Electronic criterion for categorizing the chalcogen and halogen bonds: sulfur–iodine interactions in crystals

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Diversity of mutual orientations of Y–S and I–X and covalent bonds in molecular crystals complicate categorizing noncovalent chalcogen and halogen bonds. Here, the different types of S · · · I interactions with short interatomic distances are analysed. The selection of S · · · I interactions for the categorization of the chalcogen and halogen bonds has been made using angles that determine the mutual orientation of electron lone pairs and σ-holes interacted S and I atoms. In complicated cases of noncovalent interactions with ‘hole-to-hole’ of S and I orientations, distinguishing the chalcogen and halogen bonds is only possible if the atom is uniquely determined, which also provides the electrophilic site. The electronic criterion for chalcogen/halogen bonds categorizing that is based on analysis of dispositions of electron density and electrostatic potential minima along the interatomic lines has been suggested and its effectiveness has been demonstrated.

1. Introduction

The chalcogen bond as a noncovalent interaction with an evident electrostatic component, in which the electrophilic site is provided by the sulfur atom. It is now at the heart of an IUPAC project (Terraneo & Resnati, 2017) dealing with categorizing of chalcogen, pnictogen and tetrel bonds, and other interactions involving group 14–16 elements of the periodic table. Unlike the halogen bond (Cavallo et al., 2014; Desiraju et al., 2013), owing to the presence of more than one σ-hole (Clark et al., 2007; Politzer et al., 2007) and the valence states of chalcogen atoms, it is not easy to give a clear picture of the mutual geometrical orientation of covalent bonds that lead to the typical attractive interactions between one of the chalcogen σ-holes (Bauzã & Frontera, 2018) and nucleophilic site.

The problem of identification and categorization of different types of noncovalent bonds arose a long time ago (Desiraju & Parthasarathy, 1989; Metrangolo & Resnati, 2001; Legon, 2010; Scheiner, 2011; Bauzã et al., 2017). The geometrical description indirectly treats the interactions in terms of angles and distances shorter than the sum of van der Waals radii. However, the other interactions involving Group 14-16 elements (Brammer, 2017; Cavallo et al., 2014; Gleiter et al., 2018; Legon, 2017; Scheiner, 2017) are mainly electrostatically
driven in nature (Murray et al., 2012; Politzer et al., 2010; Politzer et al., 2017) and demand the thorough analysis of the bonding features to correctly distinguish the electronic shells of atoms up to heavy ones. It can, sometimes be challenging.

The task of categorization of noncovalent interactions is not just a methodological question: it can give valuable information in the field of crystal structure prediction and directed design of crystalline materials with nonlinear optical properties that can depend on the features of halogen bonds (Yushina et al., 2018; Masunov et al., 2018).

The fundamental role in understanding the nature of nucleophilic and electrophilic regions in molecules is certainly, based on the idea of the lone pairs and the localization of σ-holes, which is inextricably linked with the features of electron density distribution (Bader et al., 1989). One of the tools that could reveal the halogen bonding in crystals is the Laplacian of electron density. On Laplacian maps, the electron concentration of the electron donor atom is directed towards the electron depletion area of the covalently bound halogen atom (Bader et al., 1987; Bader, 1990). However, the application of the Laplacian for elements with \( Z > 22 \) meets some restrictions (Shi & Boyd, 1988; Kohout et al., 1991; Eickerling & Reiher, 2008): the Laplacian does not exhibit the electron accumulation regions in the outermost valence shells of heavy atoms.

Electron Localization Function (ELF) (Becke & Edgecombe, 1990; Silvi & Savin, 1994) and One-Electron Potential (OEP) (Hunter, 1975) demonstrate the completeness of electron shell description for heavy atoms. ELF is related to Pauli electron kinetic energy density in an actual system scaled to homogeneous electron gas. It is close to 1 in regions of electron pair locations and it attains low values in σ-hole regions, where electron deficiency occurs. It provides the description of valence electron shell features for the halogen or chalcogen bonds. The negative regions of OEP approximately coincide with the maxima of the ELF function and indicate the electron concentrations in atomic shells. For example, in the \( I_3^- \ldots I_2^- \ldots I_1^- \) zigzag chain the area of electron density accumulation in the triiodide anion is oriented towards the area of electron density depletion in \( I_2^- \). The one-dimensional OEP profile clearly displays this fact (Bartashevich et al., 2017). It has been concluded (Bertolotti et al., 2014) that OEP is a more useful descriptor than the Laplacian for revealing the lone-pair orientation towards the charge depletion in heavy elements forming typical halogen bonding.

