

## Solvent-Driven Structural Changes in Anion– $\pi$ Complexes

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**Abstract:** Among the  $\pi$  interactions, the anion– $\pi$  interaction has been a novel type of interaction. In the cases of halide– $\pi$  complexes, which are the most typical examples of the anion– $\pi$  interaction, the theoretically predicted and experimentally observed structures in the gas phase are quite different from the most frequently observed crystal structures. We here investigate the structural changes in complexation of the  $F^-/Cl^-$  ion with triazine (TAz) as the number of water/acetonitrile molecules increases from 1 to 4. Both the covalent bonding type for  $F^-$ –TAz and the hydrogen-bonding type for  $Cl^-$ –TAz, which are the lowest-energy structures in the gas phase, change to the solvent-mediated anion– $\pi$ -type or displaced anion– $\pi$ -type complexes. This study explains why the (displaced) anion– $\pi$ -type complexes with some flexible orientations are most common in many crystal structures.

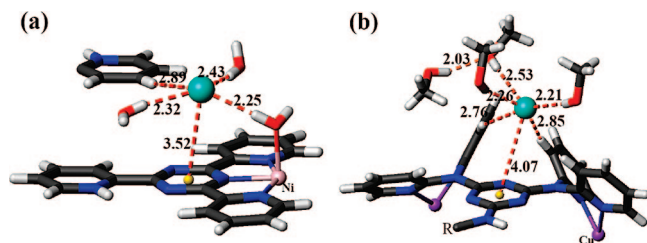
### Introduction

As intermolecular interactions involving  $\pi$  rings<sup>1</sup> play an important role in diverse chemical and biological systems, this understanding is vital for the design of nanomaterials and functional molecular systems.<sup>2</sup> Aromatic rings interact with other aromatic rings ( $\pi$ – $\pi$  interactions),<sup>3</sup> cations (cation– $\pi$  interactions),<sup>4</sup> hydrogen donors (H– $\pi$  interactions),<sup>5</sup> lone pairs (lp– $\pi$  interactions),<sup>6</sup> and anions (anion– $\pi$  interactions),<sup>7–11</sup> depending on the nature of  $\pi$ -ring systems and molecular partner systems involved. Compared with  $\pi$ – $\pi$ , cation– $\pi$ , and H– $\pi$  interactions, the lp– $\pi$  and anion– $\pi$  interactions have very recently been investigated, because aromatic rings were considered as electron sources which give repulsive interactions with anions. The anion– $\pi$  interactions are highly contrasted to the cation– $\pi$  interactions. Schneider et al.<sup>7</sup> initially published experimental evidence of  $\pi$  interactions between anions and aryl groups of several host–guest systems, and then they introduced the term “anion– $\pi$  interaction”. Gallivan and Dougherty and Danten et al. theoretically suggested the interaction of the negatively charged lone pair (lp) of water oxygen with the electron-deficient  $\pi$  ring of hexafluorobenzene.<sup>6a,b</sup> Recently, anion– $\pi$  interactions have been extensively investigated for

the strategy toward a new type of anion recognition, host architecture, and supramolecular self-assembly.<sup>8–11</sup>

Halides can interact with  $\pi$  systems in a few different complexation forms: covalent-bonding type, hydrogen-bonding type,<sup>12</sup> and noncovalent-anion– $\pi$  type. Mascal et al. and Berryman et al.<sup>11</sup> have shown that  $\pi$ -ring systems interacting with halides in the gas phase form either the H-bonding complexes or the covalent complexes (due to nucleophilic attack), whereas the complexes involving anion– $\pi$  interactions are less stable in many cases. This has been successfully demonstrated by recent experimental studies by Schneider et al.<sup>13</sup> The covalent-type complexes generally referred to as “Mesenheimer” complexes<sup>14</sup> are found to be the key intermediates in the nucleophilic aromatic substitution ( $S_NAr$ ) mechanism, and they have been characterized to be stable in the gas phase.<sup>15</sup> However, these are quite in contrast to the fact that the anions interacting with electron-deficient  $\pi$ -aromatic systems have relatively flexible orientations randomly distributed on the top of the ring in the Cambridge Structural Database.<sup>8d,11b</sup> These contrasting results between the crystal observation (noncovalent-bonding type) and the gas-phase structures (covalent-bonding/H-bonding type) demand further theoretical investigations of the anion– $\pi$  systems in the presence of solvating molecules. Additionally, as the solid-phase anion– $\pi$  complex structures are crystallized from the solvent medium, many of the crystal structures

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**Figure 1.** Fragments of the X-ray crystal structures of (a) diaqua-chloro-(2,4-bis(2-pyridyl)-6-(2-pyridinio)-1,3,5-triazine)-nickel (CCDC No. 254390) and (b)  $[\text{Cu}_3\text{Cl}_5(\text{opytrizediam})-(\text{MeOH})](\text{Cl})-6.1\text{CH}_3\text{OH}-\text{C}_4\text{H}_8\text{O}$  (CCDC No. 188817) (refs 14 and 15). Distances are in Ångstroms.

are found to be cocrystallized with the solvent molecules; thereby, the anions interact with an electron-deficient  $\pi$ -aromatic system on one side and the solvent molecules and other coordinating moieties on the other side. Figure 1 displays the representative examples of S-triazine (TAz;  $\text{C}_3\text{N}_3\text{H}_3$ )-based compounds cocrystallized with the anions, coordinating metal ions, and solvent molecules.<sup>16,17</sup>

