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Counterintuitive Substituent Effect of the Ethynyl Group in Ion−π Interactions

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In this article, we report a high-level theoretical study (SCS-RI-MP2(full)/aug-cc-pVTZ) that deals with the substituent effect of the ethynyl group on ion−π interactions in 1,3,5-triethynylbenzene systems. The ethynyl group is able to act as an electron-withdrawing group, thus favoring the anion−π interaction. Unexpectedly, it has little influence on the cation−π interaction. This behavior has been studied by examining the geometrical and energetic features of the complexes, AIM, and charge analyses and partitioning the interaction energy. The simultaneous interaction of 1,3,5-triethynylbenzene with cations and anions by opposite sides of the ring has also been studied.

Introduction

Supramolecular chemistry has expanded rapidly in recent years both in terms of potential applications and in its relevance to analogous biological systems. The formation and function of supramolecular complexes occur through a variety of noncovalent forces. An understanding and quantification of intermolecular interactions is of importance both for the rational design of new supramolecular systems, including intelligent materials, as well as for developing new biologically active agents.[1] Noncovalent interactions play a crucial role in many areas of science and technology, including materials and catalysis. They are important in chemical reactions, molecular recognition, and regulation of biochemical processes.[2] These chemical processes are accomplished with specificity and efficiency taking advantage of intricate combinations of weak intermolecular interactions of various sorts. Noncovalent interactions such as hydrogen bonding, anion−π, cation−π, and π−π interactions and other weak forces govern the organization of multicomponent supramolecular assemblies.[3] A deep understanding of these interactions is of outstanding importance for the rationalization of effects observed in several fields, such as biochemistry and materials science. A quantitative description of these interactions can be performed by taking advantage of quantum chemical calculations on small model systems.[4]

The interactions involving aromatic rings are very important in supramolecular chemistry. For instance, cation−π interactions[5] are supposed to be an important factor in several biological processes.[6] Another noncovalent interaction that involves aromatic rings is the anion−π interaction,[7] which has attracted considerable attention in the last several years. Anion−π complexes have been observed experimentally, sustaining the theoretical predictions and the promising proposal for the use of anion receptors based on anion−π interactions in molecular recognition.[8] These interactions are also important in DNA bases such as adenine.[9] Moreover, Berryman et al. have reported structural criteria for the design of anion receptors based on the interaction of halides with electron-deficient arenes.[10] Recent excellent reviews deal with anion-binding involving π-acidic heteroaromatic rings.[11] The ion−π interaction is dominated by electrostatic and ion-induced polarization terms.[12] The nature of the electrostatic term can be rationalized by means of the permanent quadrupole moment of the arene.

The π-basicity/acidity of aromatic rings can be modulated using substituents. The π-electron-rich benzene can be turned into electron-poor by substituting hydrogen atoms by electron-withdrawing groups (EWGs), for instance fluorine atoms. The electron richness of benzene can be incremented by attaching electron-donating groups (EDGs). Therefore, the strength of cation−π interactions is incremented by the addition of EDGs to benzene, and the strength of anion−π interactions is incremented by the addition of EWGs to benzene. In this article, we report a high-level theoretical study where we analyze the effect of the ethynyl group on the ion−π binding affinity of the benzene ring. The ethynyl group is not usually considered to be an EWG in textbooks. Studies on the electronic properties of the ethynyl group are scarcely found in the literature. Since the pioneering work of Landgrebe et al.[13] on the electronic nature of the acetylene group where the Hammet's substituent constants were determined, only two experimental works deal with its electron-withdrawing character.[14] For instance, the redox properties of alkynyl-substituted flavins have been studied.[14b] They agree with the fact that the ethynyl group is an EWG because the reduction potential of the ethynyl substituted flavins moves toward more positive values. In addition, the effect of the alkynyl substitution has been studied in benzoquinones using cyclic voltametry,[14a] confirming the EWG nature of the ethynyl group. In addition to these works, Diederich and collaborators have widely used scaffolds based on acetylene for constructing receptors, and they have suggested the electron-withdrawing nature of acetylene.[15] The effect of the substituent in a large set of Na^+−π complexes has recently been reported.[16] Finally, the effect of the ethynyl group on the structure and electrical properties of phenyl−thiadiazole systems has been studied theoretically.[17]

In this article, we analyze the effect of ethynyl substitution in the ion−π binding ability of benzene. To the best of our knowledge, this is the first work that studies the electronic nature of ethynyl and analyzes how it influences, as substituent of an aromatic ring, the interaction energies of anion−π and cation−π complexes. As expected, the anion−π complexes of 1,3,5-triethynylbenzene with anions are favorable and comparable to those of 1,3,5-trifluorobenzene. In contrast, the interaction energies of the complexes of 1,3,5-triethynylbenzene with

