

Cyamelic Acid as Anion- π Type Receptor for ClO_4^- and NO_3^- : π -Stacked and Edge-to-Face Structures

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Abstract: Based on the binding energies at high levels of ab initio theory including coupled cluster theory at the complete basis limit, we show that cyameluric acid ($\text{C}_6\text{N}_7\text{O}_3\text{H}_3$) is a potent receptor for ClO_4^- and NO_3^- anions through the anion- π interactions. In contrast, cyanuric acid ($\text{C}_3\text{N}_3\text{O}_3\text{H}_3$) binds Cl^- , NO_3^- , and ClO_4^- with the hydrogen bonding type structures, while their anion- π type structures show slightly weaker binding. Consequently, the cyameluric acid having the C_{3h} symmetric C_6N_7 nucleus with electron withdrawing oxygen atoms is a novel anion- π type receptor for trigonal-planar and tetrahedral anions. The structures of the cyameluric acid interacting with Cl^- and ClO_4^- are considered as the π stacking type. For the cyameluric acid interacting with NO_3^- , the π (edge) type complex is only slightly more favored over the π (stack) type in the gas phase, but the π (stack) type is likely to be as stable as the π (edge) type in the solvent phase.

Introduction

As π -rings are involved in diverse types of π -interactions¹ (π - π interactions,^{2–7} H- π interactions,^{8–10} cation- π interactions,^{11,12} and anion- π interactions^{13–15}), understanding these interactions are essential for studying protein structures,^{8,16} nucleic acids structures,¹⁷ carbon nanotube structures,¹⁸ crystal packing,¹⁹ molecular/biomolecular recognition,²⁰ and functional molecular/material systems.²¹ Indeed, there have been numerous studies on π -interactions.^{22–24} However, as compared with other types of π -interactions, the anion- π interactions have been investigated very recently. Nevertheless, in the past few years, considerable progress has been made both theoretically and experimentally on the roles of anion- π interactions in supramolecular chemistry.^{13–15} Recently, anion- π interactions have been extensively investigated for the host architecture and supramolecular self-assembly. In addition, anion- π interactions have been used for the design and synthesis of an anion host as anion recognition.¹⁵ In this regard, we have been interested in designing a new type of anion receptors which utilize the anion- π interactions.

Cyclic C_3N_3 nucleus systems are known to be a remarkable unit for supramolecular assembly.²⁵ Because of the partially

positive charge on C atoms of cyclic C_3N_3 type molecule with D_{3h} symmetry, one might expect that the cyclic C_3N_3 nucleus systems could interact favorably with trigonal-planar anions. In this regard, it would be interesting to investigate if cyclic C_6N_7 nucleus systems would be a template for the construction of tripodal and cylindrophane molecular systems for the recognition of trigonal-planar and tetrahedral anions. C_6N_7 nucleus systems are also well-known as the building blocks of the diamondlike graphitic carbon(IV) nitrides²⁶ and as the burn-rate suppressants for solid rocket propellants.²⁷

Toward this direction, using high level ab initio calculations, we here investigate how the keto forms of cyanuric acid (**1**: $\text{C}_3\text{N}_3\text{O}_3\text{H}_3$) with the C_3N_3 nucleus and the cyameluric acid (**2**: $\text{C}_6\text{N}_7\text{O}_3\text{H}_3$)^{28,29} with the C_6N_7 nucleus (in Figure 1) interact with a halide anion (Cl^-), a trigonal-planar anion (NO_3^-), and a tetrahedral anion (ClO_4^-). Indeed, we find that **2** is a novel anion receptor moiety which binds trigonal-planar or tetrahedral anions through the anion- π interaction. Cyanuric acid and cyameluric acid have five and seventeen tautomeric forms, respectively. In the gas phase, **1** and **2** are the most stable keto forms among the tautomers of cyanuric acid and cyameluric acid, respectively, and these keto forms are likely to remain stable in water and methanol.²⁸ Recently, it is experimentally noted that the keto form of cyameluric acid is favored in the crystal.²⁹ Furthermore,

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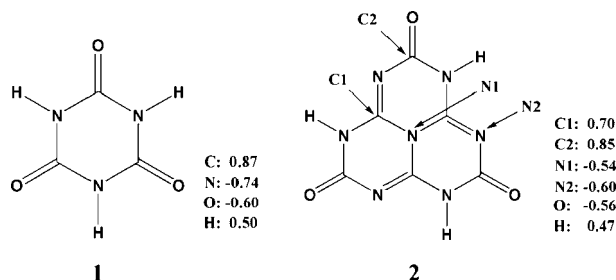