It is presumable that the crystal structure of the anion- $\pi$  complexes would reflect the way the anion interacts with the  $\pi$  system in the solvent medium or at the onset of the crystal packing. During the transition from the normal solvated state to the partially desolvated lattice (onset of crystal packing when solvent molecules start displacing out due to the evaporation of the solvent), this partially solvated status would allow both anions and  $\pi$  moieties to be more attractive. As the partially desolvated lattice slowly loses further solvent molecules, the interaction between the anion and  $\pi$  moiety would be stronger, which eventually forms the crystal packing structure. Yet, microscopic structures of the anion- $\pi$  complexes in the presence of solvating molecules are hardly predictable because the solvation of anions and  $\pi$  rings could give a drastic change in the complexation type as compared with the gas-phase structures. It is also conceivable that the electrostatic interaction, which dominates in the covalent type and H-bonding type, would become much less significant in the presence of polar solvent molecules due to the competition between the anion-solvent interaction and the anion- $\pi$  interaction. Thus, a theoretical understanding on structural changes of the anion- $\pi$  complexes in the presence of solvent molecules would help explain why covalent-bonding-type interactions are hardly observed, while the (displaced) anion- $\pi$  types are most commonly observed in many crystal structures of the anions interacting with electron-deficient  $\pi$ -aromatic systems. However, the effect including counter cations could also play a significant role, but this has not been considered in the present study since, in most cases, the counter cations tend to be solvated away from the anions in the condensed phase.

TAz is a remarkable unit for supramolecular assembly and is known to interact with anions.<sup>18</sup> In this regard, we have studied the model complexes of TAz and  $\text{F}^-/\text{Cl}^-$  solvated by up to four water/acetonitrile molecules  $[\text{TAz} \cdots \text{F}^-/\text{Cl}^- \cdots (\text{H}_2\text{O}/\text{CH}_3\text{CN})_{n=0\sim 4}]$  and show that, as the number of solvent molecules increases, the covalent- or H-bonding-type

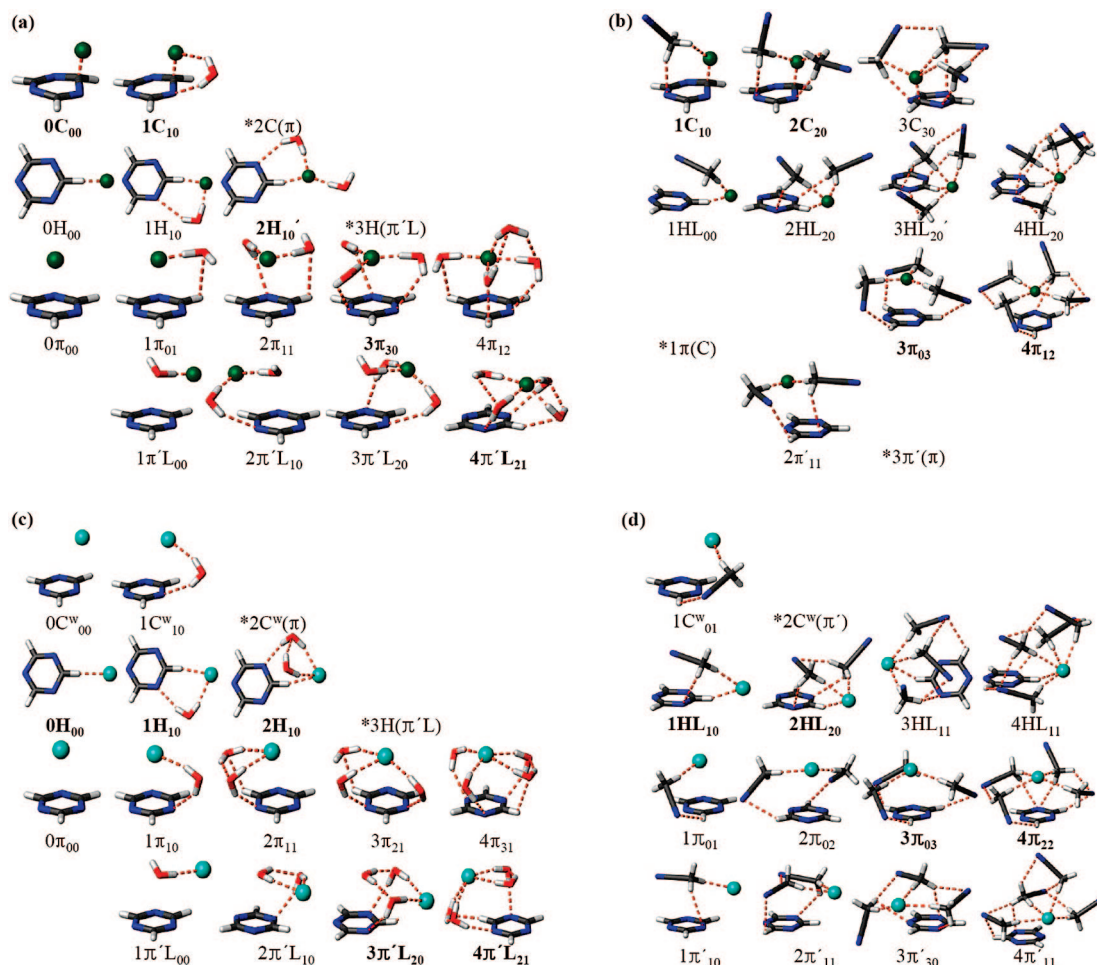
complex changes to the solvent-mediated anion- $\pi$  complex with the anion located above the  $\pi$  system.

