BOND ORDER INDICES OF IODINE:
FROM MOLECULAR COMPLEXES TO CRYSTALS

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A quantitative model to estimate bond order indices in molecular crystals is proposed for bound iodine atom I—X/I…X, where X = I, N, S. The model is based on a quantitative relationship between electron delocalization indices and bond orders. The correlations of bond orders with electronic potential and kinetic energy densities at bond critical points are found for molecular complexes and the applicability of parametric equations to the cases of molecular crystals is verified. The capacity and limitations of the models are shown.

INTRODUCTION

The sophisticated structural organization of multicomponent molecular compounds being interesting for practical applications stimulates the development of methods to search and characterize structure-forming non-covalent interactions. This is especially important at the starting stages in the design of new materials and the prediction of their functional properties determined by diverse features of the binding of molecules and ions in the condensed state. One of the tools applied for this purpose and having a clear physical base is the electron delocalization indices [1, 2] which enable the evaluation of bond order indices as a simple and universal characteristic of atomic interactions.

The problem of estimating the characteristics of chemical bonds of the iodine atom, to which this work is dedicated, has a number of practical applications. Complexes of molecular iodine with organic compounds have a structural diversity and are widely used in practice [3]. Drugs whose composition contains heteroaromatic thioamides form complexes with molecular iodine. This ability of stable and directed non-covalent interactions underlies the prediction of their antithyroid activity [4]. Iodine complexes act as intermediates in the iodine cyclization reaction [5], the electronic structure of these complexes being a useful information source and explaining the preferred directions of reactions in the synthesis of novel drugs. Iodine-containing compounds are used as ionic fluids [6, 7] and nanomaterials [8, 9].

In a quantitative description of the properties of chemical bonds and the features of intermolecular interactions in molecular crystals an approach based on partitioning the molecule space into atomic fragments within the Quantum Theory of Atoms in Molecules and Crystals (QTAIMC) is very productive [10—13]. According to QTAIMC [10, 11], atomic basins A in molecules and crystals are defined as space areas A confined by the surfaces of the zero electron density gradient and encompassing nuclei [14]. If in the theory of molecular orbitals the formal bond order is determined by the number of electrons on bonding and antibonding orbitals [15, 16], then QTAIMC proposes the electron delocalization index $\delta(A, B)$ as an analogue [1, 2]. The electron delocalization index $\delta(A, B)$ was first

introduced by Bader as a measure of the implementation of the electron correlation interaction [1]; later it has been used to estimate bond orders [2]. In the single-determinant approximation for the many-electron wave function this index determines the number of electrons distributed between two atomic basins A and B as

$$\delta(A,B) = 4 \sum_{i,j=1}^{n_{occ}} S_{ij}(A) S_{ij}(B), \tag{1}$$

where $S_{ij}(A) = \int_A \chi_i(r)\chi_j(r)dr$ is the atomic overlap matrix between two spin-orbitals i and j of the atom A; the integration is performed over the atomic basins A and B and the summation is performed over all occupied molecular orbitals n_{occ}.

The bond order can also be expressed through bond lengths and electron density parameters. Pauling [17] quantitatively estimated bond order indices for different types of covalent bonds with the use of the exponential dependence on interatomic distances. For covalent carbon—carbon bonds Matta *et al.* [18, 19] in turn have calibrated the equation proposed by Bader [14, 20] that expresses the exponential dependence of bond orders on the electron density in its critical points. They used the bond orders obtained from delocalization indices. Further Matta proposed the analysis of a matrix composed of localization indices $\lambda(A)$ [21, 11] and electron delocalization indices $\delta(A,B)$ [22—24]. It was recommended as a tool to evaluate and model the physicochemical properties and biological activity of compounds in ground and excited states [22]. The electron localization indices $\lambda(A)$ characterize the number of electrons localized in atomic basin A, which together with delocalization indices comprises the total electron occupation in a molecule. The electron localization and delocalization indices have also been successfully applied to derive quantitative structure—property and structure—activity models [22, 25] and to estimate the aromaticity of cycles [26].