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cations are almost unaffected (compared with benzene), whereas the interaction of 1,3,5-trifluorobenzene with cations is considerably reduced compared with benzene. This unexpected behavior of the 1,3,5-triethynylbenzene is studied and analyzed using high-level ab initio calculations and charge transfer effects. Moreover, we use the Bader's theory of "atoms in molecules", which provides an unambiguous definition of chemical bonding,[18] to describe the interactions. The AIM theory has been successfully used to characterize and understand a great variety of interactions, including the ones studied herein. In addition, we have used the molecular interaction potential with polarization (MIPp)[19] as a partition method to analyze the physical nature of the interactions. The MIPp is a convenient tool for predicting binding properties. It has been successfully used for rationalizing molecular interactions such us hydrogen bonding and anion$-\pi$ interactions and for predicting molecular reactivity.[20] The MIPp partition scheme is an improved generalization of the MEP where three terms contribute to the interaction energy: (i) an electrostatic term identical to the MEP,[21] (ii) a classical dispersion−repulsion term,[22] and (iii) a polarization term derived from perturbational theory.[23] The classical dispersion−repulsion term has been split up into two terms, that is, a dispersion term evaluated using quantum mechanics calculations and a repulsion term obtained by the difference. (See the Theoretical Methods for a detailed explanation.)

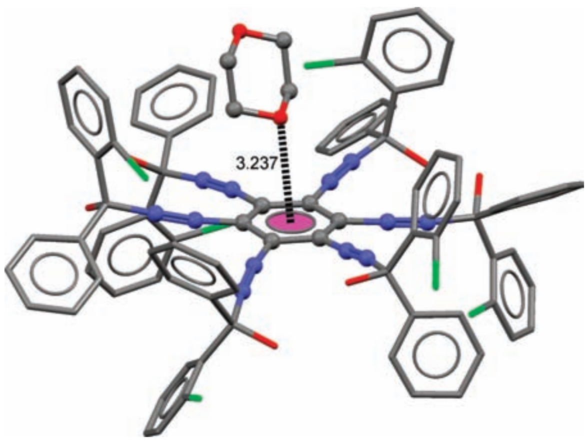
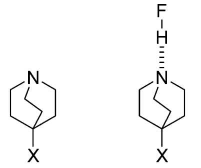


Figure 1. Partial view of the X-ray structure retrieved from the CSD (TORQAS). The hydrogen atoms have been omitted for the sake of clarity. The CC triple bonds are highlighted in blue. Distance in angstroms.



1, X=H
2, X=CCH
3, X=F
4, X=CN

5, X=H
6, X=CCH
7, X=F
8, X=CN

Figure 2. Compounds **1**−**4** and their complexes with HF **5**−**8**.

Theoretical Methods

The geometry of all of the complexes included in this study was fully optimized using the SCS-RI-MP2(full) method and the aug-cc-pVTZ basis set within the program TURBOMOLE version 5.7.[24] For Li^+ and Na^+ cations, the cc-pVTZ basis set was used. This level of theory is abbreviated as SCS-RI-MP2(full)//AVTZ′. The RI-MP2 method[25,26] applied to the study of cation$-\pi$ and anion$-\pi$ interactions is considerably faster than the MP2 method, and the interaction energies and equilibrium distances are almost identical for both methods.[27,28] Moreover, we have used the spin-component-scaled MP2 method (SCS-MP2), which is based on the scaling of the standard MP2 amplitudes for parallel- and antiparallel-spin double excitations.[29] The SCS-MP2 correlation treatment yields structures that are superior to those from standard MP2, particularly in systems that are dominated by dispersive interactions.[30] The binding energy (E) was calculated at the same level without correction for the basis set superposition error (BSSE). The basis sets used in this work are of sufficient quality that BSSEs should be rather small.[31] Moreover, it has been shown that uncorrected MP2/aug-cc-pVTZ binding energies lie between corrected and uncorrected MP2/aug-cc-pVQZ energies.[32] BSSE corrections may not always improve binding energies of weakly bonded complexes because in the counterpoise method[33] a monomer may utilize the valence and core functions of its partner, which are not available to the monomer in the complex.[34] For the anion$-\pi$ complexes, where the BSSE can be more important, we have checked this issue by computing the BSSE-corrected interaction energies of the complexes. In all cases, the difference between corrected and uncorrected energies is less than 2.6 kcal/mol, indicating that BSSE values are not very relevant. More importantly, the energetic trends using either corrected or uncorrected energies are the same. The optimization of the molecular geometries has been performed, imposing the highest abelian symmetry group for each case. Other possible conformations of complexes have not been considered because the ultimate aim of this study is to analyze the π-binding properties of substituted benzenes toward cations and anions. In this manuscript, we denote the interaction energy of the complexes using "E" and the relative energy of the complexes with respect to the related benzene complexes using "ΔE". In some complexes, the interaction energy is positive. This means that the complex is a minimum in the potential isosurface with a more positive energy than the sum of the isolated parts. However, it is possible that the observed minimum is a technical artifact.