Figure 1. NBO charges (au) of cyanuric acids (**1**: $C_3N_3O_3H_3$) and cyameluric acids (**2**: $C_6N_7O_3H_3$).

in consideration of the futuristic synthetic functionalization of the hydrogen atoms with the functional groups that could enhance the binding affinity of the trigonal-planar and tetrahedral oxyanions, we have chosen **1** and **2**. This will enable us to understand the strength of the anion- π interaction in the anion complexed with the tripodal based receptors consisting of cyameluric acid ring template.

Calculation Methods

We performed ab initio calculations using Gaussian 03 and Molpro programs.³⁰ The initial structures were optimized by using Møller–Plesset second-order perturbation theory (MP2) with the 6-31+G* basis set and then optimized at the MP2 level of theory with the aug-cc-pVDZ (abbreviated as aVDZ) basis set. To confirm their minimum energy structures, the frequency analysis was done at the MP2/aVDZ level of theory. Then, the low lying energy structures were fully optimized on the potential surfaces that are corrected for basis set superposition error (BSSE) using the counterpoise (CP) method of Boys and Bernardi³¹ for the complexes of **1**. However, these BSSE corrected geometries were obtained by optimizing only the vertical distances of the anion from the ring plane with the fixed monomer geometries using the CP method for the **2**-anion complexes. The effects of the inclusion of higher level of correlation energies were examined by performing the coupled cluster calculations with single and double excitations (CCSD) and the CCSD with perturbative triple excitations [CCSD(T)] using the aVDZ basis set on the BSSE corrected MP2/aVDZ optimized geometries. Then, the MP2/aug-cc-pVTZ (abbreviated as aVTZ) calculations were carried out, and the complete basis set (CBS) limit interaction energies at the MP2 level were obtained based on the extrapolation method exploiting that the electron correlation energy is proportional to N^{-3} for the aug-cc-pVTZ basis set.^{32,33} For **1** interacting with Cl^- , the CCSD(T)/aVTZ calculations were performed, and the CBS limit interaction energies at the CCSD(T) level [CCSD(T)/CBS] were evaluated. These CCSD(T)/CBS binding energies (which were evaluated by extrapolating the aVDZ and aVTZ values) are found to be very close to the CCSD(T)/CBS* binding energies which were evaluated from the MP2/CBS binding energies simply by adding the difference between the MP2/aVDZ and CCSD(T)/aVDZ binding energies (without the CCSD(T)/aVTZ value).³² Owing to the large size of NO_3^- and ClO_4^- , these interaction energies with **1** are reported with the CCSD(T)/CBS* binding energies. Using the MP2/aVDZ zero point energies (ZPE)

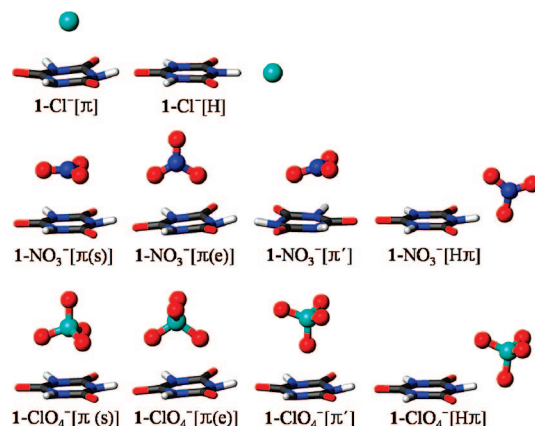


Figure 2. Structures of the $1-Cl^-[\pi, H]$, $1-NO_3^-[\pi(s): \text{stack}]$, $\pi(e): \text{edge}$, $\pi', H\pi$, and $1-ClO_4^-[\pi(s), \pi(e), \pi', H\pi]$ complexes.

and thermal energies, the ZPE-corrected interaction energies (ΔE_0), enthalpies (ΔH_{298} at 1 atm), and free energies (ΔG_{298} at 1 atm) at 298 K were evaluated. The natural bond orbital (NBO) charges were obtained at the MP2/aVDZ level. In the case of **2** interacting with anions, we evaluated the MP2/CBS and CCSD/CBS* values (but not the CCSD(T)/CBS* values due to their large size). To evaluate the interaction energies in the condensed phase, single point energy calculations were performed using self-consistent reaction field (SCRF) theory with the isodensity surface polarized continuum model (IPCM)³⁴ at the MP2/aVDZ level. The solvent dielectric constant used for water is 78.