All above-mentioned tools are usually considered in the plane of bonds arrangement thus allowing the researcher to visually understand how the electron concentration and depletion regions are located with respect to each other. This results in the spread in personal interpretation of bonding features and makes the noncovalent bond categorizing criteria qualitative and vague, to say the least.

Therefore, an actual challenge is to identify the halogen or chalcogen bonding when it is not clear which of the atoms, the halogen or chalcogen, is the electrophilic-site provider. Careful attention is paid to the particular case of noncovalent interactions between chalcogen and iodine atoms in the following investigations (Arman et al., 2010, 2012; Bartashevich et al., 2016; Konidaris et al., 2018; Jay et al., 2001; Kobré et al., 2018; Liu et al., 2009; Resnati & Pennington, 2018). If the σ-holes of the halogen and chalcogen atoms are oriented to each other in the crystal structure, and their interaction remains mainly electrostatic, it is difficult to make a decision as to which atom acts as an acceptor and, therefore, to define the name of the bonding. This problem is widespread for the mutual and competitive S···I interactions, the chalcogen and halogen bonds in \( N,S \)-heterocycles and in their crystalline polyiodides. Different mutual orientations of σ-holes located on the extension of \( X^-I \) and \( S^-Y \) covalent bonds make us face an important categorizing dilemma: which atom, S or I, delivers the electrophilic site and defines the name of the bonding. This paper aims to answer this question.

### 1.1. Theoretical background of criterion for categorizing chalcogen or halogen bonds

Within QTAIM (Bader, 1990), which gives us the most useful methodology for describing chemical bonds in molecules and crystals, the zero-flux condition \( \nabla \psi(r) \cdot \mathbf{n}(r) = 0 \) of the vector of gradient of electron density defines the boundaries of chemically bonded atoms (ED-basins), where \( \mathbf{n}(r) \) is the unit vector normal to the surface of the atomic basin in electron density. The zero-flux condition \( \nabla \varphi(r) \cdot \mathbf{m}(r) = 0 \), where \( \varphi(r) \) is the electrostatic potential and \( \mathbf{m}(r) \) is the unit vector normal to the surface of the atomic basin in electrostatic potential, describes electrically neutral bounded atomic fragments (ESP basins) within the whole system. The study of electrostatic potential topology in molecules was initiated by Gadre (Pathak & Gadre, 1990). Tsirelson et al. (2001) identified zero-flux surface in the electrostatic potential in solids using the experimental charge density. The order of saddle points in electron density and electrostatic potential along the interatomic lines was then discussed in several research papers (Tsirelson et al., 1995, 2009; Shishkina et al., 2010).

In this spirit let us consider the details of noncovalent S···I interactions in the crystal of \((Z)-4\text{-chloro-5-\{(4\text{-chloro-5H-1,2,3-dithiazol-5-ylidene amino}][phenyl]amino\)-1,2,3-di-

[Figure 1](#)

S···I interactions in the SEJQAC crystal: (a) the contour map of electron density with the bond paths and bond critical points shown; (b) disposition of zero-flux ED basins and ESP basins; (c) the contour map of ESP superimposed by the vectors showing the directions of the Coulomb forces. Note that zero-flux surfaces in ESP do not depend on the gauge choice, whereas the ESP itself does (Landau & Lifshitz, 1971).
thiazol-1-ium oligoiodide (SEJQAC) (Bol’shakov et al., 2017). Along the chalcogen bonds S1⋯I4 and S3⋯I4 (Fig. 1), the boundaries between ESP basins lie in the ED basins of the I4 atom. This means that a portion of electrons of this atom is attracted to the nuclei of S1 and S3. Note that S⋯I interactions in the SEJQAC crystal are reinforced by charges. The general observation for charge-assisted noncovalent interactions is: the boundaries of ED basins do not coincide with the boundaries of ESP basins. That means that the electrons formally belonging to one atom are attracted to the nucleus of another one. It is an efficient way to identify which atom in the pair is an electron acceptor and, correspondingly, the donor of the electrophilic site. This methodology allowed us to identify the iodine halogen bonds in polyiodide crystals (Bartashevich et al., 2014). The differences in sizes of basins for the noncovalently bound S and I atoms may be marked as \( d(I)_{\text{ED}} - d(S)_{\text{ED}} \) and \( d(I)_{\text{ESP}} - d(S)_{\text{ESP}} \), as depicted in Fig. 2.

