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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

COMPUTATIONAL ANALYSIS OF BONDING IN PhIO AND RELATED 'HYPERVALENT' IODINE COMPLEXES

RADU SILAGHI-DUMITRESCU[a]

ABSTRACT. Iodosylbenzene (iodosobenzene, PhIO) is a known oxygen atom transfer agent with interesting bioinorganic applications (e.g., formation of high-valent iron species), and is regarded as a representative member of a class of hypervalent iodine complexes. Iodine-oxygen bonding is analyzed in this and related complexes, based on molecular orbitals and Mulliken population analyses obtained from density functional theory (DFT) calculations. All data is seen to be straightforwardly interpretable in terms of a sigma dative bond between neutral iodine and oxygen units, as opposed to any alternative explanations involving iodine d-orbitals or hypervalence at the iodine.

Keywords: *hypervalence, iodosylbenzene, density functional, iodine*

INTRODUCTION

Iodosylbenzene (iodosobenzene, PhIO) is a known oxygen atom transfer agent with interesting bioinorganic applications, especially in formation of high-valent iron species with heme proteins/enzymes (e.g., peroxidases, cytochromes P450) and their models.[1-5] PhIO is regarded as a representative member of a class of hypervalent iodine complexes;[2] the term 'hypervalence' is rigorously defined as a situation where the number of valence electrons formally assignable to an atom exceeds the number of electrons that can be nominally accommodated within its valence shell. In particular, for iodine as well as for other main-group elements, 'hypervalence' would mean the presence of more than eight electrons within the valence shell. PhIO is often represented as Ph-I=O,[2] a formulation which clearly breaks the octet rule at the iodine. To avoid the apparent physical non-sense of breaking the octet rule, an alternative explanation has previously been proposed involving participation of the d-orbitals. In most cases however, it is advocated that X→O formulations be used instead of X=O. Nevertheless, the Ph-I=O notation is still widely used[2] and a clear formulation of the electronic structure of

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[a] *Universitatea Babeş-Bolyai, Facultatea de Chimie şi Inginerie Chimică, Str. Kogălniceanu, Nr. 1, RO-400084 Cluj-Napoca,Romania, rsilaghi@chem.ubbcluj.ro*

this compound would be useful, among others, in establishing reaction mechanisms and electronic structures in bioinorganic problems of general applicability.

Here, the iodine-oxygen bonding is analyzed in PhIO and related complexes, based on molecular orbitals and Mulliken population analyses obtained from density functional theory (DFT) calculations. All data is seen to be straightforwardly interpretable in terms of a sigma dative bond between neutral iodine and oxygen units, as opposed to any alternative explanations involving iodine d-orbitals or hypervalence at the iodine.

RESULTS AND DISCUSSION

Figure 1 shows relevant frontier molecular orbitals computed for PhIO employing DFT procedures (full geometry optimization with BP86/6-31G**, a standard approach for bioinorganic centers for which these results shall be relevant, as detailed in Refs.[6-9]). The C-I-O angle is computed to be 106º, indicative of an sp^3-type spatial arrangement of the orbitals at the iodine. LUMO and HOMO-7 clearly illustrate a single σ bond between I and O. HOMO-4 and HOMO also clearly illustrate no net π interaction between the two elements. The 'pseudo-σ' (or, two-electron three-center) interaction (HOMO-5 and HOMO-1) also offers no net bonding. Thus, the I-O bond has a clean σ character, and the bond order is 1.

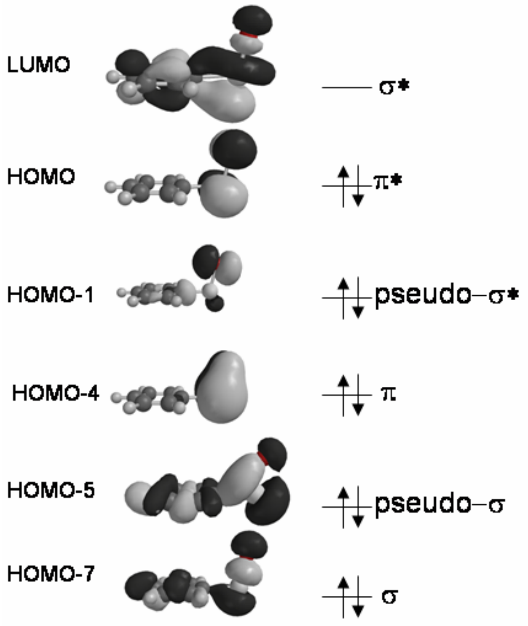

Figure 1. Bonding and anti-bonding orbitals for the I-O bond in PhIO.

