How Does a Container Affect Acidity of its Content: Charge-Depletion Bonding Inside Fullerenes

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Abstract: A recent study (Sci. Adv. 2017, 3, e1602833) has shown that FH–OH hydrogen bond in a HF-H$_2$O pair substantially shortens, and the H–F bond elongates upon encapsulation of the cluster in C$_{70}$ fullerene. This has been attributed to compression of the HF-H$_2$O pair inside the cavity of C$_{70}$. Herein, we present theoretical evidence that the effect is not caused by a mere compression of the H$_2$O-HF pair, but it is related to a strong lone-pair–π (LP–π) bonding with the fullerene cage. To support this argument, a systematic electronic structure study of selected small molecules (HF, H$_2$O, and NH$_3$) and their pairs enclosed in fullerene cages (C$_{60}$, C$_{70}$, and C$_{80}$) has been performed. Bonding analysis revealed unique LP–π$_{cage}$ interactions with a charge-depletion character in the bonding region, unlike usual LP–π bonds. The LP–π$_{cage}$ interactions were found to be responsible for elongation of the H–F bond. Thus, the HF appears to be more acidic inside the cage. The shortening of the FH bond in a simple hydrated acid, H$_2$O-HF, inside a C$_{60}$ fullerene suggests that fullerenes, though apolar, strongly interact with external anions, as was predicted from the multicenter covalency model of anion–π bonding. The similarity between anion–π and LP–π bonding suggests that fullerenes may form LP–π$_{cage}$ bonds with neutral molecules or clusters of neutral molecules enclosed inside a cage, such as H$_2$O, HF, and H$_2$O-HF. This notion has some support from other experiments, which prove that H–π$_{cage}$ type interactions influence reactivity of endohedral fullerenes. The questions to be answered are how important are potential H–π$_{cage}$ and LP–π$_{cage}$ interactions in fullerenes; and how do they affect mutual interactions of the enclosed molecules. To our surprise, though numerous bonding studies exist for endohedral metallofullerenes, the bonding interactions among fullerenes and the neutral molecules enclosed inside have not been studied in detail. Herein, we studied the structure and bonding in (HF-H$_2$O)@C$_{70}$ and selected endohedral fullerenes with small molecules (HF, H$_2$O, and NH$_3$) and their pairs enclosed inside a fullerene cage (C$_{60}$, C$_{70}$, and C$_{80}$). The series includes both experimentally known (a, b, d, e, g, h, j in Figure 1) and theoretically predicted (c, f, i, k, l in Figure 1) systems. The details on theoretical methodology are given in the Supporting Information.

Molecular structures of systems a–l in Figure 1 reveal that the H–π$_{cage}$ minimum distances increase from HF (2.42 Å in C$_{60}$ and C$_{70}$) to H$_2$O (2.65 Å in C$_{60}$; 2.70 Å in C$_{70}$) and NH$_3$ (2.62 Å in C$_{60}$; 2.77 Å in C$_{70}$) suggesting that H–π$_{cage}$ interactions weaken along this line (Figure 1). The N–π$_{cage}$ and O–π$_{cage}$ distances in NH$_3$@C$_{60}/C_{70}$ and H$_2$O@C$_{60}/C_{70}$ are within the normal ranges of LP–π interactions (Figure 1).

The most reliable probe to assess molecular interactions is the energy; herein, we define the encapsulation energy ($E_{enc}$).
interaction energy ($E_{\text{int}}$), and deformation energy ($E_{\text{def}}$) of each individual endohedral system according to Equations [1–3]:

\[
E_{\text{enc}} = E_{\text{int}} - (E_{\text{cage}} + E_{\text{HX}})
\]

(1)

\[
E_{\text{int}} = E_{\text{con}} - (E_{\text{cage}} + E_{\text{HX}})
\]

(2)

\[
E_{\text{def}} = E_{\text{rlx}} - E_{\text{con}}
\]

(3)

In the equations, $E_{\text{enc}}$, $E_{\text{int}}$, and $E_{\text{def}}$ denote the electronic energy of the complex, fullerene cage, and the endohedral molecule, respectively. $E_{\text{rlx}}$ and $E_{\text{con}}$ are electronic energies of the relaxed and the conserved (geometry in the complex) system, respectively. The calculated data for systems a–l are summarized in Table 1. Large $E_{\text{int}}$ values from $-7.8$ to $-2.2$ kcal mol$^{-1}$ imply strong interactions between the molecules and the cages.