In [27] the authors show that the electron delocalization indices linearly correlate with the formal bond orders [16] and can be employed for their estimation. However, the calculation of $\delta(A, B)$ values for crystals is very cumbersome [28]. On the other hand, there is a simple way to estimate the covalent bond orders indices from the quantum-topological characteristics of the bond critical points [29—32]. A united parametric model was proposed to describe both covalent and hydrogen O—H/O…H bonds [33]. It is shown that it describes well the topological bond orders for the distance range from 0.97 Å to 2.91 Å based on the factors such as the electron density and kinetic and potential energy densities at bond critical points. Thus, the electron delocalization indices act as a useful and convenient value to calibrate bond order indices.

In this work we consider the possibility to estimate the bond order indices of covalent and halogen bonds formed by the iodine atoms in molecular crystals. Electron delocalization indices calculated for covalent and halogen bonds in molecular complexes and structural fragments of iodine-containing compounds are used as the reference calibrating value. We aim to verify the suitability of transferring the parametric correlation models of bond order indices in the complexes of organic polyiodides to a wide range of bond lengths and interactions I—X/I…X (X = I, S, N) in iodine-containing fragments in molecular crystals. Special attention is paid to the analysis of the effect of mutual orientation of iodine-containing fragments that makes it possible to distinguish between the iodine halogen bonds and van der Waals interactions in crystals. The latter is an important step in the elaboration of recommendations for the identification of halogen interactions of types I and II [34] in crystals.

Owing to the ability of iodine atoms to participate in both covalent and numerous non-covalent interactions of different types, including halogen [35], chalcogen [36], hydrogen bonds, anion-π interactions [37], etc., the aspects of the characterization of iodine bond order indices are of special attention when research objects are selected. The research objects were iodine-containing molecular crystals based on the derivatives of quinoline, pyrimidine, benzothiazole, and other heterocyclic compounds with one and two N, S heteroatoms. Both covalent and halogen bonds of iodine were studied, including the bonds strengthened by the I⁻…I charge and strong intramolecular interactions in triiodide anions. The initial crystal structures of all compounds were taken from CSD v.5.38 [38].

EXPERIMENTAL

Parametric models for the calculation of bond order indices $n(I, X)^{cry}$, where $X = I, S, N$, in the crystals were developed by Scheme 1.
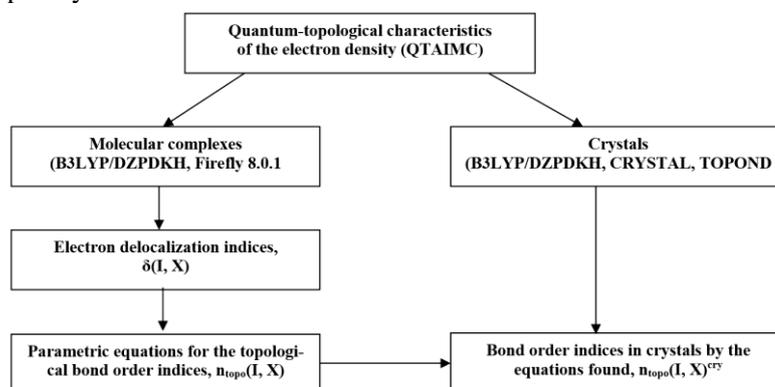
Scheme 1. Sequence of deriving the model for estimating bond order indices in the crystals based on the electron delocalization indices in the molecular complexes.

The equilibrium geometry of the considered iodine-containing molecular complexes and crystals was obtained by the Kohn—Sham method with the B3LYP functional and the Douglas—Kroll—Hess basis set (DZPDKH) [39] in the Firefly 8.0.1 [40] and CRYSTAL14 [41] programs respectively. The quantitative estimate of the correspondence of structural models to the experimental data was the root-mean-square deviation of coordinates of atomic positions (RMSD) before and after the geometry optimization. For a series of crystal structures a custom scan of the absence of imaginary frequencies was performed.

The quantum topological characteristics of the electron density were calculated using the AIMAll [42] and TOPOND16 [43] programs for molecular complexes and crystals respectively. The found local electron densities and the potential $v(r_b)$ and kinetic $g(r_b)$ energy densities at bond critical points and also the equilibrium interatomic distances for selected bonds and interactions in the isolated complex approximation are gathered in Table 1S (Table S1, Supplementary Materials*). Data obtained from the calculation of the crystals are summarized in Table 2S (Table S2, Supplementary Materials).

