

ELECTRON DELOCALIZATION INDICES AS CRITERIA FOR THE IDENTIFICATION OF STRONG HALOGEN BONDS OF IODINE

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It is found that electron delocalization indices can be efficiently used as a sorting tool for the classification of bonds between iodine atoms in a wide range of various covalent and noncovalent I...I/I–I interactions. The characteristics of bonds in a symmetrical triiodide anion can serve as benchmarks allowing to distinguish the I...I halogen bond from the I–I covalent bond.

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The interaction of halogens resulting from the predominant electrostatic attraction between the lone pairs of one halogen and the region with higher electrostatic potentials along the covalent bond of another (R–Hal⁺...Hal[–]–R) was called the halogen bonding [1]. These bonds play an important structure-forming role in many halogen-containing molecular crystals. Under that logic, one can assume that a bond strengthened by a charge in a triiodide anion should be considered as the strongest I...I halogen bond. In such a case, electron delocalization is observed over the whole subunit, and all the three iodine atoms contribute to the frontier molecular orbitals [2]. The experimental mass spectrometric determination of the dissociation energy of the triiodide anion ($I_3^- \rightarrow I_2 + I^-$) yields a value $D_e = -126.4$ kJ/mol [3]. It should be noted that a similar benchmark system for a hydrogen bond is the $[F...H...F]^-$ anion ($D_e = -155$ kJ/mol [4]).

Quantum chemical calculations of the interaction energy of iodine subunits (I_2 and I^-) in the triiodide anion indicate a wide range of values: from -113.9 kJ/mol (CCSD(T) ECP-TZ(2df)) up to -174.0 kJ/mol (B3LYP/LACVP*) [5]. The spread of these values is due to the usage of different methods of calculations. Moreover, there is a problem of attributing bonds to specific classes, which is directly related to the fact that the characteristics of the $[I...I]^-$ bond can vary with the geometry optimization of the complex or cluster removed from the continuum of its environment. Thus, for instance, the equilibrium in the gas phase configuration of the complex of the triiodide anion with a heterocyclic cation becomes more similar to the C–I...[I][–]...I–I structure rather than to C–I...[I–I][–]. Therefore, it is needed to determine the upper limit of stability, which makes it possible to distinguish a strong halogen bond from a covalent one.

In the present work we have studied the behavior of the electron delocalization indices $\delta(I, I)$ for a wide series of I–I/I...I interactions and the possibility to use them as benchmarks allowing to distinguish a halogen bond strengthened by the I...I charge from a covalent I–I bond.

Experimental. The delocalization index [6, 7] corresponds to the number of electrons delocalized or shared between atoms A and B . In the one-electron approximation the delocalization indices are determined by calculating the overlap matrix

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elements S_{ij} by the integration over the atomic basins Ω_A and the summation over all occupied molecular orbitals n_{occ} [7]

$$\delta(\Omega_A, \Omega_B) = 4 \sum_{i,j=1}^{n_{\text{occ}}} S_{ij}(A)S_{ij}(B); \quad S_{ij}(A) = \int_{\Omega_A} \chi_i(\mathbf{r})\chi_j(\mathbf{r})d\mathbf{r}.$$

According to Bader, atomic basins Ω_A are defined as regions in the real space bound by zero-flux surfaces of the gradient vector field of the electron density and embracing the nuclei [8].

The regularity of changes in the calculated delocalization indices of iodine $\delta(\text{I}, \text{I})$ has been analyzed by the example of molecular complexes and clusters described in [9, 10]. The following cases were studied: 1) N...I-I halogen bonds in molecular complexes of substituted pyridine with iodine; 2) clusters of interacting iodine molecules; 3) complexes with heterocyclic cations in which halogen bonds of iodine are strengthened by the following charges: $\text{I}_3^- \dots \text{I} \dots \text{I}_3^-$, $\text{I}_3^- \dots \text{I} \dots \text{Cat}^+$, $\Gamma \dots \text{I} \dots \text{Cat}^+$; 4) weak halogen bonds and van der Waals interactions in the C-I...I-C molecular dimers of organic molecules.

The geometry of stationary states of molecular complexes of iodine is determined by the Kohn-Sham method (B3LYP/6-311G(*d,p*)) using the Firefly program [11]. The analysis of harmonic frequencies has demonstrated that the structures correspond to a local minimum of the total energy. The calculations of the electron delocalization indices were carried out using the AIMALL software package [12].

Results and discussion. The bonds in symmetric I_3^- can be formally referred neither to covalent, nor to noncovalent bonds. However, if the triiodide anion undergoes the effect of the environment, then one of the bonds inevitably extends and another shortens. Hence, it turns out that in the asymmetric triiodide anion we can formally distinguish the I-I bond that is largely covalent and the I...I bond that can be classified as a strong halogen bond. Thus, the bond characteristics in the symmetric triiodide anion can be used as benchmarks suitable for determining the upper limit characterizing the halogen bonds of iodine.