Calculation of the MIPp energies interacting with cations and anions was performed using the HF/6-311++G**//SCS-RI-MP2(full)/aug-cc-pVTZ wave function by means of the MOPETE-98 program.[35] The ionic van der Waals parameters for F^- and Cl^- were taken from the literature.[36] The ionic van der Waals parameters used for cations come from the TRIPOS force field.[37] Some basic concepts of MIPp follow. (See refs 19 and 23 for a more comprehensive treatment.) The MEP can be understood as the interaction energy between the molecular charge distribution and a classical point charge. The formalism used to derive MEP remains valid for any classical charge; therefore, it can be generalized using eq 1, where Q_B is the classical point charge at R_B. Q_B can adopt any value; when $Q_B = 1$ corresponds to a proton, ϕ stands for the set of basis functions used for the quantum mechanical molecule A, and $c_{\mu i}$ is the coefficient of atomic orbital μ in the molecular orbital i.

$$\mathrm{MEP} = \sum_{A} \frac{Z_A Q_B}{|R_B - R_A|} - \sum_{i}^{\mathrm{occ}} \sum_{\mu} \sum_{\nu} c_{\mu i} c_{\nu i} < \phi_\mu \left| \frac{Q_B}{|R_B - r|} \right| \phi_\nu > \quad (1)$$

The MEP formalism permits the rigorous computation of the electrostatic interaction between any classical particle and the

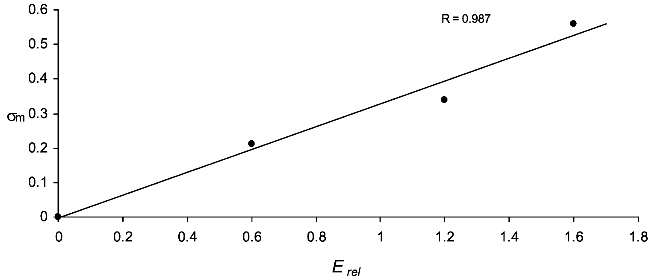


Figure 3. Regression plot of the relative energy ($E_{\rm rel}$, kilocalories per mole) versus the Hammet's $\sigma_{\rm m}$.

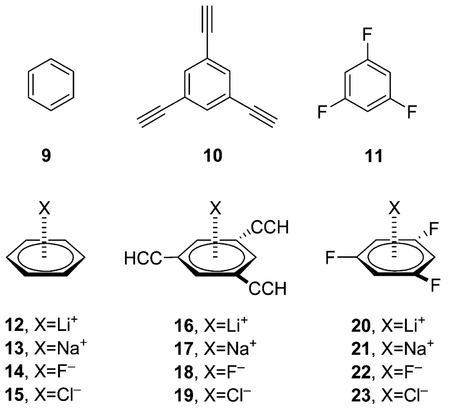


Figure 4. Compounds **9**−**11** and their ion−π complexes **12**−**23**.

molecule. Nevertheless, nuclear repulsion and dispersion effects are omitted. This can be resolved by the addition of a classical dispersion−repulsion term, which leads to the definition of MIP (eq 2), where *C* and *D* are empirical van der Waals parameters.

$$\mathrm{MIP} = \mathrm{MEP} + \sum_{\mathrm{A'B'}} \left(\frac{C_{\mathrm{A'B'}}}{|R_{\mathrm{B'}} - R_{\mathrm{A'}}|^{12}} - \frac{D_{\mathrm{A'B'}}}{|R_{\mathrm{B'}} - R_{\mathrm{A'}}|^{6}} \right) \qquad (2)$$

The definition of MIPp is given by eq 3, where polarization effects are included at the second-order perturbation level;[23] ε stands for the energy of virtual (*j*) and occupied (*i*) molecular orbitals. It is worth noting that eq 3 includes three important contributions: first, the rigorous calculation of electrostatic interactions between quantum mechanical and classical particles; second, the introduction of an empirical dispersion−repulsion term; and third, the perturbative treatment of the polarization term.

$$\mathrm{MIPp} = \mathrm{MIP} + \sum_{j}^{\mathrm{vir}} \sum_{i}^{\mathrm{occ}} \frac{1}{\varepsilon_i - \varepsilon_j} \left\{ \sum_{\mu} \sum_{\nu} c_{\mu i} c_{\nu i} < \phi_\mu \left| \frac{Q_{\mathrm{B}}}{|R_{\mathrm{B}} - r|} \right| \phi_\nu > \right\}^2 \qquad (3)$$

The dispersion energy contribution to the total interaction energy is estimated by computing the difference between the MP2 and BP86 interaction energies because the BP86 method does not take into account dispersion effects.[38] This methodology has been previously used to evaluate dispersion energies in ion−π complexes.[39] The repulsion energy contribution is evaluated using the classical dispersion−repulsion term, computed using the MIPp method and subtracting the dispersion energy.

TABLE 1: Binding and Relative Energies (*E* and $E_{\rm rel}$, respectively, kilocalories per mole) and Equilibrium Distances (*R*, angstroms) at the SCS-RI-MP2(full)/aug-cc-pVTZ Level of Theory for Complexes 5−8 (Hammet's Constants $\sigma_{\rm m}$ and Taft's $\sigma_{\rm I}$ Are Also Included)

complex	E	$E_{\rm rel}$	R	$\sigma_{\rm m}$	$\sigma_{\rm I}$
5	−17.3	0.0	1.574	0.00[a]	0.00[a]
6	−16.7	0.6	1.585	0.21[a]	0.24[b]
7	−16.1	1.2	1.593	0.34[a]	0.50[a]
8	−15.7	1.6	1.596	0.56[a]	0.59[a]

[a] From ref 14. [b] This work.

