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Hypervalent Compounds

The I=X (X = O,N,C) Double Bond in Hypervalent Iodine Compounds: Is it Real?**

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Dedicated to Professor Viktor D. Yagodovski

Abstract: *I–X (X = O, N, C) bonding was analyzed in the related hypervalent iodine compounds based on the adaptive natural density partitioning (AdNDP) approach. The results confirm the presence of a I→X σ dative bond, as opposed to the widely used I=X notation. A clear formulation of the electronic structure of these hypervalent iodine compounds would be useful in establishing reaction mechanisms and electronic structures in bioinorganic problems of general applicability.*

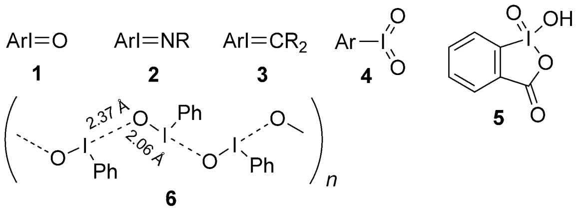

Figure 1. Common representation of hypervalent iodine compounds, with I=X bonds (structures **1**–**5**), as adopted in research literature and the polymeric structure of the iodosylbenzene **6**.

Organic derivatives of polyvalent iodine, commonly known as hypervalent iodine reagents, have found widespread application in organic synthesis as versatile, efficient, and environmentally sustainable reagents.[1] Despite extensive practical interest in these compounds, a relatively small number of computational studies on structure and reactivity of polyvalent iodine compounds have been published.[2] In particular, an important question about the existence of I=X (X = O, N, C) double bonds in organic derivatives of trivalent and pentavalent iodine has not been reliably answered. Structures of key hypervalent iodine reagents, such as iodosylarenes (**1**), iodonium imides (**2**), iodonium ylides (**3**), iodylarenes (**4**), 2-iodoxybenzoic acid (IBX, **5**), are commonly shown in the original research papers, books, and reviews in the form of compounds with a double bond at the iodine atom (Figure 1).[1,2]

X-ray structural studies of these compounds in the solid state are inconclusive because the real molecular structure of hypervalent iodine derivatives is masked by extensive networks of intermolecular secondary bonds resulting in a highly aggregated polymeric structure.[3] For example, X-ray powder diffraction and EXAFS studies of iodosylbenzene have indicated a zigzag polymeric chain structure (**6**) in which monomeric PhIO units are linked by intermolecular I···O secondary bonds.[3a] In spite of the numerous experimental structural studies of hypervalent iodine compounds,[1] the question about the real nature of the I=X bonding remains open. Bonding description in such molecules is very important for understanding the structural, physical, and chemical properties. In the current study we show the single dative [two-center two-electron (2c-2e) bond where two electrons derive from the same atom] character of chemical bonding between I and O, I and N, and I and C atoms in hypervalent iodine compounds, and it is controversial with respect to the common I=X double-bond representation.

To establish a reliable picture of the chemical bonding we have probed various hypervalent iodine molecules, such as IO_4^-, PhIO, $PhIO_2$, $PhIO_3$, PhINR ($R = SO_2Ph$), and $PhICR_2$ ($R = CO_2Me$). The geometries of all the structures were optimized at the PBE0/I/Stuttgart/H, C, N, O, S/aug-cc-pVTZ[4–8] level of theory with follow-up frequency calculations. All the structures were checked to be true minima with no imaginary frequencies. Chemical bonding analysis was performed using the adaptive natural density partitioning (AdNDP) method, which achieves a seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance.[9] The AdNDP approach has demonstrated effectiveness in the description of chemical bonding in many organic,[10] inorganic systems,[11] and clusters.[12]

It is known that the metaperiodate anion is composed of one iodine and four oxygen atoms, and is generally represented by having three double bonds between I and O, and one single I–O σ bond with a negative charge on the oxygen atom (Figure 2a). Application of the AdNDP method for the

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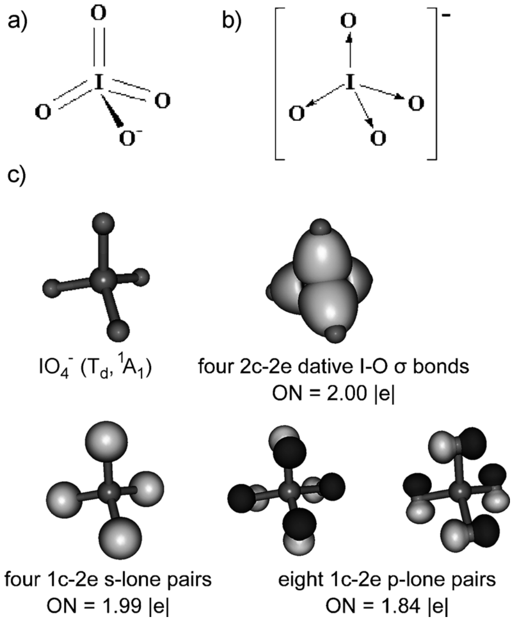

Figure 2. a) General representation of the IO_4^- structure. b) Symbolic representation of IO_4^- according to AdNDP. c) AdNDP bonding pattern of IO_4^-. The corresponding point-group symmetry and spectroscopic state of IO_4^- are given in parenthesis. ON stands for the occupation number here and elsewhere.

metaperiodate anion leads to the chemical bonding pattern shown in Figure 2.

