Modern level for the prediction of properties of iodine-containing organic compounds: iodine forming halogen bonds*

E. V. Bartashevich,a* E. A. Grigoreva,a I. D. Yushina,a L. M. Bulatova,a and V. G. Tsirelsonb

aSouth Ural State University,
76 prosp. Lenina, 454080 Chelyabinsk, Russian Federation.
E-mail: bartashevichev@susu.ru
bD. I. Mendeleev University of Chemical Technology,
9 Miusskaya pl., 125047 Moscow, Russian Federation

The modern concepts on specific features of anisotropy of the electron density of valence shells of bound atoms and chemical bonds providing the successful description of the properties of halogen bonds formed by the iodine molecule in compounds with useful physicochemical properties are generalized in the review. The prognoses of basicity by the diiodine basicity scale for the nitrogen-containing compounds are illustrated. The regularities and peculiarities of shifting bands in Raman spectra of iodine-containing organic crystals are considered. The methodical and specific problems of modeling appeared when the electronic characteristics of the iodine compounds are estimated are briefly discussed.

Key words: iodine, halogen bonds, Raman spectra, diiodine basicity scale, electron density.

Introduction

The area of practical use of compounds containing molecular iodine is rather large. These compounds are used for both the solution of problems of organic synthesis1 and elimination of iodine deficiency in the human organism.2 The search for efficient and safe bacteriostatic3 and X-ray contrast4 compounds capable of reversibly binding with proteins5 is being continued, and the problems of efficient capture of radioactive iodine contaminants are being solved.6 The emerging practical tasks stimulate permanent interest in studies of the structural and physicochemical properties of new iodine compounds (see reviews7–10).

Organic N,S-containing compounds forming molecular complexes with I2 are of special interest from both fundamental and applied points of view. The complexes of molecular iodine with heterocycles based on derivatives of thiofulvalene, phenazine, and benzimidazole are promising for the development of conducting organic materials.11 Along with widely known thyroestatics, such as methimazole, carbimazole, and 6-n-propylthiouracil, potential antithyroid drugs based on heteroaromatic thioamides evoke increased interest.12 Thioamide group in the structure of heterocyclic compounds can provide antithyroid properties at the stage of iodine organification,4 which causes interest in studying the ability of thioamides to form complexes with molecular iodine.13,14 In these complexes, numerous mutually supplementing or competing noncovalent interactions attract special attention.15,16

Among the diversity of iodine-containing organic compounds, the class of polyiodides formed by organic cations and polyiodide anions I
\[\text{n}^{-}\quad (2 < n < 30)\] of various composition and crystal structure are especially interesting. Many practically important properties and spheres of application of compounds of this series are caused by the presence of molecular iodine17 as a fragment in the polyiodide anion composition. Among these compounds, there are representatives having bacteriostatic and iodophoric properties18 and electric conductance,19 existing in the form of ionic liquid,20 and applied as components of solar cells.21

The classification of polyiodides based on structural and spectral properties has been carefully developed up to present.7,22 Much less attention was given to the description of noncovalent interactions in polyiodide anions of complicated structure. Specific features of these iodine-containing compounds are determined, to a high extent, by the presence and properties of halogen bonds23,24 formed by the iodine molecule with various electron-donor centers of adjacent molecules in the liquid and solid phases.

A number of experimental methods, including Raman spectroscopy,22 thermal analysis methods,25 and UV spectroscopy,26–29 is used for understanding the nature
of binding in organic polyiodides and crystals of neutral iodine complexes and for the evaluation of their physicochemical properties. Raman spectroscopy is widely used for the identification of the main subunits in the polyiodide anion composition: triiodide anion, pentaiodide anion, and bound molecular iodine.\(^7\) The spectral methods are actively used when studying the properties of polyiodide structures and the features of their intermolecular interactions. For these compounds, Raman spectroscopy is substantially more informative method\(^30\) than IR spectroscopy, since, according to the selection rules, some low-frequency iodine—iodine vibrations become inactive in the IR spectra.\(^31\)

