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Approximate Additivity of Anion−π Interactions: An Ab Initio Study on Anion−π, Anion−π_2 and Anion−π_3 Complexes

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We have studied the additivity of the anion−π interaction using high level ab initio calculations. We have optimized chloride and bromide complexes with one, two and three aromatic units (such as trifluoro-*s*-triazine and *s*-triazine). We have analyzed the interaction using the atoms in molecules theory and studied the charge transfer using several methods for deriving atomic charges. The results revealed additivities of both the geometries and the binding energies. We have also proposed a neutral receptor for chloride based on multiple anion−π interactions. Finally, we have simulated solvent effects within the self-consistent reaction field model.

1. Introduction

Anion coordination chemistry[1] is one of the most relevant and challenging fields of research within supramolecular chemistry.[2] It has chemical applications in, for example, catalysis,[3] analytical chemistry[4] and reactions templated[5] by anions. Additionally, it plays an important role in biochemical processes such transport and binding of amino acids and nucleotides.

A molecular interaction between an electron deficient π-electron system of aromatic compounds and an anion is an important topic that has attracted considerable attention in the last two years. We[6,7] and others[8] have demonstrated theoretically that interaction between π-electron deficient aromatic rings and anions is energetically favorable. The anion−π interaction is in general dominated by electrostatic and anion-induced polarization. The nature of the electrostatic component has been rationalized by emphasizing the function of the permanent quadrupole moment of the electron deficient aromatic ring, which is opposite to benzene. Experimentally, anion−π interactions have been shown between *s*-triazine and chloride in the solid state.[9] In solution, three important works have been recently published: first, halide recognition through aromatic receptors based on anion−π interactions;[10] second, an aromatic anion receptor based on *s*-triazine and pyridine rings, which is able to encapsulate two chloride anions;[11] third, anion binding at the peripheral nitrogen of a C_6F_5-substituted N-confused porphyrin,[12] which gives unusually high association constants that are attributed to an anion−π interaction between the anion and the C_6F_5 aromatic system. It has been proposed that receptors based on multiple anion−π interactions are promising candidates for the construction of anion-sensing receptors and understanding how they can selectively bind, functionalize, and transport anionic species in biological systems would be of great importance for the design of new drugs.[8b] In addition, the binding of anions to neutral receptors is of special significance; first, competing counterion complexes are not present if cationic hosts are used, and second, the selectivity is highest in neutral receptors due to the dominance of directional interactions.[13] For instance, the high specificity of neutral anion proteins is due to a recognition site where the anion guest is bonded simply via multiple hydrogen bonds.[14] Obviously, each noncovalent interaction is weaker than the Coulombic interaction present in charged receptors; however, a sufficiently large number of noncovalent interactions can lead to selective neutral receptors for anions.

In this paper we report a high level ab initio calculation of several complexes of chloride and bromide anions with trifluoro-*s*-triazine (TFZ) and *s*-triazine (TAZ). In particular, we have computed 1:1, 1:2, and 1:3 anion−π-system complexes to analyze the additivity of the anion−π interaction. We have chosen TAZ and TFZ because, so far, the more promising candidates to become useful receptors for the recognition of anions via anion−π interactions are based on *s*-triazine and related aromatic rings. Additionally, *s*-triazine is synthetically more versatile than other electron-deficient aromatic rings as, for instance, perfluorobenzenes or nitrobenzenes. To date, there are no previous studies in the literature dealing with the additivity of the anion−π interaction. Recently, a related work devoted to the additivity in cation−π interactions has been published.[15]

2. Computational Methods

The geometries of the complexes included in this study were initially optimized at the Hartree−Fock (HF) level using the 6-31++G** basis set by means of the Gaussian-98 program.[16] The binding energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys−Bernardi counterpoise technique.[17] Frequency calculations at the same level confirmed that the structures are at their energy minima. High level ab initio calculations are usually required to obtain accurate results, especially when π-interactions are present. In such systems, the use of a theoretical treatment that takes into account the electron correlation is mandatory. The MP2 method is the least expensive post HF procedure that takes

