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Characterizing the multiple non-covalent interactions in N, S-heterocycles–diiodine complexes with focus on halogen bonding



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ABSTRACT

The multiple non-covalent interactions in alkenylthioquinolines–diiodine complexes with conformationally flexible S-alkenyl fragments are studied from the viewpoint of the mutual influence of closely-located N and S donor sites. Despite several electron donor sites in an alkenylthioquinoline molecule (N, S and π -systems), which are capable of forming halogen bonds, the most stable complexes are observed if sulfur atom is a single donor center only. It corresponds to the most favorable mutual arrangement of the electron lone pairs of donor atoms and the depleted areas in electron localization function, which reflects the reduced shielding of iodine nucleus charge and coincides with σ -holes in the molecular electrostatic potential. Quinolines substituted at position 2 prefer to form the complexes with three-atomic non-covalent interactions: N...I, S...I and I...H. The bifurcated halogen bond with two-atomic interactions N...I and S...I turns out to be preferable for quinolines substituted at position 8. We have concluded that iodine participation in the bifurcated halogen bonding simultaneously with N and S atoms leads to reducing the binding strength in the complexes. It is found that the dipole polarization of an iodine atom provides the quantitative estimation of interaction energy in the complexes with multiple non-covalent interactions. The possibility to distinguish between the halogen bond S...I and van der Waals interaction S...I is also discussed.

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1. Introduction

The current understanding of halogen bonding (XB) as non-covalent interaction, in which a halogen atom acts as an acceptor of electron density, has been formed due to numerous studies [1–11] and is accepted now by IUPAC [12]. A certain consensus is achieved for halogen bonds in respect of strength, direction and relatively high contribution of electrostatic energy [8,13]. However the features of “attractive interaction between an electrophilic region associated with a halogen atom and a nucleophilic region in another molecule...” [12] are differently looked at in different methods and approaches.

The main methods used to establish the relative position of halogen bonds among the other non-covalent interactions are the Natural Bond Orbital analysis (NBO [14,15], Quantum Theory of Atoms In Molecules (QTAIM) [16,17] and Symmetry-Adapted Perturbation Theory (SAPT) [18–20].

QTAIM considers the bonding atoms as the nucleus-centered fragments separated by the surfaces of zero-flux of the gradient

of electron density. The bonds between atoms are associated with the lines of maximal density – the bond paths; it is valid for covalent, ionic, hydrogen, halogen bonds and van der Waals interactions. Among the functional descriptors that are successfully used to demonstrate the ability of the molecular structures for halogen bonds formation we should note the Molecular Electrostatic Potential (MEP) [8–9,21], the Electron Localization Function (ELF) [22,23], the Laplacian of electron density $\nabla^2\rho(\mathbf{r})$ [24] and the One-Electron Potential (OEP) [25]. The relatively enhanced local positive MEP areas, so called σ -holes [10], the low probability of electron pair localization, which coincides with σ -holes, the positive values of the Laplacian of electron density and OEP [25] are observed on the extension of the covalent bond formed by halogen atom, at a van der Waals radius distances. All these functions consistently reflect the relatively weak shielding of positively charged halogen nucleus along the extension of the covalent bond that engages this atom.

Nowadays the multiple interrelated and competitive non-covalent interactions of different types are in the focus of many studies [26–28]; the halogen bond is obligatory one of them. These studies showed that the proper terminology and classification of halogen bonds accompanied by the other non-covalent interactions is only

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in its development today. For example, Desiraju et al. [29] have attracted the attention to $\text{NO}_2 \cdots \text{Hal}$ ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$) supramolecular synthons in crystals and named the one halogen atom interaction with two oxygen atoms as «bifurcated three-center interaction». Lu et al. [30] have taken the same terminology using the notion «bifurcated halogen bond». Ji et al. in [31] have resorted to classification of bifurcated halogen bonds into symmetrical and asymmetrical. Note that the term «bifurcated halogen bond» is proper and really convenient only if two bonds are formed by one halogen and two electron donor centers, both of which satisfy the definition of halogen bond [12]. The term «bidentate halogen bond» has been preferred in [32] in the description of multiple charge-assisted interactions of halo-perfluorocarbons with halide anions.

To avoid confusion, it is worth to distinguish the case where one halogen atom, participating in the multiple non-covalent interactions, forms several bond paths, and only one of them corresponds to the definition of a halogen bond. We will name such interactions «two-atomic, three-atomic», etc., depending on the number of bond paths which it forms, and we will clarify whether such interactions include a halogen bond. On the other hand, two halogen bonds formed by one halogen atom can exist simultaneously. We will adhere to common terminology and call such interactions bifurcated halogen bonds.

Such accurate specification is important for characterization of the structure-forming interactions in biological systems [33] and crystal engineering [34–36]. Also, elucidation of the role of halogen bonding in multiple non-covalent interactions during description of the specific reactivity and mechanisms is of the great interest. For example, the ability of halogens to form the complexes with electron-donor centers in heterocyclic organic bases is well known

[37,38]. In particular, the complex formation with diiodine molecule is observed for the substituted quinoline systems [39,40] – see Fig. 1. These complexes exist in both solutions and crystalline state. Some tricyclic quinoline-based systems with fused N^1 and C^8 centers are known as important broad-spectrum antibiotics [41–43]. Substituted in positions 2 or 8 alkenylthio(oxy)quinolines react with an excess of diiodine yielding iodocyclization products with tricyclic thiazino(oxazolo)quinolinium systems [44–46]. Previously some of us have assumed that the iodocyclization reaction passes through the stage of halogen bond formation [47]. Alkenylthioquinolines are rich in electron-donor centers, there are several such centers in each molecule: N, S, π -systems of ethylene group and aryl ring (Fig. 2b). Thus, the study of the «alkenylthioquinolines–diiodine» complexes and halogen bond features has both fundamental and practical importance.

We suppose that iodine atom in such structures can be involved in bifurcated halogen bonding with two electron-donor centers simultaneously: $\text{N} \cdots \text{I}$ and $\text{S} \cdots \text{I}$. As we know [38], thioethers and quinoline exhibit the comparable basicity in respect to diiodine, it is bigger than that of the ethylene system [38]. However, the complex formation between iodine-containing molecules and ethylene group is probable [48] because this interaction immediately precedes the formation of a new covalent bond in the product. Thus, the electronic properties of halogen bonding in such systems are worth to be studied in detail. The aim of this work is to evaluate the mutual influence of closely-located donor N and S centers on the strength of non-covalent interactions in alkenylthioquinolines complexes with I_2 molecule.

