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Dual Binding Mode of *s*-Triazine to Anions and Cations

**Carolina Garau, David Quiñonero, Antonio Frontera,* Pablo Ballester,
Antoni Costa, and Pere M. Deyà***

*Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km
7.5, 07122 Palma de Mallorca, Spain*

tonif@soller.uib.es

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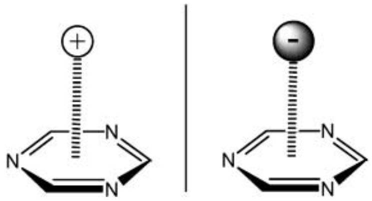
ABSTRACT



Ab initio calculations were performed on complexes between cations and *s*-triazine, which has a small and positive quadrupole moment. Minimum energy π-complexes were found between *s*-triazine and cations. Minimum π-complexes with anions were previously reported. This ability of *s*-triazine to form stable complexes with either anions or cations is studied using several theoretical methods. A likely explanation of this duality is the stabilization obtained from the ion-induced polarization.

Noncovalent interactions play an essential role in many topics of modern chemistry. In particular, cation-π interactions are significant noncovalent binding forces with great importance in many systems.[1,2] Crystallographic studies provide a great deal of information on cation-π interactions and other nonbonded interactions such as anti-hydrogen bonds, dihydrogen bonds,[3] and other nonconventional hydrogen bonds.[4] Additionally, these interactions have been extensively studied by means of computational methods. Noncovalent interactions are usually characterized by Bader's theory of "atoms in molecules" (AIM),[5] which has been used successfully to understand conventional[6] and unconventional[7] hydrogen bonds and cation-π interactions.[8] The cation-π interaction is, in general, equally dominated by electrostatic and cation-induced polarization.[9] The nature of the electrostatic component has been rationalized, emphasizing the function of the permanent quadrupole moment of benzene $Q_{zz} = -8.48$ B (buckinghams, 1 B = 3.336×10^{-40} C m^2).[10] The benzene-hexafluorobenzene favorable interaction has been studied, including the face-to-face stacking of its crystal structure.[11] A detailed analysis carried out by Williams stresses the important role of the large, permanent quadrupole moment of the two molecules, which are similar in magnitude but of opposite sign $Q_{zz}(C_6F_6) = +9.50$ B.[12] The importance of the quadrupole moment for understanding intermolecular interactions of aromatics has been discussed before.[13]

We have recently coined the term "anion-π interaction" in reporting a preliminary study of interactions between anions and hexafluorobenzene, where the anion is positioned over the ring along the C_6 axis.[14] We have also reported similar studies of interactions of anions with 1,3,5-trini-

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trobenzene (Q_{zz} = +20 B)[15] and *s*-tetrazine (Q_{zz} = +3.32 B),[16] which also present permanent quadrupole moments of sign opposite to that of benzene. Additionally, we have demonstrated that anion-π interactions are possible between anions and the π cloud of electron-rich aromatic molecules if the aromatic ring is simultaneously interacting with a cation by the opposite face of the ring.[17] Alkorta et al.[18] have also reported interactions of anions with a variety of fluoroaromatic systems.

Mascal et al.[19] have recently reported interactions of anions with the electron-deficient *s*-triazine aromatic ring. The interacting energies of *s*-triazine and anions obtained by Mascal et al. were less than −10 kcal/mol. The quadrupole moment of the *s*-triazine is very small (Q_{zz} = +0.90 B). Accordingly, the interaction is expected to be dominated by the ion-induced polarization contribution instead of the electrostatic contribution. Here, we report a study of the interaction between cations instead of anions and *s*-triazine. In these complexes the cation is positioned over the ring along the C_3 axis. Because of the polarization contribution to the total interaction energy, the *s*-triazine should be able to form stable complexes with anions and cations. The latter supposition has been confirmed by ab initio calculations and Molecular Interaction Potential with polarization (MIPp)[20] calculations. The nature of the bonding between cations and *s*-tetrazine has been analyzed by the AIM theory.

The geometries of all complexes included in this study were fully optimized at the MP2 level by using the 6-31+G* basis set in the Gaussian 98 program.[21] The binding energies were calculated with and without correction for the basis set superposition error (BSSE) by using the Boys and Bernardi conunterpoise technique[22] and zero-point energy (ZPE) corrections. Frequency calculation confirmed the structures are at their energy minima. Topological analysis of the charge density ρ(r) distribution and properties of critical points (CP) were determined by using the AIM method, which provides an unambiguous definition of chemical bonding[23] by means of the program AIM2000[24] using the MP2/6-31+G* wave function.

Table 1 reports the energies and equilibrium distances corresponding to the interaction of *s*-triazine with a series of cations. For comparison purposes the reported values by Mascal et al.[19] of complexes with anions have also been included.

Table 1. MP2/6-31+G* Energies (kcal/mol) and Noncovalent Bond Distances (Å) for Complexes of *s*-Triazine and Cations/Anions

complex	$E_{(\mathrm{MP2+ZPE})}$	$E_{(\mathrm{MP2+ZPE+BSSE})}$	R_e
s-triazine···Li^+ (**1**)	−7.4	−6.2	2.2
s-triazine···Na^+ (**2**)	−4.5	−2.5	2.7
s-triazine···K^+ (**3**)	−3.3	−1.3	3.1
s-triazine···F^- (**4**)[a]	−12.1	−9.2	2.6
s-triazine···Cl^- (**5**)[a]	−8.3	−4.8	3.2
s-triazine···N_3^- (**6**)[a]	−7.6	−4.5	2.8

[a] From ref 19.