RESULTS AND DISCUSSION

Parametric models of iodine bond order indices based on electron delocalization indices. A simple and flexible approach to the estimation of bond order indices in crystals is based on parametric correlation models in which characteristics of the electron density properties at bond critical points are used as the factors. The role of a response in expressions for the choice of parameters in a multiple linear regression can be played by electron delocalization indices in the assumption that the relationship $n_{topo}(I, X) = \delta(I, X)$ is valid. Since a direct calculation of delocalization indices is difficult in the crystals, we used the electron delocalization indices calculated by expression (1) for the sets of bonds formed by calculations of molecular complexes. The highest correlation coefficients were found for a two-factor model based on the potential $v(r_b)$ and kinetic $g(r_b)$ energy densities involved in QTAIMC

$$n_{topo}(I, X) = a_0 + a_1 \cdot v(r_b) + a_2 \cdot g(r_b). \tag{2}$$

The relationship between the electron delocalization indices $\delta(I, X)$ and topological bond order indices $n_{topo}(I, X)$ (equation (2)) based on the local electronic characteristics of electron energy densities at bond critical points is given in Fig. 1. It demonstrates that equation (2) is valid in a wide range of interatomic distances of each type: from covalent bond lengths to van der Waals interactions.

We also calculated bond order indices $n_{dist}(I, X)$ based on their exponential dependence on interatomic distances

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* Supplementary materials for this paper are available for authorized users at doi 10.26902/JSC20180819.
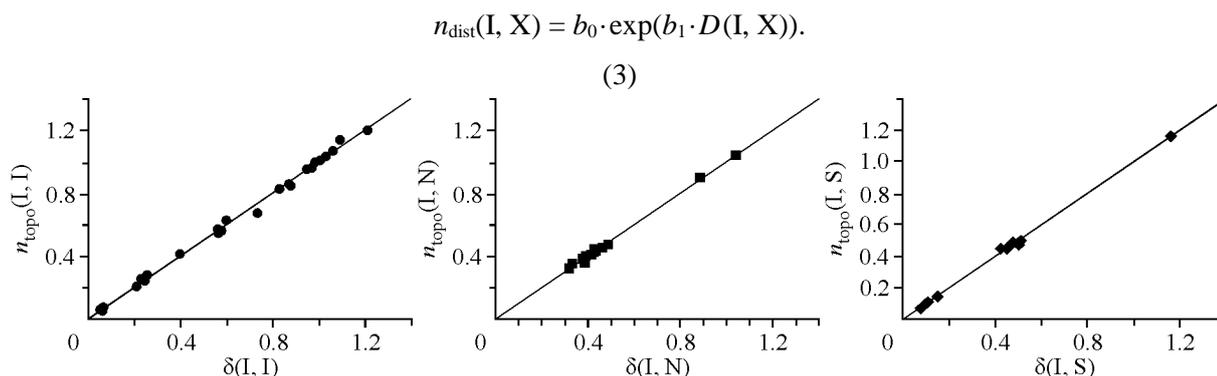
$$n_{dist}(I, X) = b_0 \cdot \exp(b_1 \cdot D(I, X)).$$

$$(3)$$

Fig. 1. Relationship between the topological bond orders $n_{topo}(I, X)$ and the electron delocalization indices $\delta(I, X)$ calculated for interactions in the molecular complexes.

The obtained parameters of models for different type bonds formed by the iodine atom I—X/I…X (X = I, S, N) are listed in Table 1. It also presents the statistical characteristics of models, square linear correlation coefficients R^2, mean square deviations *SD*, and also Δ, the maximum and minimum differences of bond order indices calculated by equations (2) and (3) and electron delocalization indices.

T a b l e   1

Statistical characteristics and parameters of the models based on the quantum topological characteristics of the electron density for non-covalent interactions of the iodine atom in molecular complexes