To understand the nature of the interaction energies, we analyzed the energy components [E_{es} : electrostatic energy, E_{ind*} : effective induction energy including the induction-induced exchange energy and the contribution of third and higher order on the uncorrelated level ($\Delta E_{ind*} = \Delta E_{ind} + \Delta E_{exch-ind} + \Delta E_{int,HF}$), E_{disp*} : effective dispersion energy including the dispersion-induced exchange energy ($\Delta E_{disp*} = \Delta E_{disp} + \Delta E_{exch-disp}$), and E_{exch*} : effective exchange repulsion energy with the induction-induced and dispersion-induced exchange energies excluded ($\Delta E_{exch*} = \Delta E_{exch} - \Delta E_{exch-ind} - \Delta E_{exch-disp}$)]. The symmetry adapted perturbation theory (SAPT)³⁵ combined with density functional theory (DFT) for monomer properties, called DFT-SAPT by Hesselmann et al.,³⁶ is known to yield reliable energy components with the asymptotically corrected PBE0 (PBE0AC) exchange-correlation (xc) functional. Using the density-fitting (DF) approximation, SAPT calculations can be successfully performed on medium sized systems. In the present study, the PBE0AC xc functional with the ALDA xc kernel was used. In the DF-DFT-SAPT calculations, a purely local ALDA xc kernel was used for hybrid xc functionals.³⁷ The aVDZ set was used as the atomic basis set, and the cc-pVTZ MP2-fitting set was employed for the DF approximations.

Results and Discussion

Figure 2 shows optimized structures of **1** interacting with Cl^- , NO_3^- , and ClO_4^- . Those anions can interact with **1** in either the hydrogen bonding type [H-type] or the anion- π type [π -type]. For $1-Cl^-$, the covalent bonding type of

Table 1. Intermolecular Distances (R in Å) and Interaction Energies (ΔE_e in kcal/mol) for the 1-Anion Complexes^a

	MP2			CCSD		CCSD(T)		
	R	aVDZ	aVTZ	CBS	aVDZ	CBS*	aVDZ	CBS*
Cl ⁻								
π	2.94	-18.00	-18.91	-19.29	-17.57	-18.86	-18.16	-19.45
H	1.84	-21.74	-22.92	-23.41	-19.61	-21.28	-20.94	-22.62
NO ₃ ⁻								
π (s)	2.90	-15.14	-16.63	-17.25	-13.61	-15.71	-14.94	-17.05
π (e)	2.56	-16.72	-17.33	-17.59	-16.32	-17.20	-17.13	-18.01
π'	2.64	-15.92	-16.63	-16.92	-14.74	-15.75	-15.87	-16.88
H π	1.55	-21.56	-22.20	-22.47	-20.16	-21.07	-21.38	-22.29
ClO ₄ ⁻								
π (s)	2.78	-14.02	-14.59	-14.84	-12.02	-12.84	-13.37	-14.19
π (e)	2.55	-13.05	-13.95	-14.32	-11.96	-13.24	-13.02	-14.29
π'	2.51	-11.54	-12.22	-12.51				
H π	1.73	-15.05	-15.60	-15.84	-13.95	-14.73	-15.00	-15.78