The questions of identification of organic compounds are tightly related to the problem of band assignment in vibrational spectra. The identification of molecular iodine in the composition of multicomponent organic compounds, in particular, in cocrystals of N,S-containing organic heterocycles, is efficiently solved using Raman spectroscopy.\(^22\) However, band assignment remains problematic for boundary cases when the I—I covalent bond is substantially elongated accompanied by the shift of the active Raman vibration band to the range characteristic of triiodide anions. In these cases, theoretical calculations of the Raman spectra can provide an additional information. A combination of theoretical and experimental approaches makes it possible to systematize information about changes in the position and intensity of molecular vibration bands.\(^32\) Therefore, quantum chemical simulation methods play important role in such studies.\(^33—35\) The modern quantum chemical calculations using the all-electron full-potential linearized augmented plane wave method\(^36—37\) were predominantly applied for inorganic halides\(^38—39\) and to study graphene-based hybrid materials doped by polyiodide anions.\(^40—41\) At the same time, the tight-binding approximation implemented in the CRYSTAL14 program\(^42—43\) is used rather often to describe the properties of iodine-containing molecular crystals.\(^44—46\)

When studying halogen bonds formed by an iodine molecule in complex compounds, it is necessary to apply a modern approach to the description of atomic and molecular interactions. Depending on specific features of anisotropy of the electron density distribution in valence shells of bonded atoms and characteristics of the formed bonds, the halogen atom can simultaneously be attracted to different adjacent atoms due to both electrophilic and nucleophilic regions of its valence shell. To describe these facts observed, one should take into account details of anisotropy of the electronic structure of the valence shells of the atoms. Thus, we speak about the study of the structure of matter at the subatomic level without using the shell atomic model. In this review, we present new achievements in the description of the properties of halogen bonds, in particular, in the iodine compounds.

For targeted search for iodophores it is important to understand the nature of iodine binding and estimations of the strength of this bond in tri- and polyiodides obtained from the calculated data of the electron density distribution, from its topological characteristics and from the calculated spectral characteristics,\(^18\) since these stages of modeling make it possible to predict a high probability of iodine sublimation from crystal and as well as the peculiarities of their thermal decomposition.\(^48—49\) This is especially significant, for example, for organic triiodides, because the formal empirical formula does not provide understanding of peculiarities of iodine atom agglomeration in a crystal, which occurs due to the formation of chains and networks of iodine—iodine halogen bonds enforced by the charge, and the existence of strongly asymmetric triiodide anions.

Thus, useful physicochemical and pharmaceutical properties of the iodine-containing compounds give reasons for the development of methods for modeling their structures at different levels of the structure: from subatomic to single-crystal, and investigation of binding sites of proteins.\(^50\) In turn, the substantiated refinement of quantitative relationships “structure—property” is the most important stage in the way for prediction of characteristics of compounds and for providing the recommendation for synthesis and functionalization of novel promising materials. The concepts on the characteristics of the electron density related to anisotropy of the electron distribution in valence shells of atoms, which provide the successful description of molecular interactions and properties of halogen bonds formed by an iodine molecule in compounds with interesting physicochemical properties, are generalized and methodical and specific problems of modeling arising when evaluating the electronic characteristics of iodine compounds are discussed in this work.

**Criteria and tools for identification of halogen bonds of iodine**

The definition of halogen bond\(^23\) was formulated in the IUPAC nomenclature: this bond is interpreted as noncovalent interaction in which halogen acts as an electron density acceptor with respect to any other atom. This definition contains a very flexible criterion that makes it possible, nevertheless, to distinguish this interaction from the van der Waals one. One should speak about halogen bond only in the case of attraction between the electrophilic region of the halogen atom and nucleophilic region of another atom. Thus, the subatomic level of analysis of matter structure is considered.

The formal definition of halogen bond does not restrict our consideration by specific frameworks of geometric characteristics, which were urgent for early classifications of halogen—halogen interactions.\(^51\) On the one hand, the length of the shortened interatomic contact
and ranges of angles between the covalent and halogen bonds are convenient for express estimations of the properties. On the other hand, structural diversity of halogen-containing compounds and evolution of methods for structure refinement permanently change reference parameters of comparison. In addition, the classification of halogen—halogen interactions is being enlarged. For example, along with interactions of types I and II,\textsuperscript{51,52} interactions of the Hal\textsubscript{3} type\textsuperscript{53—55} are observed in molecular crystals when halogen atoms are located at the vertices of an almost equilateral triangle. It should be mentioned that the modern definition of halogen bond\textsuperscript{23} gives freedom for searching for the descriptor that would confirm the nature of these interactions, indicating a significant contribution of electrostatic forces.\textsuperscript{56} Therefore, the problem arises for choosing tools that allow one to adequately examine the electronic properties of components of the system.