The "atoms-in-molecules" analysis[40] has been performed by means of the AIM2000 version 2.0 program[41] using the MP2(full)/aug-cc-pVTZ wave functions. We have used the Merz−Kollman scheme for deriving atomic charges and studying charge transfer effects at the same level of theory. It has been reported that this method provides high-quality charges.[42]

In the ternary complex effects where cation−π and anion−π interactions coexist, we have studied cooperativity effects by computing the genuine nonadditivity energies ($E - E_{\rm A}$) using eq 3. We computed the nonadditivity energies by subtracting the binding energy of the sum of all pair interaction energies ($E_{\rm A}$) from the binding energy of the complex (E)

$$E - E_{\mathrm{A}} = E_{\mathrm{abc}} - (E_{\mathrm{ab}} + E_{\mathrm{ac}} + E_{\mathrm{bc}}) \qquad (4)$$

The energy decomposition of the interaction energies into the individual electrostatic, induction, dispersion, and exchange−repulsion components was performed using density functional theory (DFT) combined with the symmetry-adapted perturbation theory (DFT-SAPT)[43] approach. For the anion complexes, we have used its density-fitting implementation (DF-DFT-SAPT).[44] The DFT-SAPT intermolecular interaction is given in terms of first-, second-, and higher-order correction interaction terms that are indicated by the superscripts (eq 5)

$$E_{\mathrm{int}} = E^1_{\mathrm{el}} + E^1_{\mathrm{exch}} + E^2_{\mathrm{ind}} + E^2_{\mathrm{ind-exch}} + E^2_{\mathrm{disp}} + E^2_{\mathrm{exch-disp}} + \delta(\mathrm{HF}) \qquad (5)$$

where $E^1_{\rm el}$ and $E^1_{\rm exch}$ are the sums of electrostatic interaction energy and the first-order exchange energy, respectively. $E^2_{\rm ind}$, $E^2_{\rm ind-exch}$, $E^2_{\rm disp}$, and $E^2_{\rm exch-disp}$ denote the induction (with response) energy, the second-order induction−exchange (with response) energy, the dispersion energy, and the exchange−dispersion contribution, respectively. δ(HF) is the Hartree−Fock correction for higher-order contributions to the interaction energy and thus is not included in DFT-SAPT calculations. Physically meaningful separation of the interaction energy may be obtained by classifying the cross terms induction−exchange $E^2_{\rm ind-exch}$ and dispersion−exchange $E^2_{\rm exch-disp}$ as a part of the induction and the dispersion, respectively.[45] In the DFT-SAPT calculations, the PBE0AC exchange-correlation (xc) potential in combination with the adiabatic local density approximation (ALDA) xc-kernel was employed using the SCS-RI-MP2(full)/AVTZ′ optimized geometries.

Results and Discussion

Preliminary Findings and Results. We have examined the Cambridge Structural Database to find evidence of anion−π interactions in polyethynyl-substituted benzenes. There is a very

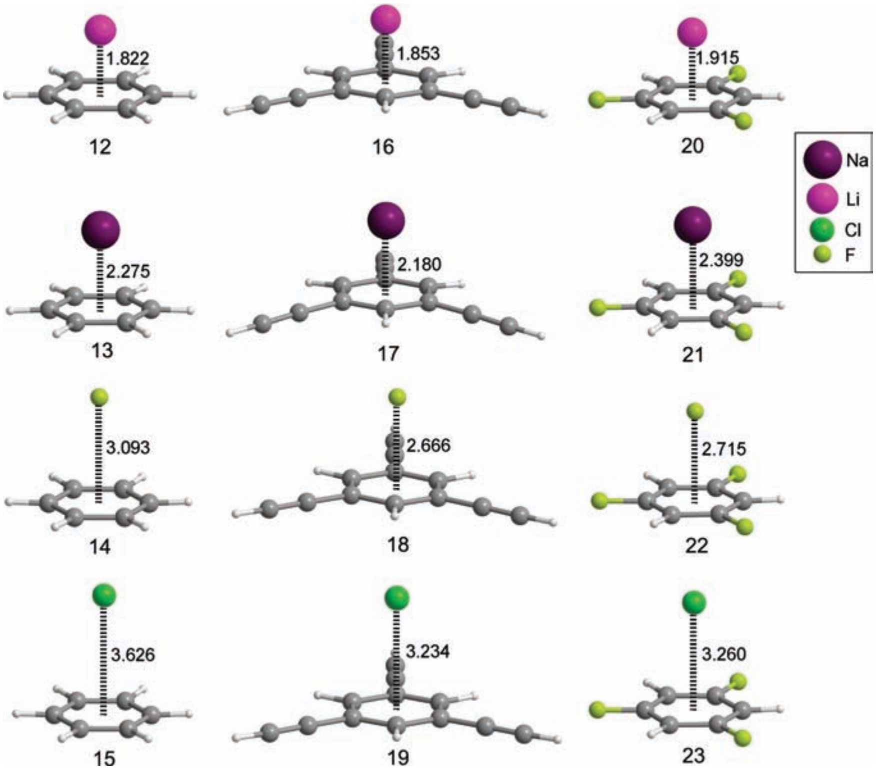


Figure 5. SCS-RI-MP2(full)/AVTZ′ optimized structures of complexes **12**−**23**. Distances in angstroms.

