^2\rho(\text{bcp})$ versus $d(I, I)$ is not a single-valued function. Covalent bonds $I-I$ in diiodine molecules in their crystalline environment show $\nabla^2\rho(\text{bcp}) \geq 0$, which grows from 0.021 to 0.031 a.u. with increasing bond lengths from 2.8 to 2.9 Å. For triiodide anions $[I-I-I]$ with $2.9 < d(I, I) < 3.2$ Å, a similar trend is kept: the values of $\nabla^2\rho(\text{bcp})$ grow from 0.033 to 0.043 a.u. However, for non-covalent interactions $I\cdots I$, among which there are charge-assisted halogen bonds and weak van der Waals interactions, the opposite tendency is observed: the values of $\nabla^2\rho(\text{bcp})$ exponentially decrease from 0.038 to 0.002 a.u. in the range $d(I, I)$ from 3.2 to 5.1 Å.

The following example illustrates the unambiguity of the $\nabla^2\rho(\text{bcp})$ versus $d(I, I)$ relationship. For both the weak non-covalent interaction $I\cdots I$ with $d(I, I) = 4.020$ Å in DOWMEJ (Bartashevich, Yushina, Vershinina et al., 2014) and the covalent bond with $d(I, I) = 2.830$ Å in ZOJPAR (Batalov et al., 2014), the same values of $\nabla^2\rho(\text{bcp}) = 0.022$ a.u. have been found. Thus, the usefulness of quantitative correlations between the Laplacian of electron density at BCPs of electron density and iodine–iodine interatomic distances, as well as the application of $\nabla^2\rho(\text{bcp})$ as the quantitative ‘structure–property’ descriptor, does appear to be doubtful.

Unlike the Laplacian of electron density, the values of the one-electron potential $P(\text{bcp})$ and the electron localization function $\eta(\text{bcp})$ at BCPs of electron density are single-valued functions of interatomic distances, and they do not exhibit extreme behaviour on the frontier between $I-I$ covalent bonds and $I\cdots I$ non-covalent interactions.

The values $P(\text{bcp})$ and $\eta(\text{bcp})$ decrease with increasing interatomic distances $d(I, I)$ in full range of various types of iodine–iodine interactions (Figs. 6b and c). Furthermore, in the range of $d(I, I)$ from 2.8 to $3.4 \pm 0.2$ Å, for which the strong bonds in $I_2$ and $I_3$ and charge-assisted halogen bonds fall in, both relationships $P(\text{bcp})$ versus $d(I, I)$ and $\eta(\text{bcp})$ versus $d(I, I)$ exhibit linear behaviour. In the distance range where the charge-assisted halogen bonds give way to typical halogen bonds, reducing $P(\text{bcp})$ and $\eta(\text{bcp})$ values with distance is slowing. The values of $P(\text{bcp})$ in the range $d(I, I)$ of $3.4 \pm 0.2$ Å to 5.1 Å have large dispersion created by the weak halogen bonds and the weak van der Waals interactions. The behaviour of $\eta(\text{bcp})$ versus $d(I, I)$ is devoid of such deficiencies in the whole range of values considered (Fig. 6c). Thus, of the three considered relationships, $\nabla^2\rho(\text{bcp})$ versus $d(I, I)$, $P(\text{bcp})$ versus $d(I, I)$ and $\eta(\text{bcp})$ versus $d(I, I)$, the most promising quantitative descriptors in the linear equations seem to be the values of the electron localization function $\eta(\text{bcp})$.

4. Conclusion

In this work we dealt with the crystalline polyiodides, which are rich in $I\cdots I$ homoatomic halogen bonds between iodine-derived organic cations and mono- or polyiodide anions. Therefore, we aimed to sort out the observed iodine–iodine bonding feature diversity. Halogen bonds between iodine subunits, such as the triiodide anion and diiodide molecule within the polyiodide chains, have also been considered.

The intra-atomic electron-density features such as electron accumulation and depletion regions, and their mutual arrangement in the bounded I atoms, have been analyzed using various modern tools. We have found that the Laplacian of electron density, the one-electron potential and the electron localization function, produced by Kohn–Sham calculations with periodic boundary conditions, differently reveal the anisotropy of the charge density distribution along and across the iodine–iodine halogen bond; this anisotropy in the Laplacian of electron density is the smallest. Besides, the last peak of function $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ in the outermost shell of the bounded iodine is usually negatively valued and it is invisible in the commonly accepted scale of $L(\mathbf{r})$.

Analysis of positions of the electronic shell boundaries for the I atoms in the crystalline environment has shown that for the halogen-bond acceptor iodine the valence electron shell is always wider than that for the halogen-bond donor iodine. In addition, we have found that the outermost electron shell, as it follows from the one-electron potential $P(\mathbf{r})$, is more highly compressed in the $\sigma$-hole direction than in the orthogonal direction, in which iodine usually serves as an electron donor in crystals.

The one-electron potential, $P(\mathbf{r})$, as the function that has clear physical meaning, helped us to identify the role of each of the I atoms in the specific non-covalent interaction. For the halogen-bond acceptor, the negative minimum of the $P(\mathbf{r})$ function in the outermost shell is usually observed, while the

Figure 6
Relationships between interatomic distances $d(I, I)$ in crystals and calculated values at the bond critical point of $I-I$ and $I\cdots I$ interactions: (a) $\nabla^2\rho(\text{bcp})$, (b) $P(\text{bcp})$, (c) $\eta(\text{bcp})$. 
positive minimum for the halogen-bond donor is expected. This simple rule is useful for the iodine–iodine halogen-bond identification and to distinguish it from Type I interactions in crystals. Therefore, we recommend the $P(r)$ function as a reference tool in halogen-bonding studies.

We also stress that the specific features of the distribution of the electron localization function allow differentiation of the diiodine molecule tightly interacting with the monoiiodide anion from the typical triiodide anion in crystals.

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