## Calculation Methods

We performed ab initio calculations using the Gaussian 03, Molpro, and Turbomole programs.<sup>19</sup> To search for low-lying energy structures, we have extensively investigated many possible configurations on the basis of our previous experiences to generate low-lying energy structures from various molecular clusters.<sup>20</sup> For hundreds of structural isomers, we have carried out geometry optimization using Moller-Plesset second-order perturbation theory (MP2) for smaller systems and the resolution of the identity approximation (RI) of MP2 (RI-MP2)<sup>21</sup> for larger systems with the 6-31+G\* basis set. Then, a number of lower-energy structural isomers were optimized using the MP2 method with the aug-cc-pVDZ (abbreviated as aVDZ) basis set. The frequency analysis was made at the MP2/aVDZ level of theory to confirm the minimum-energy structures. For this low-energy conformer search, the cases for mono- to trisolvation are rather intuitive, while the cases for tetra-solvation require extensive investigation. The present study is indeed an extensive study to search for the low-lying energy structures for nanosolvation. Thus, we believe that the structures reported here would be the lowest-energy structures for each given cluster because practically all possible topological isomers have been investigated, and high-level ab initio calculations have been made along with the frequency analysis. Energies were obtained with the basis set superposition error correction. On the MP2/aVDZ geometries, we carried out the MP2/aug-cc-pVTZ (abbreviated as aVTZ) calculations, and the complete basis set (CBS) limit interaction energies at the MP2 level were obtained on the basis of the extrapolation method exploiting the fact that the electron correlation energy is proportional to  $N^{-3}$  for the aug-cc-pVNZ basis set.<sup>22,23</sup> Coupled cluster calculations with single and double excitations (CCSD) with aVDZ basis set on the MP2/aVDZ-optimized geometries were performed. Given the importance of a higher level of correlation energies, the CCSD/CBS limit interaction energies ( $\Delta E_c^{\text{C}}$ ) were evaluated from the MP2/CBS limit interaction energies by adding the difference between the MP2/aVDZ and CCSD/aVDZ interaction energies. Using the MP2/aVDZ zero-point energies (ZPE), the ZPE-corrected interaction energies ( $\Delta E_0$ ) at the CBS limit were evaluated. The amount of intermolecular charge transfer based on the natural bond orbital (NBO) analysis<sup>24</sup> was computed at the MP2/aVDZ level.

## Results and Discussion

Figure 2 shows the low-lying energy structures of  $\text{TAz} \cdots \text{F}^-/\text{Cl}^- \cdots (\text{H}_2\text{O}/\text{CH}_3\text{CN})_{n=0\sim 4}$  (a/b/c/d) complexes optimized at the MP2/aVDZ level of theory. TAz interacts with  $\text{F}^-/\text{Cl}^-$ , forming a few different kinds of isomers: (i) covalent interactions [C type] (where the  $\text{F}^-$  ion attacks a C atom of TAz, resulting in transformation from the  $\text{sp}^2$  to  $\text{sp}^3$  hybrid orbital), (ii) weakly covalent interactions [ $\text{C}^{\text{W}}$  type] (where the carbon atom of TAz to which the  $\text{Cl}^-$  ion is attached holds the  $\text{sp}^2$  type), (iii) H-bonding interactions [H type]



**Figure 2.** MP2/aVDZ low-lying energy structures of  $\text{TAz} \cdots \text{X}^- \cdots (\text{Solv})_{n=1 \sim 4}$ , where  $\text{X} = \text{F}/\text{Cl}$  and  $\text{Solv} = \text{H}_2\text{O}/\text{CH}_3\text{CN}$ . (a)  $\text{X}/\text{Solv} = \text{F}/\text{H}_2\text{O}$ , (b)  $\text{X}/\text{Solv} = \text{F}/\text{CH}_3\text{CN}$ , (c)  $\text{X}/\text{Solv} = \text{Cl}/\text{H}_2\text{O}$ , and (d)  $\text{X}/\text{Solv} = \text{Cl}/\text{CH}_3\text{CN}$ . For each interaction type (C, covalent-bonding;  $\text{C}^w$ , weakly covalent-bonding; H, H-bonding;  $\pi$ , anion- $\pi$  interaction;  $\pi'$ , displaced anion- $\pi$  interaction; HL, H-bonding and lp(solvent)- $\pi$  combined interaction;  $\pi'L$ , displaced anion- $\pi$  and lp(solvent)- $\pi$  combined interaction), the prefix “ $n$ ” and suffix subscripts “ $n1/n2$ ” in notations “ $nY_{n1n2}$ ” ( $Y, \text{C}^w/\text{H}/\pi'/\text{HL}/\pi'L$ ) are the number of solvent molecules and the number of  $\text{H}(\text{solvent})-\text{N}(\text{TAz})/\text{lp}(\text{solvent})-\text{H}(\text{TAz})$  H bonds ( $<3 \text{ \AA}$ ), respectively. The lowest-energy conformer for each solvated structure is marked in bold. A structure marked “\*” denotes that it changes to another lower-energy structure. Namely, in a, for  $n = 2$ , the C-type complex merges to the anion- $\pi$  complex [ $2\pi_{11}$ ], while for  $n = 3$ , the H-type complex merges to the  $\pi'L$ -type complex [ $3\pi'L_{20}$ ]. In b, for  $n = 1$ , the  $\pi$ -type complex merges to the C-type complex, while for  $n = 3$ , the  $\pi'$ -type complex merges to the  $\pi$ -type complex [ $3\pi_{03}$ ]. In c, for  $n = 2$ , the  $\text{C}^w$ -type complex merges to the anion- $\pi$  complex [ $2\pi_{11}$ ], while for  $n = 3$ , the H-type complex merges to the  $\pi'L$ -type complex [ $3\pi'L_{20}$ ]. In d, for  $n = 2$ , the  $\text{C}^w$ -type complex merges to the  $\pi'$ -type complex [ $2\pi'_{11}$ ].