The complexes with halogen bonds are characterized\textsuperscript{57} as compounds with “interactions controlled by electrostatics.” The authors\textsuperscript{58} agree with this definition, since the electrostatic energy component makes the highest contribution determining attraction of molecules in the complex. The molecular electrostatic potential (MEP) \( \phi(r) \) mapped on the isosurface surrounding the molecule with the electron density \( \rho(r) \) was proposed\textsuperscript{56} for the clear description of the ability of halogens to act as electron density acceptors. The contour \( \rho(r) \) close in value to the contour of the van der Waals surface of the molecule and equal to 0.001 au is chosen for this purpose. This approach gives the clear pattern of the region of enhanced values of the \( \rho(r) \) function along the covalent bond of halogen, which is named the \( \sigma \)-hole.\textsuperscript{59} In the series of halogens, the \( \sigma \)-hole is manifested most strongly for iodine atoms because of their high polarizability.\textsuperscript{60}

However, the elucidation of anisotropy of the electrostatic potential \( \phi(r) \) on the interatomic and van der Waals surface in complexes and crystals have a number of restraints. First, the absolute values of \( \phi(r) \) cannot be quantitatively compared for structures with different empirical composition. For example, for chalcogenazino(olo)-quinolinium series,\textsuperscript{61} the \( \phi(r)_{\text{max}} \) value on the \( \sigma \)-hole of the covalently-bonded iodine atom did not allow even qualitative assignment of these cations to the group of cations capable of acting as donors of halogen bond with triiodide anions in crystals. Second, for a complex or a crystal, \textit{i.e.}, for the system in which noncovalent binding has already taken place, the MEP on the \( \rho(r) \) isosurface can lose its clearness because of the influence of adjacent atoms. For instance, it is seen for triiodide anions having a pronounced \( \sigma \)-hole in the isolated state, but its traces disappear if the same \( \rho(r) \) contour is analyzed in crystals of triiodides and polyiodides.\textsuperscript{35}

Unlike the maps on the isosurface, the superposition of gradient fields \( \phi(r) \) and \( \rho(r) \) retains its informativity for crystals.\textsuperscript{35} Both contour maps of gradients of the functions applied\textsuperscript{44} for crystalline \( I_2 \) and constructed using the WinXPRO program\textsuperscript{62,63} and a simpler representation for analysis of the superposition of boundaries of atomic basins in the electron density and electrostatic potential performed for molecular complexes (Fig. 1, \textit{a}) can be used.\textsuperscript{64} This procedure is available for any level of structural modeling: from isolated complexes to crystals, the wave functions of which were obtained with allowance of periodical boundary conditions. A comparison of the queue of appearance of one-dimensional minima of the \( \upsilon(r) \) and \( c(r) \) functions between the atoms bonded by the halogen bond (see Fig. 1, \textit{b}) remains informative in simplest cases. If \( \upsilon(r)_{\text{min}} \) precedes \( c(r)_{\text{min}} \) along the line of interatomic interaction \( B..I \) from atom \( B \) (electron donor) to atom \( I \) (electron acceptor), this means that the fraction of electrons formally belonging to atom \( B \) is attracted to the core of atom \( I \), and this is the main attribute of the formed halogen bond.

