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Towards the Design of Neutral Molecular Tweezers for Anion Recognition

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Abstract: Molecular tweezers are simple molecular receptors that can be characterized by the presence of two flat pincers separated by a more or less rigid tether. They have the ability to form complexes with a substrate molecule by gripping the substrate between the tips of the tweezers in a similar manner to that of mechanical tweezers. Klärner et al. synthesized one of the structurally simplest molecular tweezers, which is reported to bind electrodeficient aromatic and aliphatic substrates as well as organic cations. Complexes between these molecular tweezers and electron-rich aromatic, aliphatic, or anionic substrates have not been observed. Inspired by several recent reports that describe the interaction of hexafluorobenzene with electron-rich sites of molecules, we conducted a theoretical study to show the possibility of building molecular tweezers, based on those synthesized by Klärner, which were able to bind to anions and thus increase their potential as molecular receptors. We characterized complexes formed between several fluorinated derivatives of simple tweezers and an iodine anion, and analyzed the nature of the intermolecular interactions as well as the energetics for the process of complexation. The stabilization trend reflected by the energetic results when fluorine substituents were added to benzene rings confirms our hypothesis about the possibility of obtaining neutral tweezers composed of aromatic rings that can bind anions.

Keywords: ab initio calculations · anions · fluorine · molecular recognition · Umpolung

Introduction

The process of molecular recognition of guest molecules by synthetic hosts is of great interest in areas of supramolecular chemistry, such as chemical detection, separation and encapsulation, enantioselective synthesis,[1] and the design of new materials by means of molecular self-assembly. These processes and the properties of nano- and sub-nano-scale materials depend, to a large extent, on the nature of the intermolecular interactions. For this reason, their study and characterization has experienced enormous growth in recent years. Among the different intermolecular forces, the interactions of arenes with other aromatic units or with charged ions (π–π and ion–π interactions)[2,3] are of particular relevance for protein–ligand recognition. Their detailed study would help the design of efficient synthetic receptors with the ability to bind selectively to different kind of substrates, and consequently, lead to the construction of new synthetic, more highly organized chemical systems that could mimic the complex functions of biological systems.

Molecular tweezers are simple molecular receptors that can be characterized by the presence of two flat pincers separated by a more or less rigid tether. They have the ability to form complexes with a substrate molecule by gripping the substrate between the tips of the tweezers in a similar manner to that of mechanical tweezers. Since the pioneering work by Whitlock and Chen,[4] a plethora of new molecular tweezers have been synthesized,[5–8] most of which were designed to bind aromatic guest molecules. Klärner and Kahlert synthesized one of the structurally simplest pairs of molecular tweezers (**1** in Figure 1), which is reported to bind electrodeficient aromatic and aliphatic substrates, as well as organic cations.[8] Thermodynamic data for the complexation process for these molecular tweezers binding different substrates were obtained by using ^{1}H NMR spectroscopy[9] and luminescent titration.[10] Based on these results, complex formation mainly appears to be as a result of the enthalpic receptor–substrate interaction in which the entropy varies over a relatively wide range.[9] Calculations of the potential-energy surface suggest that the receptor–substrate interac-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains Cartesian coordinates and total energies of the compounds presented herein.

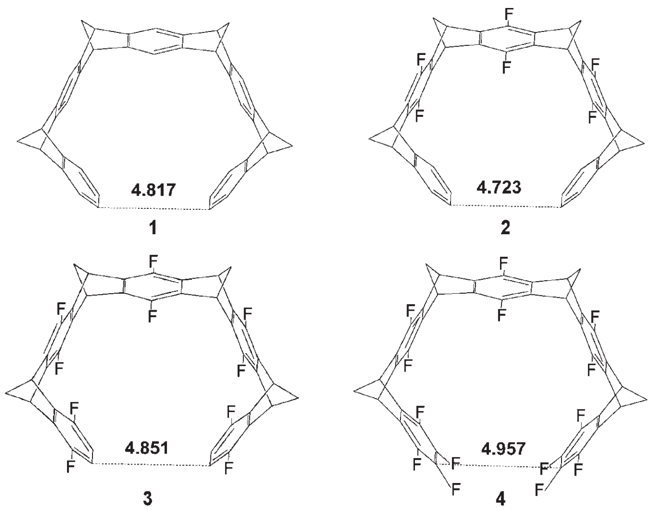

Figure 1. Structures of the tweezers studied. Distances between the terminal carbon atoms in Å are shown.

tions are mostly electrostatic.[11] Substituents on the benzene ring of the molecular tweezers alter their binding parameters, but the effect seems to be related to steric rather than electrostatic factors.[9,12] Complexes between these molecular tweezers and electron-rich aromatic, aliphatic, or anionic substrates have not been observed.