For that purpose we performed the following studies.

- We considered the electron density properties in alkenylthioquinolines–diiodine complexes with multiple non-covalent interactions which included a halogen bonds from the viewpoint of QTAIM [17].
- We analyzed the effects of mutual influence of closely-located donor centers on the halogen bonding in the studied alkenylthioquinolines and examined whether the bifurcated halogen bonds were preferable to the conventional halogen bond.
- We discussed the efficiency of different approaches and descriptors to quantify the halogen bond properties.

Our approach consisted of analysis of electron density and interatomic bond paths in terms of QTAIM [17] and comparison

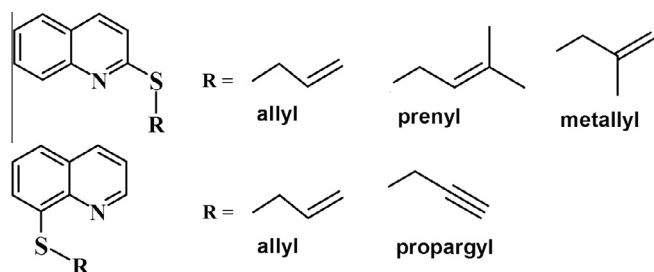


Fig. 1. The set of alkenylthioquinolines substituted in the 2 or 8 positions.

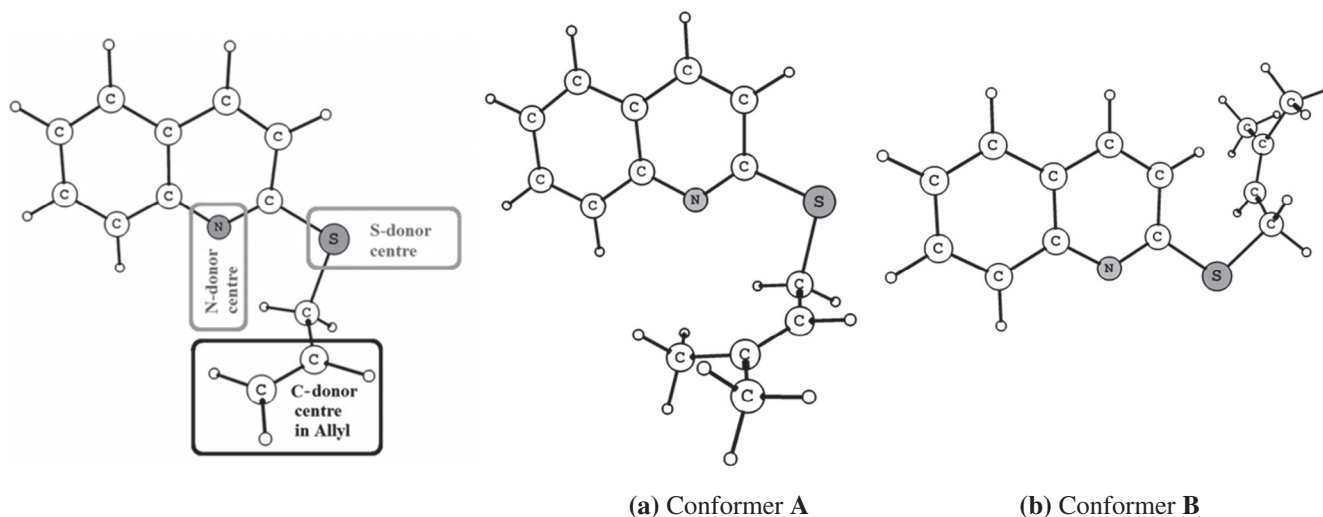


Fig. 2. Donor centers (N, S, π -systems of ethylene group and aryl rings) in substituted 2- and 8-alkenylthioquinolines. The most stable conformers for 2-prenylthioquinolines: the atom N is shielded by alkenyl group in conformer A (a), the atoms N and S are available for the attack in conformer B (b).

of atomic dipole moments for acceptor atoms in different conformations of alkenylthioquinolines in their complexes with diiodine. We also evaluated the properties of ELF and MEP. Finally, we studied a capability of the employed approaches to characterize the strength of halogen bonds in complexes with multiple non-covalent interactions involving the diiodine molecule.

2. Methodology

The sample set of complexes formed by alkenylthioquinolines substituted in positions 2 or 8 with diiodine has been prepared for analysis of halogen bonds and other non-covalent interactions (see Fig. 1 and Table 1). The computations of the wave functions for the abovementioned alkenylthioquinolines and diiodine molecules and their molecular complexes have been carried out by the Kohn–Sham method [49] in the B3LYP/6-311** approximation; the software package Firefly, version 8.0.0 [50]. The procedure of geometry optimization has been based on the early results of conformational analysis of initial alkenylthioquinolines structures [47] which has been done using methodology described in [51]. The minimum-energy equilibrium structures of all systems have been confirmed by harmonic frequencies calculating. The interaction energy of alkenylthioquinolines and diiodine molecules in complexes has been calculated as follows: $E_{\text{int}} = E_{\text{Qin} \cdots \text{I-I}} - (E_{\text{Qin}} + E_{\text{I-I}}) - E_{\text{CP}}$. Here $E_{\text{Qin} \cdots \text{I-I}}$ is the total energy of complex, E_{Qin} and $E_{\text{I-I}}$ are total energies of the donor and diiodine molecules, respectively, and E_{CP} is the correction that compensates for the basis set superposition error [52].

