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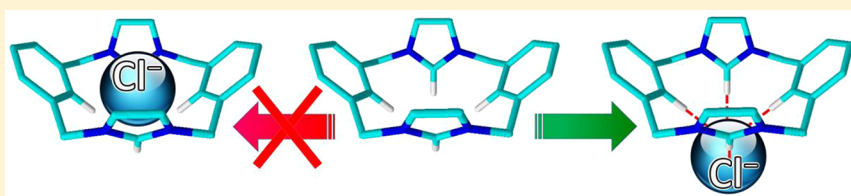
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S Supporting Information



ABSTRACT: The supramolecular bonding contacts driving the recognition of chloride ions by macrocyclic imidazolium-based receptors have been investigated by density functional theory calculations, both in vacuo and in solution (DMSO). This computational study reveals that the most stable host–guest complexes in vacuo and solution are different. While the anion interacts by means of two C–H···Cl[−] hydrogen bonds with the host molecule in vacuo (in a similar manner to that observed in the published single-crystal X-ray structure of the Cl[−]–host complex), four C–H···Cl[−] contacts are clearly present in solution, as observed experimentally by earlier studies. In addition, the computed optimal Cl[−]–host complex in solution confirms that the cavity of the host macrocycle, formed by four aromatic rings, does not include the anions, which are located outside the cyclic receptor with which they interact through two C_{ph}–H···Cl[−] hydrogen bonds and two unconventional (C_{im}–H)⁺···X[−] interactions.

■ INTRODUCTION

Anion-recognition chemistry has become a major area of supramolecular chemistry, driven by the central role played by anions in biological and chemical systems,¹ and also due to environmental concerns.² Hence, the design and preparation of (selective) anion receptors represents an important area of current research.^{3–8}

Macrocyclic-based compounds provide a well-defined host environment for guest inclusion; therefore, such molecules have been intensively used to develop anion receptors.^{9,10} In that context, imidazolium-containing macrocyclic frameworks have been used in anion recognition,^{11,12} as the result of the ability of protonated imidazole rings (i.e., imidazolium cations) to undergo strong bonding interactions with anions that can be established through charged N⁺–H···X[−] or hydrogen bonds, electrostatic interactions, or (C–H)⁺···X[−] interactions.^{13,14} It should be mentioned that, as the imidazolium moiety is a charged aromatic ring, another type of noncovalent bonding contact between imidazolium and an anion may be considered, namely, the anion– π interaction;^{15,16} actually, such interactions have been observed recently in a calix[4]pyrrole anion–host molecule¹⁷ and in a flexible tetracationic imidazolium-based macrocycle.¹⁸

The binding interactions of anions with receptors are directed by a number of factors, for example, receptor–anion

strength, influence of solvent(s) and cosolute(s), crystal packing (in the case of solid-state structures), and energetic cost characterizing the conformational arrangements that must be adopted by both the host and the guest to promote an optimal recognition process.^{19,20}

In the present study, the potential contact interactions occurring between a chloride anion and dicationic imidazolium-based receptors have been investigated theoretically, both in the solid state and in solution (DMSO). The dicationic [1₄]-imidazoliophanes depicted in Figure 1 are capable of binding distinct anions in polar media, by means of unconventional (C–H)⁺···X[−] (X[−] = F[−], Cl[−], Br[−], I[−], CN[−], H₂PO₄[−], PF₆[−], AcO[−]) charge-assisted hydrogen bonds.^{21,22} The different possible conformations adopted by the cyclophane Host (Figure 1B) upon interaction with Cl[−] in DMSO have been first explored, with the aim to determine which Cl–Host complex(es) is(are) likely to exist in solution and the types and numbers of supramolecular contacts (hydrogen-bonding, anion– π interactions, and so on) involved in the formation/stabilization of the host–guest systems. The computational