Whereas the interaction of cations with aromatic systems has been widely studied, very few reports deal with anion–aromatic interactions despite their relevance in vast areas of biology,[13] for example, in the removal of contaminants such as nitrates,[14] and in the removal of radioactive materials such as pertechnates.[15] Moreover, the design of neutral receptors that are capable of binding anions is of particular interest, because it avoids the presence of counterions complexes and improves selectivity, owing to the relevance of directional interactions.[16] Several recent reports describe the interaction of hexafluorobenzene with electron-rich sites of molecules such as H_2O, HCN, HF, and so forth,[17–19] and also theoretical investigations describe the interactions of electron-deficient π systems with several anions.[20–26] The total anion–π-complex interaction energies are similar to those of the corresponding cation–π complexes. The most important contributions to the total interaction energies are electrostatic and induction energies; however, unlike the cation–π complexes, the dispersion energies have a non-negligible contribution.[23] Inspired by these later studies, we carried out a theoretical study designed to investigate the possibility of building molecular tweezers similar to **1** that were able to bind to anions, and thus increasing the possibility for their use as molecular receptors. We chose **1** as the host molecule because it is the simplest one of the family developed by Klärner and the iodine anion as the guest molecule because it is a medium-sized atomic anion. We characterized the complexes formed from one of several fluorinated derivatives of **1** and I^- and analyzed the nature of the intermolecular interactions as well as the energetics for the complexation process.

Computational Methods

In the present study, the geometry of different tweezers and tweezer–ion complexes was fully optimized by the Gaussian 03 program[27] by using density functional theory (DFT) and the B3LYP[28,29] functional. The atoms of the tweezers were described by a 6-31+G* basis set, and the iodine atom was represented by the basis set and the effective core potential of Christiansen et al.[30] Calculations were performed on structures in which the anion is located within the concave cavity of the tweezers. Vibrational analysis was conducted at the same level of theory for each of the stationary points found to ascertain whether or not they corresponded to actual minima on the potential-energy surface. Enthalpies were determined at 298.15 K by using the quantum statistical thermodynamics expressions for ideal gases.[31] To obtain the intermolecular binding energy of the ion–tweezer dimers, a basis set superposition error (BSSE) correction for all of the complexes was carried out by using the counterpoise method developed by Boys and Bernardi.[32] As it is well known that DFT calculations using the B3LYP functional fail to provide accurate binding energies for van der Waals complexes, single point calculations at the second-order Møller–Plesset[33] (MP2) level on the B3LYP optimized geometries have been carried out. These calculations will help to provide insight into the relevance of the dispersive interactions in the stability of a tweezer–anion complex. To estimate the effects of different solvents on the complexes, DFT calculations that included the integral equation formalism polarizable continuum model[34] were also performed.

To shed more light on the nature of the binding energy between an anion and the tweezers, and to aid the efficient design of the latter, we used the symmetry-adapted perturbation theory (SAPT)[35] to obtain a physical interpretation of the interaction energy. In this method, the interaction energy is expressed as a sum of perturbative corrections in which each correction results from a different physical effect. The different intermolecular terms obtained from this method can be summarized in electrostatic, exchange–repulsion, induction, and dispersion contributions.[23,35] The interaction energy, E_{inter}, is given by Equation (1):

$$E_{\text{inter}} = E_{\text{es}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{disp}} \qquad (1)$$

in which E_{es} is the electrostatic energy, E_{exch} is the exchange–repulsion energy, E_{ind} is the induction energy, and E_{disp} is the dispersion energy.

Results and Discussion

Aside from parent molecule **1**, we have also optimized the molecular structures of several fluorinated derivatives of **1** that contain 6, 10, and 14 fluorine atoms, which are denoted as **2**, **3**, and **4**, respectively (Figure 1). All tweezers show C_{2v} symmetry despite the fact that no symmetry constraints were used during the optimization process. Cartesian coordinates of all the optimized structures are included in the Supporting Information.