**Table 1.** Encapsulation, $E_{\text{enc}}$, interaction, $E_{\text{int}}$, and deformation, $E_{\text{def}}$, energies for endohedral systems a–l calculated at the BSSE-corrected B3D97/def2-SVP level. $E_{\text{enc}}$ at the BSSE-corrected SCS-MP2/def2-TZVPP level is given for comparison (kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{enc}}$</th>
<th>$E_{\text{int}}$</th>
<th>$E_{\text{int}}$(SCS-MP2)</th>
<th>$E_{\text{def, cage}}$</th>
<th>$E_{\text{def, HX}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. HF@C$_{60}$</td>
<td>$-7.2$</td>
<td>$-8.3$</td>
<td>$-7.1$</td>
<td>$1.1$</td>
<td>$0.0$</td>
</tr>
<tr>
<td>b. H$<em>2$O@C$</em>{60}$</td>
<td>$-12.6$</td>
<td>$-16.7$</td>
<td>$0.1$</td>
<td>$0.0$</td>
<td></td>
</tr>
<tr>
<td>c. NH$<em>3@C</em>{60}$</td>
<td>$-15.2$</td>
<td>$-15.3$</td>
<td>$0.0$</td>
<td>$0.0$</td>
<td></td>
</tr>
<tr>
<td>d. HF@C$_{70}$</td>
<td>$-7.8$</td>
<td>$-8.1$</td>
<td>$0.0$</td>
<td>$0.0$</td>
<td></td>
</tr>
<tr>
<td>e. H$<em>2$O@C$</em>{70}$</td>
<td>$-12.1$</td>
<td>$-10.3$</td>
<td>$0.0$</td>
<td>$0.0$</td>
<td></td>
</tr>
<tr>
<td>f. NH$<em>3@C</em>{70}$</td>
<td>$-15.4$</td>
<td>$-15.5$</td>
<td>$0.0$</td>
<td>$0.0$</td>
<td></td>
</tr>
<tr>
<td>g. (HF-HF)@C$_{70}$</td>
<td>$-9.7$</td>
<td>$-11.5$</td>
<td>$0.1$</td>
<td>$2.0$</td>
<td></td>
</tr>
<tr>
<td>h. (H$<em>2$O-HF)@C$</em>{70}$</td>
<td>$-13.8$</td>
<td>$-14.4$</td>
<td>$0.2$</td>
<td>$1.6$</td>
<td></td>
</tr>
<tr>
<td>i. (NH$<em>3$-HF)@C$</em>{70}$</td>
<td>$-13.9$</td>
<td>$-15.4$</td>
<td>$0.2$</td>
<td>$3.3$</td>
<td></td>
</tr>
<tr>
<td>j. (H$_2$O-H$<em>2$O)@C$</em>{70}$</td>
<td>$-9.8$</td>
<td>$-12.6$</td>
<td>$0.3$</td>
<td>$3.5$</td>
<td></td>
</tr>
<tr>
<td>k. (NH$_3$-H$<em>2$O)@C$</em>{70}$</td>
<td>$-8.9$</td>
<td>$-11.8$</td>
<td>$0.4$</td>
<td>$4.6$</td>
<td></td>
</tr>
<tr>
<td>l. (NH$_3$-NH$<em>3$)@C$</em>{70}$</td>
<td>$-2.2$</td>
<td>$-8.1$</td>
<td>$0.7$</td>
<td>$8.2$</td>
<td></td>
</tr>
</tbody>
</table>
–15.5 kcal mol\(^{-1}\) for systems with a single molecule enclosed and –11.1 to –17.4 kcal mol\(^{-1}\) for systems with enclosed pairs (Table 1) infer clearly bonding interactions between the fullerene cage and the enclosed molecule(s). DFT-D3-calculated \(E_{\text{int}}\) are in a good agreement with the more accurate SCS-MP2/def2TZVPP data (Table 1). The deformation energy of the fullerene cage, \(E_{\text{def,cage}}\) in Table 1, is small in all cases, as was expected.\(^{[16]}\) \(E_{\text{def,HX}}\) of the enclosed molecules is relatively large and reflects structural rearrangement due to the encapsulation. It is highest for the most sterically demanding pair, \(\text{NH}_3\cdot\text{NH}_3\), and negligible for the systems with a single molecule enclosed (a–f in Figure 1 and Table 1).