TABLE 2: Binding Energies and Their Variation with Respect to Benzene (*E* and Δ*E*, respectively, in kilocalories per mole) and Equilibrium Distances (*R*, angstroms) at the SCS-RI-MP2(full)/AVTZ′ Level of Theory for Complexes 12−23 as well as Merz−Kollman-Derived Charges (Q_{MK}, e), the Values of the Charge Density at the Cage CP (ρ, a.u.), and Their Variation with Respect to Benzene Complexes (Δρ, a.u.)

complex	*E*	R	Q_{MK}	$10^2\rho$	$10^3\Delta\rho$	Δ*E*
12 (**9** + Li^+)	−41.8	1.822	0.616	1.44		
13 (**9** + Na^+)	−30.3	2.275	0.743	1.05		
14 (**9** + F^-)	0.5 (1.5)[a]	3.093	−0.861	0.41		
15 (**9** + Cl^-)	0.0 (1.1)[a]	3.626	−0.904	0.32		
16 (**10** + Li^+)	−38.4	1.853	0.618	1.39	−0.57	3.4
17 (**10** + Na^+)	−33.3	2.180	0.718	1.20	1.52	−3.0
18 (**10** + F^-)	−7.5 (−5.3)[a]	2.666	−0.803	0.79	3.77	−8.0 (−6.8)[a]
19 (**10** + Cl^-)	−5.8 (−3.2)[a]	3.234	−0.856	0.58	2.57	−5.8 (−4.2)[a]
20 (**11** + Li^+)	−25.5	1.915	0.662	1.32	−1.27	16.3
21 (**11** + Na^+)	−17.0	2.399	0.788	0.91	−1.42	13.3
22 (**11** + F^-)	−9.7 (−8.1)[a]	2.715	−0.831	0.76	3.46	−10.2 (−9.6)[a]
23 (**11** + Cl^-)	−7.6 (−5.8)[a]	3.260	−0.879	0.57	2.48	−7.6 (−6.9)[a]

[a] Values in parentheses correspond to the BSSE corrected energies.

limited number of X-ray structures that contain polyethynyl-substituted benzenes and anions. In addition, most of them have other substituents like F and CN that do not allow us to extract any reliable conclusion concerning the electron-withdrawing nature of acetylene. However, a search in the CSD of structures where polyethynyl benzenes participate in lone pair (l.p.)-π interactions gives one interesting structure (CSD code TORQAS).[46] This structure is shown in Figure 1. It can be observed that the oxygen atom is located approximately over the center of the central ring at a 3.237 Å, which is characteristic of this type of interaction.[47] The central ring is substituted with six ethynyl groups. Each ethynyl is also bonded to a sp^3 carbon atom; therefore, additional substituent effects that may influence the electronic nature of the ring through the CC triple bond are not present. An interesting aspect is the directionality of the interaction because one l.p. of the oxygen atom of dioxane (equatorial l.p.) is pointing to the center of the ring. This structure confirms the assumption that polyethynyl-substituted benzenes can favorably interact with concentrations of negative charge using the π-system.

As aforementioned, the aim of this work is to study the electronic nature of the ethynyl group by analyzing its ability to modify the π-electron cloud of the benzene ring. Because the ethynyl is able to affect the electronic nature of benzene using either the π-electrons or by inductive effects, we have first studied a model system where only inductive effects are operative. We have used quinuclidine derivatives (Figure 2) where the X group is H (**1**), CCH (**2**), F (**3**), or CN (**4**). This system allows us to analyze the inductive effect of ethynyl by computing and comparing the hydrogen bonding interaction energies of complexes **5**−**8**. Quinuclidine derivatives have been successfully used before to obtain inductive parameters calculating the ionization constant of the protonated amine.[48]

The binding energies and equilibrium distances of the complexes **5**−**8** are gathered in Table 1. It can be observed that the interaction energy of complex **6** is less favorable than **5**,

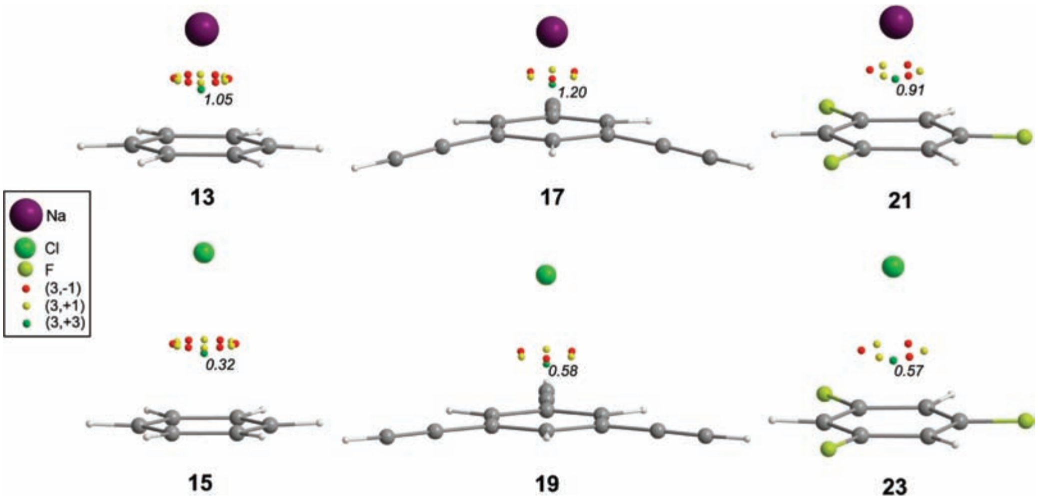


Figure 6. Distribution of critical points of several complexes is shown. The value of $10^2\rho$ at the cage CPs is shown in italics (a.u.).