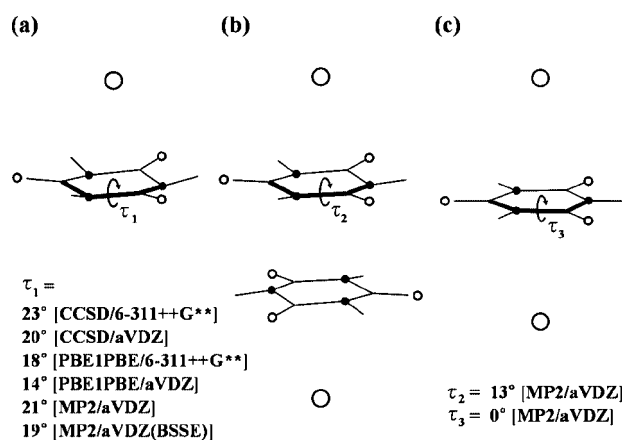
^a The BSSE-corrected MP2/CBS and CCSD(T)/CBS energies were estimated based on the extrapolation method exploiting that the electron correlation energy is proportional to N^{-3} for the aVNZ basis set. The CCSD(T)/CBS* energies were estimated using $[E_{\text{CCSD(T)/CBS}} = E_{\text{MP2/CBS}} + (E_{\text{CCSD/aVDZ}} - E_{\text{MP2/aVDZ}})]$. R is either the vertical distance from the ion to the ring plane of **1** (for π complexes) or the shortest H-bond distance from the ion to the N atom of **1** (for H complexes). In the case of 1-Cl⁻, we also calculated the CCSD(T)/aVTZ energies (-18.94/-22.30 kcal/mol for π -type/H-type). By using these aVTZ values, the extrapolated CCSD(T)/CBS energies for the π -type/H-type are -19.27/-22.87 kcal/mol, which are very close to the CCSD(T)/CBS* energies (-19.45/-22.62 kcal/mol). Structures NO₃⁻: π' and ClO₄⁻: π (e) are transition states, and structure ClO₄⁻: π' is a saddle point with three imaginary frequencies.

Table 2. Thermodynamic Quantities (in kcal/mol at the CCSD(T)/CBS* Level) for the 1-Anion Complexes

	Cl ⁻		NO ₃ ⁻			ClO ₄ ⁻	
	π	H	π (s)	π (e)	H π	π (s)	H π
ΔE_0	-18.95	-23.64	-16.27	-17.18	-22.40	-13.46	-15.12
ΔH_{298}	-19.15	-23.81	-15.92	-16.77	-22.01	-13.03	-14.62
ΔG_{298}	-12.15	-18.13	-4.99	-7.52	-13.54	-3.45	-7.26

complex (where an anion attacks a partially positive carbon atom of π system, resulting in transformation from the sp² to sp³ hybrid orbital) is not observed. For the complexes of **1** with NO₃⁻ and ClO₄⁻, the H-type is combined with the π -type [π (edge)-type]. In the case of π -type, three different isomers [π (stack), π (edge), and π' types] are observed. 1-NO₃⁻ [π'] and 1-ClO₄⁻ [π (edge)] complexes with one small imaginary frequencies would be the transition states of the H π -type. 1-ClO₄⁻ [π'] has three imaginary frequencies. Other optimized geometries are the local or global minima geometries. Similar structural and energetic studies for the case of s-triazine with NO₃⁻ and BF₄⁻ have been done by other groups.³⁸ We have listed the CBS limit interaction energies (ΔE_e) at the MP2/CCSD/CCSD(T) level in Table 1. The ΔE_0 , ΔH_{298} and ΔG_{298} are obtained from the CCSD(T)/CBS* binding energies with the MP2/aVDZ ZPE and thermal energies corrections (Table 2). In tables and figures, π (stack)/ π (edge) will be simply denoted as π (s)/ π (e) for brevity.

At the MP2/CBS* level of theory, the π (edge)-type complex is 0.3 kcal/mol more stable than the π (stack)-type for 1-NO₃⁻, while the π (stack)-type is 0.5 kcal/mol more stable than the π (edge)-type for 1-ClO₄⁻. For 1-ClO₄⁻, however, the π (edge)-type is 0.1 kcal/mol more stable than the π (stack)-type at the CCSD(T)/CBS* level of theory. For the complexes of **1** with Cl⁻, NO₃⁻, and ClO₄⁻, the interaction energies of the H(π)-type complexes are lower than the most stable π -type complexes by 3.2, 4.2, and 1.5 kcal/mol at the CCSD(T)/CBS* level, respectively. For Cl⁻, the interaction energy for the H-type/ π -type is -19.27/-22.87 kcal/mol at the CCSD(T)/CBS level and -19.45/

**Figure 3.** The C-N-C-N torsion angles (τ : dihedral angles) in the optimized geometries of 1-Cl⁻ (a), Cl⁻-1-1-Cl⁻ (b), and Cl⁻-1-Cl⁻ (c).