Interaction type	Parameter		Statistical characteristic	
	$n_{dist}(I, X)$	$n_{topo}(I, X)$	$n_{topo}(I, X)$	$n_{dist}(I, X)$
I—I/I…I (32)	$b_0 = 427.43\pm42.38$	$a_0 = 0.04\pm0.01$	$R^2 = 0.99$	$R^2 = 0.99$
	$b_1 = -2.12\pm0.03$	$a_1 = -38.04\pm0.88$	$\Delta_{max} = 0.05$	$\Delta_{max} = 0.05$
		$a_2 = -20.08\pm2.03$	$\Delta_{min} = -0.04;\ SD = 0.02$	$\Delta_{min} = -0.05;\ SD = 0.02$
I—N/I…N (15)	$b_0 = 51.33\pm4.04$	$a_0 = 0.11\pm0.02$	$R^2 = 0.99$	$R^2 = 0.99$
	$b_1 = -1.91\pm0.03$	$a_1 = -7.54\pm2.21$	$\Delta_{max} = 0.03$	$\Delta_{max} = 0.04$
		$a_2 = -0.20\pm4.48$	$\Delta_{min} = -0.02;\ SD = 0.01$	$\Delta_{min} = -0.02;\ SD = 0.01$
I—S/I…S (15)	$b_0 = 233.83\pm12.10$	$a_0 = 0.01\pm0.01$	$R^2 = 0.99$	$R^2 = 0.99$
	$b_1 = -2.14\pm0.02$	$a_1 = -19.30\pm0.22$	$\Delta_{max} = 0.03$	$\Delta_{max} = 0.02$
		$a_2 = -0.05\pm0.04$	$\Delta_{min} = -0.03;\ SD = 0.01$	$\Delta_{min} = -0.01;\ SD = 0.01$

Estimation of the effect of the environment on the calculated iodine bond orders. Before we pass to the crystals, let us analyze the effect of the environment on I—I bond delocalization indices in an iodine molecule halogen-bonded in molecular complexes (Table 3S, Supplementary Materials). In an isolated iodine molecule, $\delta(I, I) = 1.210$. Without external interactions the average number of electrons of I atom shared with the neighboring atom is $N^\delta(I, I)_b = 0.605$. Here $N^\delta(A, B)_b$ is the average number of electrons of A atom shared with the B atom bonded to the A atom [42]. In the complex $I_2…I_2…I_2$ of three molecules bonded with each other by two halogen bonds, the central iodine atom additionally contributes 0.185 to the bonds with other atoms. The fraction of delocalized electrons per atoms not bonded to the considered one is $N^\delta(I, I)_{nb} = 0.057$, $N^\delta(I, I)_{nb} = N^\delta(I) - N^\delta(I, I)_b$, where $N^\delta(I)$ is the number of A atom electrons delocalized over other atoms of the system. In a stable complex of seven iodine molecules the central atom forms four bond paths with the neighbors and delocalizes only 0.147 electrons with the bound atoms. The delocalization with unbound atoms is $N^\delta(I, I)_{nb} = 0.134$, and the delocalization index of the I—I covalent bond decreases to $\delta(I, I) = 0.984$. This means that the additional delocalization of electrons in the crystal, which is associated with the environment, involves not only the fraction of electrons belonging to this atom but also the fraction of electrons shared with

the atoms to which it is bonded. Thus, in the crystal the covalent bond order indices must be lower than those obtained in the models based on isolated molecular complexes.

In a series of substituted nitrogen-containing heterocycles forming complexes with I_2, in which the iodine atom making only two bond paths (with iodine and nitrogen) a monotonic change of delocalization indices for the I—I bond is observed, depending on the strength of the N…I halogen bond. A detailed analysis of changes in the delocalization indices of halogen bonds in this series is given in [44]. Note that the weakest N…I halogen bond in a 3-chloropyridine molecule has $\delta(N, I) = 0.391$. The electron delocalization index for I—I bond and the covalent bond order index decreases to $\delta(I, I) = 1.026$ during complexation respectively, i.e. it noticeably changes as compared to the isolated I_2 molecule. Here the average number electrons of I atom shared with the nitrogen atom due to the halogen bond is $N^\delta(I, I)_b = 0.104$ e (Table 2). The strongest halogen bond with the delocalization index $\delta(N, I) = 0.462$ is observed in the complex with 4-dimethylaminopyridine, the covalent bond becoming weaker $(\delta(I, I) = 0.972)$ and the fraction of electrons shared with other base atoms being $N^\delta(I, X)_{nb} = 0.057$. However, in the 2,2′-diazabicyclo[2.2.2]octane complex with the same N…I bond length, as well as in the 4-dimethylaminopyridine complex, the electron sharing with unbound atoms (no bond paths) is almost two times larger: $N^\delta(I, X)_{nb} = 0.106$. It turns out that just due to this electron sharing the delocalization indices of both covalent and halogen bonds appreciably decrease in the 2,2′-diazabicyclo[2.2.2]octane complex (Table 3S, Supplementary Materials).