The obtained wave functions have been further used in the QTAIM analysis of electron density [17]. In particular, the electron density values and Laplacian of electron density $\nabla^2 \rho(\mathbf{r}_b)$ values at the bond critical points, $\rho(\mathbf{r}_b)$ of halogen bonds $\text{C}=\text{C} \cdots \text{I}$, $\text{N} \cdots \text{I}$, $\text{S} \cdots \text{I}$ and $\text{I} \cdots \text{H}$ have been found (see Table 1). The ELF [53] and atomic

electric dipole moments have also been calculated. According to [54], the total electric dipole moment of the molecular complex, μ^{Complex} , is a vector sum of the atomic dipole moments $\mu(\Omega_i)$: $\mu^{\text{Complex}} = \sum_i \mu(\Omega_i)$. Each atomic dipole moment consists of the intra-atomic component, $\mu^{\text{Intra}}(\Omega_i)$, originating from electron density redistribution within the QTAIM-basin of a bonded atom, and the bonding component, $\mu^{\text{Bond}}(\Omega_i)$ resulting from the charge transfer between the basins [54,55]: $\mu(\Omega_i) = \mu^{\text{Intra}}(\Omega_i) + \mu^{\text{Bond}}(\Omega_i)$. The magnitude of the total atomic dipole moment is $|\mu(\Omega_i)| = (|\mu_x(\Omega_i)|^2 + |\mu_y(\Omega_i)|^2 + |\mu_z(\Omega_i)|^2)^{1/2}$. The AIMALL software [56] has been used.

Electrostatic potential of the alkenylthioquinolines–diiodine complexes mapped on the 0.001 a.u. contours of electron density (as proposed in [16]) has been considered qualitatively for alkenylthioquinolines donor centers. All the MEP features have been determined using the MoleCoolQt and Mollso programs [57,58]. Also, the superposition of gradient fields in the electron density $\rho(\mathbf{r})$ and MEP, $\varphi(\mathbf{r})$, for the alkenylthioquinolines complexes with I_2 has been investigated in the plane of quinolone ring. Zero-flux conditions $\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$ [17,59] and $\nabla \varphi(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$ [60,61] (see below) allow us to identify the boundaries of atomic ρ -basins and φ -basins in corresponding $\rho(\mathbf{r})$ and $\varphi(\mathbf{r})$ gradient fields [62–65].

All figures in this work have been prepared with program Multiwfn 3.2.1 [66].

3. Results and discussion

3.1. QTAIM analysis of electron density

Alkyl-substituted thioethers exhibit comparable basicity with quinoline in respect to molecular iodine: $\text{pK}_{\text{B12}}(\text{diethyl sulfide})^{\text{in Hept}} = 2.29$, $\text{pK}_{\text{B12}}(\text{quinoline})^{\text{in Hept}} = 2.06$ [38]. In the absence of steric hindrances blocking the nitrogen atom, it would be expected

Table 1

Interaction energies and characteristics of the halogen bonds and other non-covalent interactions in the set of alkenylthioquinolines–diiodine complexes.

Complexes	Intermolecular contacts	$R(\text{D} \cdots \text{I})$, Å	$\rho(\mathbf{r}_b)$ (D \cdots I), a.u.	$\nabla^2 \rho(\mathbf{r})$ (D \cdots I), a.u.	Eint, kcal/mol
2-Allyl-thioquiniline- I_2	N \cdots I	2.861	0.026	0.058	−5.7
	S \cdots I	3.637	0.009	0.025	
	I \cdots H	2.938	0.010	0.027	
	N \cdots I	2.921	0.023	0.053	
	I \cdots H	3.064	0.008	0.020	−4.3
	I \cdots H	3.147	0.007	0.021	
	S \cdots I	3.133	0.025	0.044	
	C $=$ C \cdots I	3.164	0.016	0.035	
8-Allyl-thioquiniline- I_2	S \cdots I	3.719	0.008	0.023	−4.0
	N \cdots I	3.093	0.016	0.041	−6.8
	S \cdots I	3.105	0.026	0.046	
	C $=$ C \cdots I	3.162	0.016	0.035	
2-Propargyl-thioquiniline- I_2	N \cdots I	2.865	0.026	0.058	−5.5
	S \cdots I	3.633	0.009	0.025	
	I \cdots H	2.943	0.011	0.045	
8-Propargyl-thioquiniline- I_2	S \cdots I	3.749	0.007	0.022	−3.7
	N \cdots I	3.106	0.016	0.040	
2-Prenyl-thioquiniline- I_2	N \cdots I	2.847	0.027	0.060	−6.0
	S \cdots I	3.632	0.009	0.025	
	I \cdots H	2.931	0.010	0.027	
	S \cdots I	3.121	0.025	0.045	
	C $=$ C \cdots I	3.139	0.018	0.036	
2-Metallyl thioquiniline- I_2	N \cdots I	2.854	0.026	0.059	−5.8
	S \cdots I	3.633	0.009	0.025	
	I \cdots H	2.933	0.010	0.027	
	N \cdots I	2.963	0.021	0.049	
	I \cdots H	3.253	0.006	0.020	
	I \cdots H	3.022	0.008	0.021	
	S \cdots I	3.139	0.024	0.044	
	C $=$ C \cdots I	3.087	0.018	0.037	

that the stability of alkenylthioquinolines–diiodine complexes with $N_{sp^2} \cdots I$ or $S \cdots I$ interactions is comparable. But it is impossible to give preference to some of the electron-donor centers due to the conformational flexibility of S-alkenyl fragment in position 2 or 8 of quinoline.

Our experience shows that both 2- and 8-alkenylthioquinolines can form two kinds of relatively stable conformers. In conformer **A** (Fig. 2a), N atom is shielded by alkenyl group and the cyclization reaction centers are drawn together (N in quinoline and C in allyl group) [48]. In conformer **B** (Fig. 2b), the N and S atoms are available for attack. However, in this case the calculated interaction energy E_{int} in complexes with diiodine is in range of $-(3.7$ to $6.8)$ kcal/mol; it is significantly less than the interaction energy in the unsubstituted quinoline (-8.7 kcal/mol) or isoquinoline (-9.8 kcal/mol). A sulfur atom in both 2 and 8 positions is located sufficiently close to the nitrogen atom in the quinoline system. It can be assumed that in such structures the iodine atom can be coordinated with $S-C-C-N$ and $S-C-N$ fragments by means of two electron-donor centers $N \cdots I$ and $S \cdots I$ simultaneously.