Based on these observations, we propose to analyze the dispositions of one-dimensional minima of electron density \( (\text{ED}_{\text{min}}) \) and of electrostatic potential \( (\text{ESP}_{\text{min}}) \) along the line between considered atoms. The suggested electronic criterion for categorizing, which the electrophilic site dictates the type and name of bonding, can be formulated as follows: the minimum of electrostatic potential \( (\text{ESP}_{\text{min}}) \) is always located at the side of atom that donates electrons; the minimum of electron density \( (\text{ED}_{\text{min}}) \) is placed closer to the atom that delivers its electrophilic site for bonding. Obviously, the latter atom must prescribe the name of bonding.

Of course, the one-dimensional criterion is just a simplification of the actual disposition of boundaries of atomic basins. Nevertheless, this approach was previously successfully used for hydrogen bonds (Mata et al., 2007b) and the comparisons of atomic basins in electron density and electrostatic potential were applied in some works (Mata et al., 2007a; Crespo, 2014). It was claimed that the central region between zero-flux surfaces in electron density and electrostatic potential was related to the electrostatic interaction between the electron donor and acceptor atoms. When these two basin boundaries significantly mismatched, we can clearly see that part of the electron density of one atom is electrostatically attracted to the nucleus of the neighbour atom. This uniquely defines which atom acts as an acceptor of electrons and provides it electrophilic site for bonding. That is particularly important for categorizing of the halogen and chalcogen bonds and the other noncovalent interactions involving Group 14–16 elements.

Thus, the suggested electronic criterion is suited for complicated cases of mutual halogen and chalcogen orientation and for categorizing the halogen and chalcogen bonds in crystals. This study compares different types of S⋯I noncovalent interactions in crystals: the typical chalcogen and halogen bonds and the ‘hole-to-hole’ interactions sometimes established between sulfur and iodine atoms. Below we focus on the noncovalent interactions between thiol-group and iodine-substituted compounds with the short S⋯I contacts in organic crystals.

2. Experimental

2.1. Selection of subset of S⋯I interactions

Comprehensive characterization of all possible mutual orientations and types of bonding can be made on the basis of the systematic choice of analyzed structures among a great number of S⋯I short contacts from the CSD database (Groom et al., 2016). The set of crystals for this study, taken from CSD (Version 5.39), includes only organic derivatives without disorder which fit the following limiting conditions: (1) only thiol-like derivatives \( Y–S–Z \), where \( Y, Z = C, O, S, Se, Te, N, P, Hal \); (2) interatomic distance \( d(S, I) \leq r_{vdw}(S) + r_{vdw}(I) \), where \( r_{vdw} \) is the atomic radius in the Bondi scale (Bondi, 1964). Among these interactions, S⋯I⋯X, there are short contacts with I₂ tri- or polyiodide anions \((X = I)\) that found out established the I⋯X bond order. Fig. 1 illustrates the nomenclature of abbreviations used in this work for characterization of diversity of mutual S⋯I orientations. Due to ambiguity in \( \theta_1 \) and \( \theta_2 \) angle assignment, the largest values of \( \theta_1 \) and \( \theta_2 \) are attributed to the \( \theta \) angle in all cases. The angle \( \varphi \) indicates the covalent bond I–X deviation from the normal to the plane Y–S–Z.

Due to the time-consuming calculations of electronic characteristics, we compiled a testing set in which only iodine atoms are presented as heavy atoms: \( Y, Z = C, S \). We calculated geometric and electronic descriptors for 27 crystals with 51 S⋯I short contacts in total. Representation of the obtained angular \( \varphi-\theta \) distribution is shown in Fig. S1, exhibiting a representative cut of all S⋯I contacts and focusing on all possible \( \theta \) values at 160° < \( \varphi \) < 180°. A comparison of calculated and experimental values of the S⋯I distance and \( \theta, \varphi \) angles for the testing set is given in the Table S1.

2.2. Quantum chemical calculations

Periodic Kohn–Sham calculations were performed in CRYSTAL17 (Dovesi et al., 2018) package using the B3LYP (Lee, Yang & Parr, 1988; Becke, 1988) functional. Structure optimizations were made with fixed unit-cell parameters and an \( 8 \times 8 \times 8 \) k-point net. The following crystalline atomic basis sets were applied: modified DZVP set for iodine atoms and 6-31G** for all other atoms (Gatti et al., 1994). Truncation...
Table 1
Deviations of calculated distances and angles from X-ray diffraction data for HOVLUA and absolute distances from S atom to the minima of ED and ESP, respectively.