T a b l e   2

Bond order indices in the crystals obtained by Eq.(3), $n_{dist}(I, I)^{cry}$ and Eq.(2), $n_{topo}(I, I)^{cry}$

Compound	Interaction type	DZPDKH		DZP	
		$n_{dist}(I, I)^{cry}$	$n_{topo}(I, I)^{cry}$	$n_{dist}(I, I)^{cry}$	$n_{topo}(I, I)^{cry}$
Benzopyrazine·I_2	I—I	0.923	0.952	1.110	0.933
1,4-Diiodobuta-1,3-diene	I…I	0.073	0.066	0.119	0.096
1,5-Diiodonaphthalene	I…I	0.096	0.088	0.102	0.088
1,3-Dithiolane-2-thione·I_2	I—I	0.766	0.791	0.887	0.686
7-Iodo-3-isopropyl-1-methyl-2,3-dihydro-indol-2-one	I…I	0.078	0.080	0.088	0.072
Tetramethylammonium iodide 2I_2	I—I	0.922	0.932	0.990	0.789
	I…I⁻	0.552	0.576	0.463	0.314
1,3,5-Triiodo-2,4,6-trimethylbenzene	I…I	0.102	0.087	0.112	0.091
	I…I	0.111	0.096	0.082	0.087
	I…I	0.093	0.080	0.073	0.080

Thus, the effects on the electron delocalization indices, and correspondingly, the I—I covalent bond order indices in molecular complexes of iodine are produced by both strength of halogen bonds and number of the nearest atoms with which iodine atoms may not make bonds but are involved in the electron delocalization process having the quantum mechanical nature.

Iodine bond order indices in molecular crystals. Equation (2) with the found parameters, which was obtained for molecular complexes, was applied to calculate bond order indices involving iodine atoms in the crystals. To this end, we used local electronic characteristics $v(r_b)$ and $g(r_b)$ obtained for the crystals with the CRYSTAL14 program by the Kohn—Sham method and the B3LYP functional, and formally, the same basis set localized on the atoms but involving, however, a periodic component. The I—I covalent bonds in the crystals are characterized by bond order indices ranging from 0.98 to 0.80. The smallest bond order indices <0.1 in the crystals were found for weak I…I van der Waals interactions, with the halogen bond order indices in the crystals being nearly two times smaller than those in the molecular complexes. This fact is well explained by that the total number of interactions per iodine atom increases in the crystal; correspondingly, the fraction of electrons involved in the formation of halogen bonds decreases.
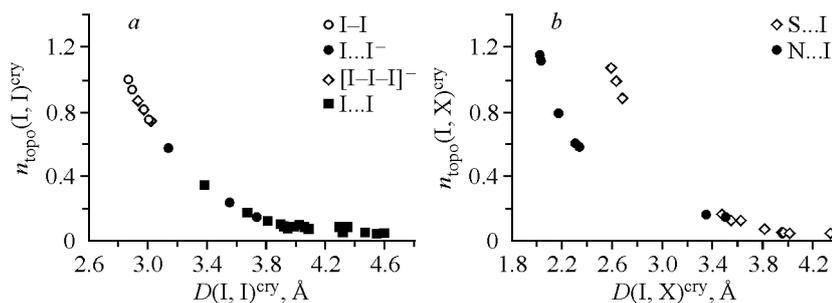
Fig. 2. Dependences of the topological bond order indices (equation 2) on I—X/I…X (X = I, S, N) interatomic distances in the crystals.

Fig. 2 *a,b* depicts the dependences of bond order indices on interatomic distances I—X/I…X in the crystals $n_{topo}(I, X)^{cry}$ (Table S1, Supplementary Materials). The bond order indices in the complexes are systematically shifted to larger values of 1.193÷0.053 in comparison with those in the crystals

of 1.000÷0.040. The region of non-covalent interactions in crystals extends to 4.6 Å. The halogen bond order indices involving nitrogen and sulfur atoms (I…N and I…S) are on average lower in the crystals than those in the complexes. This situation agrees well with the statement that in the crystals each atom contacting with its crystal environment more greatly delocalize electrons, which decreases the order indices of both covalent bonds and non-covalent interactions.