The Mulliken population analysis shows that the oxygen atom in Figure 1 formally contains two electrons in each of its 2s, $2p_x$ and 2 p_y orbitals (assuming the z-axis to be along the I-O bond), with occupancies of 1.96, 1.61, and 1.87, respectively. In addition to these six electrons, the oxygen $2p_z$ orbital contains 1.17 electrons (equally distributed between the spin-up and spin-down orbitals). This data can be taken as indication of dative bonding between neutral PhI and an oxygen atom, PhI:→O; within this dative bond, the electrons are almost equally shared between the iodine and the oxygen, as illustrated in Figure 1 and by the -0.60 partial atomic charge on the oxygen atom. Gradual elongation of the I-O bond from the equilibrium length of 1.90 Å to 2.50 Å led to a gradual decrease in partial atomic charge on the oxygen, from -0.60 to -0.49; an *increase* would have been expected if the oxygen in PhIO was formally charged, O^{2-} or O^- - although one can also simply interpret these changes as evidence that heterolytic cleavage of the bond to generate on oxo moiety is not favoured. Such electronic structure description is completely consistent with the ability of PhIO to function as oxygen *atom* donor.

A similar situation is seen in the simpler aliphatic analogue, CH_3IO. The oxygen atom features a partial atomic charge of -0.61, and the orbital picture (not shown) is similar to that of Figure 1.

In the related $CH_3I(OH)_2$ species, the oxygen atoms feature partial atomic charges of -0.62 and -0.63, respectively, i.e. very similar to the oxygen atom in CH_3IO and in turn very similar to the water oxygen. $CH_3I(OH)_2$ formally results from CH_3I and two neutral hydroxyl radicals, HO, as opposed to CH_3IO resulting formally from CH_3I and a neutral oxygen atom. As the CH_3I iodine already has a formally closed-shell configuration, it can only engage in dative bonding. With a $2s^2$ $2p^4$ oxygen atom, such dative bonding is straightforward, as the oxygen can engage with an empty p orbital. On the other hand, with a hydroxyl radical-type oxygen ($2s^2$ $2p^5$), the I-O bond will contain one extra electron; in $CH_3I(OH)_2$, there will be a total of two extra electrons in the I-O σ systems, leading to a formal bond order of 0.5, and an expectedly longer I-O distance compared to CH_3IO. Indeed, the I-OH distances in $CH_3I(OH)_2$ are 2.16 Å and 2.17 Å, respectively, as opposed to 1.90 Å in CH_3IO. These two extra electrons in the σ system of $CH_3I(OH)_2$ also explain why although iodine engages in two dative bonds as opposed to only one in CH_3IO, the partial atomic charge on I is essentially the same in the two systems (0.47 vs 0.49, respectively).

In the related $CH_3I(O)(OH)_2$ species, the oxygen atoms feature partial atomic charges of -0.60 (on the OH oxygens) and -0.58 (on the non-protonated oxygen), respectively, suggesting that the three oxygen atoms have identical oxidation states. As expected (see above discussion on $CH_3I(OH)_2$), in $CH_3I(O)(OH)(OH)$ the I-OH bond lengths are distinctly longer than I-O, i.e.

2.10 Å, vs. 1.85 Å. The partial atomic charge on the iodine in $CH_3I(O)(OH)_2$ is 0.93, essentially double compared to CH_3IO or $CH_3I(OH)_2$ and reflecting a cumulative effect of the three dative bonds towards oxygenic ligands.

CONCLUSIONS

The partial atomic charges and bond lengths are consistent with an assignment of the I-O bond in PhIO as single dative, i.e. I→O. Within this bond, the electrons are distributed evenly between iodine and oxygen. An important point is that in none of the complexes examined is the octet rule *effectively* violated: there are indeed more than eight electrons in the non-participating and bonding orbitals around the iodine, but of all these electrons only 8 can be effectively assigned to iodine while the others effectively belong to oxygen. The I-O system holds 11 electrons (i.e., 10 electrons as shown in Figure 1, plus one electron of iodine involved in I-C bonding). We, therefore, see no need for the use of the term 'hypervalent' in connection to the complexes of this class (i.e., RIO, $RIO(OH)_2$, etc., where R is an organic substituent). The situation seen here appears in no way different from what is seen with other oxyanions (e.g. sulfate, nitrate), for all of which we advocate against the use of the term 'hypervalent' as well as against the use of a double-bond symbol, i.e., X→O with an oxygen atom accepting the dative bond, rather than X=O.

EXPERIMENTAL SECTION

The models were subjected to full geometry optimizations unless otherwise specified. Geometries were optimized for each spin state without any geometrical constraints, with the BP86 functional, which uses the gradient-corrected exchange functional proposed by Becke (1988),[10] the correlation functional by Perdew (1986),[11] and the DN** numerical basis set (comparable in size to 6-31G**), as implemented in Spartan.[12] For the SCF calculations, a fine grid was used, and the convergence criteria were set to 10^{-6} (for the root-mean square of electron density) and 10^{-8} (energy), respectively. For geometry optimization, convergence criteria were set to 0.001 au (maximum gradient criterion) and 0.0003 (maximum displacement criterion). Charges and spin densities were derived from Mulliken population analyses after DFT geometry optimization.

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