The electron delocalization index for the isolated and consequently symmetric triiodide anion is $\delta^{\text{III}} = 0.832$. Judging from Fig. 1a, it is impossible to classify the charge strengthened bond between the iodine atoms as belonging to this or that type if we consider only the delocalization indices for the I-I/I...I bonds lying in the range from 1.055 to 0.565.

Let us consider how a quantitative criterion based on the delocalization indices enables the division of the selected I-I/I...I iodine bonds into groups on the principle of similarity of their interaction nature. Firstly, let us calculate the value $\Delta\delta^{\text{II}}$ which characterizes how the electron delocalization index of the I-I bond under consideration in the particular structure differs from that for the isolated iodine molecule: $\Delta\delta^{\text{II}} = \delta(\text{I}_2) - \delta(\text{I}, \text{I})$. Assume as a benchmark the maximum value of the electron delocalization index in the iodine molecule, $\delta(\text{I}_2) = 1.335$, obtained according to the chosen method of computer simulation. Obviously, any noncovalent interaction of the iodine molecule either with a donor or with an electron acceptor would reduce the delocalization index of the I-I bond. Secondly, let us determine the values $\Delta\delta^{\text{III}}$ showing how the delocalization indices of the bond under consideration deviate from that in the triiodide anion: $\Delta\delta^{\text{III}} = \delta(\text{I}_3^-) - \delta(\text{I}, \text{I}) = 0.832 - \delta(\text{I}, \text{I})$. The value $\Delta\delta^{\text{III}}$ can be both positive and negative. Participating in the noncovalent interaction, the triiodide anion becomes asymmetric; and the delocalization index of one of these bonds increases and another decreases. Thirdly, let us introduce the criterion $D = \Delta\delta^{\text{II}}/\Delta\delta^{\text{III}}$ reflecting the degree of involvement of the iodine subunit under consideration in the noncovalent interactions.

Fig. 1b illustrates that the D criterion enables the division of all the bonds into two groups. The bonds with the delocalization indices lower than that of the isolated triiodide anion refer to the first group with $D > 0$. The D criterion has high positive values for the I...I halogen bonds of iodine strengthened by the charges. If the electron delocalization index is higher than that in the triiodide anion, then these bonds refer to the second group where the covalent bonds of iodine are extended and weakened due to noncovalent interactions. The reference parameter to distinguish these two groups is the internuclear distance being $\sim 3.0 \text{ \AA}$.

According to the proposed criterion the I...I halogen bonds should belong only to the first group of noncovalent interactions if they are charge strengthened.

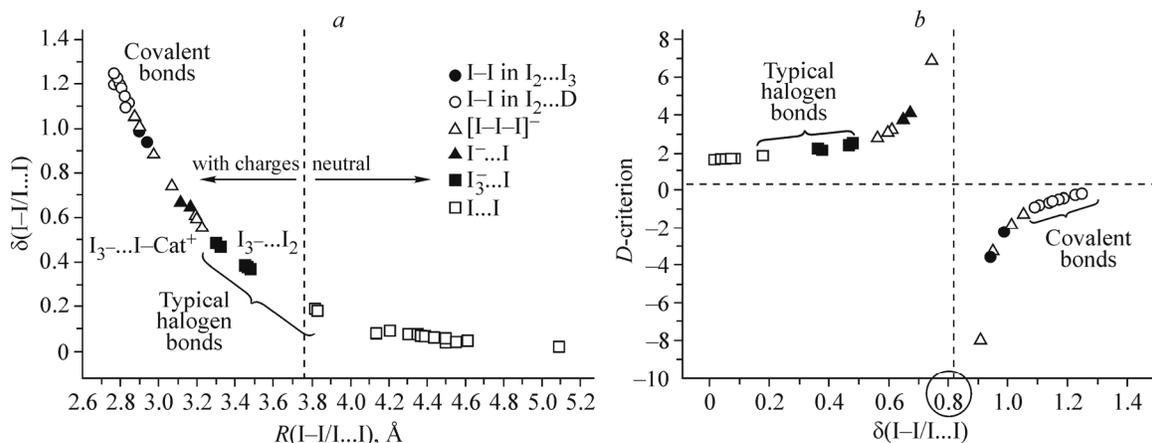


Fig. 1. Dependence of the electron delocalization indices $\delta(I, I)$ on the $R(I-I/I...I)$ Å bond lengths (a); D -criterion and delocalization indices $\delta(I, I)$ in iodine-containing complexes and clusters (b).

Conclusions. Based on the analysis of the behavior of the electron delocalization indices we have proposed a quantitative criterion allowing to draw the line between the I–I covalent and halogen bonds of iodine strengthened by I...I charges. It is demonstrated that the relationship of changes in the electron delocalization indices $\Delta\delta^{II}/\Delta\delta^{III}$ calculated for the iodine bonds distorted as a result of the participation of the iodine subunit under consideration in noncovalent interactions can be taken as a benchmark value determining the region of existence of halogen bonds. The proposed classification of bonds in complex systems with elements of iodine aggregation is clear and simple and it offers an opportunity for a relative, but objective evaluation of the features of halogen bonds of iodine.

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