Let us compare the non-covalent interactions which have been identified by the QTAIM bond paths in electron density for several types of complexes. All these systems have been formed on the basis of the most probable conformations of substituted alkenylthioquinolines. Substituted at position 2 quinolines prefer to form the diiodine complexes with multiple, for example, three-atomic non-covalent interactions manifested by the $N \cdots I$, $I \cdots S$ and $I \cdots H$ bond paths (Type 1) – see Fig. 3a. Quinolines substituted at position 8 can form complexes with two-atomic interactions $N \cdots I$ and $I \cdots S$ (Type 2) – see Fig. 3b. Moreover, probably both 2- and 8-substituted quinolines can form the complexes only via the single reaction center – the S atom and involve it in $S \cdots I$ interaction (Type 3) – see Fig. 3c. The biggest value of electron density at the bond critical point in complex **1** corresponding to the $N \cdots I$ bond is $\rho(r_b) = 0.027$ a.u. and for $S \cdots I$ bond in complex **3**, $\rho(r_b) = 0.026$ a.u. At the same time, for bifurcated interactions in 8-allylthioquinoline (Type 2), the largest values $\rho(r_b) = 0.016$ a.u. and $\rho(r_b) < 0.010$ a.u. are observed for $N \cdots I$ and $S \cdots I$ bonds, respectively. We can suppose that interactions, which involve the two donor centers in 8-alkenylthioquinoline, are not synergistic. Also we can speculate that the two donor centers competing for the coordination of diiodine molecule reduce the strength of the halogen bonding.

3.2. Molecular electrostatic potential (MEP)

Let us now apply another method for characterization of investigated interactions. Molecular electrostatic potential mapped to peculiar surface of the electron density illustrates the specific interactions in complexes whose driving factor is electrostatics (Fig. 4). For each type of complexes, the selected contour corresponds to the electron density at the bond critical point of the strongest halogen bond (see above) and the following features of MEP become obvious. The depleted MEP values forming the σ -hole areas [8] around the iodine atom which involved in multiple bonding become apparent clearly. For Type 2 complex, the extended areas of low MEP values attributed both to the N and S atoms are well seen. Mutual influence of electron localization areas on I atom and on the S atom – the secondary donor center, favors additional repulsion leading to decreasing of total bonding strength in the complex. Indeed, for such type of complexes we have observed the highest interaction energy – see Table 1. In the Type 1 and Type 2 complexes, the different orientations of low-MEP regions are noticeable for S atom. They correspond to the regions of sulfur electron lone pairs (LP) localization. In this case the difference in orientation of the MEP maxima for sulfur and quinoline ring is determined by the conformational factors.

Halogen bonding in complexes of N-heterocyclic with diiodine and multiple non-covalent interactions $N \cdots I \cdots N$ are discussed in [67–68], and the effect of the mutual influence of two allied donor centers is emphasized. For example, 1,10-phenanthroline ($pK_{B12} = 1.91$) as the base is weaker than pyridine ($pK_{B12} = 2.22$). Two lone pairs of two nitrogen atoms in 1,10-phenanthroline form extended area of the very low negative MEP ($V_{min}^S = -246.8$ kJ/mol) [38]. For pyridine, on the contrary, no deep minimum -159.0 kJ/mol has been found. These estimations do not fit the experimental values of the N-heterocyclic basicity. Thus, the MEP is not self-contained descriptor in estimations of halogen bonding strength in the case of the multiple non-covalent interactions.

3.3. Electron localization function

For the Type 1 complexes with multiple non-covalent interactions, the ELF (Fig. 5a) on the plane defined by I, N and S atoms reveals the following features. First, the LP maximum of N atom is strictly directed along the $N \cdots I$ bond path towards the region

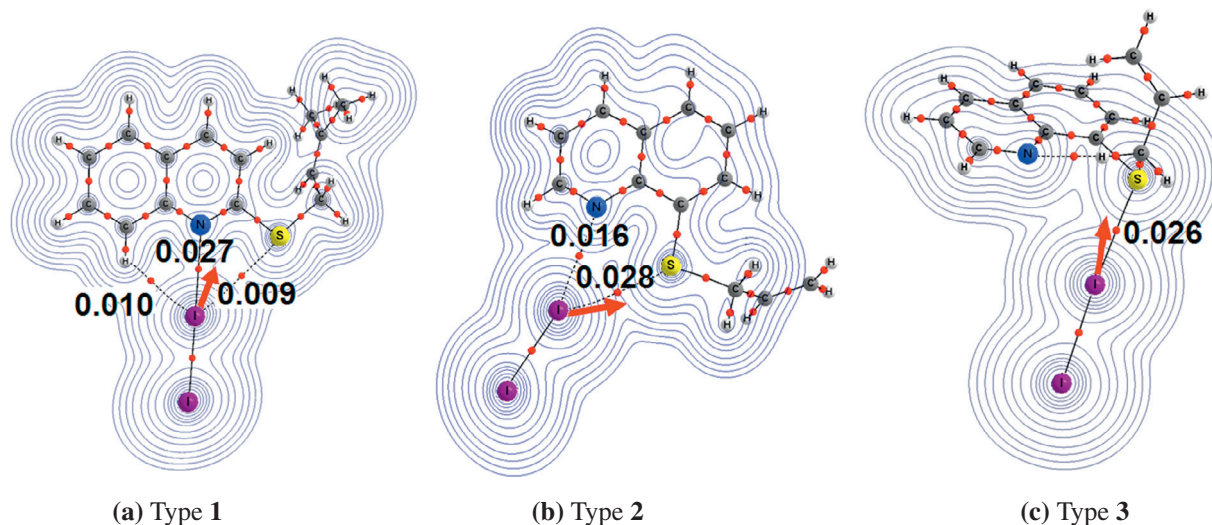


Fig. 3. The electron density in the iodine complexes superimposed with the bond paths, bond critical points and directions of the iodine atomic dipole polarization (red arrows): a) 2-prenylthioquinoline ($E_{int} = -5.98$ kcal/mol), b) 8-allylthioquinoline ($E_{int} = -4.05$ kcal/mol) and c) 8-allylthioquinoline ($E_{int} = -6.77$ kcal/mol).