It was demonstrated\textsuperscript{24,35} that one of the tools that accessibly and clearly elucidates the property of the iodine—iodine halogen bond is the one-electron potential (OEP)\textsuperscript{65}

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

The OEP function is characterized by the alternation of regions of negative and positive values corresponding to the shell atomic electron structure. For the Laplacian \( \nabla^2 \rho(r) \), this alternation shows the regions of concentration and depletion of the electron charge density.\textsuperscript{66} However, for atoms of medium periods, for example, in crystalline \( Cl_2 \), the Laplacian \( \nabla^2 \rho(r) \) illustrates the mutual orientation of the regions of charge concentrating and depleting in the external electron shells,\textsuperscript{67} whereas the possibility of using the Laplacian \( \nabla^2 \rho(r) \) as a clear criterion of halogen bond is lost for crystalline \( I_2 \). The matter is that the fifth from the core minimum of the \( \nabla^2 \rho(r) \) function of iodine atom remains in the region of positive values,\textsuperscript{68} which does not allow one to conclude about the concentration/deconcentration of electron density in the external electron shell of iodine atom. Therefore, the Laplacian of electron density is not suitable as a criterion for the identification of a halogen bond involving iodine.\textsuperscript{69} Note that iodine manifests this behavior of the \( \nabla^2 \rho(r) \) function regardless of the choice of functional and basis set. The exceptions are only some approximations taking into account relativistic effects, for example, the basis set constructed using the Douglas—Kroll—Hess formalism.\textsuperscript{70,71}

The one-electron potential function is free of this drawback. The utmost minimum of the OEP of an isolated iodine atom lies in the region of negative values and is close to the position of the utmost maximum of the electron localization function\textsuperscript{72} (ELF) (Fig. 2, \textit{a}). This
region corresponds to positive values of the density of the local kinetic energy of the electron and can be used as an indicator of details of the external electron shell.

It was examined how the shell structure of two iodine atoms undergo changes if they are involved in the common halogen bond in crystalline (3E)-8-chloro-3-iodomethylidene-2,3-dihydro-1,4-oxazino[2,3,4-ij]quinolinium triiodide (EJUPOQ) (Fig. 2, b). When examining the migration from the position of the same I(1) atom along the I(1)...I(2) halogen bond in which it is involved as an electron acceptor and along the weak van der Waals interaction I(1)...I(3), it can be seen that the external electron shell of the I(1) atom is significantly compressed in the direction in which this atom acts as an electron acceptor and is broadened in the direction in which it is an electron donor.

The role performed by each atom in the considered noncovalent interaction can be identified from the char-
characteristics of 1D extremes of the OEP in the region of external atomic shells of pairs of iodine atoms bound by the typical halogen bond. In other words, it can be revealed whether the specific iodine atom is a donor or acceptor of electrons, which is important for halogen bond identification in crystals with multiple interactions of iodine atoms, which are entangled in the network of non-covalent interaction formed by polyiodide anions. As shown by the analysis,\textsuperscript{35,73} the appearance of the minimum of the OEP function with negative values should be expected for the electron donor iodine atom in the region of external valence shell, whereas positive values should be expected for the OEP minimum fifth from the core (Fig. 3).

It seems noteworthy to evaluate the possibility of using the Laplacian values at the saddle points of the electron density\textsuperscript{66} (bond critical points) as quantitative descriptors of bond properties. When considering tendencies for changes in $\nabla^2 \rho(r_b)$ in a wide series\textsuperscript{74} of covalent bonds, halogen bonds, and weak van der Waals interactions I–I/I…I, it is seen that $\nabla^2 \rho(r_b)$ is not an unambiguous function of the corresponding interatomic distances\textsuperscript{75} (Fig. 4).

Positive values of $\nabla^2 \rho(r_b)$ increase with the elongation of bond lengths for covalent bonds elongated due to the interaction with the environment in crystals and for triiodide anions. However, an opposite tendency is observed for all noncovalent interactions, from halogen bonds strengthened by the charges I–…I to weak van der Waals interactions I…I: the $\nabla^2 \rho(r_b)>0$ values decrease in the range from ~3.4 to ~5.5 Å. For instance, approxi-
mately the same value \( \nabla^2 \rho (r_b) \sim 0.022 \) au is typical of the weak noncovalent interaction with a distance of 4.020 Å in crystalline 1-iodomethyl-1,2-dihydro-[1,3]thiazolo-[3,2-4]quinolinium polyiodide (DOWMEJ)\(^\text{76}\) and of the bond in the iodine molecule with a distance of 2.830 Å involved in the chain motif in crystalline \((E)-3\text{-iodomethyl-}
oline[2,3,4-ij]quinolinium polyiodide (ZOJPAR)\(^\text{7,78}\). Thus, the use of \( \nabla^2 \rho (r_b) \) at the critical points of electron density as a descriptor in relationships “structure—property” is impossible, because the dependence of the \( \nabla^2 \rho (r_b) \) on interatomic distances is ambiguous.