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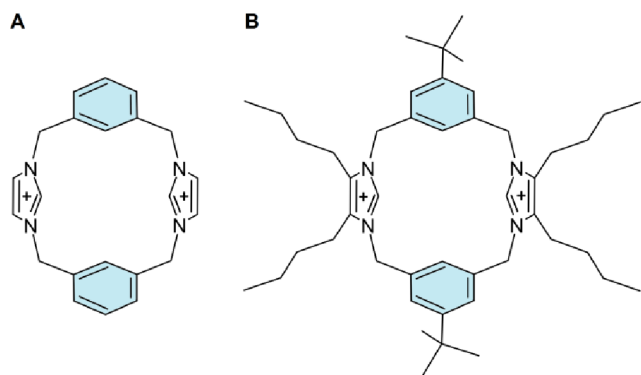


Figure 1. (A) Representation of dicationic 3,5(1,3)-dibenzena-1,5(1,3)-di-imidazoliocyclooctaphanedium, $\text{Host}^{\text{cryst}}$, whose X-ray structure of the dichloride salt has been reported;²³ (B) Di-imidazolacyclooctaphanedium cation, symbolized as Host, used for solution anion-binding studies.²¹

results obtained are compared to the available experimental data.

■ COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian09 suite of programs.²⁴ As discussed in detail in the main text of this contribution, a four-step procedure was applied to find the most stable Cl–Host conformers that may be present in solution. To this end, geometry optimizations were performed at the B3LYP/6-31+G(d,p) level of theory. As revealed by previous studies,^{25,26} this level of theory is a good tradeoff between computational cost and accuracy to describe complexes governed by H-bonding and anion– π interactions, with a dominant electrostatic contribution. To estimate the formation energies in DMSO, single-point calculations on the optimized geometries in vacuo were carried out at the B3LYP/6-311++G(d,p) level of theory using an implicit solvation scheme, PCM;^{27a} the energies were corrected from basis-set superposition error (BSSE).^{27b} In addition, the most stable structures obtained in vacuo were reoptimized in DMSO, at the B3LYP/6-31+G(d,p) level with the PCM method to simulate the effect of the solvent. Subsequently, single-point calculations were carried out on these structures at the B3LYP/6-311++G(d,p) level of theory (with PCM) to assess the energies of the most stable conformers in DMSO. In particular, the formation, interaction, and strain energies were calculated. These different energies are defined as follows:

ΔE (formation energy) is calculated as the difference between the energy of the single components of the complex (at their most stable geometry) and the energy of the complex (at its most stable geometry); hence, the most stable complex will be characterized by the lowest ΔE value.

ΔE^{int} (interaction energy) is calculated as the difference between the components of the complex (at their geometry in the complex) and the energy of the complex (at the most stable geometry); ΔE^{int} thus represents the energy obtained when the different components of the complex are “rigidly assembled”.

ΔE^{str} (strain energy) is calculated as the difference between the energy of the host at its most stable geometry and the energy of the host calculated at the complex geometry; ΔE^{str} therefore reflects the energetic

cost for the host to adopt the adequate geometry (conformation) to interact efficiently with the anion. It should be noticed that $\Delta E = \Delta E^{\text{int}} + \Delta E^{\text{str}}$.

For the solid-state studies, the asymmetric unit of the single-crystal X-ray structure of $\text{Host}^{\text{cryst}}$,²³ showing the interaction between one chloride anion and a cyclophanes unit (Supporting Information, Figure S1A),²³ was used to perform single-point calculations at the MP2/6-31+G(d,p) level of theory, which allowed to provide the wave function required to analyze the electron density of the complex Cl– $\text{Host}^{\text{cryst}}$. It should be mentioned here that $\text{Host}^{\text{cryst}}$ is involved in the binding of a second chloride guest, symmetrically positioned on the opposite side of the host, thereby ensuring charge balance of the system (since the cyclic receptor is dicationic).

The Atoms in Molecules (AIM)²⁸ theory was employed to quantify the noncovalent interactions present in the supramolecular complexes investigated herein. AIM is based upon those critical points where the gradient of the electron density vanishes. Within this approach, two bonded atoms are connected with a *bond path* through a *bond critical point*. It is known that the electron density at the bond critical points roughly correlates with the strength of the chemical bonds and interactions.