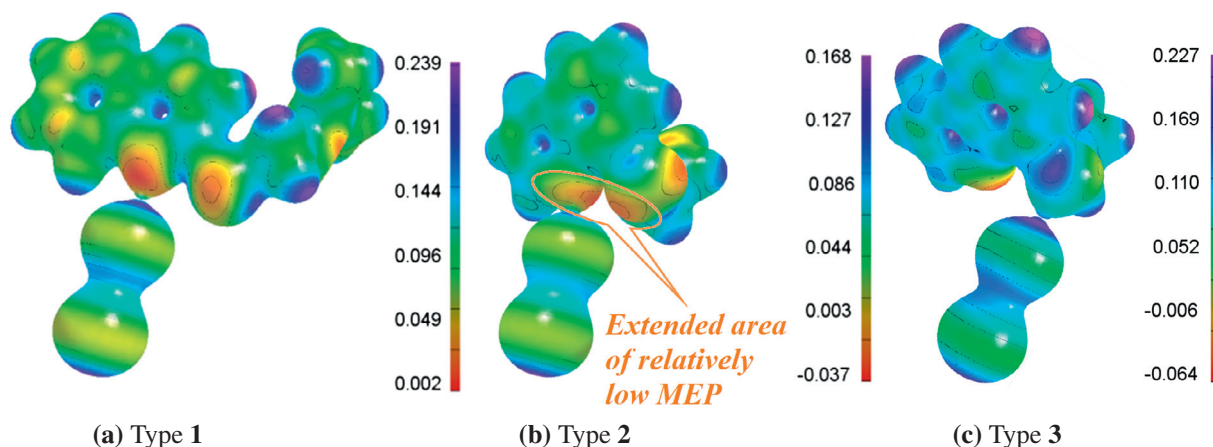


Fig. 4. MEP on surfaces of electron density, which correspond to electron density value at the bond critical point of the strongest halogen bonds (the range is of 0.020–0.030 a.u.): (a) 2-prenylthioquinoline (Type 1), (b) and (c) 8-allylthioquinoline (Type 2) and (Type 3).

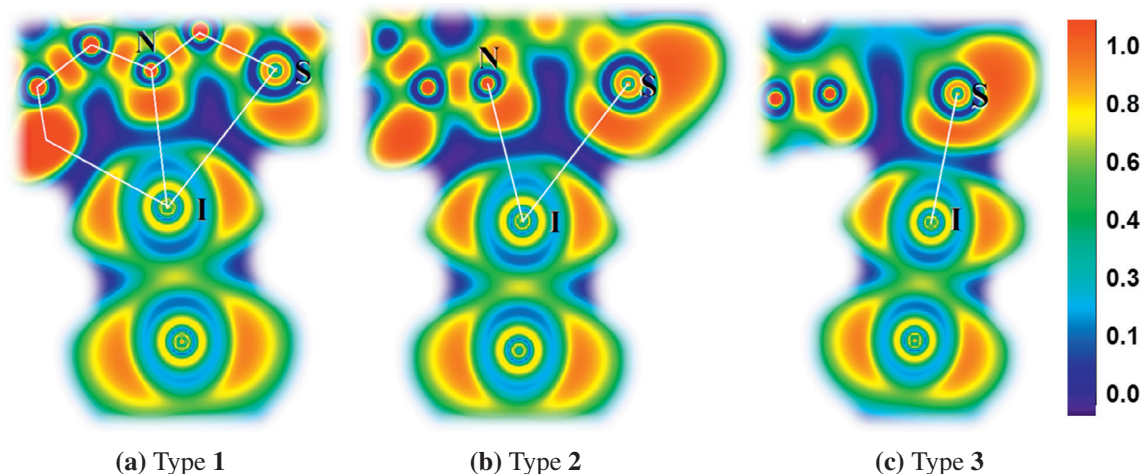


Fig. 5. ELF for (a) 2-prenylthioquinoline (Type 1), (b) and (c) 8-allylthioquinoline a) (Type 2) and (Type 3).

of low ELF area on the iodine atom. Similar orientation is observed for the conventional halogen bond in Type 3 complexes (Fig. 5c). Second, the mutual orientation of the high ELF values of iodine and sulfur atoms along the S...I bond path is observed.

For usually weaker bonding, the angular orientation of the ELF maximum of N atom to the area of low ELF values of iodine atom can be seen (Fig. 5b) for Type 2 complex. A small part of ELF maximum around S atom is orientated to the low ELF values of I atom. At the same time, the larger part of the sulfur ELF maximum is orientated towards the high ELF values of I atom.

The lower ELF area on the extension of the covalent bond I—I indicates the smaller shielding of the iodine nuclei in complexes in this direction, and the formation of the halogen bonding with the electron-donor center is the most efficient. The N atom still dominates, as the most effective electron donor center in complexes with multiple non-covalent interactions.

It should be noted that the ELF more clearly reflects the qualitative differences between N—C—S fragment in quinolines substituted in positions 2 and N—C—C—S fragment in quinolines substituted in positions 8 – see Fig. 6. Moreover, free rotation of the alkenyl fragment around the bond C_{Ar} —S not only determines the steric hindrances in I and N juxtaposition. The bend of chain C_{Ar} —S—C—C leads to the different disposition of ELF maxima on the S atom in 8-allylthioquinoline conformers. The fragment of 3D ELF presentation illustrates the different variants of back-to-

back orientation of electron pair localization on N and S atoms. In conformer A (Fig. 6a) the S atom lone pairs LP(S) of the tetragonal atom are oriented orthogonally to the plane of the quinoline ring. In conformer B (Fig. 6b), both sulfur lone pairs LP(S) and nitrogen lone pair LP(N) are in the plane of the quinoline system. The interaction energy in the complex is slightly lower (–4.73 kcal/mol) for conformer A, than for conformer B (–4.05 kcal/mol).

Thus, the ELF demonstrates the possible orientations and complementarity of σ -holes of iodine and electron-pairs in different donor centers. However, the qualitative pattern does not provide quantitative estimation of halogen bonding strength in these complexes under consideration.

3.4. Atomic dipole moments

We have recently shown [69] that in the complexes of small molecules the dipole polarization of the acceptor atom correlates with the stretching force constant [7] of a conventional halogen bond.