Fluorine substitution does not significantly affect the global structure of the tweezers. As expected, the main changes in the structures are located in the benzene rings, which leads to an increase in the ipso angle (for example, it varies from 116.9° in **1** to 119.3° in **2**) and shortening of the C···C distance at the same position (it varies from 1.396 Å in **1** to 1.388 Å in **2**). An estimate for the difference in the opening of the molecular tweezers can be obtained through measuring the distance between the terminal carbon atoms of the tweezers. In the parent molecule this distance is 4.817 Å. In the case of **2**, the distance is reduced to 4.723 Å, which indicates a small closing of the tweezers. In **3** this distance increases to 4.850 Å and in **4** the opening is even larger, which is reflected in a terminal C atom distance of 4.957 Å. The decrease in the C···C distance in **2** may be a result of the lower repulsive interactions between a substituted benzene ring and a nonsubstituted one than the repulsive interactions between two nonsubstituted ones. These electrostatic interactions will be very important for the analysis of how the tweezers clasp anions. The balance of positive/negative charge controlling the electrostatic interactions will be noticeably affected by the tendency of the dipole moment to decrease, because a zero value in the dipole reflects a totally symmetric charge disposition. The dipole moments of **1**, **2**, **3**, and **4** are 1.098, 0.020, 1.404, and 5.824 debyes, respectively. The value of the dipole moment for **2** reflects a very symmetric charge disposition. It does not happen in **3** and **4**, possibly owing to the existence of repulsive interactions between the terminal fluorine atoms in the tweezers. In all the tweezers, the smallest frequency was the opening–closing movement of the tweezers (with values ranging from 14.55 cm^{-1} in **1** to 12.04 cm^{-1} in **4**). The low frequency values emphasize the flatness of the potential-energy surface for that movement.

As electrostatic interactions seem to play a significant role in the global interaction energy of anions with π systems, we calculated the molecular electrostatic potential (MEP) of the tweezers (Figure 2). The convex side of the tweezers always presents a more positive MEP than the concave one, which is independent of the degree of fluorine substitution. The same type of behavior was observed by the group of Klärner, in which they report no meaningful changes in the differences between the convex versus concave MEP of several NH_2, OH, and OAc substituted molecular clips.[11] We did not try to evaluate these differences because our main goal was to characterize the interactions of the anion in the concave side of the tweezers and to analyze its potential as a molecular receptor site for anions. However, some changes in the fragments that join the benzene rings in the frame of the tweezers can noticeably alter the MEP sign of the convex side. Work is being carried out to find the most suitable hinges for the tweezers.

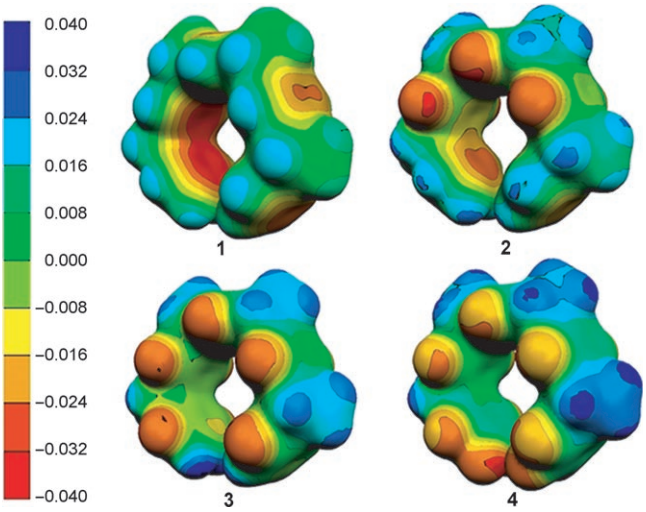

Figure 2. Electrostatic molecular potential (atomic units) of the tweezers.