(where  $\text{F}^-/\text{Cl}^-$  interacts with a H atom of TAz by H-bonding), (iv) noncovalent anion- $\pi$  interactions [ $\pi$  type] (where the  $\text{F}^-/\text{Cl}^-$  ion is located above the centroid of TAz), and (v) solvent-mediated displaced anion- $\pi$  interactions [ $\pi'$  type]. The  $\text{F}^-/\text{Cl}^-$  ion and TAz are connected with water/acetonitrile molecules mainly with  $\text{H}(\text{TAz}) \cdots \text{N}/\text{O}(\text{solvents})$ ,  $\text{N}(\text{TAz}) \cdots \text{H}(\text{solvents})$ , and  $\text{H}(\text{solvents})^{\delta+} \cdots \text{F}^-/\text{Cl}^-$  H-bonding. In our notation of the structures, the solvent hydrogen bonds are not taken into account because these are always present. The O/N lone pair of a water/acetonitrile molecule hydrogen-bonded to a  $\text{F}^-/\text{Cl}^-$  ion has a lp- $\pi$  interaction [L type] with TAz.<sup>6</sup> These are represented as either a  $\pi'L$  type (displaced anion- $\pi$  and lp(solvent)- $\pi$  combined interaction) or an HL type (H-bonding and lp(solvent)- $\pi$  combined interaction). In the figure, for each interaction type ( $Y: \text{C}/\text{C}^w/\text{H}/\pi/\pi'/\pi'L/\text{HL}$ ), prefix “ $n$ ” in notation “ $nY_{n1n2}$ ” is the number

of solvent molecules, and the suffix “ $n1/n2$ ” is used to designate notation between different structures. “ $n1/n2$ ” is correlated to the number of  $\text{H}(\text{solvent})-\text{N}(\text{TAz})$  or  $\text{lp}(\text{solvent})-\text{H}(\text{TAz})$  H bonds ( $<3.0 \text{ \AA}$ ), respectively (but not the real number of H bonds). Although the  $\text{O} \cdots \text{O}$  bond length indicating the radius of the first hydration shell (reflecting the direct interaction) in the liquid water is often given as  $3.4\text{--}3.5 \text{ \AA}$  (or the  $\text{H} \cdots \text{O}$  distance as  $2.5 \text{ \AA}$ ),<sup>25</sup> the  $\text{H} \cdots \text{N}$  or  $\text{lp} \cdots \text{H}$  distances within  $3.0 \text{ \AA}$  are denoted as pseudo H bonds in Figure 2, because in clusters, even long H-bond distances show the direct interaction because of the absence of the second solvation shell. Since the distance to represent the on/off H bond cannot be clearly defined in clusters, the above H-bond distances are not used to count the correct number of H bonds but are used for the proper designation of each cluster to distinguish between different structures.



**Table 1.** CCSD/CBS Limit Interaction Energies (in kcal/mol)<sup>a</sup>

<i>n</i>	C <sup>(w)</sup> type				H(L) type				$\pi$ type				$\pi'$ (L) type			
	conf	$\Delta d_c$	$\Delta E_e^C$	$\Delta E_0$	conf	$\Delta d_H$	$\Delta E_e^C$	$\Delta E_0$	conf	$\Delta d_{\text{face}}$	$\Delta E_e^C$	$\Delta E_0$	conf	$\Delta d_{\text{cen}}$	$\Delta E_e^C$	$\Delta E_0$
TAz...F <sup>−</sup> ...(H <sub>2</sub> O) <sub><i>n</i>=0~4</sub>																
0	<b>0C<sub>00</sub></b>	1.51	−33.99	−32.73	0H <sub>00</sub>	1.53	−18.28	−18.70	0 $\pi$ <sub>00</sub>	2.54	−11.27	−11.23				
1	<b>1C<sub>10</sub></b>	1.53	−17.04	−14.43	1H <sub>10</sub>	1.66	−13.68	−11.48	1 $\pi$ <sub>01</sub>	2.65	−10.00	−9.15	1 $\pi'$ <sub>L00</sub>	3.50	−10.36	−9.46
2					<b>2H<sub>10</sub></b>	1.75	−11.21	−10.18	2 $\pi$ <sub>11</sub>	2.72	−9.35	−8.01	2 $\pi'$ <sub>L10</sub>	3.59	−9.69	−8.27
3									<b>3<math>\pi</math><sub>30</sub></b>	2.76	−8.71	−8.44	3 $\pi'$ <sub>L20</sub>	3.67	−9.02	−8.30
4									4 $\pi$ <sub>12</sub>	2.92	−7.65	−6.78	<b>4<math>\pi'</math><sub>L21</sub></b>	3.78	−8.94	−7.28
TAz...F <sup>−</sup> ...(CH <sub>3</sub> CN) <sub><i>n</i>=0~4</sub>																
1	<b>1C<sub>10</sub></b>	1.52	−19.39	−17.11	1HL <sub>00</sub>	1.75	−11.91	−10.85								
2	<b>2C<sub>20</sub></b>	1.56	−11.25	−9.17	2HL <sub>20</sub>	1.82	−9.92	−8.88					2 $\pi'$ <sub>11</sub>	3.39	−8.53	−7.23
3	3C <sub>30</sub>	1.60	−5.71		3HL <sub>20</sub>	1.88	−8.34		<b>3<math>\pi</math><sub>03</sub></b>	2.79	−9.33					
4					4HL <sub>20</sub>	2.00	−7.76		<b>4<math>\pi</math><sub>12</sub></b>	2.79	−8.82					
TAz...Cl <sup>−</sup> ...(H <sub>2</sub> O) <sub><i>n</i>=0~4</sub>																
0	0C <sup>w</sup> <sub>00</sub>	2.90	−7.04	−6.83	<b>0H<sub>00</sub></b>	2.30	−9.39	−9.25	0 $\pi$ <sub>00</sub>	3.14	−6.63	−6.52				
1	1C <sup>w</sup> <sub>10</sub>	2.97	−8.23	−6.96	<b>1H<sub>10</sub></b>	2.31	−9.97	−8.75	1 $\pi$ <sub>10</sub>	3.15	−7.48	−6.17	1 $\pi'$ <sub>L00</sub>	4.24	−7.37	−6.73
2					<b>2H<sub>10</sub></b>	2.40	−9.84	−8.53	2 $\pi$ <sub>11</sub>	3.21	−8.39	−7.19	2 $\pi'$ <sub>L10</sub>	4.28	−8.79	−7.61
3									3 $\pi$ <sub>21</sub>	3.22	−6.48	−6.18	<b>3<math>\pi'</math><sub>L20</sub></b>	4.34	−7.57	−6.68
4									4 $\pi$ <sub>31</sub>	3.25	−4.98	−5.66	<b>4<math>\pi'</math><sub>L21</sub></b>	4.35	−6.57	−6.47
TAz...Cl <sup>−</sup> ...(CH <sub>3</sub> CN) <sub><i>n</i>=0~4</sub>																
1	1C <sup>w</sup> <sub>01</sub>	3.04	−7.65	−6.92	<b>1HL<sub>10</sub></b>	2.40	−7.70	−7.07	1 $\pi$ <sub>01</sub>	3.20	−6.94	−6.32	1 $\pi'$ <sub>10</sub>	4.44	−6.97	−6.39
2					<b>2HL<sub>20</sub></b>	2.41	−7.78	−6.78	2 $\pi$ <sub>02</sub>	3.24	−7.47	−6.29	2 $\pi'$ <sub>11</sub>	4.36	−7.70	−6.54
3					3HL <sub>11</sub>	2.49	−6.59		<b>3<math>\pi</math><sub>03</sub></b>	3.31	−7.57		3 $\pi'$ <sub>30</sub>	4.38	−6.86	
4					4HL <sub>11</sub>	2.54	−6.80		<b>4<math>\pi</math><sub>22</sub></b>	3.31	−7.50		4 $\pi'$ <sub>11</sub>	4.21	−6.89	