-22.62 kcal/mol at the CCSD(T)/CBS* level, showing that both CBS and CBS* values are almost the same. In Table 1, the MP2/CBS interaction energies are close to the CCSD(T)/CBS* values, while the CCSD/CBS* values are slightly underestimated but consistently lower than the CCSD(T)/CBS* values. In this regard, in the case of **2** interacting with the anions, we report the CCSD/CBS* energies.

For 1-Cl⁻/NO₃⁻/ClO₄⁻ complexes, $\Delta\Delta E_0$ [ΔE_0 (π -type)- ΔE_0 (H(π)-type)] is 4.7/5.2/1.7 kcal/mol, and $\Delta\Delta G_{298}$ [ΔG_{298} (π -type)- ΔG_{298} (H(π)-type)] is 6.0/6.0/3.8 kcal/mol, respectively. Therefore, for all the three cases, the H(π) types are much more stable.

The MP2/aVDZ optimized geometry of 1-Cl⁻ [π] shows that the ring plane is significantly distorted with the C-N-C-N torsion angles of 21° in Figure 3a, which is in good agreement with the value (20°) at the CCSD/aVDZ level. This ring distortion is due to the partial change in the hybridization from sp² to sp³ of both peripheral carbon and nitrogen atoms. Since **1** does not show strong electron delocalization in contrast to the aromatic ring systems, **1** can

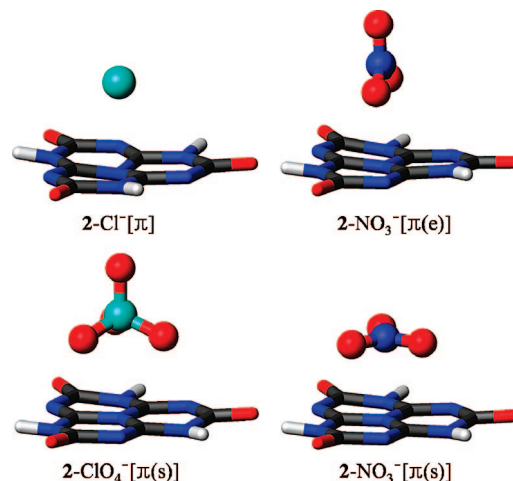
Table 3. DFT-SAPT (Density Fitting) Interaction Energy Components (kcal/mol) for the **1**-Anion Complexes^a

	Cl ⁻		NO ₃ ⁻			ClO ₄ ⁻	
	π	H	π(s)	π(e)	Hπ	π(s)	Hπ
ΔE _{int}	-17.40	-21.22	-13.85	-15.61	-20.02	-11.77	-14.07
ΔE _{deform}	2.91	5.10	1.99	2.46	4.60	1.83	2.31
ΔE _{sapt}	-20.31	-26.32	-15.84	-18.07	-24.62	-13.60	-16.37
ΔE _{es}	-28.33	-32.61	-17.09	-21.99	-33.06	-19.48	-19.41
ΔE _{ind*}	-8.07	-24.55	-5.90	-7.33	-20.83	-6.20	-10.95
ΔE _{disp*}	-6.97	-6.60	-8.57	-7.63	-6.99	-9.96	-5.73
ΔE _{exch*}	23.07	37.45	15.72	18.89	36.25	22.04	19.72

^a The DFT-SAPT values without density fitting are also calculated. In the case of **1**-Cl⁻, ΔE_{int} = -17.86/-21.74, ΔE_{sapt} = -20.77/-26.84, ΔE_{es} = -28.32/-32.61, ΔE_{ind*} = -8.06/-24.53, ΔE_{disp*} = -7.44/-7.13, and ΔE_{exch*} = 23.05/37.43 kcal/mol. ΔE_{deform}: CCSD(T)/aVDZ deformation energy (ΔE_{int} = ΔE_{sapt} + ΔE_{deform}).