Complexation with an iodine anion: In a computational study of the anion–π interactions by employing the SAPT method, Kim et al.[23] have performed the decomposition of the intermolecular-interaction energy into several terms, namely, electrostatic, induction, exchange–repulsion, and dispersion terms. The authors show that for different halogen complexes with several π systems the electrostatic term follows the same tendency as the total interaction energy. This tendency can be understood by taking into consideration the fact that both dispersion and induction energies can be ascribed, to a large extent, to interactions between the molecular orbitals (MOs) of the anion and the π system. The attractive induction and dispersion energies increase as the diffuse electron cloud of the anion interacts with the substrate. The repulsive exchange interaction, which also depends on the overlap of the MOs, increases too. This has the effect of establishing a balance between the exchange–repulsion energy on one side and the induction and dispersion energies on the other, and results in a direct correlation between the remaining term, the electrostatic energy, and the total intermolecular energy. Fluorine substitution does not significantly affect the MOs in the concave cavity of the molecules, and therefore, we expect that the balance between dispersion–inductive and the exchange–repulsion terms would be almost constant for the different tweezers analyzed herein. Therefore, the total interaction energy would vary according to the electrostatic term, which can be estimated by analyzing the MEP inside the concave cavity. The MEP in the concave cavity of **1** is notably negative and becomes less and less negative as the degree of fluorine substitution increases, as shown in Figure 2. The values of the MEP in the center of the convex cavity are −21.26, −10.25, −5.79, and −0.64 $kcal\,mol^{-1}$. Clearly the best candidate to accommodate I^- in its cavity is **4**, in which the MEP in the center of the cavity is almost neutral.

The stability of the complex between the anion and the tweezers must be determined through the magnitude of the dispersion and induction energies. These energies will depend on the characteristics of the anion. To analyze the features of the intermolecular interactions for the complexation of the tweezers with iodine, calculations by using the SAPT method in the iodine–hexafluorobenzene system have been done. The results of these calculations are shown in Table 1, together with the results obtained by Kim and coworkers[23] for hexafluorobenzene with the rest of halides. This table shows that the induction and dispersion energies have a larger contribution to the total interaction energy as the size of the halide anion increases. If the electrostatic energy is subtracted from the interaction energy ($E_{\text{inter-es}}$) then the resulting repulsive interaction decreases as the anion size increases. This repulsive interaction compensates to some extent for the depletion of the attractive electrostat-

Table 1. MP2 equivalent interaction energy[a] (kcal mol^{-1}) components of different halides-hexafluorobenzene complexes obtained by using the SAPT program.

	F$^-$	Cl$^-$	Br$^-$	I$^-$
E_{inter}	−17.86	−12.92	−12.28	−11.24
E_{es}	−28.49	−22.71	−22.13	−19.98
E_{exch}	42.54	43.44	48.72	48.31
E_{ind}	−25.39	−26.16	−29.54	−31.01
E_{disp}	−6.52	−7.48	−9.33	−8.56
$E_{\text{MP2−BSSE corrected}}$	−18.87	−12.97	−12.68	−11.25
$E_{\text{inter−es}}$	10.63	9.8	9.85	8.74

[a] Results for F$^-$, Cl$^-$, and Br$^-$ are from ref. [23]. Results for I$^-$ are from this work.

ic energy that also appears when the anion size increases, and keeps the value of the total energy in the same range. The results obtained for iodide, in which induction and dispersion energies play an important role, are similar to the results given by Kim and co-workers for some organic anions (NO_3^-, CN^-, etc.).[23] In fact, for these anions the dispersion term is even more important than in our case and the electrostatic term is less important, therefore, larger attractive interaction energies can be expected for these organic anions bound to the tweezers than those we would find with iodide.

To study the complexation process, we performed geometric optimizations of the complexes formed between the different molecular tweezers and the iodine anion located in their concave cavities. The interaction energies were corrected for BSSE by employing the counterpoise method. By using the B3LYP frequencies, we calculated the zero-point vibrational energy (ZPVE) corrected energies and the differences in enthalpy at 298 K. The results of these calculations are summarized in Table 2 and Figure 3. The interaction energy is positive for compounds **1–I**$^-$ and **2–I**$^-$, but negative for **3–I**$^-$ and **4–I**$^-$ (see Table 2). The value for **4–I**$^-$ is within the expected range of binding energies for several cations binding similar molecular tweezers.[8] It can also be seen in Table 2 than the zero-point energy and thermal corrections used to obtain the enthalpy values slightly increase the stability of the complexes. The stabilizing trend reflected in the energetic results when fluorine substitutions are performed confirms our hypothesis about the possibility of obtaining neutral tweezers composed of aromatic rings that can bind anions.

Table 2. Obtained BSSE, deformation, interaction and total complexation energies (kcal mol^{-1}) of the investigated tweezer–ion complexes.