<table>
<thead>
<tr>
<th>DFT functional</th>
<th>( d(S\cdot I)_{\text{calc}} )</th>
<th>( \theta_{\text{calc}} ) (°)</th>
<th>( \varphi_{\text{calc}} ) (°)</th>
<th>( \Delta )</th>
<th>( d(S)_{\text{ED}} ) (Å)</th>
<th>( d(S)_{\text{ESP}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSE06</td>
<td>-0.033</td>
<td>0.6</td>
<td>-1.2</td>
<td>0.041</td>
<td>1.700</td>
<td>1.741</td>
</tr>
<tr>
<td>WC1LYP</td>
<td>-0.051</td>
<td>0.0</td>
<td>-1.7</td>
<td>0.045</td>
<td>1.692</td>
<td>1.732</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-0.032</td>
<td>-0.9</td>
<td>-2.7</td>
<td>0.046</td>
<td>1.701</td>
<td>1.746</td>
</tr>
<tr>
<td>B3LYP-D*</td>
<td>-0.003</td>
<td>-0.8</td>
<td>-2.3</td>
<td>0.046</td>
<td>1.693</td>
<td>1.739</td>
</tr>
</tbody>
</table>

criteria for bielectronic integrals have been set as follows: overlap threshold for Coulomb integrals and Hartree–Fock exchange integrals equals \( 10^{-10} \) a. u., penetration threshold for Coulomb integrals is \( 10^{-10} \) a. u.; the first and second criteria for pseudo-overlap are \( 10^{-10} \) and \( 10^{-20} \) a. u., respectively; these values are much higher than the default ones in order to increase the quality of calculations. Control of the absence of these values are much higher than the default ones in order to increase the quality of calculations.

Quantum-topological analysis of electron density and electrostatic potential was performed by the program 3DPlot (Stash & Tsirelson, 2014).

3. Results and discussion

3.1. Analysis of \( S \cdot I \) short contacts distribution in crystals

Our analysis starts from the distribution of \( S \cdot I \) contacts that provided varying angles \( \theta (Y - S \cdot I) \) and \( \varphi (S \cdot I - X) \) (Fig. 3). The range of possible values for the angles is as follows: \( 70^\circ \leq \theta \leq 125^\circ \) and \( 60^\circ < \varphi < 120^\circ \); the range of \( S \cdot I \) distances varies from 2.75 A to 3.78 A. The latter value limiting the upper limit of distances is the sum of the van der Waals radii of sulfur and iodine on the Bondi (1964) scale. For convenience, let us divide the scattering diagram (Fig. 3a) into four regions.

(1) Lower left rectangle includes structures with the values of parameters \( 70^\circ \leq \theta \leq 125^\circ \), \( 60^\circ < \varphi < 120^\circ \), \( S \cdot I \) distance from 3.53 Å to 3.78 Å. This case includes 4.7% of all considered interactions and corresponds to the area where orientation of the lone pair of the sulfur atom, \( \text{Lp(S)} \), towards the electronegative belt of the iodine atom dominates: \( \text{Lp(S)} \rightarrow \text{Lp(I)} \).

(2) Upper left region with angles \( 70^\circ \leq \theta \leq 125^\circ \) and \( 120^\circ < \varphi < 180^\circ \) and distances from 2.75 Å to 3.78 Å (15.2% of all contacts) mainly refers to orientation of the sulfur lone pair, \( \text{Lp(S)} \), towards the \( \sigma \)-hole of the iodine atom, \( \sigma \)-hole (I), which corresponds to halogen bonding. It is worth mentioning that the majority of significantly shortened contacts are located mainly in this field (blue and green circles in Fig. 3).

Figure 3
(a) Prevalent types of \( S \cdot I \) interactions, (b) the distribution of \( \theta \) and \( \varphi \) angles and \( S \cdot I \) interatomic distances. The legend of color dots is shown on the right: the shorter distances are marked in blue, while the longer distances are marked in red.
(3) Upper right part of diagram with angles $125^\circ \leq \theta \leq 180^\circ$ and $120^\circ \leq \varphi < 180^\circ$ and distances from $3.400 \text{ Å}$ to $3.780 \text{ Å}$ (19.7% of all contacts) consists of the various types of mutual S and I orientations, including the cases of $\text{Lp}(S) \rightarrow \text{Lp}(I)$ that cannot be attributed to interactions involving the electrophilic sites. Note that all possible types of $\text{S} \cdots \text{I}$ electrophilic site orientations are found in this area. They are as follows: (a) the halogen bonds in which sulfur lone pair is oriented to $\sigma$-hole of iodine $\text{Lp}(S) \rightarrow \text{\sigma\text{-hole}(I)}$; (b) the chalcogen bonds in which $\sigma$-hole of sulfur is directed to electronegative belt of iodine $\text{Lp}(I) \rightarrow \text{\sigma\text{-hole(S)}}$; (c) hole-to-hole S $\cdots$ I orientations.