■ RESULTS AND DISCUSSION

Computational Studies in Vacuo. The single-crystal X-ray data of the dicationic [1₄]imidazoliophane ($\text{Host}^{\text{cryst}}$; Figure 1A) interacting with chloride ions²³ were used to investigate the interactions taking place between one chloride anion and the host (that is the Cl– $\text{Host}^{\text{cryst}}$ complex corresponding to the asymmetric unit of the X-ray structure of $\text{Host}^{\text{cryst}}$; Supporting Information, Figure S1A²³). As shown in previous studies,^{21,23} two “unconventional C–H \cdots Cl[–] hydrogen bonds” stabilize the Cl– $\text{Host}^{\text{cryst}}$ complex, namely, the C_{ph}–H \cdots Cl[–] (the distance between the Cl[–] and the interacting atom, i.e., a hydrogen atom, is 2.81 Å) and C_{im}–H \cdots Cl[–] (2.54 Å) bonds. In addition, the potential involvement of the aromatic rings in weak anion– π interactions was considered. Indeed, it appears that the guest chloride anion is located exactly above the ring centroid of both the phenyl (Cl \cdots Ph_{centroid}, the distance between the Cl[–] and the centroid of the aromatic ring is 4.25 Å) and the imidazolium (Cl \cdots Im_{centroid} = 4.47 Å) moieties (Supporting Information, Figure S1). In addition, the solid-state structure of $\text{Host}^{\text{cryst}}$ reveals that the macrocycle is also involved in strong π – π interactions (through its benzene rings) with neighboring molecules. Hence, single-point calculations at MP2/6-31+G(d,p) level of theory and subsequent AIM analysis were performed on a model taking into account these supramolecular contacts. Two views of the Cl– $\text{Host}^{\text{cryst}}$ complex obtained after AIM analysis are depicted in Figure 2.

The present calculations corroborate the presence of two atypical C–H \cdots Cl[–] hydrogen bonds, whose electron densities at the bond critical points are 0.0090 au for C_{ph}–H \cdots Cl[–] and 0.0142 au for C_{im}–H \cdots Cl[–]. In addition, the AIM analysis suggests the occurrence of a third type of C–H \cdots Cl[–] contacts (H \cdots Cl[–] separation distance of 3 Å; not shown in Figure 2) with an electron density of 0.0053 au, which are realized between methylene groups belonging to adjacent cyclophanes and the anion. π – π stacking interactions occur between phenyl rings of neighboring molecules (see Figure 2, blue lines) that are characterized by an overall electron density at the two critical points (between the arenes) of 0.0169 au. It should be

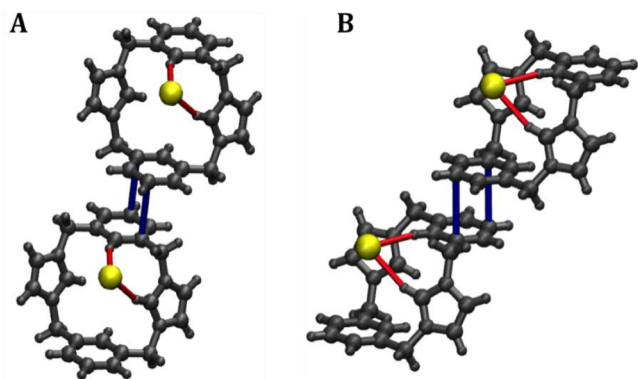


Figure 2. (A) Top view and (B) side view of the Cl–Host^{cryst} complex. Single-point calculations were carried out on a model extracted from the crystal structure at the MP2/6-31+G(d,p) level of theory to characterize the interactions between the host and the anion using the AIM analysis. The red and blue lines represent the bond paths corresponding to respectively H-bonding and π – π stacking interactions.