<sup>a</sup>  $\Delta E_0$  is the ZPE-corrected  $\Delta E_e^C$  (CCSD/CBS). The frequencies for ZPE were evaluated at the MP2/aVDZ level. The CCSD/CBS energies were obtained as  $[E_{\text{CCSD/CBS}} = E_{\text{MP2/CBS}} + (E_{\text{CCSD/aVDZ}} - E_{\text{MP2/aVDZ}})]$ , where the MP2/CBS energies were estimated on the basis of the extrapolation method exploiting the fact that the electron correlation energy is proportional to  $N^{-3}$  for the aVNZ. The distance between F<sup>−</sup> and C(TAz)/H(TAz)/Face(TAz)/Center(TAz) is  $\Delta d_c/\Delta d_H/\Delta d_{\text{face}}/\Delta d_{\text{cen}}$ . The lowest-energy conformers are denoted in bold characters.

We have listed the  $\Delta E_e^C$  (CCSD/CBS energy) and  $\Delta E_0$  (ZPE-corrected CCSD/CBS energy) of the complexes (Figure 2) in Table 1.

We first consider the case of TAz...F<sup>−</sup>...(H<sub>2</sub>O)<sub>*n*=0~4</sub> complexes (Figure 2a). For *n* = 0 and 1, the C-type complexes [0C<sub>00</sub>, 1C<sub>10</sub>] are the lowest-energy structures. As in the previous gas-phase ab initio studies by Mascal et al. and Berryman et al.,<sup>11</sup> we note that the C-type complex of 0C<sub>00</sub> is more stable than the H-type-[0H<sub>00</sub>]/ $\pi$ -type-[0 $\pi$ <sub>00</sub>] complex by 22/14 kcal/mol in  $\Delta E_0$ . For *n* = 1, 1C<sub>10</sub> is lower than 1H<sub>10</sub>/1 $\pi$ <sub>01</sub>/1 $\pi'$ <sub>L00</sub> by 3/5/5 kcal/mol. For *n* = 2, the H type [2H<sub>10</sub>] is the most stable, while the covalent-bonding type merges to the  $\pi$  type [2 $\pi$ <sub>11</sub>]. For *n* = 3, the H type merges to the water-mediated displaced anion- $\pi$  complex [3 $\pi'$ <sub>L20</sub>], while 3 $\pi$ <sub>30</sub> is the lowest-energy structure, which is nearly isoenergetic to 3 $\pi'$ <sub>L20</sub>. For *n* = 4, the displaced anion- $\pi$  complex [4 $\pi'$ <sub>L21</sub>] is nearly isoenergetic to or only 0.5 kcal/mol more stable than 4 $\pi$ <sub>12</sub>. This small energy difference between the displaced anion- $\pi$  type and the anion- $\pi$  type explains that these complexes would have relatively flexible orientations. The successive interaction energies [ $\Delta\Delta E_0 = \Delta E_0(n) - \Delta E_0(n-1)$ ] of the most favorable complexes by the sequential addition of water molecules from *n* = 1 to *n* = 4 are 18.30, 4.25, 1.74, and 1.16 kcal/mol, showing a dramatic change in complex type (C type for *n* = 1, H type for *n* = 2,  $\pi$  type for *n* = 3, and  $\pi'$ L type for *n* = 4).