The directions of the atomic dipole moments on the iodine atom in complexes of all three types (Fig. 3) do not coincide with the bond path of halogen bonding. In most cases, these deviations are small; they are probably caused by the influence of the second donor center. We remind that in the investigated 2- and 8-alkenylthioquinolines both donor centers (N and S) are placed very close

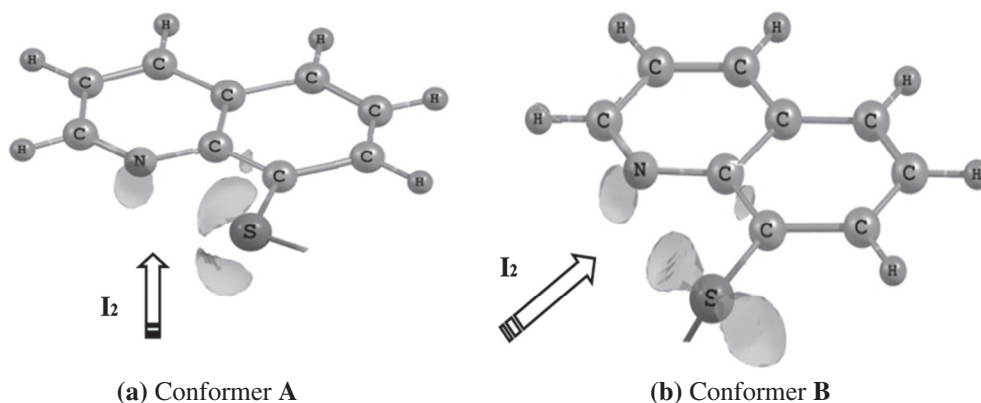


Fig. 6. Sulfur electron lone pair orientation expressed through 3D diagrams of ELF = 0.9 in 8-allylthioquinoline conformers. Arrows indicate the direction of the iodine attack.

to each other. If the axis Z is directed from acceptor atom (I) to donor atom (N or S) along the strongest halogen bond, the relationship between the component of iodine dipole moment $\mu_z(I)$ and the complex interaction energy E_{int} is detected. The magnitudes of the total iodine dipole moment $|\mu(I)|$ and its components along each axis are listed in Table 2. Atomic dipole moments of orthogonal components $\mu_x(I)$, $\mu_y(I)$ of acceptor atom do not provide any significant contribution to quantitative relationship with interaction energy in the complexes.

The two linear relations (E_{int} vs. $\mu_z(I)$) with nearly equal inclination angles are observed for the three types of investigated complexes with a sets of bond paths $N\cdots I$, $S\cdots I$, $I\cdots H$ (Type 1), $N\cdots I$, $S\cdots I$ (Type 2) and $S\cdots I$ (Type 3), as well as for additional set encountered in such structures $N\cdots I$, $I\cdots H$, $I\cdots H$ (Type 1) and $C\equiv C\cdots I$ (Type 3) (Fig. 7a). All conventional halogen bonds $S\cdots I$ and $C\equiv C\cdots I$ fit the red line, while both the three- and two-center interactions with iodine atom (such as Type 1 and Type 2) fit the green line. Thus, the iodine atom dipole polarization along the strongest halogen bond in complexes with multiple non-covalent interactions has systematically lower magnitudes $\mu_z(I)$ than those in the conventional halogen bonds (such as Type 3). This fact is in good agreement with the following conclusion: the participation of iodine atom in the multiple non-covalent interactions with several donor centers simultaneously reduces the dipole polarization along each particular bond.

According to Table 2, the intra-atomic component, $\mu_z^{\text{Intra}}(I)$, has negative values for the complexes with conventional bond (Type 3)

and positive values in case of iodine atom involved in the multiple interactions (Type 1 and Type 2). The behavior of bonding component of dipole moments in these complexes is opposite. When the interaction energy has comparable values, the bonding dipole moment $\mu_z^{\text{Bond}}(I)$ for atoms with multiple interactions is lower than that for conventional halogen bonds. Intra-atomic component of iodine is leveled under influence of differently oriented multiple interactions. It means that the multiple non-covalent interactions reduce the intra-atomic contribution in the total dipole polarization of iodine atom. However the bonding dipole-moment component quantitatively dominates the intra-atomic component.

We found that the separation into intra-atomic, $\mu_z^{\text{Intra}}(I)$, and the bonding dipole moment, $\mu_z^{\text{Bond}}(I)$, improves the relationship between the atomic dipole polarization and the interaction energy (Fig. 7b) and makes it quantitative. Two-factor equation that describes the correlation between the interaction energy and the components of the atomic dipole moment of the iodine has been established:

$$E_{\text{int}} = -[1.0 \pm 0.2] - [15.4 \pm 0.9]\mu_z^{\text{Intra}}(I) - [7.7 \pm 0.4]\mu_z^{\text{Bond}}(I) \quad (1)$$

The correlation coefficient is 0.98; standard error of estimations is 0.21; Fisher's factor is 197.2. It can be seen that the parameters in Eq. (1) increase the influence of intra-atomic dipole polarization factor $\mu_z^{\text{Intra}}(I)$ on the interaction energy in the complex. Probably it is a crucial factor in reducing total atomic moment and interaction energy in the complex.

Table 2

Atomic dipole moments (a.u.) and its components for the acceptor iodine atom for the set of alkenylthioquinolines–diiodine complexes.

Complexes	Intermolecular contacts	$\mu_x(I)$	$\mu_y(I)$	$\mu_z(I)$	$ \mu(I) $	$\mu_z^{\text{Intra}}(I)$	$\mu_z^{\text{Bond}}(I)$
2-Allyl-thioquiniline- I_2	$N\cdots I$, $S\cdots I$, $I\cdots H$	0.218	−0.002	0.540	0.582	0.048	0.492
	$N\cdots I$, $I\cdots H$, $I\cdots H$	−0.059	−0.378	0.394	0.549	0.027	0.367
	$S\cdots I$	−0.209	−0.053	0.691	0.724	−0.110	0.801
	$C\equiv C\cdots I$	−0.019	0.019	0.404	0.405	−0.137	0.542
8-Allyl-thioquiniline- I_2	$N\cdots I$, $S\cdots I$, $I\cdots H$	0.508	0.025	0.407	0.651	0.018	0.389
	$S\cdots I$	−0.025	−0.017	0.820	0.821	−0.081	0.901
	$C\equiv C\cdots I$	−0.023	0.016	0.422	0.423	−0.137	0.559
2-Propargyl-thioquiniline- I_2	$N\cdots I$, $S\cdots I$	0.203	−0.003	0.508	0.547	0.042	0.466
8-Propargyl-thioquiniline- I_2	$C\equiv C\cdots I$	0.480	−0.013	0.382	0.613	0.002	0.379
2-Prenyl-thioquiniline- I_2	$N\cdots I$, $S\cdots I$, $I\cdots H$	0.237	−0.002	0.570	0.617	0.054	0.516
	$S\cdots I$	0.023	0.002	0.759	0.759	−0.103	0.862
	$C\equiv C\cdots I$	0.021	0.000	0.526	0.526	−0.104	0.630
2-Metallyl thioquiniline- I_2	$N\cdots I$, $S\cdots I$, $I\cdots H$	0.225	−0.012	0.554	0.598	0.051	0.503
	$N\cdots I$, $I\cdots H$, $I\cdots H$	−0.031	0.378	0.338	0.508	0.011	0.326
	$S\cdots I$	0.015	−0.012	0.679	0.679	−0.116	0.795
	$C\equiv C\cdots I$	−0.024	0.010	0.515	0.516	−0.119	0.635