mentioned here for comparison purposes that a π – π stacked benzene pair exhibits two bond paths between two pairs of carbon atoms, which correspond to an overall electron density of 0.0111 au (as calculated at the at MP2/6-31++G(d,p) level of theory).²⁹

It is important to note that the AIM analysis of the system does not reveal the existence of anion– π interactions therefore indicating that the chloride–host interaction is only driven by hydrogen bonds and electrostatics. In fact, effective anion– π interactions are characterized by anion–centroid distances below 3.8 Å;³⁰ in the present case, distances well above 4 Å are observed (Supporting Information, Figure S1) therefore confirming the calculation results and earlier findings.¹⁵

Computational Studies in Solution. The di-imidazola-cyclooctaphanediium cation Host, bearing *tert*-butyl and butyl substituents that increase its solubility in organic solvents (see Figure 1B) has been used for solution binding studies (in DMSO and acetonitrile) with different anions.²¹ In the present study, the nature of the possible conformation(s) between one host macrocyclic molecule and one chloride anion (Cl–Host complex) has been investigated in solution, and the different types of supramolecular contacts that stabilize this(these) conformer(s) have been assessed. To achieve these objectives, a four-step procedure was applied.

Step i 24 starting geometries were considered for the Cl–Host complex (see the Supporting Information, Figures S2 and S3), which were obtained by variation of three parameters, namely, the position of the chloride anion in the macrocyclic cavity of the Host, the orientation of the aromatic rings constituting the macrocycle, and the dihedral angles of the butyl substituents (Supporting Information, Figure S2). These different factors allowed obtaining 24 possible types of initial structures for the Cl–Host complex, which are depicted in the Supporting Information, Figure S3. These model structures were subsequently fully optimized at the B3LYP/6-31+G(d,p) level of theory.

Step ii The full optimization of the 24 initial structures considered (Supporting Information, Figure S3) generated 12 types of complexes, from which 5 “unique” structural types were clearly identified

(Supporting Information, Figure S4). These five categories of host–guest molecules are characterized by the presence of four, three, two, one, or no hydrogen bonds; hence, these compounds are respectively symbolized as Cl–Host^{4HB}, Cl–Host^{3HB}, Cl–Host^{2HB}, Cl–Host^{1HB}, and Cl–Host^{0HB}. It should be noticed that the categories Cl–Host^{3HB} and Cl–Host^{2HB} present more than one possible conformer, which mostly vary by the orientation of the butyl substituents (see the Supporting Information, Figure S4) and whose energy differences are ranging within 2–3 kcal mol^{−1} (Supporting Information, Figure S5).

Step iii Single-point calculations on the five structural types obtained in vacuo were performed at the B3LYP/6-311++G(d,p) level of theory, using an implicit solvation scheme (PCM, see the Computational Details Section) to evaluate their energies in solution. While the relative energies of the most stable host–guest molecular pairs hardly change (data not shown), the absolute energies are significantly affected. For instance, the formation energy of the most stable complex, Cl–Host^{4HB}, amounts to −140 kcal mol^{−1} in vacuo, while it is −6 kcal mol^{−1} in solution. In addition, the calculated formation energies in solution for Cl–Host^{2HB} and Cl–Host^{0HB} are above zero, therefore indicating that the structures optimized in vacuo most likely do not exist in solution (a detailed analysis of the corresponding energetics and of the solvent effect are discussed in the following section). This also suggests that the simple approach consisting of performing single-point calculations on the structures determined in vacuo is not appropriate.

Step iv Full optimization at the B3LYP/6-31+G(d,p) level of theory of the most stable complexes found in vacuo was performed in DMSO (Figure 3), followed by single-point calculations at the B3LYP/6-311++G(d,p) level (with the inclusion of implicit solvent).