To reveal the spatial charge redistribution upon encapsulation of the studied molecules, the real-space electron deformation density (EDD)\(^{[10,17]}\) was plotted in Figure 2 for selected systems (see Figures S2–S4 in the Supporting Information for the rest of systems). The most significant features of EDD plots are the missing electron density concentration regions between the heteroatom X (F, N, and O), and the \(C\) cage atoms that are usual in LP–\(\pi\) interactions.\(^{[10]}\) To provide a comparison, we analyzed bonding in an exohedral HF@\(C_{60}\) complex. The EDD maps of HF@\(C_{60}\) and two isomers of HF@\(C_{60}\) are compared in Figure 2. Both endo- and exo-hedral H–\(\pi\) bonded complexes showed general patterns of H–\(\pi\) bonding, that is, regions of charge concentration between the hydrogen and the cage (blue regions in the EDD maps of the systems between the H atoms and the \(\pi\)-systems).\(^{[17]}\) On the other hand, the depletion of the electron density between the heteroatoms and the cage (the red regions between X and cage atoms in Figure 2) in endohedral systems is in a striking contrast to what is usually observed for LP–\(\pi\) interactions, that is, charge concentration.\(^{[10]}\) These features can be interpreted in terms of Pauli repulsion between the lone pair of the heteroatom amplified by dipole-induced polarization of fullerene’s charge density that is responsible for masking the dipole of the endohedral molecules (Table S2 in the Supporting Information).\(^{[16]}\) The regions of ED concentration/depletion are more prominent in systems with encapsulated pairs because of the proximity of heteroatoms to the cage walls (see Figure 2 for \(\text{H}_2\text{O-HF@C}_{70}\) and Figures S2–S5 in the Supporting Information for the other systems).

Intuitively, charge polarization can account for stabilization of the polar endohedral molecules, but comparison of Hartree–Fock (HF) and SCS-MP2 tells a different story. Interaction energies computed at the HF/def2-TZVPP level presented in Table S3 in the Supporting Information are all positive, suggesting that the electrostatic interaction between the fullerenes and endohedral systems is insufficient to account for the bonding. The Hartree–Fock method does account for charge polarization, but not for the dispersion. Thus, charge polarization can be ruled out as the source of stabilization in these systems. This finding is in agreement with a physical model previously presented for description of fullerene interaction with neutral molecules.\(^{[14]}\)

A more quantitative picture of bonding can be obtained from the second-order density matrix of electron density by mapping the electron sharing between the atoms within the context of quantum theory of atoms in molecules (QTAIM).\(^{[18]}\) Our previous studies demonstrated that delocalization index (DI)\(^{[19]}\) is a useful tool for assessing the nature of chemical bonds.\(^{[10,19,20,21]}\) Furthermore, recent studies have proven that DI is quantitatively linked to the exchange-correlation component of interaction energy.\(^{[22,23]}\)

Our DI analysis confirms the presence of H–\(\pi\) and LP–\(\pi\) interactions between the endohedral species and the fullerenes (Figure 3). Comparing the DI values for molecules and pairs inside the fullerene cavities and in gas phase, but in the con-