	BSSE[a]	ΔE_{deform}[a]	$\Delta E_{\text{complex}}$[a,b]	ΔH	BSSE[c]	$\Delta E_{\text{inter−MP2}}$[c]
1–I$^-$	14.60	0.79	12.87	12.56	20.35	4.45
2–I$^-$	14.78	0.71	5.20	4.21	21.66	−4.06
3–I$^-$	15.11	0.54	−0.28	−1.05	22.59	−9.72
4–I$^-$	15.23	0.44	−5.95	−6.00	23.55	−15.82

[a] Obtained by using the B3LYP functional. [b] $\Delta E_{\text{complex}} = \Delta E_{\text{inter}} + \Delta E_{\text{deform}}$. [c] Obtained by performing single point MP2 calculations on the optimized B3LYP geometries.

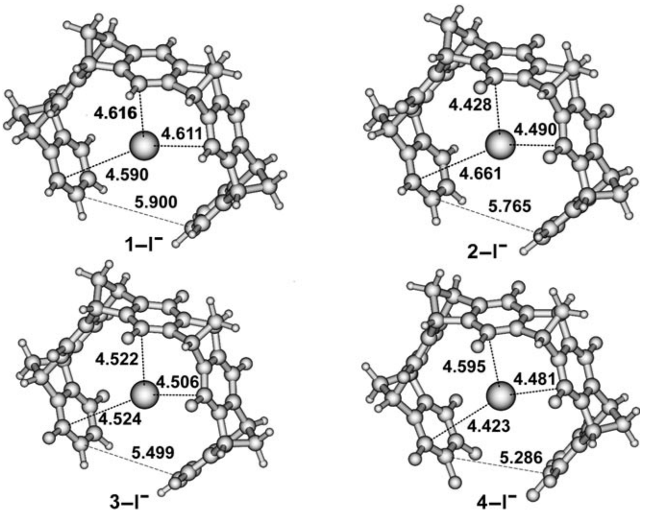

Figure 3. Optimized structures of the iodide–tweezer complexes. Distances are given in Å.

A comparison between the binding energies and the MEP value in the cavity of the tweezers highlights the fact that the stability comes from the depletion of the electrostatic repulsion between the anion and the π clouds of the aromatic rings, which have a lower electron density owing to the influence of the fluorine atoms. This decrease in the electrostatic repulsion is accompanied by a decrease in the distance between the anion and the tweezer (see Figure 3) together with an increase in attractive energies (induction and dispersion), which gives more stability and produces more stable complexes. To further investigate the relationship between the MEP and the binding energy, we performed a linear regression between them. The regression coefficient value was 0.9902. The expression obtained cannot be used to obtain quantitative results owing to the small amount of data used; however, it gives a qualitative insight into the close relationship between these two properties. Complexes **1–I**$^-$, **2–I**$^-$, and **3–I**$^-$ were characterized as transition states with imaginary frequencies of 13.5i, 11.04i, and 7.4i cm^{-1}. These frequencies correspond to the movement of the iodine anion out of the molecular tweezers. Complex **4–I**$^-$ is a real minimum in which the smallest frequency (5 cm^{-1}) is the movement of the iodine anion out of the molecular tweezers.

A comparison between Figures 1 and 3 shows that all molecular tweezers open after complexation with the iodine anion. This general opening movement is probably as a result of the anion size. However, the degree that the molecule opens is not the same for the different tweezers. The distance that the tweezers open was measured from the distance between the terminal carbon atoms in the monomer and the corresponding complex. The distance that the tweezers open decreases as the fluorine substitution increases (1.08, 1.04, 0.6, and 0.3 Å). This trend is also reflected in the energetic cost of the opening movement (deformation energy), which is less than 1 kcal mol^{-1} in all cases, and ranges from 0.79 kcal mol^{-1} in **1–I**$^-$ to 0.44 kcal mol^{-1} in **4–I**$^-$

(Table 2). Therefore, both the extent that the tweezers open and the deformation energy decrease as the binding energy increases. This trend occurs because they are related through electrostatic interactions as follows: the electrostatic repulsion between the anion and the π-electron density decreases, and the tweezers can approach the optimized geometry of the isolated molecule, which decreases the extent of the opening and the deformation energy. The frequencies calculated for the vibration of the tweezers opening in the complexes are 22.5, 21.8, 20.6, and 20.6 cm^{-1} for the series, which decrease as the binding energy increases.