be easily distorted when interacting with a highly electronegative anion. However, in the crystal structures of cyanuric acid nucleus that shows favorable anion-π interactions with anions, the planarity of the ring is well restored. For example, the crystal structure of Fe-pseudocryptand [CCDC No. 623175] in which the cyanuric acid nucleus interacts with Cl⁻ through the anion-π interactions³⁹ shows the C-N-C-N torsion angle of 8° (see the Supporting Information). Here, the cyanuric acid ring plane interacts with Cl⁻ in one side, with another cyanuric acid ring plane in the other side through the π-π interactions, forming an anion-π-π-anion complex. Another crystal structure of the cyanuric acid with Cl⁻ is found to have the Cl⁻-**1**-Cl⁻ complex with the C-N-C-N dihedral angle of 0°. ⁴⁰ In the MP2 calculated geometries of the Cl⁻-**1**-Cl⁻ complex and the Cl⁻-**1**-Cl⁻ complex, the C-N-C-N torsion angle is 13° and 0°, respectively, which is in good agreement with the crystal structures. Therefore, the difference between the calculated geometry of the isolated **1**-Cl⁻ complex and the X-ray structure in the crystal form arises from the fact that the X-ray structure is for the condensed phase, while the calculated structure is for the isolated molecule in the gas phase.

Table 3 shows the DFT-SAPT interaction energy components. It should be noted that ΔE_{sapt} is the interaction energy between individual monomers on the complex geometries. Upon the complexation with an anion, there are some deformations in geometries of the π-rings and anions. At the CCSD(T)/aVDZ level, ΔE_{deform} for the H-type/Hπ-type of **1**-Cl⁻/NO₃⁻ complex is 5.1/4.6 kcal/mol. What distinguishes the interactions between the H(π)-type and the π-type is the magnitude of the induction energies and dispersion energies. In the case of the H(π)-type, the induction contribution (38/34/30% for Cl⁻/NO₃⁻/ClO₄⁻) to the total attractive interaction energies (ΔE_{es} + ΔE_{ind*} + ΔE_{disp*}) is much larger than that for the π-type (19/20/17%), while the dispersion contribution (10/11/16%) is much smaller than that for the π-type (16/21/28%). The electrostatic energy components of both the H(π)-type (51/54/54% for Cl⁻/NO₃⁻/ClO₄⁻) and the π-type (65/60/55%) are large. Owing to the large diffuse nature of the electron cloud in the anionic systems, the magnitude of the exchange repulsion energies in these anion complexes, which is similar to the

**Figure 4.** Structures of the **2**-Cl⁻[π], **2**-NO₃⁻[π(e), π(s)], and **2**-ClO₄⁻[π(s)] complexes.**Table 4.** Intermolecular Distance (R in Å), Interaction Energies (ΔE_e in kcal/mol), and SAPT(DF-DFT(PBE0AC)/aVDZ) Interaction Energy Components (in kcal/mol) for the **2**-Anion Complexes

	Cl ⁻	NO ₃ ⁻		ClO ₄ ⁻
	π	π(s)	π(e)	π(s)
R ^a	2.94	2.74	2.54	2.72
MP2/aVDZ	-32.19	-29.84	-30.74	-28.08
MP2/aVTZ	-33.44	-31.11	-31.68	-29.40
MP2/CBS	-33.96	-31.64	-32.08	-29.96
CCSD/aVDZ	-30.94	-27.23	-29.58	-25.81
CCSD/CBS*	-32.71	-29.30	-30.92	-27.69
ΔE _{int}	-31.38	-27.39	-29.14	-25.69
ΔE _{def}	2.59	2.01	2.46	2.15
ΔE _{sapt}	-33.97	-29.40	-31.60	-27.84
ΔE _{es}	-44.16	-32.99	-36.90	-30.17
ΔE _{ind*}	-12.66	-10.52	-11.86	-9.05
ΔE _{disp*}	-9.64	-13.46	-11.07	-12.85
ΔE _{exch*}	32.49	27.57	28.23	24.24
ΔE _{ipcm(water)} ^b	-11.94	-15.89	-15.30	-18.14

^a R is the shortest vertical distance from an anion atom (O) to the ring plane. ^b Interaction energies in water (dielectric constant: ε = 78) are estimated using SCRFP/PCM(MP2/aVDZ).

magnitude of the electrostatic interaction energy, is substantially larger than that in the case of the complexes involving cations.^{12f}

Since the structure of **1** with D_{3h} symmetry has a highly positive charge on each C atom (0.87 au) due to the neighboring N atoms (with larger electronegativity than the C atom) and the electron withdrawing substituents of =O (Figure 1), it favors interacting with trigonal-planar and tetrahedral anions. Similarly, we note that the structure of **2** with C_{3h} symmetry also has highly positive charge on each C1 carbon atom (0.70 au) surrounded by three N atoms including the centroid N atom (-0.54 au) and on each C2 carbon atom (0.85 au) surrounded by two N atoms and one =O atom. Therefore, we can expect that **2** would be a novel anion receptor recognizing trigonal-planar and tetrahedral anions.