**Figure 2.** EDD plots for selected species using different isosurfaces (0.005, 0.001, and 0.0005 e). Blue and red colors represent electron-density concentration and depletion, respectively. The orientation of endohedral species is the same as in Figure 1, except for \(\text{H}_2\text{O@C}_{70}\) that is presented from a different angle for better clarity.
served geometry of the complexes shows that encapsulation weakens the covalent character of H–X bonds, because both H and X employ their valence shell in interaction with the cage. The DI values for H–π bonds between hydrogens and the interior of the π-system of the fullerenes are comparable to those of ordinary hydrogen bonds. The H–π bonds of the endohedral HF with C_{60} and C_{70} are the strongest with a substantial DI value > 0.2 a.u., suggesting that HF is close to a position to protonate C=π bonds of fullerenes from the interior.

The DI analysis reveals the LP–π interactions between heteroatoms and the cage. The LP–π interactions strengthen from HF to NH_{3} in line with Lewis basicity of the lone-pair donor, with the distance of the donor atom from the cage carbons (Figure 1), and with increasing interaction energies, E_{int} (Figure 1 and Table 1). The magnitude of the DI values for LP–π interactions are two to three times greater than those reported previously for classic LP–π interactions, suggesting formation of weak bonds with a substantial multi-center character.

The formation of LP–π bonds inside fullerenes accompanied with a depletion of electron density between the interacting fragments is a reminiscent of charge-shift bonding proposed within the context of valence bond theory. In the present cases, correlation (dispersion) plays the main role in the bonding as it is known for systems, such as F_{2} (see relevant discussion in the Supporting Information).

LP–π bonds decrease the basicity of LP-donating heteroatoms, because they are engaged in interactions with the cage.
walls. However, once the HF and the base are encapsulated inside $C_{2p}$, the lone pair of the base interacts with the acidic proton of HF instead of the $\pi$ system of $C_{2p}$. Simultaneously, less basic F employs its valence shell to interact with the cage $\pi$ system. Consequently, the H–F bond becomes weaker (less covalent), and the acidity of the H atom increases. The same scenario repeats for other acid/base interactions, such as $\text{H}_2\text{O}$ or $\text{NH}_3$ and enhances acidity of the proton donors.

To test this hypothesis, we studied structure and electronic properties of $(\text{H}_2\text{O}$–$\text{HF})$@$C_{2p}$. The fluorine atom in $(\text{H}_2\text{O}$–$\text{HF})$@$C_{2p}$ strongly interacts with the $\pi$ system of $C_{2p}$ (Figure S5 in the Supporting Information). The H–F bond length is almost the same as that in $(\text{H}_2\text{O}$–$\text{HF})$@$C_{17}$ (0.964 Å in $C_{2p}$ vs. 0.967 Å in $C_{17}$; 0.948 Å in gas phase) suggesting enhanced acidity of HF. Although the inner cavity of $C_{2p}$ is large enough for the $\text{H}_2\text{O}$–HF pair to be able to adopt its gas-phase geometry, in this system, the (F)–O–(H) distance remains still shorter than in the free molecular complex but by 0.1 Å longer than in $(\text{H}_2\text{O}$–$\text{HF})$@$C_{17}$. This observation proves that both the (F)–O–(H) distance shortening and the H–F bond elongation originates from the electronic effects and is not primarily governed by the endohedral compression.

In summary, we investigated bonding between small neutral closed-shell molecules (HF, $\text{H}_2\text{O}$, and $\text{NH}_3$) and their pairs encapsulated inside a fullerene ($C_{60}$, $C_{70}$, and $C_{80}$). Electron-density analyses showed that enhanced acidity of the proton donor molecules is not merely because the endohedral compression is caused by the small cavity. The fullerenes influence acidity of the endohedral species rather by affecting the covalency of the H–X through strong LP–π*σ bond formation. The predicted systems are potential candidates for experimental synthesis on the basis of their encapsulation energies.

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Conflict of interest

The authors declare no conflict of interest.

References