AdNDP recovered one s-type and two p-type electron lone pairs (1c-2e) on each oxygen atom with occupation numbers (ONs) in the range of 1.84-1.99 |e|. Four 2c-2e I−O σ bonds (ON = 2.00 |e|) originate from the donation of electron density directly from iodine, thus indicating the dative character of these bonds. In addition, NBO analysis was performed to determine a charge distribution in this species. According to it, every oxygen atom bears a negative charge of −1.14, while iodine is positively charged (+3.56). Thus, our analysis shows that single dative I:→O bonds should be used to describe chemical bonding in IO_4^-. The appropriate symbolic representation according to the AdNDP analysis is demonstrated in Figure 2b.

Iodosylbenzene was first synthesized by C. Willgerodt from iodobenzene in 1892 and it has the empirical formula PhIO.[13] Similar to the IO_4^- case, it has been described as having a I=O bond (structure **1**, Figure 1), a formulation which clearly breaks the octet rule at iodine. The results of the AdNDP analysis and the corresponding symbolic representation of PhIO are summarized in Figure 3. As expected, AdNDP revealed three lone pairs (ON = 1.75–1.99 |e|) on the oxygen atom, one dative 2c-2e I→O σ bond with ON = 2.00 |e|. The bonding between iodine and the carbon atom of the Ph group derives from the sharing of an electron pair between these atoms and thus represents a common single covalent I−C σ bond (ON = 1.97 |e|). The remaining electrons of I form two lone pairs with ON = 1.99 |e| as shown in Figure 3. Complete AdNDP analysis of PhIO is given in Figure S1 in the Supporting Information. We obtained a similar bonding pattern for $PhIO_2$ (see Figure S2 in the Supporting Information) and $PhIO_3$ (see Figure S3 in the Supporting Information), where the bonding between the oidine and oxygen atoms represents a single dative 2c-2e I→O σ bond and confirms the absence of I=O bonds. The situation described here appears to be akin to other oxyanions, including the well-known sulfate, nitrate, and phosphate anions (all of which we do not represent with a double-bond symbol) with an oxygen atom accepting the dative bond.

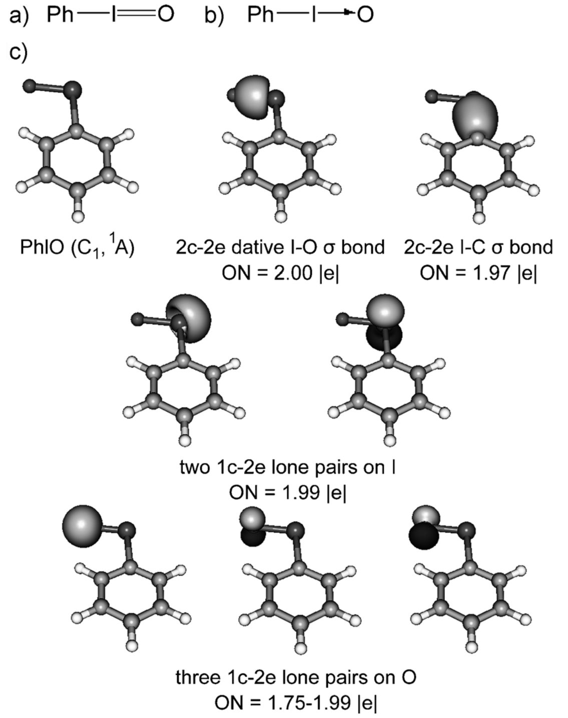

Figure 3. a) General representation of the PhIO structure. b) Symbolic representation of PhIO according to AdNDP. c) AdNDP bonding pattern for PhIO. Complete AdNDP analysis of PhIO is given in the Supporting Information (Figure S1). The corresponding point-group symmetry and spectroscopic state of PhIO are given within parenthesis.

More complicated cases where the nature of the I−X bonding remains contentious were investigated using an iodonium imide and iodonium ylide (structures **2** and **3**; Figure 1). Results of the AdNDP analyses on I−N and I−C fragments and nearby atoms are shown in Figure 4 and Figure 5, respectively.