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into account dispersion forces, which are neglected in currently popular DFT approaches. Nevertheless, the main obstacle to a more widespread use of the MP2 method continues to be its high computational requirement, principally in medium to large systems. Because of the time-consuming nature of the MP2 calculations on these systems, we have used a computationally faster treatment than the traditional MP2 method. This method is the resolution of the identity MP2 (RI-MP2),[18,19] which uses an auxiliary fitting basis to avoid treating the complete set of two-electron repulsion integrals. The RI-MP2(full) calculations without imposing any symmetry constraint were done using the program TURBOMOLE version 5.7.[20] The RI-MP2 method applied to the study of cation and anion−π interactions is considerably faster than the MP2 and the interaction energies and equilibrium distances are almost identical for both methods.[21] We have also computed single point energy calculations at the MP2(full)/6-31++G**//RI-MP2(full)/6-31++G** level of theory to further validate the reliability of the RI-MP2 values. It is worth mentioning that the interaction energies reported here are not zero-point energy (ZPE) corrected. The RI-MP2 method is much faster than MP2; however, frequency analysis calculations are not available, which is a drawback. Fortunately, we have previously demonstrated that the ZPE corrections in the binding energies of anion−π complexes are very small, being in all the cases studied less than 1 kcal/mol.[6,7,22] For instance, Cl^- complexes **1** and **3**, which have been previously reported by us at MP2/6-31++G** level of theory,[7] were true minima with ZPE values of 0.22 and 0.24 kcal/mol, respectively. Br^- complexes **2** and **4** (this work) were true minima at the MP2/6-31++G** level of theory with ZPE of 0.08 and 0.02 kcal/mol, respectively. We have also performed frequency calculations for the computationally more affordable 1:2 complex, i.e., complex **7**, at the MP2/6-31++G** level. We have found that it is a true minimum with a ZPE value of 0.13 kcal/mol. We have also done calculations using the fluoride anion; however, F^- complexes are not stationary points and the minimum-energy structures correspond to the nucleophilic attack of the anion at one of the carbon atoms. For some complexes, we have carried out calculations simulating two solvents ($CHCl_3$ and H_2O) within the self-consistent reaction field model at the MP2(full)/6-31++G**//RI-MP2(full)/6-31++G** level of theory. We have used a polarizable continuum (PCM) model as currently implemented in Gaussian-03 program.

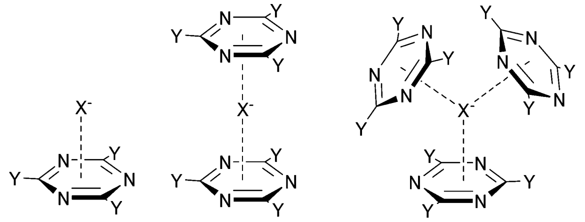
The charge transfer from the anion to the aromatic rings has been evaluated using several methods for deriving atomic charges, i.e., Mulliken population analysis,[23] Merz−Kollman scheme[24] and the atoms-in-molecules method (AIM).[25] In addition, we have evaluated the charge density and its Laplacian at the cage critical point that is present in the complexes linking the anion with the center of the aromatic rings. These values can be directly associated with the strength of the interaction.[6] The AIM charges were computed using the AIM2000 v2.0 program[26] at the MP2(full)/6-31++G**//RI-MP2(full)/6-31++G** level.

3. Results and Discussion

TABLE 1: Binding Energies (kcal/mol) with (E_{CP}) and without (E) the Basis Set Superposition Error (BSSE) Correction and Equilibrium Distances (R_e, Å) at Several Levels of Theory for Complexes 1−12

	RI-MP2			MP2//RI-MP2	
complex	E	E_{CP}	R_e	E	E_{CP}
1 (TFZ-Cl^-)	−20.3	−15.1	3.008	−20.3	−15.0
2 (TFZ-Br^-)	−18.8	−14.2	3.176	−21.8	−14.2
3 (TAZ-Cl^-)	−9.0	−5.3	3.220	−9.0	−5.2
4 (TAZ-Br^-)	−8.4	−5.0	3.338	−10.7	−5.1
5 (TFZ_2−Cl^-)	−38.2	−28.6	3.006	−38.5	−28.5
6 (TFZ_2−Br^-)	−36.4	−26.8	3.170	−41.7	−26.8
7 (TAZ_2−Cl^-)	−17.3	−10.4	3.213	−17.4	−10.4
8 (TAZ_2−Br^-)	−16.8	−10.2	3.370	−20.6	−10.0
9 (TFZ_3−Cl^-)	−64.2	−41.0	3.019[a]	−65.6	−41.0
10 (TFZ_3−Br^-)	−60.7	−38.6	3.172[a]	−75.3	−38.6
11 (TAZ_3−Cl^-)	−39.2	−22.2	3.015[a]	−39.6	−22.2
12 (TAZ_3−Br^-)	−37.6	−21.7	3.372[a]	−49.2	−21.7

[a] Mean distances.