Combination of calculated and experimental Raman spectra in investigation of the nature of iodine bonds

The identification of molecular iodine in the composition of multicomponent organic compounds, in particular, in cocrystals of N,S-containing heterocycles, is efficiently solved using Raman spectroscopy.\(^\text{22}\) This method is most informative with respect to the properties of iodine—iodine bonds\(^\text{31}\) and is sensitive to effects of noncovalent interactions involving iodine. The characteristic range of wave numbers in the Raman spectra for the vibration band of the iodine molecule\(^\text{7}\) bound in crystal corresponds to 140—180 cm\(^{-1}\). The electron density redistribution during the formation of halogen bonds is accompanied by the shift of wave numbers of the \( \nu (I—I) \) stretching vibration toward the range of lower values. The substantial shifts of the wave numbers relative to the reference band in iodine crystal\(^\text{7} \) (180 cm\(^{-1}\)) to lower values indicates a higher involvement of the iodine atom in the halogen bond and the respective weakening of its covalent bond. As a rule, the weakening of the covalent bond of iodine detected in the Raman spectra is a consequence of the halogen bond involving I\(_2\) molecule. Therefore, the shift of the vibration band of bound iodine relative to the reference band in iodine crystal indirectly characterizes the strength of the halogen bond.

Examples of shifting beyond the limits of the designated range of wave numbers characteristic of the iodine molecule to a range of 100—140 cm\(^{-1}\), which corresponds to the symmetric vibration of triiodide anion, were reported.\(^\text{79}\) These observations possibly indicate the formation of a single three-center system of the \([S—I—I]\) type in which the covalent and halogen bonds of iodine become close in length and their vibrations shift to the range non-typical of I\(_2\).\(^\text{22}\) A correlation between the wave number of the \( \nu (I—I) \) stretching vibration and \( \delta (I—I) \) bond length presented earlier\(^\text{79}\) makes it possible to distinguish the threshold value at which the linear character of the interaction \(\nu (I—I) vs \delta (I—I)\) is violated. This value corresponds to a distance of 2.86 Å between iodine atoms\(^\text{79}\) and can serve as a criterion for the formation of the three-center system, including such a system as triiodide anion. Another criterion derived on the basis of the ratio of indices of electron delocalization in asymmetric and symmetric triiodide anion\(^\text{80}\) makes it possible to distinguish halogen bonds strengthened by the I—...I—I bond and bonds in the typical three-center system \([I—I—I]\). Along with the classification of polyiodides on the basis of structural characteristics proposed in the review,\(^\text{7}\) the spectroscopic classification\(^\text{22}\) is widely used for the compounds containing bound molecular iodine. Based on the data on bond lengths and experimental Raman spectra, it is proposed to divide iodine-containing complexes into three types of adducts: types \([B—I—I]\) (A), \([B—I—I]\) (B), and \([B—I—I]^{—}\) (C), where B is the electron donor. Types A, B, and C can be considered as stages corresponding to the movement along the reaction coordinate from the initial state of the electron donor and isolated molecule I\(_2\) to the corresponding salt \((B—I—I)^{—}\) formed as the final product. As a rule, an inverse dependence between the shortening of the length of noncovalent interactions B...I\(_2\) and elongation of I—I bonds, which is exponential, is observed.\(^\text{22}\) The types of binding A and C correspond to two flat slope regions of the exponent, whereas compounds with binding according to type B correspond to points in the inflection of the exponent. For the three-center systems \([B—I—I]\), the corresponding vibrations B—I and I—I, as a rule, interact with each other. The structures I—...I\(_2\) (see Fig. 2, b) and I\(_3\)...I\(_2\) (Fig. 5, b) are classified as adducts of type A in the series of polyiodides. In this case, the Raman spectra exhibit only the band of bound iodine.\(^\text{81,82}\) In addition, the symmetric vibration band at 100—120 cm\(^{-1}\), which is characteristic of triiodide anions, is not detected for the pentaiodide structures of the I\(_2\)...I—I type.\(^\text{7}\)

The combined consideration of theoretical and experimental Raman data makes it possible to solve a number of such difficult problems as, e.g., vibration assignment in the case of boundary values of wave numbers. Good correspondence of calculated and experimental characteristics of the Raman spectra serves as an additional criterion for reliability of electronic descriptors used in the structure—property problems.