(4) Lower right side contains $125^\circ \leq \theta \leq 180^\circ$, $60^\circ \leq \varphi \leq 120^\circ$ and distances from $3.430 \text{ Å}$ to $3.780 \text{ Å}$. It is the greatest part of all possible contacts, 60.4%, which predominantly demonstrates the following mutual orientations: (a) the typical chalcogen bonds, $\text{Lp}(I) \rightarrow \text{\sigma\text{-hole(S)}}$; (b) the noncovalent interactions $\text{Lp}(I) \rightarrow \text{Lp}(S)$ which can be attributed to the typical van der Waals interactions.

Thus, the wide range of mutual orientations of the electrophilic and nucleophilic regions for S and I atoms in crystals creates objective difficulties in categorizing a given sort of noncovalent bond. Moreover, owing to the two $\sigma$-holes exhibited by the S atom in sulfide molecules, we face a more complex procedure for categorizing the S $\cdots$ I chalcogen or halogen bonds. Therefore, in this study we give priority to orientations in which one $\sigma$-hole of S is involved in a noncovalent interaction. To do this, of two possible $\theta_1$ and $\theta_2$ angles ($Y$ $\cdots$ $S$ $\cdots$ I and $Z$ $\cdots$ S $\cdots$ I) we choose only the larger one, which is suited for consideration as the electrophilic site. In general, three types of orientation for the electrophilic site of sulfur and iodine are possible: $\text{Lp}(S) \rightarrow \text{\sigma\text{-hole(I)}}$, $\text{Lp}(I) \rightarrow \text{\sigma\text{-hole(S)}}$, $\text{\sigma\text{-hole(I)}\rightarrow \sigma\text{-hole(S)}}$. It should be noted that the tricky cases are the hole-to-hole orientations. The cases of $\sigma$-hole(I)$\rightarrow \sigma$-hole(S) interactions are realized when both the $\theta$ and $\varphi$ angles lie in the range $150^\circ$ to $180^\circ$, falling into the upper right part of scattering diagram in Fig. 3(a). Such a situation leads us to recognize that the geometric criterion is not enough to make a decision about the type and name of the noncovalent interaction. The choice between the I and S electrophilic sites requires the application of electronic criteria for identification of which atom provides its electrophilic site and accepts electrons. The latter step allows us to conclude whether we are dealing with a halogen or a chalcogen bond.

Moving on the next stage of analysis of the noncovalent types of bonding, we have to limit our choice by a more concrete series of $\text{S} \cdots \text{I}$ interactions, which are characterized by sequential behaviour of at least one of the geometrical parameters. Continuity of bonding types cannot be achieved if we move along $\varphi$ with fixed $\theta$ values as in the upper and bottom right parts on the scattering diagram shown in Fig. 3(a). Orientations of covalent bonds $Y(Z) \cdots$ S and I $\cdots$ X are rather more random than regular and, moreover, the S $\cdots$ I distances in this region are significantly larger: the majority of dots are in red which means that these distances are only slightly shorter than the sum of van der Waals radii. In contrast, tracing along the changes of the $\theta$ angle for fixed $\varphi$ values, corresponding to the most populated area of contacts, namely at $\varphi = 170^\circ \pm 10^\circ$, we get the option to chose and examine S $\cdots$ I short contacts; the strong halogen bonds, the typical chalcogen bonds, as well as hole-to-hole S $\cdots$ I-oriented interactions, are among them. Such a set of S $\cdots$ I contacts and their properties was compiled and is listed in Table S1.

### 3.2. Application of electronic criteria for categorizing the halogen and chalcogen bonds

Let us examine the implementation of electronic criterion for our set of S $\cdots$ I noncovalent interactions (Table S1) at the condition of $\theta$ angle increasing. To simplify arrival at the decision about the type of bonding, we take advantage of the analysis of the one-dimensional minima of electron density, ED$_{min}$, and electrostatic potential, ESP$_{min}$, along the line between the S and I atoms, as Fig. 2 recommends. It has been verified that the values at the minima of the one-dimensional ED function between S and I atoms and the values of ED at the BCP, $\rho_{\text{BOSP}}$, correlate well and for many cases are similar in magnitude (Table S2).