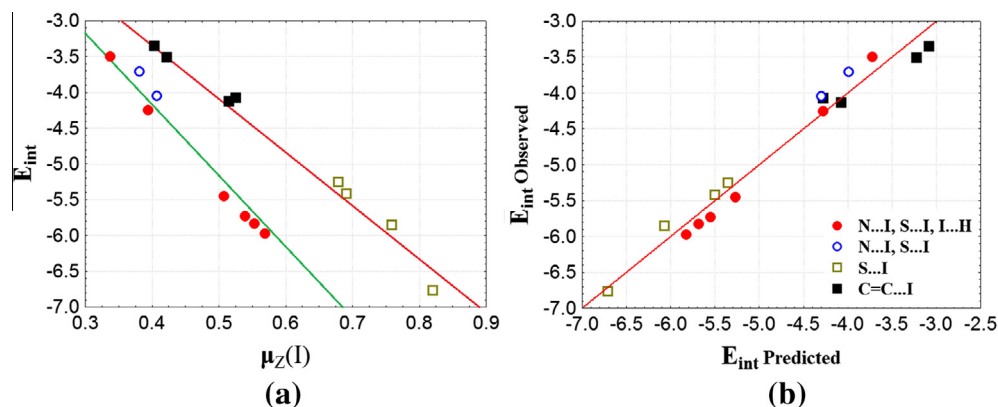


Fig. 7. (a) Two linear relationships between component of the total atomic dipole moment on iodine atom involved in the non-covalent bond, $\mu_Z(I)$, and interaction energy E_{int} in complexes; (b) Values E_{int} estimated (predicted) from Eq. (1) (see text) and directly computed (observed) in the B3LYP/6-311** approximation accounting for BSSE correction.

Thus, the dipole polarization is systematically lower in complexes with the bifurcated halogen bonds and the halogen bond with multiple non-covalent interactions. We suppose that iodine participation in the bifurcated halogen bonding with N and S atoms simultaneously leads to reducing the polarization along each particular N...I or S...I interaction.

3.5. Superposition of the gradient fields of electron density and electrostatic potential

Zero-flux condition $\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$ [17,59] highlights the ρ -basin boundaries of a bounded atom. The nuclei of neighboring atoms in any molecular system are also separated in the inner electrostatic field, $\mathbf{E}(\mathbf{r}) = -\nabla\varphi(\mathbf{r})$ by surfaces $P(\mathbf{r})$, satisfying the zero-flux condition $\mathbf{E}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = -\nabla\varphi(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$, $\forall \mathbf{r} \in P(\mathbf{r})$ [60,61], where $\mathbf{n}(\mathbf{r})$ is a unit vector normal to the surface $P(\mathbf{r})$ at \mathbf{r} . Each surface $P(\mathbf{r})$ defines the φ -basin of the electrically-neutral i th atom in a molecule, inside of which the electrons are attracted to the nucleus i [63].

The superposition of the $\nabla\rho(\mathbf{r})$ and $\nabla\varphi(\mathbf{r})$ gradient fields, supplemented by the bond paths in electron density, allows to elucidate the electrostatic forces acting in complexes [62–65] and to provide the specific information about kinds of each non-covalent interaction in a complicated system with multiple bonds. Indeed, if the part of electron density of electron-donor atom D falls into

φ -basin of the neighboring halogen atom, this part of electron density of atom D will be attracted to the halogen nucleus. This fact is equivalent to implementation of the basic feature of the halogen bond. Thus, failure to fulfill this condition casts doubts upon the possibility to define the observed interaction as a halogen bond.

The different dispositions of ρ - and φ -basin boundaries for atoms participating in multiple non-covalent interactions with iodine atom are shown in Fig. 8. The boundary of N ρ -basin invades the region of I φ -basin in all cases where N...I bond path exists. Such picture reflects that some fraction of the electron density of the N atom is attracted to the iodine nucleus for the charge compensation along the given direction of bonding. This fact corresponds to the fundamental definition of halogen bonding: a halogen atom should act as an acceptor of electron density. For the sulfur atom two different situations are observed. In complexes Type 2 and Type 3, the boundary of sulfur ρ -basin penetrates into the region of iodine φ -basin. It is a typical halogen bond S...I in both cases. So we can identify the multiple two-atomic iodine interactions in Type 2 complexes as bifurcated halogen bonds. In complex Type 1 the situation is opposite. Boundaries of the ρ - and φ -basins are not only close to each other, but ρ -basin of iodine is invading into the φ -basin of sulfur atom. That raises the question: can we identify this interaction as halogen bonding? Our observations do not allow us to define the interaction S...I in Type 1 complex as a halogen bond. It is rather van der Waals interaction