TABLE 3: Electrostatic (E_e), Polarization (E_p), Dispersion (E_d), and Repulsion (E_r) Contributions to the Total Interaction (E_t) Energy (kilocalories per mole) for 9−11 Interacting with Li$^+$, Na$^+$, F$^-$, and Cl$^-$ at the Distance of the MP2 Optimized Complex[a]

compound	E_e	E_p	E_d	E_r	E_t	E_{MP2}
9 + Li$^+$	−15.9	−31.7	−5.2	15.4	−37.4	−41.8
9 + Na$^+$	−14.8	−19.0	−8.8	11.0	−31.7	−30.3
9 + F$^-$	9.5	−7.9	−1.9	1.9	1.5	0.5
9 + Cl$^-$	6.8	−4.7	−3.2	1.8	0.6	0.0
10 + Li$^+$	−1.6	−41.7	−5.5	13.4	−35.4	−38.4
10 + Na$^+$	−3.5	−29.5	−16.6	20.0	−29.6	−33.3
10 + F$^-$	3.7	−17.6	−2.6	7.6	−8.9	−7.5
10 + Cl$^-$	3.2	−10.0	−5.8	4.3	−8.3	−5.8
11 + Li$^+$	6.1	−28.4	−3.4	8.8	−16.9	−25.5
11 + Na$^+$	3.2	−16.3	−6.4	7.6	−11.9	−17.0
11 + F$^-$	−2.6	−11.4	−3.7	8.1	−9.6	−9.7
11 + Cl$^-$	−2.1	−6.3	−5.2	3.9	−9.9	−7.6

[a] For comparison purposes, the binding energies of complexes **12**−**23** at the SCS-RI-MP2(full)/AVTZ′ (E_{MP2}, kilocalories per mole) are included.

confirming the fact that ethynyl is electron-withdrawing. The interaction energy of **7** is less favorable than that of **6**, indicating that fluoride is more electron-withdrawing than ethynyl. As expected, the least favorable complex is **8** because the CN group is the most electron-withdrawing group. These results are in agreement with the Hammet σ_m values of C≡C, F, and CN. (See Table 1.) In fact, we have found a good relationship ($r = 0.987$) between the relative energies and the Hammet σ_m values. (See Figure 3.) The value of Taft's inductive parameter (σ_I) of C≡C is not available.[49] We have estimated its value from a similar representation using the known σ_I of the other groups and interpolating the value for C≡C, which is 0.24.

Ion−π Interactions. From the preliminary results, we learn that the ethynyl group is electron-withdrawing by induction. However, the triple bond has π-electrons that are suitable for interacting with the π-cloud of benzene. This issue can be very important in the π-complexes of ethynyl-substituted benzene. To shed light on this subject, we have computed the ion−π complexes shown in Figure 4. The geometric and energetic results are summarized in Table 2. As expected, the interaction energies of benzene with cations (**12** and **13**) are large and negative. In addition, the interaction energies of benzene with anions are almost negligible (0.5 and 0.0 kcal/mol for **14** and **15**, respectively). Previous studies demonstrate that the unfavorable electrostatic contribution to the total interaction energy of the anion−π complexes of benzene is almost completely compensated by the ion-induced polarization term.[50] Very interesting energetic results are obtained for the complexes of **10** interacting with anions and cations. It can be observed that the presence of three ethynyl groups attached to benzene clearly favors the interaction with anions. For instance, the interaction energy of fluoride complexes goes from positive for benzene (complex **14**, $E = 0.5$ kcal/mol) to negative for 1,3,5-triethynylbenzene (complex **18**, $E = -7.5$ kcal/mol). Moreover, the interaction energies of the anion−π complexes **18** and **19** (−7.5 and −5.8 kcal/mol, respectively) are comparable to the ones observed for 1,3,5-trifluorobenzene complexes **22** and **23** (−9.7 and −7.6 kcal/mol, respectively), indicating that the electron-withdrawing substituent effect of the ethynyl group is almost comparable to fluorine favoring anion−π interactions. A counterintuitive finding is discovered by analyzing the cation−π complexes of compounds **10** and **11** compared with that of **9**. That is, the interaction energies of the cation−π benzene complexes **12** and **13** (−41.8 and −30.3 kcal/mol, respectively) are considerably more favorable than 1,3,5-

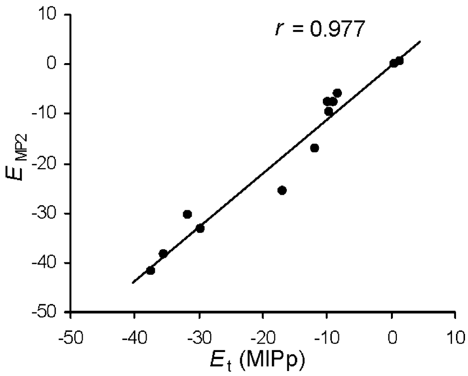


Figure 7. Regression plot of the total interaction energy (E_t, kilocalories per mole) computed using the MIPp partition scheme versus the SCS-RI-MP2(full)/AVTZ′ binding energy of complexes **12**−**23** (E_{MP2}, kilocalories per mole).