1, X=Cl, Y=F **5**, X=Cl, Y=F **9**, X=Cl, Y=F

2, X=Br, Y=F **6**, X=Br, Y=F **10**, X=Br, Y=F

3, X=Cl, Y=H **7**, X=Cl, Y=H **11**, X=Cl, Y=H

4, X=Br, Y=H **8**, X=Br, Y=H **12**, X=Br, Y=H

Figure 1. Anion−π complexes (**1**−**12**) studied in this work.

Table 1 reports the complexation energies with (E_{CP}) and without (E) the basis set superposition error (BSSE) correction and equilibrium distances of complexes **1**−**12** at two levels of theory. The E_{CP} values computed at the MP2(full)/6-31++G**//RI-MP2(full)/6-31++G** level of theory are almost identical to the values computed at the RI-MP2/6-31++G** level. This result confirms the consistency of the RI-MP2 method. The E_{CP} values shown in Table 1 correspond to the interaction of chloride and bromide with one, two, and three TFZ or TAZ units. First, we have analyzed the additivity of the anion−π interaction in terms of the binding strength. The results computed for the TFZ complexes show that the binding energy computed for the 1:2 sandwich complexes **5** and **6** (see Figure 1) is almost twice the value of the binding energy computed for the 1:1 complexes **1** and **2**, respectively. Likewise, the binding energy computed for the 1:3 complexes **9** and **10** is approximately 3 times the binding energy obtained for the 1:1 complexes **1** and **2**, respectively. This result suggests that the binding energy between either Cl^- or Br^- and two or three TFZ rings could be estimated using the binding energy of the 1:1 complex and it is a clear indication of the additivity of the interaction. The latter is also supported by the geometry of the complexes, where the R_e of the anion to the ring center is basically insensitive to the stoichiometry of the complex. The behavior of TAZ_2-X (X = Cl^- and Br^-) complexes is the same as TFZ_2-X complexes; i.e., the binding energy computed for the sandwich complexes **7** and **8** (see Figure 1 and Table 1) is almost twice the value of the binding energy computed for the 1:1 complexes **3** and **4**, respectively. The binding energies and equilibrium distances obtained for the TAZ_3-X complexes **11** and **12** have a different behavior when compared to the TFZ_3-X complexes **9** and **10**. Although the E_{CP} value of complexes **9** and **10** is almost 3 times the values of complexes **1** and **2**, respectively, the E_{CP} value of complexes **11** and **12** is significantly more than 3 times the value of complexes **3** and **4**, respectively, indicating an apparent cooperativity. However, by analyzing the geometries of the TAZ_3-X complexes **11** and **12** (see Figure 3), some extra interactions can be noticed; i.e., several hydrogen bonds between the N atoms and the C−H bonds of the *s*-triazine units are formed, giving rise to E_{CP} values more negative than expected. We have