DMSO was chosen for these solution studies because it is more polar than acetonitrile (the other solvent used

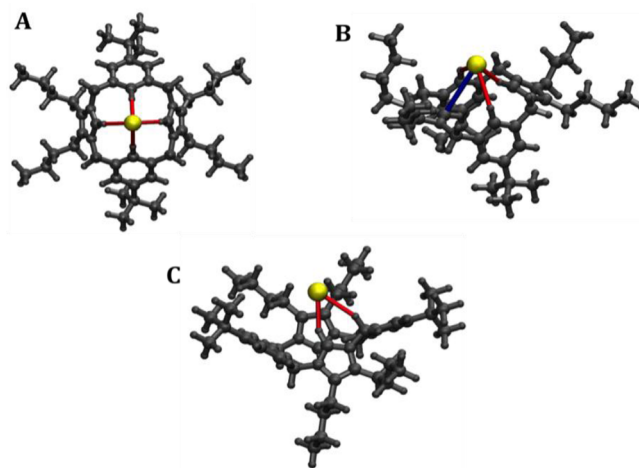


Figure 3. Most stable Cl–Host conformers obtained in DMSO by full optimization through a four-step procedure: (A) Cl–Host^{4HB}, (B) Cl–Host^{3HB}, and (C) Cl–Host^{2HB}. The results of the corresponding AIM analyses are illustrated by red lines for the H-bonding interactions and by a blue line for the anion– π interactions.

Table 1. Formation (ΔE), Relative (ΔE^{rel}), Interaction (ΔE^{int}), and Strain (ΔE^{str}) Energies (in kcal mol⁻¹), Electron Densities (au), and Structural Parameters (Å) of the Cl–Host Conformers in DMSO^a

	ΔE^{rel}	ΔE	ΔE^{int}	ΔE^{str}	interaction ^b	ρ	d
Cl–Host ^{4HB}	0.0	−5.6	−7.5	+1.9	C _{Im} –H...Cl	0.0124	2.57
					C _{Im} –H...Cl	0.0124	2.57
					C _{Ph} –H...Cl	0.0091	2.76
					C _{Ph} –H...Cl	0.0091	2.76
Cl–Host ^{3HB}	+4.1	−1.4	−4.8	+3.4	C _{Im} –H...Cl	0.0167	2.42
					C _{Ph} –H...Cl	0.0064	2.98
					C _{Ph} –H...Cl	0.0057	3.05
					C _{Im} ...Cl	0.0027	4.01
					C _{CH2} –H...Cl	0.0014	3.85
Cl–Host ^{2HB}	+2.8	−3.0	−4.7	+1.7	C _{Im} –H...Cl	0.0143	2.50
					C _{CH2} –H...Cl	0.0095	2.74

^aBoth the energies and electron densities are evaluated at the B3LYP/6-311++G(d,p) level of theory with the inclusion of DMSO effects (PCM).

^bDistances between the anion and the interacting atom, namely, hydrogen or carbon, are indicated as C–H...Cl and C...Cl, respectively.

experimentally) and is thus expected to provide stronger effects on the structures.²¹ This final step of computational procedure produced 3 favorable complexes out of the 24 initial structures depicted in Figure S3 of the Supporting Information.