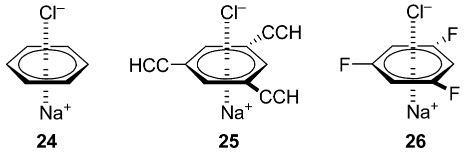


Figure 8. Ternary complexes **24**−**26**.

TABLE 4: Binding Energies (*E*, kilocalories per mole) and Equilibrium Distances (*R*, angstroms) at the SCS-RI-MP2(full)/aug-cc-pVTZ Level of Theory for Complexes 24−26 as well as Merz−Kollman-Derived Charges (Q_{MK}, e), the Values of the Charge Density at the Cage CPs (ρ, a.u.), and Their Variation with Respect to the Binary Complexes ($\Delta\rho$, a.u.)[a]

compd	E	$E - E_{\mathrm{A}}$	R(C−π)	R(A−π)	Q_{MK}(C)	Q_{MK}(A)	$10^2\rho$(C−π)	$10^2\rho$(A−π)	$10^3\Delta\rho$(C)	$10^3\Delta\rho$(A)
24	−101.5	−8.9	2.156	2.957	0.706	−0.767	1.26	0.86	2.07	5.34
25	−111.0	−7.2	2.081	2.817	0.683	−0.715	1.39	1.05	1.84	4.71
26	−96.7	−9.9	2.249	2.876	0.748	−0.781	1.16	1.00	2.46	4.23

[a] C stands for cation and A stands for anion.

trifluorobenzene complexes **20** and **21** (−25.5 and −17.0 kcal/mol, respectively). Therefore, the existence of three fluorine atoms bonded to the aromatic ring clearly favors the anion−π interaction ($\Delta E = -10.2$ kcal/mol for **22** and −7.6 kcal/mol for **23**) and disfavors the cation−π interaction ($\Delta E = +16.3$ kcal/mol for **20** and +13.3 kcal/mol for **21**) compared with benzene. Similarly, the presence of three ethynyl groups favors the anion−π interaction ($\Delta E = -8.0$ kcal/mol for **18** and −5.8 kcal/mol for **19**) compared with benzene. Interestingly, it does not worsen the cation−π interaction in excess ($\Delta E = +3.4$ kcal/mol) for **16**, and remarkably, it favors the cation−π interaction in complex **17** ($\Delta E = -3.0$ kcal/mol) compared with benzene. These results indicate an interesting duality behavior of the ethynyl group, which is able to proceed as a fluorine substituent favoring the anion−π interaction without excessively changing the cation−π binding properties of the aromatic ring.

The optimized structures of the complexes are shown in Figure 5. It can be observed that the equilibrium distances of the complexes are in agreement with the energetic analysis. The anion−π complexes of triethynyl and trifluorobenzene have shorter equilibrium distances than the anion−π complexes of benzene. In contrast, the cation−π distances of triethynyl and trifluorobenzene complexes have longer equilibrium distances than benzene apart from complex **17**, which has a shorter distance than benzene complex **13**, which is in agreement with the interaction energy.

Charge Transfer and AIM Analyses. We have also summarized in Table 2 the charge of the ion in the complexes to examine the charge transfer from the ion to the aromatic ring and vice versa. We have used the Merz−Kollman method for deriving atomic charges. Charge transfer is higher in cation−π than in anion−π complexes, principally because the cations are closer to the π-system than anions. Interestingly, charge transfer from the arene to the sodium is higher in complex **17** than in complex **13**, which is in agreement with the energetic results. That is, the ethynyl substituent is able to improve the interaction energy of benzene with sodium. Moreover, the equilibrium distance in **17** is shorter than that in **13**, favoring the charge transfer.