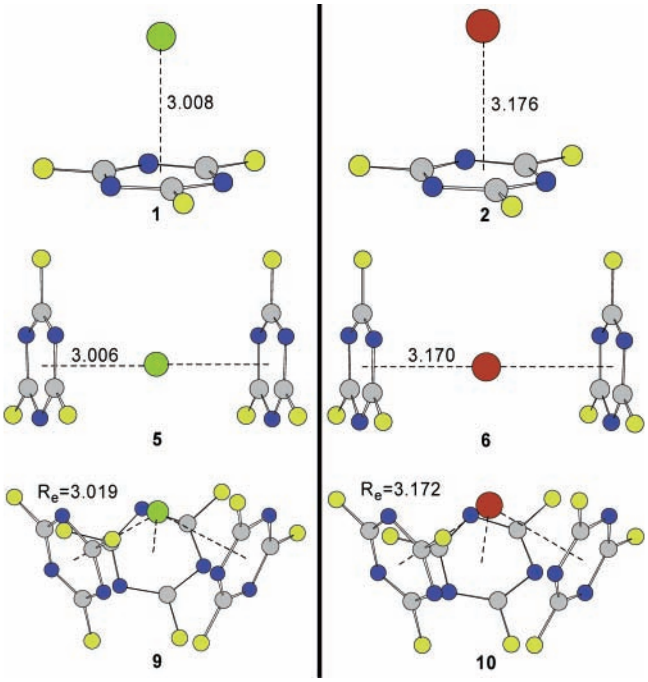


Figure 2. RI-MP2(full)/6-31++G** fully optimized structures of the two groups of TFZ complexes. The equilibrium distances shown in the 1:3 complexes **9** and **10** are mean distances. All distances are in Å.

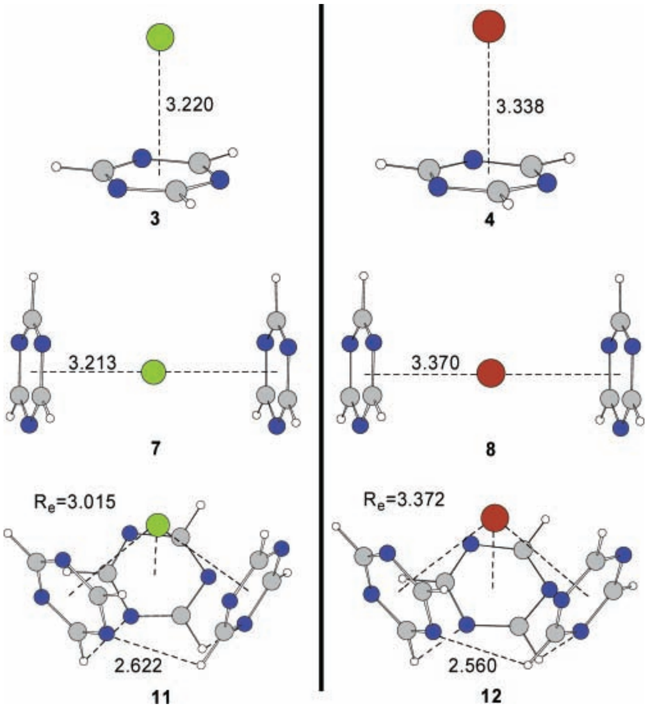


Figure 3. RI-MP2(full)/6-31++G** fully optimized structures of the two groups of TAZ complexes. Distances in Å. The hydrogen bond between the N atom and the C−H bond of the *s*-triazine units and its distance is shown. The distances shown in complexes **11** and **12** are mean distances.

TABLE 2: Atomic Charge of Cl$^-$ and Br$^-$ in the Complexes (*q*, e) and the Values of the Electron Charge Density (ρ, au) and Its Laplacian ($\nabla^2\rho$, au) at the Cage Critical Point Formed upon Complexation at the MP2//RI-MP2 Level of Theory

complex	q_{AIM}	$q_{\mathrm{M-K}}$	q_{Mull}	$10^2\rho$	$10(\nabla^2 r)$
1 (TFZ-Cl$^-$)	−1.006	−0.871	−0.856	0.853	0.323
2 (TFZ-Br$^-$)	−1.050	−0.882	−0.839	0.801	0.282
3 (TAZ-Cl$^-$)	−1.021	−0.902	−0.956	0.595	0.223
4 (TAZ-Br$^-$)	−1.106	−0.917	−0.959	0.599	0.216
5 (TFZ$_2$−Cl$^-$)	−0.943	−0.692	−0.790	0.832	0.326
6 (TFZ$_2$−Br$^-$)	−1.103	−0.762	−0.448	0.789	0.284
7 (TAZ$_2$−Cl$^-$)	−1.065	−0.724	−0.989	0.594	0.227
8 (TAZ$_2$−Br$^-$)	−1.125	−0.748	−1.099	0.568	0.205
9 (TFZ$_3$−Cl$^-$)	−0.769	−0.653	−0.773	0.838	0.324
10 (TFZ$_3$−Br$^-$)	−1.135	−0.734	−0.964	0.794	0.286
11 (TAZ$_3$−Cl$^-$)	−1.015	−0.692	−0.939	0.599	0.220
12 (TAZ$_3$−Br$^-$)	−1.113	−0.686	−0.660	0.573	0.203