In their analysis of the molecular interactions in several anion–π systems, Kim and co-workers[23] found that the frequency of the intermolecular stretching mode is correlated with the BSSE and ZPVE corrected binding energies. Therefore, the magnitude of this vibration was an indication of the strength of the intermolecular forces in those particular systems. As the anion is surrounded by three different benzene rings in our case, we cannot expect any quantitative indication of the strength of the interaction from the values of the anion–benzene stretching frequencies perpendicular to the plane of the aromatic rings. Instead, we found that there was a second-order polynomial correlation between the square of the anion vibration as the anion moves in and out of the tweezers and the binding energies in such a way that imaginary frequencies correspond to positive binding energies and vice versa. This parabolic correlation indicates that the value of the frequency will increase with the value of the energy; larger positive energies will give higher imaginary frequencies and larger negative energies will yield higher real frequencies.

The interaction between the p HOMO of the anion and the π LUMO of the tweezers is primarily responsible for the induction energy. In these systems, this kind of interaction must be accompanied by a charge transfer from the anion to the molecular tweezers, Δq. Mulliken charges calculated by using the MP2 wave functions show that this Δq increases as the fluorine substitution increases. Relative to its value in the nonfluorinated complex (**1–I**$^-$), this increase in charge transfer from I^- to the tweezers is 0.015 (**2–I**$^-$), 0,035 (**3–I**$^-$), and 0.050 (**4–I**$^-$). Fluorine substitution does not significantly change the π LUMO, so the difference in charge transfer must be owing to a change in molecular orbital overlap, which is achieved as a result of a smaller distance between the anion and the π system, as shown in Figure 3. For this reason, **4–I**$^-$ is the complex with the biggest charge transfer. This charge transfer is accompanied by a bigger induction energy and a bigger dispersion energy, which eventually results in the formation of a more stable complex.

The most common current density functionals are known to have poorly described dispersion forces. In the complexation of anions with π systems, the main contributors to the interaction energy are the electrostatic and induction terms,[23] which are quite well described by DFT methods, but there is a non-negligible contribution of the dispersion term that is stabilizing, and as previously stated, not well described with density functionals. Clearly our results obtained by using the B3LYP functional suffer from this defect. Nevertheless, the fact that the complexation energy for **4–I**$^-$ is stabilizing is encouraging because a better description of the intermolecular interactions would definitely increase this value, which supports the hypothesis proposed in this work. To see the effect of using a better method to calculate the intermolecular forces, we evaluated the interaction energy by means of MP2 single point calculations on the B3LYP optimized geometries by employing the same basis set. Owing to the rigidity of the system and the fact that the iodine anion has a considerable size and almost fills the cavity, we do not expect a significant change between the molecular geometries optimized by using the B3LYP and the MP2 methods. The interaction energy corrected for BSSE ($\Delta E_{\text{inter-MP2}}$ in Table 2) is -15.82 kcalmol^{-1} for complex **4–I**$^-$, which is significantly more negative than that obtained by DFT and similar to that reported for cation–π systems.[22] A similar decrease in the interaction energy with respect to the B3LYP calculation can be observed for the other complexes (Table 2). An estimate of the relevance of the dispersion energy in the total interaction is given by the ratio of the ΔE_{corr} (the difference in energy between the complex and the monomers computed at the MP2 level vs. the same quantity calculated at the HF level) to the corrected interaction energy. This ratio is 1.42 for **4–I**$^-$ compared with the values of 0.66 for $Cl^-\cdots C_6F_6$ and 0.67 for $Br^-\cdots C_6F_6$ dimers reported by Kim et al.[23] and the value of 0.69 for the $I^-\cdots C_6F_6$ dimer that we calculated by using the same basis set as for the tweezers. No quantitative estimations can be obtained from these results because ΔE_{corr} contains contributions from other energy terms and the structure of the tweezers (composed of several aromatic rings) is more complicated than the structure of the C_6F_6 molecule. However, these results show the relevant role played by the dispersion term in the tweezer–anion binding energy.

Influence of the solvent: To get an estimate of the effects of solvent in the complexes, we have performed single point DFT calculations that include a polarizable continuum model.[34] For each of these calculations, the geometry of the complex in the gas phase was used as the reference and the iodine anion was moved out of the molecular tweezers along the axis perpendicular to the symmetry plane of the molecule. Figure 4 shows the results obtained by using water as the solvent for the different tweezers. Distances and energy differences are given with respect to the values of the gas-phase geometry. In all the tweezers, the structure in which the anion is out of the tweezers is the most stable. This result is not surprising because water is a very polar solvent and the binding energy in the tweezers studied is not large enough to keep the ion inside. However, it is obvious that as the number of fluorine atoms is increased the difference in energy decreases and the slope of the curve is lower. Taking this information into account, we think that if there are enough aromatic rings in the tweezers (bigger tweezers), which provide more binding sites, then the anion inside the tweezers could be more stable than in the solvent.