The distances from S and I nuclei to the common minimum of electron density, $d(S)_{\text{ED}}$ and $d(I)_{\text{ED}}$, as well as the distances to electrostatic potential minimum, $d(S)_{\text{ESP}}$ and $d(I)_{\text{ESP}}$, have been estimated. The sum of corresponding distances is equal to the length of the noncovalent interaction S $\cdots$ I. The difference in distances $d(S)_{\text{ED}} - (S)_{\text{ESP}}$ or $d(I)_{\text{ED}} - (I)_{\text{ESP}}$ determined as the gap between the minima ED$_{min}$ and ESP$_{min}$, and called $\Delta$, have also been analyzed. Such a semi-quantitative criterion seems quite convenient. If the inequality $d(S)_{\text{ED}} - (S)_{\text{ESP}} > 0$ holds, it means that the one-dimensional minimum, ESP$_{min}$, is closer to the S atom and the minimum ED$_{min}$ is closer to the I atom. This situation is possible when a certain small fraction of electrons belonging to the atomic basin of S is attracted to the I nucleus. Thus, for halogen bonds, the $\Delta$ values must be positive. If the inequality $d(S)_{\text{ED}} < (S)_{\text{ESP}}$ is true, the one-dimensional minimum, ED$_{min}$, is closer to S and a fraction of electrons from the atomic basin of I is attracted to the S nucleus. A situation such as this describes typical chalcogen bonding for which the determined $\Delta$ value is negative.

We have checked the influence of the calculation method on the resulting values of $d(S)_{\text{ED}}$, $d(S)_{\text{ESP}}$ and the gap $\Delta$. The effect of DFT functionals was studied on the example of HOVLUA (Table 1). For all examined DFT functionals, we have observed slight shortening of the S $\cdots$ I distance in comparison with experimental one; at the same time the angular orientation is excellently preserved. This fact is particularly important in the part of the present work concerning hole-to-hole orientation of S $\cdots$ I short contacts. It is worth noting that the locations of ED$_{min}$ and ESP$_{min}$ remain stable for the case of a medium $\Delta$ value in HOVLUA in all checked DFT functionals. It varies just slightly due to the variation of the S $\cdots$ I distance. While the absolute value of $\Delta$ depends on the chosen method of estimation of electrostatic interactions, the order of the minima is free of methodological details and this particular feature is the essence of discussed criterion providing categorization ability.
The effect of the Grimme dispersion correction (B3LYP-D*) is manifested in a significant decrease of \( d(S \cdot \cdot I)_{\text{exp}} - d(S \cdot \cdot I)_{\text{calc}} \) values although corresponding changes in \( \theta \) and \( \psi \) values are rather small. Dispersion correction on D* level does not influence obtained values of \( d(S)^{\text{ED}} \) and \( d(S)^{\text{ESP}} \) on the lines of S \( \cdot \cdot \cdot I \) bound atoms (Table 1).

Note that the calculated values of \( \theta \) and \( \psi \) angles for all selected contacts reproduce well not only the values observed in the crystals but also the features of their distribution in the total set of S \( \cdot \cdot \cdot I \) contacts represented in Fig. 3. For clarity, we present a 3D scatterplot (Fig. 4) of calculated angles \( \theta \), \( \psi \) and the gap \( \Delta \). For considered S \( \cdot \cdot \cdot I \) interactions, the gap varies in the range \(-0.18 < \Delta < 0.29 \) Å. It is clearly seen [Fig. 4(a)] that relatively a large gap with positive \( \Delta \) values, for which \( d(S)^{\text{ED}} > d(S)^{\text{ESP}} \) or, in other words, when \( d(I)^{\text{ED}} < d(I)^{\text{ESP}} \), is observed for the low values of \( \theta \) and the high values of \( \psi \). According to our electronic criterion, these are the halogen bonds. It is important that in the chosen coordinates the ranges of \( \Delta \) values practically do not overlap for the halogen and chalcogen bonds. The latter have high values of \( \theta \) and significantly wider range of \( \psi \) than the previous ones.

We did not find correlation of the gap value \( \Delta \) with either the bond length S \( \cdot \cdot \cdot I \), or the local properties such as the electron density and electrostatic potential at their minima. At the same time, the gap \( \Delta \) grows with the increasing of the difference in sizes of ED basins for S and I: \( d(S)^{\text{ED}} - d(I)^{\text{ED}} \), and it decreases with the increasing of the difference in sizes of ESP basins: \( d(S)^{\text{ESP}} - d(I)^{\text{ESP}} \) along S \( \cdot \cdot \cdot I \) interatomic line. A more detailed consideration of the quantitative relationships of the gap \( \Delta \) with the properties of halogen and chalcogen bonds is planned to carry out in further studies.