Energies of the Cl–Host Conformers in DMSO. The three molecular pairs obtained with the four-step procedure are of the types Cl–Host^{4HB} (Figure 3A; four hydrogen bonds), Cl–Host^{3HB} (Figure 3B; three hydrogen bonds), and Cl–Host^{2HB} (Figure 3C; two hydrogen bonds). In contrast to the calculations carried out in vacuo, Cl–Host^{0HB} does not show a minimum of the potential energy surface in DMSO; in particular, the anion moves away from the aromatic groups of the host molecule with which it establishes very weak C–H...Cl[−] bonds with the butyl chains (data not shown). The geometries exhibited by Cl–Host^{4HB} and Cl–Host^{3HB} are similar to those observed in vacuo (Figure 3A, B and Figure S4 of the Supporting Information), with C–H...Cl[−] bonds solely involving aromatic moieties (phenyl or imidazolium groups). However, for Cl–Host^{2HB}, the optimization performed in solution gives rise to a geometry that is significantly different than the one obtained in vacuo. Indeed, the chloride anion is more exposed to the solvent, and one of the two hydrogen bonds is provided by a methylene group connecting a phenyl and an imidazolium rings (Figure 3C). Next, the energies (at the B3LYP/6-311++G(d,p) level of theory) of the Cl–Host complexes showing the highest stabilities in DMSO have been analyzed. As is evidenced in Table 1, Cl–Host^{4HB} displays the largest interaction energy, which most likely is due to the presence of four hydrogen bonds and fairly small strain energy. Thus, for Cl–Host^{4HB}, the anion can strongly interact with the host without affecting its most stable geometry, having the largest formation energy of all complexes. Cl–Host^{2HB} and Cl–Host^{3HB} have comparable interaction energies (of about 5 kcal mol⁻¹), but the latter requires twice more energy (3.4 vs 1.7 kcal mol⁻¹) to adopt the adequate conformation to generate three hydrogen bonds. Accordingly, the Cl–Host complex with four hydrogen bonds, that is, Cl–Host^{4HB}, whose estimated formation energy is −5.6 kcal mol⁻¹, is the most stable; Cl–Host^{3HB} and Cl–Host^{2HB} are energetically accessible (Table 1) and therefore may exist in solution. In fact, the structure Cl–Host^{2HB} resembles that observed by X-ray diffraction studies for the Cl–Host^{cryst} complex,²³ which indicates that it is the most stable geometry in the solid state. Thus, in line with experimental studies,²¹ our computations corroborate the

crucial role played H-bonding interactions in the stabilization of the host–guest complexes.

AIM Analysis: Hydrogen-Bonding and Anion– π Interactions in Solution. As observed in vacuo (see above), the most stable conformer obtained by full optimization in DMSO is Cl–Host^{4HB}, which is stabilized by four hydrogen bonds, involving the C–H groups of two phenyl and two imidazolium rings. This hydrogen-bonding motif is symmetric, with two C_{Ph}–H...Cl bonds of 2.76 Å and two C_{Im}–H...Cl bonds of 2.57 Å (Table 1). The AIM analysis confirms the existence of these supramolecular interactions, which are reflected by electron densities at the critical points of 0.0091 au for C_{Ph}–H...Cl and 0.0124 au for C_{Im}–H...Cl (Table 1 and Figure 3A). As already mentioned, the complexes bearing three and two hydrogen bonds show very similar interaction energies, with values around −5 kcal mol⁻¹. Cl–Host^{3HB} is stabilized by quasi-symmetric C_{Ph}–H...Cl bonds (Figure 3B), with distances of 2.98 and 3.05 Å, and electron densities of 0.0064 and 0.0057 au (Table 1). The third strong hydrogen bond involves the imidazolium ring and is characterized by a C_{Im}–H...Cl separation distance of 2.42 Å and an electron density of 0.0167 au (Table 1). Interestingly, the AIM analysis reveals the presence of anion– π interactions in Cl–Host^{3HB}, between one of the imidazolium rings and the anion, with an electron density at the bond critical point equal to 0.0027 au (Table 1). In the case of Cl–Host^{2HB}, the anion–host complex is stabilized by two C–H...Cl hydrogen bonds (Figure 3C), with a fairly large overall electron density of 0.0238 au (Table 1).

Solvation Effect on the Anion– π Interactions. The Cl–Host conformers obtained via optimization in vacuo exhibit stabilization energies that are one order of magnitude greater than those calculated in solution. Such a feature may logically be anticipated as in vacuo the anion can solely interact with the host (no solvent molecules are involved) and the electrostatic interactions are therefore emphasized. The stabilization energies of Cl–Host^{0HB}, Cl–Host^{1HB}, Cl–Host^{2HB}, Cl–Host^{3HB}, and Cl–Host^{4HB} estimated in vacuo range between −140 and −120 kcal mol⁻¹ (Supporting Information, Figure S5). All the hydrogen bonds are shorter and thus stronger than those determined in solution (Supporting Information, Table S1). In addition, all host–guest complexes, except Cl–Host^{4HB}, show anion– π interactions. These chloride–aromatic interactions (one anion– π contact for Cl–Host^{3HB}, two for Cl–Host^{2HB}, two for Cl–Host^{1HB}, and four for Cl–Host^{0HB}) are characterized by a mean electron density at the bond critical