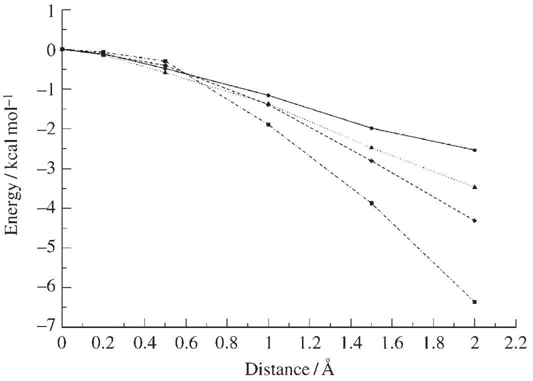

Figure 4. Energy profile of the iodide–tweezer complexes in water when the iodine anion is moved out of the molecular tweezers along the axis that is perpendicular to the symmetry plane of the molecule. Each complex is denoted with the number of the tweezers as follows: ■ = **1**, ◆ = **2**, ▲ = **3**, and ● = **4**. Distance = 0.0 corresponds to that of the equilibrium geometry in the gas phase.

The same type of calculations that have been conducted in water have also been performed in chloroform. Results for **4**–**I**$^-$ are shown in Figure 5. In this case, and as a consequence of the lower dielectric constant of chloroform, the anion is more stable inside the tweezer than in the solvent. However, the energy minimum is not the same as that of the gas phase and it occurs at about 1.5 Å along the axis, which approximately corresponds to the outer border of the aromatic rings. As an attractive interaction exists between the anion and the hydrogen atoms of the methylene-bridged groups in this position, modification of these bridged structures so that no attraction exists can render the energy minimum to occur when the anion is in the center of the cavity.

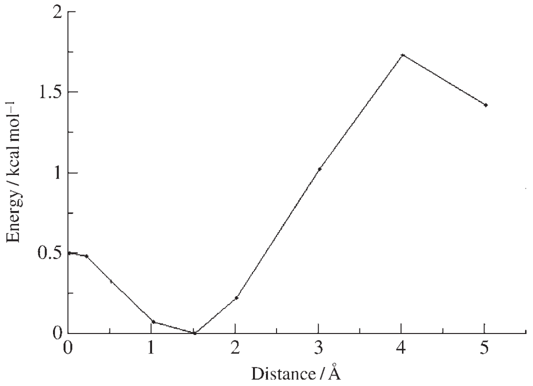

Figure 5. Energy profile of the **4**–**I**$^-$ complex in chloroform when the iodine anion is moved out of the molecular tweezers along the axis perpendicular to the symmetry plane of the molecule. Distance = 0.0 corresponds to that of the equilibrium geometry in the gas phase.

Conclusions

In the present study, we have provided theoretical support to the idea that molecular tweezers composed of aromatic rings, which are generally used for molecular recognition of electrodeficient aromatic and aliphatic substrates as well as organic cations, could also bind anions after fluorine substitution of the hydrogen atoms of the aromatic rings. Thus, in **4**–**I**$^-$ the binding energy obtained is close to that observed for similar molecular tweezers binding cations. Considering the energy results obtained, it seems quite clear that the same behavior will occur with other anionic compounds and with electron-rich aromatic or aliphatic substrates. It should be noted that, for computational efficiency, the present study has been conducted on small molecular tweezers, and that if bigger tweezers are considered then the number of binding sites will probably increase, which would result in a bigger stabilization energy.

In the benzene–anion complexes studied there is a balance between the exchange–repulsion energy on one side and the dispersion and induction energies on the other. As a consequence of this situation, there is a correlation between the binding energies and the electrostatic terms. We have found the same type of correlation between the variation of the binding energy of the molecular tweezer complexes along the series and the value of the electrostatic potential inside the cavity of the tweezers. It must be noted that in the **4**–**I**$^-$ complex we have a large attractive binding energy even though the electrostatic potential inside the cavity is slightly negative.

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