For complexes **1**−**3** exploration of the CPs revealed the presence of three (3,−1) and three (3,+1) CPs symmetrically distributed. The bond CPs connect the cation with the nitrogen atoms, and the ring CPs connect the cation with the carbon atoms (see Figure 1). The Laplacian of the bond CPs is positive (see Table 2) indicating a depletion of the electron density, as is common in closed-shell interactions.[5] Finally, the interaction is further described by the presence of a cage CP located over *s*-triazine molecule along the C_3 axis, connecting the cation with the center of the ring.

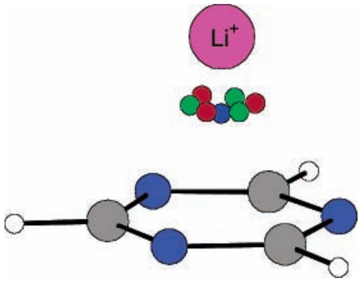

Figure 1. Representation of the location of the (3,−1) CPs (red circles), the (3,+1) CPs (green circles), and the (3,+3) CP (blue circle) originating from the interaction of *s*-triazine with lithium.

Different studies point out that the formation of π-interactions is associated to the appearance of a cage CP connecting the ion with the center of the aromatic ring.[8,14] In all complexes studied here the cation-π interaction is characterized by the presence of a cage CP. The results present in Table 2 show that the electron density at the cage CP

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Table 2. Selected Electron Density Topological Properties for Complexes of *s*-Triazine with Cations

complex	CP[a]	n	$10^2\rho$	$10^2\nabla^2\rho$
s-triazine···Li$^+$ (**1**)	(3,−1)	3	0.821	4.381
	(3,+1)	3	0.810	4.468
	(3,+3)	1	0.763	4.161
s-triazine···Na$^+$ (**2**)	(3,−1)	3	0.566	2.820
	(3,+1)	3	0.549	2.892
	(3,+3)	1	0.499	2.807
s-triazine···K$^+$ (**3**)	(3,−1)	3	0.521	2.252
	(3,+1)	3	0.498	2.338
	(3,+3)	1	0.429	2.807

[a] The electron density (ρ) and its Laplacian ($\nabla^2\rho$) in atomic units at the critical points (CP) originated upon complexation are given, as well as the total number (n) of each CP in the complex.

decreases on going from complex **1** to **3**, indicating a relationship between the interaction energy and the electron density at the cage CP. This issue is important because the value of the density and its Laplacian at the cage CP can be used as a measure of the strength of the π-interaction.

To analyze the physical nature of the ion-π interaction in the electron-deficient *s*-triazine ring and whether polarization is important, we have computed its contribution to the total interaction energy using the recently developed MIPp,[20b] which is a powerful tool for the prediction of binding properties of aromatic compounds.[25] MIPp is an improved generalization of the molecular electrostatic potential (MEP) where three terms contribute to the interaction energy: (i) an electrostatic term identical to the MEP,[26] (ii) a classical dispersion-repulsion term, and (iii) a polarization term derived from perturbational theory.[27] Therefore, it provides a natural partitioning of the interaction energy into intuitive components.

Calculation[28] of the MIPp of *s*-triazine interacting with Li$^+$ and F$^-$ was performed using the HF/6-31+G* wave function. As a result, a MIPp minimum was found at 2.21 Å over the ring along the C_3 axis for lithium and at 2.80 Å for fluoride. In the calculations either Li$^+$ or F$^-$ was considered as a classical nonpolarizable particle. The van der Waals parameters used to describe the classical particles are present in Table 3. We have explored the electrostatic (E_e), polarization (E_p), and van der Waals (E_{vw}) contributions to the total interaction energy when a fluoride anion or a lithium cation approach a *s*-triazine molecule perpendicular to the center of the aromatic ring. The results in Table 3 point out that the electrostatic contribution to the total energy is modest as a result of the small quadrupole moment of *s*-triazine. In contrast the polarization term dominates the interaction and is responsible for the unusual behavior of *s*-triazine, which is able to interact with anions and cations favorably.

Table 3. Contributions to Total Interaction Energy (kcal/mol) Calculated with MIPp for *s*-Triazine Interacting with F$^-$ and Li$^+$ as Classical Particles at the MIPp Minimum

ion	distance (Å)	E_e	E_p	E_{vw}	E_t
Li$^+$	2.21	8.69	−15.43	−0.59	−7.33
F$^-$	2.80	−4.19	−7.75	2.18	−9.77

[a] The van der Waals parameters used are $R_{vw} = 1.200$ Å and $\epsilon = 0.400$ kcal/mol for Li$^+$ and $R_{vw} = 2.170$ Å and $\epsilon = 0.061$ kcal/mol for F$^-$.

In summary, the results derived from theoretical calculations reported in this study reveal the suitability of *s*-triazine for interacting with anions and cations. This behavior is explained by the ion-polarization contribution to the total interaction energy and by a very small Q_{zz}, which is essential for dual binding modes. It can be then generalized that aromatic molecules with a very small quadrupole moment will be able to interact favorably with either anions or cations. Finally, the characteristics of the interaction of *s*-triazine with cations have been studied using a topological analysis of the electron density and MIPp calculations.

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