As one can see, in the iodonium imide PhINR ($R = SO_2Ph$) there are two lone pairs on N with ON = 1.84–1.97 |e| and two lone pairs on I with ON = 1.97–1.99 |e| (Figure 4). Covalent bonds at the studied fragments are represented by 2c-2e I−C and 2c-2e N−S σ bonds with ON = 1.91 |e| and ON = 1.96 |e|, respectively. Again, the bonding between I and N has a dative character and is represented by the single 2c-2e I→N σ bond according to our analysis. The chemical bonding picture of the iodonium ylide $PhICR_2$ ($R = CO_2Me$) shows one dative I→C σ bond (ON = 1.96 |e|), one 2c-2e bond between I and C of the Ph fragment with ON = 1.97 |e|, two lone pairs on I (ON = 1.96–1.99 |e|), two 2c-2e C−C σ bonds (ON = 1.98 |e|), and one 3c-2e π bond (ON = 1.80 |e|) delocalized over three carbon atoms (Figure 5).

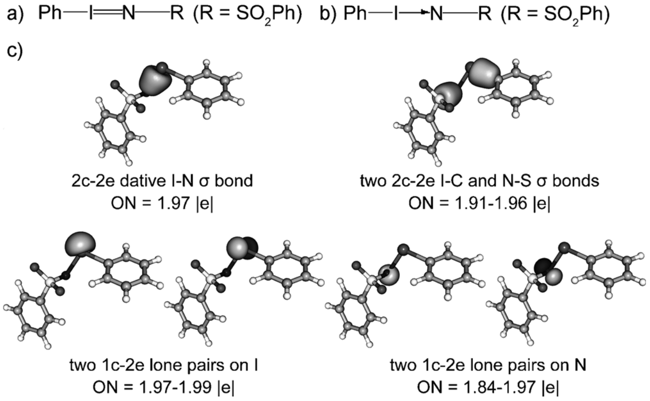

Figure 4. a) General representation of the PhINSO$_2$Ph structure. b) Symbolic representation of PhINSO$_2$Ph according to AdNDP. c) AdNDP bonding pattern of the PhINSO$_2$Ph molecule for the I—N, I—C, and N—S fragments. Complete AdNDP analysis of PhINSO$_2$Ph is given in the Supporting Information (Figure S4).

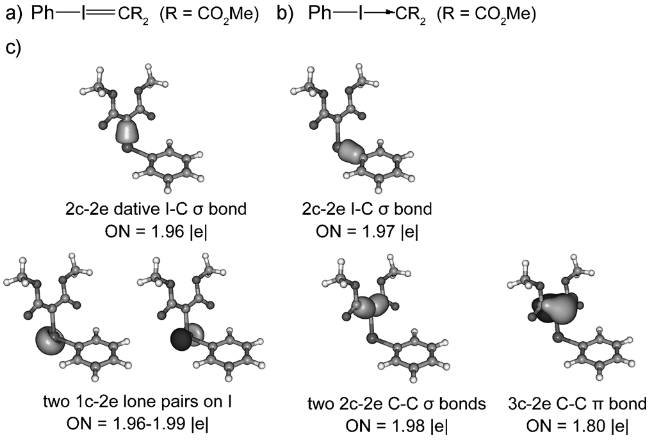

Figure 5. a) General representation of the PhIC(CO$_2$Me)$_2$ structure. b) Symbolic representation of PhIC(CO$_2$Me)$_2$ according to AdNDP. c) AdNDP bonding pattern of the PhIC(CO$_2$Me)$_2$ molecule for the I—C, and C—C fragments. Complete AdNDP analysis of PhIC(CO$_2$Me)$_2$ is given in the Supporting Information (Figure S5).

The 3c-2e π bond is responsible for the bending of the C-C-C fragment and can actually be represented by a lone pair on the central carbon atom with a somewhat lower occupation number (ON = 1.48 | e |). This data is supported by the NBO analysis, thus showing a positive charge of + 0.75 on two flanking carbon atoms and a negative charge of −0.58 on the central carbon atom. The need to form the 3c-2e π bond comes from the fact that the carbon atom is less electronegative than either N or O and needs some help from its neighboring carbon atoms, thus transforming a lone pair into the 3c-2e π bond. The presence of this 3c-2e π bond seems to explain the C—C bond length (1.44 Å) on this fragment which is something average between the single and double C—C bond lengths. Similar cases wherein a 3c-2e π bond originates from the lone pair on the central carbon atom and makes the corresponding C–C distances shorter than a typical C—C bond length, are exemplified by such molecules as $C_8B_2^-$, C_9B^-, and C_{10}^-.[10g]

The bonding picture developed for PhIC(CO$_2$Me)$_2$ through the AdNDP analysis shows that the single dative I→C σ bond can be formed only if electron-withdrawing groups like CO$_2$Me take some electron density from the carbon atom (its charge is not −1.0 but only −0.58) connected to the iodine atom because the carbon atom is not electronegative enough to acquire two electrons from the iodine atom alone.