Nonetheless, we have revealed a number of problems in the use of the two-factor model of bond order indices in iodine-containing crystals, which is obtained based on the topological characteristics of the electron density.

When different DZPDKH and DZP basis sets are used, the values obtained for the test sampling (Table 2) demonstrate substantial distinctions. In the case of taking into account relativistic effects for iodine atoms by means of DZPDKH, for weak I…I interactions lower bond orders $n_{topo}(I, I)^{cry}$ obtained by equation (2) are observed in comparison with $n_{dist}(I, I)^{cry}$ values obtained by equation (3) (Table 2). For DZP we observed lower bond orders $n_{topo}(I, I)^{cry}$ as compared to $n_{dist}(I, I)^{cry}$ in the whole range of interactions, except weak van der Waals ones in 1,3,5-triiodine-2,4,6-trimethylbenzene (Table 2). Thus, the choice of the basis set for iodine atoms appreciably affects the bond order indices.

There are also other restrictions on the application of parametric models based on of the local electron density the properties. Firstly, with the help of these models it is possible to estimate only those interatomic interactions that are identified based on the critical bond points. Secondly, the disadvantages of the above model may be the use of the densities of kinetic $g(r_b)$ and potential $v(r_b)$ energies in one equation because these functions are already related by the local virial theorem [45]: $2g(r_b) + v(r_b) = 1/4\nabla^2\rho(r_b)$. Then, $\nabla^2\rho(r_b)$ is an ambiguous function of interatomic distances for iodine atoms [46] because both strong covalent bonds and rather weak I…I interactions may have the same $\nabla^2\rho(r_b)$ values. All this worsens the universality of the presented approach to the estimation of bond order indices in the crystals.

Nonetheless, the results of our work demonstrate that the parametric models are useful for the quantitative estimation of halogen and covalent bond order indices of iodine atom I—X/I…X (X = I, S, N) in molecular crystals if we stay within one level of calculations. Due to the fact that in the crystal each structure-forming interaction is, as a rule, accompanied by the occurrence of a saddle point in the electron density, it is possible to assume that this approach enables one to encompass the whole range of significant non-covalent interactions necessary to estimate the properties of the crystal structure. It is important that if the interatomic interaction of interest is not accompanied by the occurrence of the bond path and the critical bond point, the opportunity remains to use equation (3) which allows the estimation of bond order indices $n_{dist}(I, X)$ from the empirical dependence of these values on interatomic distances.

Thus, we have demonstrated the possibilities and designated the applicability boundaries of the parametric model for the calculation of bond order indices, which is based on the local properties of

the kinetic $g(r_b)$ and potential $v(r_b)$ energy densities. This model can be useful for the description of halogen and covalent bonds formed by the iodine atom in the crystals. Parameters of the model obtained in this study are suitable for the characterization of iodine interactions with sulfur and nitrogen. Further expansion of parameter sets may be helpful in the description of other non-covalent interactions in molecular crystals.

CONCLUSIONS

The two-factor equation depending on the potential $v(r_b)$ and kinetic $g(r_b)$ electronic energies at bond critical points is proposed to estimate bond order indices of I—X/I…X (X = I, S, N) bonds formed by iodine atoms in organic crystals. This model is parameterized by electron delocalization indices calculated for pair interactions of iodine atoms in isolated molecular complexes. The obtained bond order indices regularly decrease with increasing interatomic distances, which indicates in favor of the applicability of this equation for the estimation of iodine bond order indices in the crystals in a wide range of bond lengths from covalent to van der Waals.

The analysis shows that bond order indices for I—I/I…I interactions are, as a rule, lower in the crystals than those in the molecular complexes. The crystal environment effect on the electron delocalization in organic crystals involving iodine atoms is numerically estimated. The total number of interactions per iodine atom in the crystal increases in comparison with that in the molecular complex. In most cases, this results in a greater degree of electron delocalization and a decrease the covalent bond order indices.

It is found that the transferability of parameters of the proposed equation on passing from the complexes to the crystals may be considered to be satisfactory only within one level of calculations of the electron delocalization indices and the local properties of electron energies at bond critical points. The change of the basis set on passing to the crystal level of the structural description significantly affects the numerical values of the estimated bond order indices. Thus, the transferability of parameters of the found equations is limited by the choice of the basis set for the iodine atom.

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