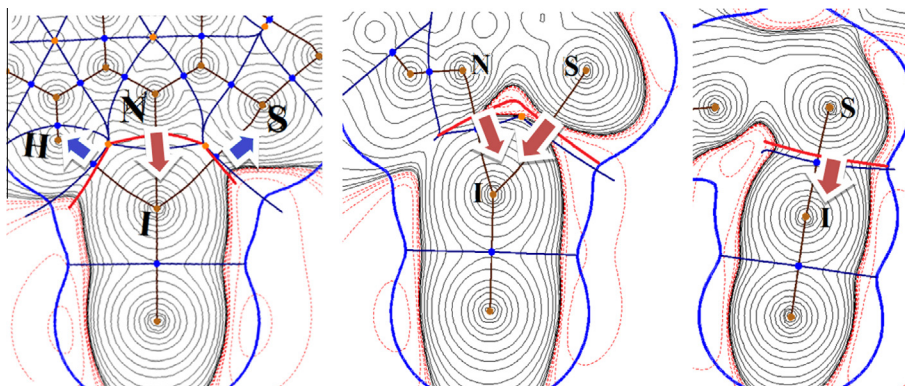


Fig. 8. Variations of boundaries of ρ - and φ -basins: (a) 2-prenylthioquinoline (Type 1), (b) and (c) 8-allylthioquinoline (Type 2) and (Type 3). (Brown arrows show the directions of the atomic electron attraction to I nucleus, which acts as acceptor. Blue arrows show the directions of attraction of valence electron shells of I atom to the neighboring nuclei which are involved in the secondary interactions. The separatrices of φ - and ρ -basins are showed by the red and blue solid lines, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

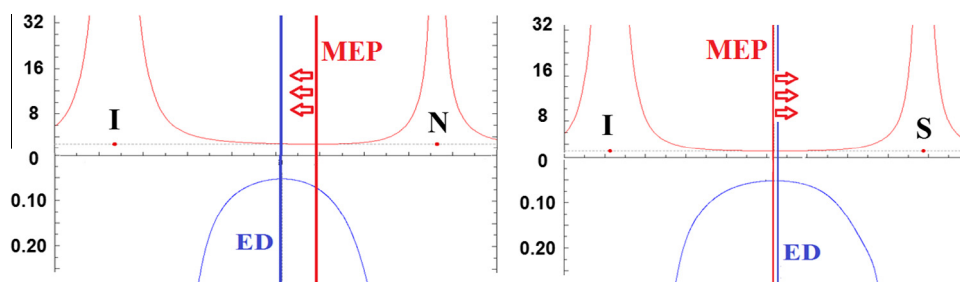


Fig. 9. Variations of MEP minima (red) and electron density minima (blue) along the halogen bond and other secondary interactions: (a) N...I halogen bond (Type 1), (b) I...S van der Waals interaction in 2-prenylthioquinoline (Type 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

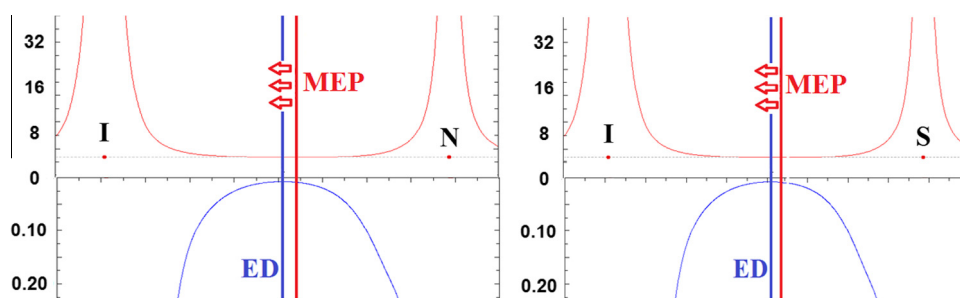


Fig. 10. Variations of MEP minima (red) and electron density minima (blue) along the halogen bond and other secondary interactions: (a) N...I halogen bond (Type 2), (b) S...I halogen bond in 8-allylthioquinoline (Type 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which is realized by S and I intra-basin redistribution of electron density (with corresponding change in its attraction to their own nuclei) and by dispersion mechanism.

The variation of ρ - and φ -basins boundaries illustrates the interatomic and intermolecular electrostatic interactions in complexes with non-covalent interaction and halogen bonding. Figs. 9 and 10 demonstrate even more clearly the variation of minima of MEP and electron density functions along the internuclear lines. Thus, not any halogen non-covalent interaction in the complexes with closely-located donor centers can be defined as a halogen bond.

The idea that every halogen-halogen interaction cannot be classified as halogen bonds recently has been consistently discussed in [70]. Moreover the latter statement was confirmed by the experimental data [71]: the different kinds of plastic deformation were observed for the compounds with different types of halogen interactions. Larger size and polarizability of iodine quite clearly illustrate principal difference between “type I” and “type II” halogen-halogen contacts [72]. Such a classification has become foundation for the classification of halogen interactions based on the geometric consideration since the first studies dedicated to this problem [73].

In our case, considering the multiple non-covalent contacts between iodine atom and donor atom D, we find an opportunity to distinguish the halogen bonding S...I and van der Waals interaction S...I with both electrostatic and dispersion components. However, in this case for contact D...I, where D=N, S, the geometrical principle is not manifested quite clearly. The organization and the principle of redistribution of the electron density play the key role in the differentiation of D...I interactions.

4. Conclusion

The most stable complexes of 2- and 8-substituted thioquinolines are formed if the diiodine molecule is oriented towards only one donor center – the S atom. In this case only one S...I halogen bond (Type 3) is formed on the “external” side of the molecule, without any harmful effect from the other donor center. The N

atom in quinoline ring experiences steric hindrances produced by the alkenyl group. The presence of alternative donor centers and the hydrogen atom in position 2 of substituted compounds leads to multiple N...I, I...S, and I...H interactions with diiodine molecule. Among all the non-covalent interactions in these Type 1 complexes only N...I interaction can be classified as a halogen bond. The strength of bonding in complexes with bifurcated halogen bonds N...I and S...I (Type 2) is lower than in the systems with one conventional halogen bond S...I or N...I. The electron shell repulsion of the iodine atom and the alternative donor center – the S atom – can serve as the reason of the bond strength decreasing. Thus, not each multiple intermolecular interaction, which involves the diiodine molecule, even if it is oriented along the direction of the extension of I–I covalent bond, can be referred to as a halogen bond.

We note that the analysis of superposition of gradient fields of electron density and electrostatic potential has allowed establishing the important differences between van der Waals interactions and halogen bonding in diiodine complexes with multiple interactions. On the qualitative level, the ELF perfectly copes with the demonstration of mutual orientation of the localized electron lone pairs of the donor atom and σ -hole on halogen atom, which is important for understanding the halogen bond features. Furthermore, the dipole polarization of iodine atom involved in the multiple interactions provides the quantitative estimation of the binding strength in the complexes.

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