In the case of TAz...F<sup>−</sup>...(CH<sub>3</sub>CN)<sub>*n*=0~4</sub> complexes (Figure 2b), for *n* = 0 to *n* = 2, the C-type complexes [0C<sub>00</sub>, 1C<sub>10</sub>, 2C<sub>20</sub>] are the lowest-energy structures. Although the anion- $\pi$  complex for *n* = 1 merges to the covalent-bonding-type complex [1C<sub>10</sub>], the anion- $\pi$  complexes for *n* = 3 and

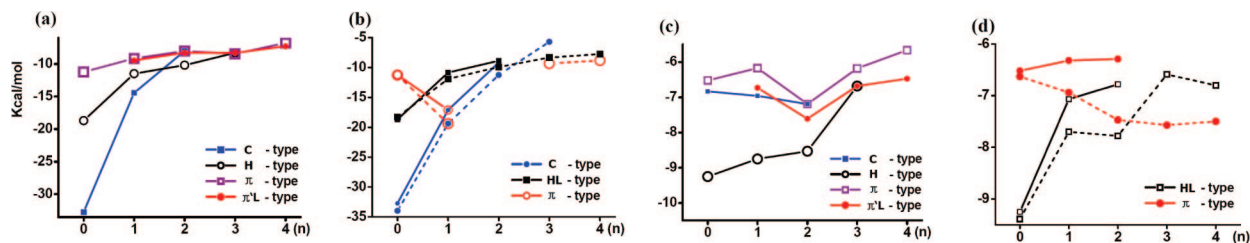
4 are the lowest-energy structures. The  $\pi$ -type complex of 3 $\pi$ <sub>03</sub>/4 $\pi$ <sub>12</sub> is 1 kcal/mol lower than the HL-type complex of 3HL<sub>20</sub>/4HL<sub>20</sub>.

In the case of TAz...Cl<sup>−</sup>...(H<sub>2</sub>O)<sub>*n*=0~4</sub> complexes (Figure 2c), for *n* = 0 to *n* = 2, the H types [0H<sub>00</sub>, 1H<sub>10</sub>, 2H<sub>10</sub>] are the most stable complexes, while for *n* = 3 and 4, the  $\pi'$ L types are the most stable. In the gas phase, the H-type complex of 0H<sub>00</sub> is 2/3 kcal/mol less stable than the C<sup>w</sup>-type/ $\pi$ -type complex. For *n* = 2, the C<sup>w</sup>-type complex merges to the  $\pi$  type, while for *n* = 3, the H-type complex merges to the solvent-mediated displaced anion- $\pi$  complex [3 $\pi'$ <sub>L20</sub>], which is the lowest-energy structure. The  $\Delta\Delta E_0$  values of the most preferable structures by the sequential addition of water molecules (*n* = 1–4) are 0.5, 0.22, 1.85, and 0.21 kcal/mol, respectively. A large change from  $\Delta E_0(2)$  to  $\Delta E_0(3)$  reflects a conformational change from the H type to the  $\pi'$ L type.

In the case of TAz...Cl<sup>−</sup>...(CH<sub>3</sub>CN)<sub>*n*=0~4</sub> complexes (Figure 2d, Table 1), for *n* = 0, 1, and 2, the H-type complexes are the most stable isomers, while the lowest-energy structures for *n* = 3 and 4 are the anion- $\pi$ -type complexes where the Cl<sup>−</sup> ion is above the centroid of TAz, as in the case of the F<sup>−</sup> complex.

In the absence of solvent molecules, the C type is the lowest-energy structure in the TAz...F<sup>−</sup> complex, and the H type is the lowest-energy structure in the TAz...Cl<sup>−</sup> complex. However, for both cases, in the presence of three water/acetonitrile molecules, the solvent-mediated anion- $\pi$ -type complexes become the lowest-energy structures. These interesting trends are depicted in Figure 3.

For the TAz...F<sup>−</sup> complexes, the covalent-bonding C-type interactions are characterized by the substantial



**Figure 3.** ZPE-corrected CCSD/CBS limit interaction energies [ $\Delta E_0$ ], (a) X/Solv = F/H<sub>2</sub>O, (b) X/Solv = F/CH<sub>3</sub>CN, (c) X/Solv = Cl/H<sub>2</sub>O, and (d) X/Solv = Cl/CH<sub>3</sub>CN for the low-lying energy structures of TAZ...X<sup>−</sup>...(Solv)<sub>n=1–4</sub>. Dotted lines are for the ZPE-uncorrected values.

**Table 2.** Charge Transfer (in MP2/aVDZ NBO Charge in au) from the F<sup>−</sup> Ion to the  $\pi$  System ( $\Delta q_\pi$ ) and the Solvent Molecules (Water/Acetonitrile;  $\Delta q_s$ )