Let us compare the calculated and experimental wave numbers of the stretching vibration of the iodine molecule and corresponding lengths of halogen bonds for a series of crystal structure selected from the CSD.\(^\text{83}\) This sampling (Table 1) supplemented by the compounds studied\(^\text{75}\) contains both molecular iodine complexes with interactions of the S...I\(_2\) and \([S—I—I]\) types and tri- and polyiodides of the alkylammonium and chalcogenazolo-(azino)quinolinium series containing bound molecular iodine. All ranges of bond lengths of iodine and their characteristic vibration ranges are presented in Table 1: 100—120 cm\(^{-1}\) in triiodide anions, 100—140 cm\(^{-1}\) for compounds of the \([S—I—I]\) group, 140—180 cm\(^{-1}\) for...
neutral complexes with molecular iodine, and finally, 180 cm\(^{-1}\) for crystalline iodine itself.

The calculated wave numbers of stretching vibrations of iodine obtained in the isolated complex approximation are systematically overestimated, as a rule, compared to the experimental data: the average deviation is 21 cm\(^{-1}\), the root-mean-square deviation is 15 cm\(^{-1}\), and the maximum one is 51 cm\(^{-1}\). The correlation coefficient between experimental and calculated wave numbers obtained in the isolated complex approximation is rather low being 0.73. At the same time, the "strong bond" approximation for crystal accomplished in the CRYSTAL14 program\(^{42,43}\) provides a better agreement with experimental data than the MO LCAO approximation for the isolated complexes.

The average deviation of the wave number for \(d(I—I)\) is 4.7 cm\(^{-1}\), the maximum one is 15.7 cm\(^{-1}\), and the correlation coefficient between experimental and calculated data is 0.97 (Fig. 6, a).

It can be assumed that the main reason for insufficient accuracy of the spectral data reproducibility for molecular iodine complexes is a substantial distinction of the geometry in a crystal and equilibrium geometry of the complex extracted from crystalline continuum. For instance, that data presented in Table 1 show the systematic overestimation of halogen bond lengths in isolated complexes by 0.3 Å on the average. The maximum deviation of the S…I halogen bond length was 0.5 Å for the 5-chlorobenzothiazole-2-thione•I\(_2\) complex (HAFLEG),\(^{88}\)

![Fig. 5. (a) Raman spectrum of polyniodide ZOJPAR\(^{77,78}\) (114 and 134 cm\(^{-1}\) are symmetric and antisymmetric stretchings of triiodide anion, respectively; vibration of iodine molecule is 172 cm\(^{-1}\)); (b) fragment of the structure of the I\(_1^–...I_2^–...I_3^–\) zigzag in polyniodide ZOJPAR.](image-url)

### Table 1. Experimental and calculated wave numbers of stretching vibrations \(\nu(I—I)\) obtained in different approximations and deviations \(\Delta d(S…I)\) and \(\Delta d(I—I)\) of the calculated bond lengths from the values observed in crystals