evaluated these extra interactions energetically, performing some single points of the TAZ$_3$-X geometries by removing the anion and freezing the rest of the structure, to estimate the contribution of the hydrogen bonds to the total interaction energy. For chloride (complex **11**) this contribution (denoted as E^{HB}) is −12.5 kcal/mol, which turns into $E_{\mathrm{CP}}^{\mathrm{HB}} = -5.8$ kcal/mol when the BSSE correction is applied. Therefore, the binding energy of complex **11** due to the effect of the three anion−π interactions can be estimated as follows: $E_{\mathrm{CP}} - E_{\mathrm{CP}}^{\mathrm{HB}} = -22.2 - (-5.8) = -16.4$ kcal/mol, which is approximately 3 times the E_{CP} of complex **3**. For bromide (complex **12**), the $E^{\mathrm{HB}} = -12.2$ kcal/mol and the $E_{\mathrm{CP}}^{\mathrm{HB}} = -5.8$ kcal/mol; therefore, the binding energy of complex **12** without the contribution of the hydrogen bonds can be estimated to be −15.9 kcal/mol, approximately three times the E_{CP} of complex **4**. These results confirm the additivity in TAZ$_3$-X complexes of the anion−π interaction and explain the fictitious cooperativity observed in the binding energies of **11** and **12**. The optimized geometry of the 1:3 complexes does not involve the three aromatic rings in a D_{3h} arrangement; instead, it forms a cone-shaped structure (see Figures 2 and 3). For TAZ complexes this fact can be easily explained by the presence of several N···H−C hydrogen bonds; however, for TFZ this rationalization is not valid. A likely explanation for the conical arrangement of the TFZ 1:3 complexes is that the repulsion between the fluorine atoms attached to the TFZ rings is lower in comparison with a D_{3h} arrangement.

Second, the additivity of the interaction has been analyzed from different and interesting points of view. In Table 2, we report the charge transfer from the anion to the aromatic rings in the complexes and we also report the values of the charge density and its Laplacian at the cage critical point (CP) that appears upon complexation. The charge transfer has been evaluated using several methodologies, and the values derived from the Mulliken, AIM, and Merz−Kollman (M−K) approaches are summarized in Table 2. Mulliken and AIM charge variation of chloride and bromide on going from 1:1 to 1:3 complexes is not intuitive and does not follow an understandable rule. In addition, the AIM charges predict a counterintuitive charge transfer from the electron deficient ring to the anion for all complexes apart from **5** and **9**. This lack of relationship between the charge of the anion (either AIM or Mulliken) and the stoichiometry of the complexes is in complete disagreement with the energetic and geometric analyses. However, the analysis from the M−K method for deriving charges gives a completely different picture. The charge of the anion in the complexes is gradually reduced when going from the 1:1 to 1:3 complex for the four series studied here, in agreement with the expected behavior whether the interaction presents additivity. The disagreement between AIM and M−K has been observed and discussed before in the literature.[27] The M−K method is considered to give high quality charges.[27]

Topological analysis of the charge density distribution ρ(*r*) and properties of critical points (CP) were determined by using the AIM method by means of the program AIMPAC using the MP2(full)/6-31++G** wave function. It provides an unambigu-

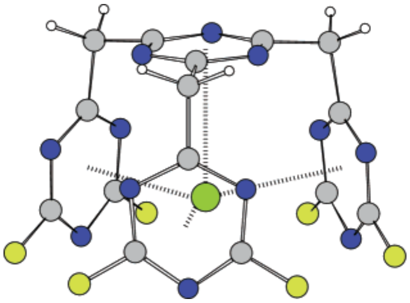


Figure 4. RI-MP2(full)/6-31++G** fully optimized structure of a host−guest complex, where the receptor binds the anion via multiple anion−π interactions.