Note that for all considered S \( \cdot \cdot \cdot I \) interactions (Table S1), the distance from I to the minimum of electrostatic potential \( d(I)^{\text{ESP}} \) is typically longer than that from the S atom: \( d(I)^{\text{ESP}} > d(S)^{\text{ESP}} \). However, the distances to the minimum of electron density between the S and I atoms, \( d(S)^{\text{ED}} \) and \( d(I)^{\text{ED}} \), may occur in different proportions. The proportion of corresponding distances \( d(S)^{\text{ED}} \) and \( d(I)^{\text{ED}} \) changes with increasing angle \( \theta \) and grows from left to right on the histogram in Fig. 5 (see the green line). As a rule, in the \( \theta \) interval from \( \sim 90^\circ \) and up to \( \sim 120^\circ \), the distance to the minima of electron density is somewhat shorter from atom I than from atom S: \( d(S)^{\text{ED}} > d(I)^{\text{ED}} \). It means that in this direction the atomic basin of I is more compressed than that for S, despite the fact that the van der Waals radius of I is greater. Exceptions in our set are present, for example, the interaction in PIPXUJ (Shin et al., 2014) showing a relatively small \( \theta \) angle and a long interatomic distance. For large angles (\( \theta > 120^\circ \)), as a rule the situation is opposite: \( d(I)^{\text{ED}} > d(S)^{\text{ED}} \).

The histogram in Fig. 6 compares the corresponding distances from atomic nuclei to the minima of electron density, \( d(S)^{\text{ED}} \) and electrostatic potential \( d(S)^{\text{ESP}} \). Generally, the picture is similar to the previous histogram in Fig. 5, but this time it is free of exceptions. The disposition \( d(S)^{\text{ED}} > (S)^{\text{ESP}} \) takes place for relatively small \( \theta \) angles. In our set the last case with \( \theta = 142.6^\circ \) is observed for interactions in 1,4,7-trithia-cyclononane diiodine, the crystal structure with CSD refcode...
YEWPAR (Cristiani et al., 1993). Starting from $\theta > 147^\circ$ which is observed in IFOSUL01 (Wolstenholme et al., 2006) crystal structure, the S···I interactions in further part of the histogram in Fig. 6, the considered set are characterized by the longer distances $d(S)_{ESP}$ and the shorter $d(S)_{ED}$. It is easy to estimate that according to the proposed electronic criterion: the S atom delivers the electrophilic site when $d(S)_{ED} > (S)_{ESP}$, the gap $\Delta$ is positive, and it means that these types of interaction are the halogen bonds.

For large angles $\theta > 150^\circ$, the situation is opposite and $d(S)_{ED} < (S)_{ESP}$. According to the electronic criterion above, it means that the electrophilic site for S···I interactions is provided by the S atom, electrons are accepted by S, and these are the chalcogen bonds.

The S···I bonds located on the left and right edges of the histograms do not cause difficulties for the assignment of the halogen and chalcogen bonds with the traditional geometric criteria. To illustrate this statement, let us consider two structures with typical $\sigma$-hole orientations and compare the dispositions of $ED_{\text{min}}$ and $ESP_{\text{min}}$ along the lines of S···I bound atoms. Indeed, for the halogen bond in IFOSUL01 it is easy to identify [Fig. 7(a)] that the I atom provides its electrophilic site for bonding, as $ED_{\text{min}}$ is closer to the I atom. In HOVLUA [Fig. 7(b)], it is evident that the electrophilic site is delivered by the S atom: a portion of electrons belonging to the I atom is attracted to S; this can be identified by the fact that $ED_{\text{min}}$ is closer to S atom.

The structures with hole-to-hole orientation for the S···I short contacts clearly contrast with many cases of typical orientation for the chalcogen bonding, where the $\sigma$-hole of S is oriented towards the electronegative equatorial belt of the atom, i.e. the lone pair of the I atom. Thus, this antithesis shows that hole-to-hole orientation is much less common than the typical chalcogen bond and is beneficial at short S···I distances. However, this particular case of hole-to-hole orientation is of special interest from the point of categorizing S···I noncovalent interactions. Actually, the geometric definition of electrophilic site is not applicable in this case anymore.