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_{\text{calc}}/\text{cm}^{-1})</th>
<th>(\nu_{\text{exp}}/\text{cm}^{-1})</th>
<th>(\Delta d(S…I)/\Delta d(I—I)/\text{Å})</th>
<th>Referral code</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,5-Dimethylsulfonyl-1,3-dithiolan-2-thione•I(_2)</td>
<td>172.0</td>
<td>135.0</td>
<td>–0.38/–0.01</td>
<td>BIMMEP(^{84})</td>
</tr>
<tr>
<td>N-Methylbenzothiazole-2-thione•I(_2)</td>
<td>169.9</td>
<td>160.5</td>
<td>–0.26/–0.03</td>
<td>DAXXQ(^{13})</td>
</tr>
<tr>
<td>1,3-Dithiacyclohexane-2-thione•I(_2)</td>
<td>172.9</td>
<td>136.5</td>
<td>–0.37/0.00</td>
<td>DAYBOT(^{85})</td>
</tr>
<tr>
<td>N-Methyl-1,3-thiazolidine-2-thione•I(_2)</td>
<td>168.9</td>
<td>133.5</td>
<td>–0.40/0.07</td>
<td>DIJYUR(^{86})</td>
</tr>
<tr>
<td>1-Methylimidazolide-2-thione•I(_2)</td>
<td>161.7</td>
<td>141.0</td>
<td>–0.38/0.13</td>
<td>EGEREO(^{87})</td>
</tr>
<tr>
<td>6-Propyl-2-thiouracil•I(_2)</td>
<td>151.0</td>
<td>141.0</td>
<td>–0.25/–0.01</td>
<td>HAFLAC(^{88})</td>
</tr>
<tr>
<td>5-Chlorobenzothiazole-2-thione•I(_2)</td>
<td>172.1</td>
<td>139.6</td>
<td>–0.46/0.11</td>
<td>HAFLEG(^{88})</td>
</tr>
<tr>
<td>5,5-Dimethylimidazolidine-2,4-dithione•I(_2)</td>
<td>168.0</td>
<td>152.0</td>
<td>–0.30/–0.02</td>
<td>KUWDEL(^{89})</td>
</tr>
<tr>
<td>5,5-Dimethyl-2-thiooximidazolidin-4-one•I(_2)</td>
<td>167.0</td>
<td>158.0</td>
<td>–0.26/–0.04</td>
<td>KUWDOV(^{89})</td>
</tr>
<tr>
<td>1,3-Dithiolan-2-thione•I(_2)</td>
<td>172.9</td>
<td>149.5</td>
<td>–0.39/0.01</td>
<td>PEKJY(^{91})</td>
</tr>
<tr>
<td>4,5-Bis(2-nitrobenzylthio)-1,3-dithiole-2-thione•I(_2)</td>
<td>164.8</td>
<td>162.2</td>
<td>–0.20/–0.06</td>
<td>TIJLUU(^{90})</td>
</tr>
<tr>
<td>1-(2-(N,N-Dimethylammonio)ethyl)-1H-tetrazole-5-thiolate•I(_2)</td>
<td>155.0</td>
<td>112.5</td>
<td>–0.27/0.05</td>
<td>WURGEW(^{87})</td>
</tr>
<tr>
<td>1H-Benzothiazole-2-thione•I(_2)</td>
<td>170.9</td>
<td>147.0</td>
<td>–0.34/0.26</td>
<td>XOVRJ(^{92})</td>
</tr>
</tbody>
</table>
plexes and triiodide anions I$_3^-$ with close or the same bond lengths.

The low value $\eta(r_b) = 0.38$ is observed for the 1-(2-dimethylammonioethyl)tetrazole-5-thiolate $\cdot$ I$_2$ (WURGEX) structure$^{87}$ close to type C. The spectrum of this compound exhibits one band at 104 cm$^{-1}$ falling in a range of typical symmetric vibrations of triiodide anion, indicating the loss of the covalent character of the bond in I$_2$ with the length $d$(I$\cdot$I) = 3.031 Å.

The value $\eta(r_b) = 0.5$ corresponding to the state of homogeneous electron gas can be named the conventional boundary in Fig. 6, b. Our observations$^{95}$ make it possible to note that for a series of organic triiodides the character of the iodine—iodine bond changes at $\eta(r_b) < 0.5$, which is manifested in the spectral and thermal properties of these crystals: the bands typical of triiodide anion in the Raman spectra are shifted,$^{48}$ and the early stage of iodine sublimation on heating can appear.$^{49}$

The found interrelations between active vibrations in the Raman spectra and topological characteristics based on the calculated electron density in crystals are useful for the classification of various types of binding in iodine-containing systems, appropriate for quantitative estimation of spectral characteristics, and suitable in procedures of assignment of experimentally observed bands in Raman spectra. In this case, the predictive aspect is the possibility of estimating the strength of binding and retention of iodine, which is reflected in the description of iodophoric properties of organic compounds,$^{18}$ the possibility of prognosis of iodine sublimation from crystals on heating, and specific features of thermal decomposition of polyiodides depending on the composition and structural peculiarities of polyiodide anion.$^{48,77}$