F <sup>−</sup> (solv) <sub>n</sub>		C type		H(L) type		$\pi$ type		$\pi'$ (L) type	
n	$\Delta q_s$	conf	$\Delta q_\pi/\Delta q_s$	conf	$\Delta q_\pi/\Delta q_s$	conf	$\Delta q_\pi/\Delta q_s$	conf	$\Delta q_\pi/\Delta q_s$
TAZ...F <sup>−</sup> ...(H <sub>2</sub> O) <sub>n=0–4</sub>									
0		0C <sub>00</sub>	0.51	0H <sub>00</sub>	0.11	0 $\pi$ <sub>00</sub>	0.02		
1	0.12	1C <sub>10</sub>	0.46/0.04	1H <sub>10</sub>	0.06/0.07	1 $\pi$ <sub>01</sub>	0.02/0.11	1 $\pi'$ <sub>L00</sub>	0.04/0.11
2	0.17			2H <sub>&gt;10'</sub>	0.05/0.12	2 $\pi$ <sub>11</sub>	0.02/0.15	2 $\pi'$ <sub>L10</sub>	0.02/0.15
3	0.18					3 $\pi$ <sub>30</sub>	0.02/0.15	3 $\pi'$ <sub>L20</sub>	0.02/0.17
4	0.18					4 $\pi$ <sub>12</sub>	0.02/0.17	4 $\pi'$ <sub>L21</sub>	0.02/0.16
TAZ...F <sup>−</sup> ...(CH <sub>3</sub> CN) <sub>n=0–4</sub>									
1	0.10	1C <sub>10</sub>	0.48/0.03	1HL <sub>00</sub>	0.06/0.08				
2	0.13	2C <sub>20</sub>	0.44/0.05	2HL <sub>20</sub>	0.04/0.11			2 $\pi'$ <sub>L11</sub>	0.03/0.13
3	0.15	3C <sub>30</sub>	0.39/0.07	3HL <sub>20'</sub>	0.03/0.13	3 $\pi$ <sub>03</sub>	0.01/0.15		
4	0.18			4HL <sub>20</sub>	0.02/0.16	4 $\pi$ <sub>12</sub>	0.01/0.17		
TAZ...Cl <sup>−</sup> ...(H <sub>2</sub> O) <sub>n=0–4</sub>									
0		0C <sup>w</sup> <sub>00</sub>	0.07	0H <sub>00</sub>	0.06	0 $\pi$ <sub>00</sub>	0.02		
1	0.06	1C <sup>w</sup> <sub>10</sub>	0.05/0.05	1H <sub>10</sub>	0.04/0.05	1 $\pi$ <sub>10</sub>	0.01/0.05	1 $\pi'$ <sub>L00</sub>	0.03/0.06
2	0.10			2H <sub>10</sub>	0.04/0.08	2 $\pi$ <sub>11</sub>	0.01/0.08	2 $\pi'$ <sub>L10</sub>	0.02/0.08
3	0.10					3 $\pi$ <sub>21</sub>	0.01/0.10	3 $\pi'$ <sub>L20</sub>	0.03/0.10
4	0.11					4 $\pi$ <sub>31</sub>	0.01/0.11	4 $\pi'$ <sub>L21</sub>	0.01/0.11
TAZ...Cl <sup>−</sup> ...(CH <sub>3</sub> CN) <sub>n=0–4</sub>									
1	0.05	1C <sup>w</sup> <sub>01</sub>	0.04/0.05	1HL <sub>10</sub>	0.04/0.05	1 $\pi$ <sub>01</sub>	0.02/0.05	1 $\pi'$ <sub>L10</sub>	0.03/0.05
2	0.08			2HL <sub>20</sub>	0.02/0.09	2 $\pi$ <sub>02</sub>	0.03/0.08	2 $\pi'$ <sub>L11</sub>	0.02/0.08
3	0.12			3HL <sub>11</sub>	0.02/0.11	3 $\pi$ <sub>03</sub>	0.02/0.11	3 $\pi'$ <sub>L30</sub>	0.02/0.11
4	0.14			4HL <sub>11</sub>	0.02/0.13	4 $\pi$ <sub>22</sub>	0.01/0.14	4 $\pi'$ <sub>L11</sub>	0.02/0.13

charge transfer from the F<sup>−</sup> ion to the  $\pi$  system, whereas the charge transfer is small for the H type and insignificant for the  $\pi$  type and  $\pi'$ L type (Table 2). The anion– $\pi$  interactions related to the  $\pi$  type/ $\pi'$ L type have substantial dispersion energies, while the H-bonding related to the H type is mostly electrostatic. In particular, the charge-transfer-driven C-type interactions are highly susceptible to polar solvents like water because these interactions compete with the charge-transfer-driven ionic H-bonding, similar to the special type of H-bonding species (F–H–OH)<sup>−</sup>. In the presence of water molecules, for  $n = 1$ , the C-type interaction dominates (a charge transfer of 0.46 au from the F<sup>−</sup> ion to the  $\pi$  system), so that the (F–H–OH)<sup>−</sup> ionic H-bonding interaction is not properly formed. However, for  $n = 2$ , the ionic H-bonding interaction dominates, so the carbon atom to which the F<sup>−</sup> ion was attached when  $n = 0/1$  is no longer of the sp<sup>3</sup> type, and it returns to the sp<sup>2</sup> type. As a result, in the presence of more than two water molecules, H/ $\pi$ / $\pi'$ L-type interactions are more stable than the C-type interaction.

These charge-transfer-driven C-type interactions are less susceptible to the solvents of the relatively lower dielectric

constant. Therefore, in contrast to the case in the aqua phase, in the presence of the acetonitrile molecules, the (F–H–CH<sub>2</sub>CN)<sup>−</sup> ionic H-bonding interaction does not compete with the charge-transfer-driven C-type interaction. The charge transfer from F<sup>−</sup> to TAZ by forming the sp<sup>3</sup>-type carbon is 0.48/0.44/0.39 au for  $n = 1/2/3$ . In the F<sup>−</sup>...(CH<sub>3</sub>CN)<sub>n=1–3</sub> complexes, the charge transfer from the F<sup>−</sup> ion to the acetonitrile molecules is only 0.03/0.05/0.07 au. For  $n = 3/4$ , the complexation is characterized by the N(acetonitrile)...H(TAZ) H-bonding and the acetonitrile-mediated  $\pi$ -type interaction. This is because the solvation by acetonitrile molecules drives the anion to be located above the  $\pi$  ring, allowing a large empty space for the stabilization of the excess electron around the anion.