bonds of 0.0088 au (see the Supporting Information, Table S1). The inclusion of solvation is crucial to have a more realistic view of the actual interactions between the host and the guest molecules. Indeed, in the presence of solvent, the hydrogen bonds become significantly weaker; for instance, the mean electron densities of the H-bonds in vacuo and in solution are 0.0150 and 0.0097 au, respectively. In addition, most of the anion- π interactions present in vacuo disappear in solution; actually, Cl-Host^{0HB} is not stable in DMSO, and for Cl-Host^{2HB}, the anion is significantly exposed to the solvent molecules and consequently too far to efficiently interact via anion- π interactions with the host aromatic rings. The only complex that still features anion- π bonding contacts in solution is Cl-Host^{3HB}.

CONCLUSIONS

In summary, the possible host-guest complexes formed between an imidazolium-based macrocyclic receptor and chloride have been investigated theoretically both in vacuo and in solution. Earlier nontheoretical studies suggest that the recognition process is realized exclusively by means of ionic and hydrogen-bonding interactions.^{21,23} Accordingly, the purpose of the present, thorough computational analysis was to evaluate the nature and strength of the supramolecular contacts between the host and the guest and whether other type(s) of noncovalent interactions (such as anion- π interactions) were also present (and were playing an additional stabilizing role). To this end, single-point calculations were first performed on the asymmetric unit of the single-crystal X-ray structure of the complex Cl-Host^{Crystal} (namely, to investigate the nature of the bonding interactions involved in the formation of a supramolecular complex between a chloride anion and the macrocyclic receptor) at the MP2/6-31+G(d,p) level of theory. These calculations confirmed the H-bonding pattern suggested by the experimentalists but also revealed the occurrence of weak interactions between C_{CH2}-H hydrogen atoms (from the macrocyclic host) and the anion. No anion- π interactions were found in the crystal structure of Cl-Host^{Crystal}. Subsequently, a four-step calculation procedure was applied to assess the possible conformations of the Cl-Host complex that may exist in DMSO. Full optimization of 24 starting structures (conformers) led to 3 stable host-guest complexes in solution. These were fully characterized by means of AIM analysis. The most stable conformer, that is, Cl-Host^{4HB}, exhibits four hydrogen bonds (between the chloride and the host molecule). The other two conformers, which are energetically accessible in solution, display three or two hydrogen bonds (Cl-Host^{3HB} and Cl-Host^{2HB}, respectively). In addition, Cl-Host^{3HB} is further stabilized by weak anion- π interactions. Thus, the present computational study confirms earlier experimental results suggesting the crucial involvement of hydrogen bonds in the interaction between the guest anion and the host macrocycle.

This initial study will serve as a basis for future computational work aimed at characterizing the bonding contacts between other anions and this family of anion receptors and at assessing the role played by hydrogen-bonding and anion- π interactions in the recognition process. In particular, the selectivities observed experimentally²¹ will be investigated theoretically.

ASSOCIATED CONTENT

Supporting Information

Figures showing the position of a chloride anion above two aromatic rings, in the crystal structure of Cl-Host^{cryst}; figures illustrating the procedure that was applied for the theoretical calculations; a table of electron densities and structural parameters of the most stable Cl-Host conformers in vacuo; and XYZ coordinates of Cl-Host^{2HB}, Cl-Host^{3HB}, and Cl-Host^{4HB}. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS USED

DMSO, dimethyl sulfoxide; DFT, Density Functional Theory; Ph, phenyl; Im, imidazole; PCM, Polarizable Continuum Model; B3LYP, Becke, three-parameter, Lee-Yang-Parr; AIM, Atoms in Molecules

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