### Basicity prediction for organic compounds by the diiodine basicity scale

For the formation of the B...I$_2$ complex by iodine molecule and organic base, the basicity factor by the diiodine basicity scale ($pK_{B(I2)}$)$^{96}$ is determined by the equilibrium constant $K_c$

$$pK_{B(I2)} = \log K_c.$$

The large array of experimental data$^{96}$ allows one to perform correlation analysis between the basicity and structural properties of compounds and to predict basicity for the new synthesized compounds. Interrelations of $pK_{B(I2)}$ to such factors as peculiarities of the base structure, the nature of the electron-donating center, multiple noncovalent interactions, steric effects, and effect of the solvent and temperature were shown.$^{96-98}$ The authors$^{99}$ used the methods of reference vectors$^{100}$ and multiple linear regression to develop a predictive quantitative model for basicity by the diiodine basicity scale applying...
the characteristic fragments of molecules as quantitative descriptors.

The N…I halogen bond is formed between the basic center and iodine molecule, and its electronic characteristics can act as quantitative descriptors of basicity by the diiodine basicity scale: the stronger the halogen bond with iodine, the more stable the complex and the higher basicity. Therefore, to predict \( pK_{B(I_2)} \) in the series of substituted pyridines, it was enough to characterize halogen bonds using, for instance, electron delocalization indices or topological characteristics of electron density. This approach makes it possible to take into account directly the influence of solvents, reveals steric hindrances for the formation of a bond with the basic center, and estimates enhancing or weakening effects of multiple interactions with \( I_2 \) molecule in a complex. The halogen bond N…I is weakened, as a rule, under the influence of multiple noncovalent interactions, for example, hydrogen bonds I…IH in iodine complexes with aliphatic amines, which shows quantitatively the decreasing of the electron delocalization index.

Note that the properties of only one halogen bond are insufficient for qualitative prognosis of basicity when different classes of nitrogen-containing organic bases are considered in combination (Fig. 7). Although the characteristics of the N…I halogen bond are sensitive to the formation of additional noncovalent interactions in a complex with iodine, aliphatic amines need to take into account their structural diversity owing to their conformational mobility.

**Conclusion**

It can be stated that the subatomic level of the matter structure provides a wide arsenal of tools for reliable recognition of halogen bonds regardless of the choice of the calculation approximation. The extremes precede of the electron density and electrostatic potential functions along the line of interatomic interactions, which comes from the electron shell structure, and the values and signs of the one-electron potential in the minima corresponding to these shells. Note that the electron density Laplacian is least informative for revealing halogen bonds of iodine, because it cannot show specific features of the shell structure of heavy atoms.

The modern subatomic level of prediction of the properties of substances provides new possibilities for enlargement of the range of efficient electron descriptors, such as topological characteristics of functions based on electron density, operating in quantitative relationships "electronic structure—property of substance." For example, the approach proposed for prognosis of the basicity indicators by the diiodine basicity scale for a number of nitrogen-containing organic compounds is based on the description of the properties of the halogen bonds formed by the iodine molecule with the basic site. In this case, the electron localization indices or topological properties of electron density determined for the formed halogen bonds act as subatomic descriptors.

The use of Raman spectroscopy for the classification of various types of iodine bonds, including those in new crystals of the series of chalcogenazolo(azino)quinolone tri- and polyiodides was demonstrated. The regularities of the behavior of the calculated characteristics of the Raman spectra are successfully used in procedures of assignment of the experimentally observed bands of iodine subunits in the structures of polyiodide anions of complicated composition. The iodophoric properties of organic polyiodides caused by the presence and strength of binding of \( I_2 \) in the composition of polyiodide anions can be predicted on the basis of the values of electron localization function. Such a descriptor calculated at the critical
point of the bond in the electron density for iodine—iodine interactions in crystals is quantitatively interrelated to the characteristics of the experimentally obtained Raman spectra of the compounds containing iodine molecules.

To conclude, efficiency of the modern level of analysis for revealing properties of halogen bonds of iodine is rather high at the stages of both interpretation of the results and modeling of novel compounds.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 17-03-00406) and the Government of the Russian Federation (resolution no. 211 of March 16, 2013, agreement no. 02.A03.21.0011).

References


Received March 28, 2017; in revised form July 5, 2017