Essentially, the studied iodine compounds can be described as Lewis bases bonded to Lewis acids [-O, -NSO$_2$Ph, and -C(CO$_2$Me)$_2$]. This description means that the Lewis acidity of the three latter species should be related to the strength of the bonding to the iodine-containing Lewis base. Hence, the strength of donor–acceptor interactions would be defined by the Lewis basicity/acidity of the components. The computed interaction energies between donor (PhI-) and corresponding acceptors suggest that -O (−211.4 kcal mol^{-1}) is a stronger Lewis acid than -NSO$_2$Ph (−132.0 kcal mol^{-1}) and -C(CO$_2$Me)$_2$ (−163.6 kcal mol^{-1}) and that the strength of the donor–acceptor bonds follows the trend for the acceptors: O > C(CO$_2$Me)$_2$ > NSO$_2$Ph. Thus, we believe that the derived description of the presented hypervalent iodine compounds as donor–acceptor complexes might be a very useful model for classifying known iodine compounds as well as for the design and prediction of novel molecules where the Lewis base and/or the Lewis acid are changed. Furthermore, our results might also be relevant to a broader range of existing compounds such as the carbodiphosphorane Ph$_3$P═C═PPh$_3$,[14] the borylene complex (BH)L$_2$,[15] the silylones SiL$_2$,[16] as well as the germylones GeL$_2$[17] (with different N-heterocyclic carbenes as ligands L), where a single dative bond rather than the double-bond character was confirmed based on their electronic structures and chemical behavior.[18–21]

According to the obtained chemical bonding pictures of all the studied molecules, it is clearly seen that the octet rule is obeyed in each case. Although we have used the term hypervalent throughout our discussion, it is noteworthy that it was purposely used to describe molecules which contain elements in any of their oxidation states other than their lowest oxidation state, and is in concordance with Musher's definition of a hypervalent molecule.[22] However, we agree with Gillespie and Silvi[23] who concluded that hypervalence is not a useful concept as hypervalent molecules are not different in any significant way from Lewis octet molecules.

In conclusion, we performed chemical-bonding analyses on several hypervalent iodine compounds where the presence of I═O, I═N, and I═C bonds was questionable. The AdNDP approach for the analyses of the MO wave functions of the corresponding compounds revealed only single I→X dative-bond character. The significant advancement made in the current study is that the bonding patterns and formulas are derived from the MO wave function by a unified and well-defined quantum chemical procedure. In particular, we believe that our representation of the studied hypervalent compounds might clarify the question of I—X double/single bond notation used in student courses and in current textbooks. We also believe that our theoretical findings can serve as a general guideline for the synthesis of new molecules with unusual bonds and reactivities.

Experimental Section

Calculations: The detailed description of the AdNDP algorithm developed by Zubarev and Boldyrev can be found elsewhere.[9] From the computational point of view, AdNDP is a generalization of the NBO analysis by Weinhold.[24] AdNDP performs analysis of the first-order reduced density matrix with the purpose of obtaining its local block eigenfunctions with optimal convergence properties for describing the electron density. The local blocks of the first-order reduced density matrix correspond to the sets of n atoms (from one to all the atoms of the molecule) which are tested for the presence of a two-electron object (nc-2e bonds, including core electrons and lone pairs as a special case of $n=1$) associated with this particular set of n atoms. The n atomic sets are formed and checked in an exhaustive manner, so that the recovered nc-2e bonding elements always correspond to the point group symmetry of the system after these bonding elements are superimposed onto the molecular frame. For the given n atomic block those eigenvectors are accepted whose occupation numbers (eigenvalues) exceed the established threshold value, usually close to $2.00|e|$. Thus, Lewis's idea of an electronic pair as the essential element of bonding is preserved. The AdNDP procedure is numerically efficient because it involves only a series of diagonalizations of density matrix blocks. It is unbiased in the sense that no preliminary ideas of the bonding pattern are required to perform analysis. The AdNDP code is a stand-alone program that uses output from Gaussian 09. The density matrix used for the basis of the natural atomic orbitals as well as for the transformation between atomic orbital and natural atomic orbital basis sets, which are used by the AdNDP program, was generated at the B3LYP/LANL2DZ[25,26] level of theory by means of the NBO code[27] incorporated into Gaussian 09.[28] It is known that the results of NBO analysis do not generally depend on the quality of the basis set, so the choice of the level of theory for the AdNDP application is adequate. The visualization of the results of the calculations was performed by using MOLEKEL 5.4.0.8.[29]

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