For the TAZ...Cl<sup>−</sup> complexes, in the presence of solvent molecules, weakly covalent-bonding C<sup>w</sup>-type interactions are characterized not only by small charge transfer (0.07/0.05 au for  $n = 0/1$ ) from the Cl<sup>−</sup> ion to the  $\pi$  system like the H-type interactions (0.06/0.04 au) but also by the sp<sup>2</sup>-type carbon (different from the sp<sup>3</sup>-type carbon in the F<sup>−</sup> complexes). Also, for the TAZ...Cl<sup>−</sup> complexes, the covalent-bonding-type complexes are not the lowest-energy structures in the presence of water/acetonitrile molecules. For  $n = 0/1/$

2, the complexation is characterized by the N(acetonitrile)··· $\pi$  lp- $\pi$  interaction and the H(solvent)···N(TAz) and  $\text{CH}^{\delta+}$ ··· $\text{Cl}^-$  hydrogen-bond interactions. The  $\text{C}^{\text{W}}$ -type complexes merge to the other type of complexes for  $n = 2$ . For  $n = 3/4$ , the anion is above the  $\pi$  ring as the  $\text{Cl}^-$  ion interacts with water or acetonitrile molecules, like in the case of the  $\text{F}^-$  complexes. In the presence of three and four water molecules, the complexation is characterized by both the H(water)···N(TAz) and H(water) $^{\delta+}$ ··· $\text{Cl}^-$  H bonds and the O(water)··· $\pi$  lp- $\pi$  interaction. In the presence of three and four acetonitrile molecules, the complexation is characterized by the N(acetonitrile)···H(TAz) H-bonding and the  $\pi$ -type interaction.

In crystal structures, each anion involved in the anion- $\pi$  interaction is surrounded by several other coordinating moieties. In addition, one or more solvent molecules per anion- $\pi$  complex are often present. Thus, the anion in the anion- $\pi$  complexes would have relatively flexible orientations toward the  $\pi$ -ring system, in agreement with a recent experiment.<sup>26</sup> Thus, the present results explain some of the real situations of the anion- $\pi$  interaction in crystals. Furthermore, the anion- $\pi$  complexes with a few water molecules or other solvent molecules in the gas phase can be experimentally observable, as in the case of halide-water clusters or benzene-water clusters.<sup>27</sup> Water molecules can act to pull the  $\text{F}^-/\text{Cl}^-$  ion away from TAz, so that the TAz can be fully hydrated (with minimal anion- $\pi$  interaction) by a large number of water molecules in the aqua phase, consistent with the result of the diminished  $\text{TAz}\cdots\text{Cl}^-$  interaction energy described on the basis of continuum solvent models.<sup>11a</sup>

Understanding the nature of anion- $\pi$  interaction in the presence microsolvants around the complex is important not only for the structural insight into these clusters, which would be observed in the gas-phase experiments, but also for the conceptual understanding of crystal growth in the solvent medium as the solvent molecules would eventually be displaced out during the crystal packing.

## Concluding Remarks

It is known that there is a distinct difference between the theoretically predicted or experimentally observed most-stable form of halide- $\pi$  complexes in the gas phase and the most frequently observed crystal structures of halide- $\pi$  complexes. However, the anion binding patterns are expected to change significantly in the presence of polar solvent molecules. As a  $\text{F}^-/\text{Cl}^-$  ion interacts with TAz, the binding pattern shows an intriguing structural change depending on the number of solvating molecules.

For the complexes with the  $\text{F}^-$  ion, in the absence of solvent molecules, covalent bonding is clearly the most preferable because the  $\text{F}^-$  ion attacks an  $\text{sp}^2$ -type C atom in TAz and transforms it into an  $\text{sp}^3$ -type C atom. This covalent-type complex is well-known as a "Jackson-Meisenheimer" or "Meisenheimer" complex. In the presence of a monohydrated  $\text{F}^-\cdots\text{TAz}$  system, the covalent-bonding type is still the lowest-energy structure. In the presence of two water molecules, the covalent-bonding type changes to the H-bonding type, which competes with

the anion- $\pi$  type and the water-mediated displaced anion- $\pi$  type. For three and four water molecules, the displaced anion- $\pi$  interaction is most preferable. In the presence of acetonitrile molecules, for one and two acetonitrile molecules, the covalent-bonding-type complexes are the most preferable, while for the complexes with three and four acetonitrile molecules, the anion- $\pi$ -type structures are the most stable. For the complexes with the  $\text{Cl}^-$  ion, the H-bonding type is the most preferable up to two solvent molecules. However, in the presence of three solvent molecules, the H-bonding type changes to the solvent-mediated anion- $\pi$  type. For three and four solvent molecules, the anion- $\pi$  types are the lowest-energy structures. Since both the anion- $\pi$  type and the displaced anion- $\pi$  type are nearly isoenergetic, it explains why both types with relatively flexible orientations are most common in many crystal structures.

The intriguing role of hydration/solvation on the structure of anion- $\pi$  complexes will shed light on various  $\pi$  systems interacting with anions and help resolve the differences between the gas-phase results and the crystal data. Furthermore, the understanding of microscopic structures of anions interacting with  $\pi$  systems in the solution phase would practically aid the design and development of novel anion receptors.<sup>28</sup>

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**Supporting Information Available:** Structures and interaction energies of low lying energy complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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