TABLE 3: Computed Binding Energies (*E*, kcal/mol) for TFZ Complexes with Chloride Simulating Two Solvents within the Self-Consistent Reaction Field Model and in the Gas Phase at the MP2(full)/6-31++G//RI-MP2(full)/6-31++G** Level of Theory**

	MP2//RI-MP2		
complex	(CHCl$_3$ *E*	H$_2$O *E*	gas phase E_{CP}
1 (TFZ-Cl$^-$)	−5.9	−3.5	−15.0
5 (TFZ$_2$−Cl$^-$)	−11.1	−7.0	−28.5
9 (TFZ$_3$−Cl$^-$)	−31.7	−24.2	−41.0
receptor	−15.8	−11.9	−31.0

ous definition of chemical bonding[28] including ion−π interactions.[6,29] A common feature in all complexes is the presence of a cage CP linking the anion with the center of the rings. The value of the charge density at the cage critical point is directly related to the strength of the interaction,[6] and it has been proposed that it can be used as a measure of the bond order in cation−π[29] and anion−π[7] interactions. In Table 2, we summarize the values of ρ and its Laplacian derivative ($\nabla^2\rho$), computed for the complexes **1**−**12** at the cage CPs. The variation of the values of both parameters is very small in each group of complexes (on going from 1:1 to 1:3 complexes). For instance, in the chloride complexes with TFZ (**1**, **5**, **9**) the values of ρ ($\times 10^2$) are 0.853, 0.832, and 0.838 au, respectively. Taking into consideration that the values of ρ and $\nabla^2\rho$ are very sensitive to little changes in the strength of the interaction,[7] this result indicates that the bond order of each anion−π interaction is approximately constant in the complexes of each series and it is not affected by the number of interacting aromatic units, thus confirming the additivity of the anion−π interaction.

The main expectation of the anion−π interaction is its application in the field of the molecular recognition of anions using neutral receptors based on this noncovalent interaction. Figure 4 shows the optimized structure of a receptor that we propose for the molecular recognition of chloride, which is based on multiple anion−π interactions and the binding units are derivatives of *s*-triazine. It is composed of a central platform of *s*-triazine substituted by three 2,4-difluoro-6-methylene-1,3,5-triazine groups, resulting in a tripodal architecture. Therefore, the anion binds the receptor via four anion−π interactions. The computed binding energy for this system is $E_{CP} = -31.0$ kcal/mol at the RI-MP2(full)/6-31++G** level of theory.

Finally, we have performed calculations simulating two solvents within the self-consistent reaction field PCM model using the RI-MP2(full)/6-31++G** geometries. We have studied the additivity for one set of complexes (TFZ with chloride) and the receptor simulating CHCl$_3$ ($\epsilon = 4.9$) and H$_2$O ($\epsilon = 78.39$). The results are summarized in Table 3. In comparison with the gas-phase results, the binding energies are drastically reduced in water, especially for 1:1 and 1:2 complexes (**1** and **5**, respectively), although the interaction is still favorable. In chloroform, a significant reduction is also observed for complexes **1** and **5**. The additivity of the interaction is maintained in both solvents; i.e., the binding energy of the 1:2 complex is twice the value of the 1:1 complex. Unexpectedly, the reduction, in comparison with the gas phase, is less important in the 1:3 complex. As a matter of fact, the binding energy is reduced by a factor of 4 in water for the 1:1 and 1:2 complexes and by a factor of approximately 3 in chloroform with reference to the gas-phase binding energies. For the 1:3 complex (**9**), it is only reduced by a factor of 2 in water and less than 2 in chloroform. This differentiating behavior of the 1:3 complex is difficult to explain at this stage of the study and it requires further investigation. The theoretical study simulating chloroform and water have been extended to the receptor. The energetic results are present in Table 3. In comparison with the gas phase, the binding energy is reduced in both solvents, but it is appreciably favorable, indicating that receptors based on the anion−π interaction are expected to be competitive in organic solvents.

4. Conclusion

In conclusion, the results present in this study on anion−π, anion−π_2 and anion−π_3 complexes reveal additivity in both binding energies and geometries. The charge transfer (M−K) and AIM (ρ, $\nabla^2\rho$) analyses are in agreement with the energetic and geometric results. As far as we know, this is the first study on the additivity of the anion−π interaction and it is expected to open further investigations for the design and synthesis of a new class of neutral receptors for the molecular recognition of anions. A preliminary study simulating two solvents has been included, indicating that receptors based on this interaction can be competitive.

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