Figure 4 shows the optimized structures of **2**-complexes interacting with Cl⁻, NO₃⁻, and ClO₄⁻, and Table 4 lists the CBS interaction energies and the SAPT interaction energy components.

For the 2-Cl⁻/NO₃⁻/ClO₄⁻ complexes, the interaction energies of the π -type complexes are \sim 30 kcal/mol, which are greater than those of the charged H-bonding complexes. Any H-types of the 2-NO₃⁻/ClO₄⁻ complexes and any covalent types of the 2-Cl⁻/NO₃⁻/ClO₄⁻ complexes merged to the π -type complexes during the geometry optimization. The H-type of the 2-Cl⁻ complex, though it exists, is much less stable than the π -type complex. As compared with the π (stack)-type of **1**, in the π (stack)-type of **2** the electrostatic energy increases almost twice (from -17 to -33 kcal/mol) for the binding with NO₃⁻, while it increases only 1.5 times (from -28/-19 to -44/-30 kcal/mol) for the binding with Cl⁻/ClO₄⁻. It is because the positive N on the centroid of **2** favorably interacts with the negative N on the center of NO₃⁻. Nevertheless, in the case of the 2-NO₃⁻ complex, the π (edge)-type (i.e., edge-to-face type) is slightly more stable than the π (stack)-type by \sim 1 kcal/mol, because the π (edge)-type (wherein the highly positively charged N atom of NO₃⁻ stays away from the highly positive C atoms on the rings of **2**) has the larger electrostatic energy gain by \sim 4 kcal/mol (-33.0 vs -36.9 kcal/mol in ΔE_{es} for the edge vs stack form). However, both π (edge)-type and the π (stack)-type are nearly isoenergetic, so that the structure can be changed depending on the solvation and packing effects. The π (edge)-type which has a larger electrostatic energy gain is expected to be slightly less stabilized than the π (stack)-type in the condensed phase, so that the π (stack)-type would be easily observable in crystals. Indeed, the SCRFP/PCPM(MP2/aVDZ) calculations show that in water the π (stack)-type is \sim 0.6 kcal/mol more stable than the π (edge)-type (Table 4). Thus, all the structures of the 2-Cl⁻/NO₃⁻/ClO₄⁻ complexes would have the anion- π interactions in the π -stacked form in solvents and crystals, while for the 2-NO₃⁻ complex the π (edge)-type is also compatible. What is more important is that the interaction energy of **2** with Cl⁻/NO₃⁻/ClO₄⁻ in the gas phase changes from -32/-31/-28 kcal/mol (at the MP2/aVDZ level) to -12/-16/-18 kcal/mol in water. Thus, ClO₄⁻ and NO₃⁻, which have smaller binding energies than Cl⁻ in the gas phase, have larger binding energies in water, indicating that **2** is a selective receptor for ClO₄⁻ and NO₃⁻ in solution.

Conclusions

Using high levels of ab initio theory including coupled cluster theory at the complete basis limit, we have investigated the possibility of designing anion receptors which strongly bind trigonal-planar and tetrahedral anions. The cyanuric acid (C₃N₃O₃H₃) binds Cl⁻, NO₃⁻, and ClO₄⁻ as H(π)-type structures, while its anion- π type structures are less stable. Thus, we studied the cases of the cyameluric acid (C₆N₇O₃H₃) having the C_{3h} symmetric C₆N₇ nucleus with electron withdrawing O atoms and Cl⁻, NO₃⁻, and ClO₄⁻ anions having π -type structures with the binding energies of \sim 30 kcal/mol in the gas phase. Although Cl⁻ has larger binding energies than NO₃⁻ and ClO₄⁻ in the gas phase, this trend is reversed in water. The cyameluric acid is a novel anion- π type receptor for ClO₄⁻ and NO₃⁻, and consequently, it would be used as a template for building tripodal and cylindrophane receptors for the selective recognition of

trigonal-planar and tetrahedral anions toward the design of novel anion receptors.⁴¹

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Supporting Information Available: XYZ coordinates of the MP2/aug-cc-pVDZ BSSE-corrected optimized geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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