Figure 7
Disposition of minima of electron density (vertical dashed line) and electrostatic potential (vertical solid line) along the S···I interactions for typical cases of (a) the halogen bond (YEWPAR) and (b) the chalcogen bond (HOVLUA). The arrow points to the electrophilic site provider.

Figure 8
Three-dimensional electron localization function (ELF) with contour 0.85 for the NAKROH crystal structure.
The 3D representation of ELF in NAKROH (Werz et al., 2005) structure with isosurface ELF = 0.85 (Fig. 8) illustrates the fragment of planar motif in which the S atoms of 1,2,3-tris(methylthio)cyclopropenium cation interact with the I atoms of the neighboring triiodide anion. In the case of S2−I2 interactions, the Lp accumulation region of terminal I2 is accommodated opposite the electron depletion region of S2. This type of orientation, Lp(I)→σ-hole(S), is a characteristic of the chalcogen bond. In the other case of S1−I2 interactions, the electron accumulation region in the equatorial part of I2 atom is oriented towards the electron accumulation region of S2 atom. In the S1−I3 interaction, atoms face each other resulting in hole-to-hole orientation, which is shown in Fig. 8. In the latter case, the characterization of the bonding type is ambiguous, as it is impossible to identify which atom provides the electrophilic site and which one donates electrons. Thus, this interaction cannot be classified reliably in terms of electrophilic site interactions using the ELF point of view only. Therefore, we have to complement and expand our observations for categorizing chalcogen or halogen bonds with the electrostatic properties of interatomic interactions in crystals and rely on the electronic criteria in complicated cases.

In contradistinction with Fig. 9 which illustrates the cases of the typical halogen and chalcogen bonding, Fig. 8 shows the more complicated cases in the NAKROH structure. Both S2−I2 and S1−I3 interactions are located closer to the right end of the histograms in Figs. 5 and 6, and are characterized by large θ angles. Using the ELF-based visualization only, we could not reliably identify an acceptor of electrons, but according to the electronic criterion we are able to make a concrete decision based on the condition $d(S)_{ED} < d(S)_{ESP}$. The graphical representation of the suggested electronic criterion is suitable for the typical halogen and chalcogen bonding, Fig. 8 shows the typical halogen and chalcogen bonds in the same compound, chalcogen bonds demonstrate lower Δ values (close to zero) and longer S−I distances.

**Figure 9**
Disposition of minima of electron density (vertical dashed line) and electrostatic potential (vertical solid line) along the S−I interactions in complicated cases (NAKROH) (a) the chalcogen bond and (b) hole-to-hole orientation as the chalcogen bond. The arrow points to the electrophilic site provider.

**4. Conclusion**
Analysis of the mutual orientation of the sulfur atom in the thiol group and the bound iodine atom in organic crystals reveals the different types of sulfur and iodine electrophilic site dispositions: Lp(S)→σ-hole(I), Lp(I)→σ-hole(S), σ-hole(I)→σ-hole(S). Unlike the typical chalcogen bond, where there is a clear geometric orientation of the sulfur electrophilic site, some short contacts S−I, where the σ-hole of the S atom is orientated towards the σ-hole of the I atom, still require consideration. In such cases we have to complement the geometrical considerations by the electrostatic field features to trust the electronic criteria for categorizing the chalcogen or halogen bonds.

To categorize the type of bonding in complicated cases of S−I noncovalent interactions, we suggest the following rule. **The minimum of electrostatic potential is located along the interatomic line closer to the atom that has excess of electron density. The minimum of electron density is always closer to the atom that has excess of electron density.** Therefore, we have to complement and expand our observations for categorizing chalcogen or halogen bonds with the electrostatic properties of interatomic interactions in crystals and rely on the electronic criteria in complicated cases.
The disposition of electron density and electrostatic potential minima can be quantitatively analyzed by the comparison of estimated distances from the referenced atoms (S or I in our study) to the minima of corresponding functions. In addition, Fig. 2 gives an example of the graphical representation of electronic criterion. The comparison of characteristic segments of electron density and electrostatic potential along the interatomic line facilitates the categorization of both the typical and controversial cases of S···I chalcogen and halogen bonds.

5. Related literature


Acknowledgements

The authors express their gratitude to Dr Silvia M. Casassa from University of Torino for the assistance in specifying computations with the use of TOPOND and to Dr Adam I. Stash from Karpov Institute of Physical Chemistry, Moscow for help with 3DPlot program.

Funding information

The following funding is acknowledged: Russian Foundation for Basic Research (grant No. 17-03-00406); Ministry of Education and Science of the Russian Federation (grant 4.1157.2017/4.6, contract No. 02.A03.21.0011).

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