Topological analysis of the charge density ρ(r) distribution and properties of critical points (CPs) were determined for complexes **12**−**23** using the Bader's theory of "atoms in molecules", which provides an unambiguous definition of chemical bonding,[51] using the MP2(full)/aug-cc-pVTZ//SCS-RI-MP2(full)/AVTZ′ wave function. The AIM theory has been successfully used to characterize ion−π interactions.[52] For complexes **12**−**15**, the exploration of the CPs revealed the presence of six bond and six ring CPs that connect the ion to the six carbon atoms and the middle of the six CC bonds of the ring, respectively. For complexes **16**−**23**, the exploration of the CPs revealed the presence of three bond and three ring CPs that connect the ion to the six carbon atoms of the ring. In addition, the interaction is further described by a cage CP that connects the ion to the center of the ring. In Figure 6, we represent the distribution of CPs that is generated upon complexation of the ion in several representative complexes. The value of the charge density (ρ) computed at the cage CP has been related to the strength of the interaction and can be used as a measure of the bond order.[7b] Therefore its variation ($\Delta\rho$) upon going from the benzene (**12**−**15**) to the trisubstituted complexes (**16**−**23**) is a good measure of the strengthening or weakening of the ion−π interactions. These values are summarized in Table 2. It can be observed that the cation−π complexes of 1,3,5-trifluorobenzene have negative values of $\Delta\rho$, indicating a weakening of the interaction with respect to benzene. The contrary is found for the anion−π complexes, that is, positive values of $\Delta\rho$ and, consequently, a strengthening of the anion−π interaction, which is in agreement with the energetic and geometric results. The same behavior is observed for the anion−π complexes of 1,3,5-triethynylbenzene, which have positive values of $\Delta\rho$ indicating a strengthening of the anion−π interaction. For the cation−π complexes of 1,3,5-triethynylbenzene, a different behavior is obtained for Li^+ and Na^+. Whereas the lithium complex **16** has a negative value of $\Delta\rho$ (weakening of the interaction), complex **17** has a positive value of $\Delta\rho$ (strengthening of the interaction), which is in agreement with the energetic, geometric and charge transfer features of this complex. To give a feasible explanation for these findings, we have performed a partition of the interaction energy, which is discussed below.

MIPp Analysis. With the purpose of analyzing the nature of the ion−π interactions in complexes **12**−**23** and understanding the importance of electrostatic, polarization, and dispersion terms, we have performed a partitioning of the interaction energy using an "in house" modification of the MIPp method. (See the computational methods for details.) The results are gathered in Table 3. The binding energies obtained from the partition method are similar to the binding energies summarized in Table 2. As a matter of fact, we have found a good relationship ($r = 0.977$) between both energies, as can be observed in the regression plot of Figure 7. This result gives reliability to the MIPp method. Very interesting points arise from the analysis of the results. First, in benzene complexes, the interaction is governed by the electrostatic and polarization terms. Both terms are negative in the cation−π complexes. In anion−π complexes the electrostatic term is positive, and the polarization term is negative. Second, in 1,3,5-trifluorobenzene complexes, the electrostatic term is very small, which is in agreement with the almost negligible quadrupole moment ($Q_{zz} = 0.57$ B) of **11**.[53] The interaction is dominated by polarization and dispersion terms. Third, the partition energy scheme gives an explanation for the counterintuitive behavior of the 1,3,5-triethynylbenzene complexes. It can be observed that the polarization term, which is negative for both cations and anions, is large in comparison with benzene and trifluorobenzene complexes. This fact explains the duality of the ethynyl group. On one hand, it is able to favor the π-interaction with anions because it is an EWG, as confirmed by the preliminary calculations on the quinuclidine system. They clearly showed that the ethynyl group was able to induce electron-withdrawing effects via the σ bonds because it de-

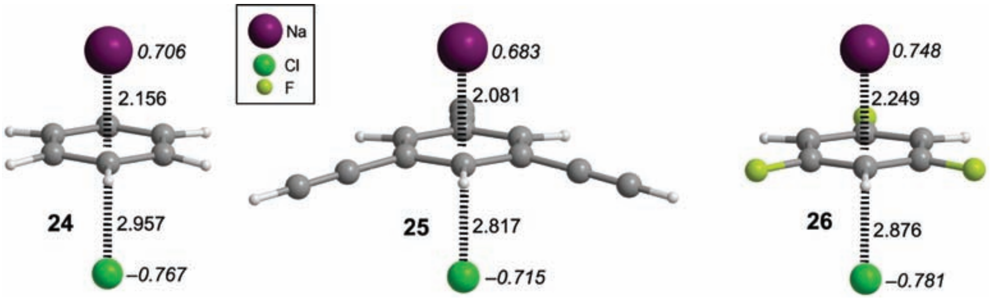


Figure 9. SCS-RI-MP2(full)/aug-cc-pVTZ optimized structures of complexes **24**−**26**. Distances (angstroms) are indicated in plain text. The Merz−Kollman charges (*e*) are indicated in italics.

TABLE 5: Energetic Contributions to the Total Interaction Energy (E_{int}) Using DFT-SAPT

complex	E^1_{el}	E^1_{exch}	E^2_{ind}	$E^2_{ind-exch}$	E^2_{disp}	$E^2_{exch-disp}$	δ(HF)	E_{int}
12 (**9** + Li^+)	−17.4	14.6	−39.9	10.7	−0.8	0.1	−2.9	−35.6
13 (**9** + Na^+)	−17.3	13.3	−31.4	13.7	−0.8	0.2	1.4	−20.9
14 (**9** + F^-)	4.8	6.3	−15.0	7.9	−4.5	1.4	0.3	1.2
15 (**9** + Cl^-)	3.3	4.9	−10.0	6.0	−4.6	1.2	0.1	0.9
16 (**10** + Li^+)	−5.5	12.5	−45.1	10.6	−0.9	0.1	−3.2	−31.5
17 (**10** + Na^+)	−8.9	16.5	−41.7	17.7	−1.2	0.2	1.5	−15.9
18 (**10** + F^-)	−5.0	17.4	−35.0	21.7	−9.2	3.2	0.1	−6.9
19 (**10** + Cl^-)	−2.9	12.7	−24.1	16.7	−9.0	2.7	0.0	−3.9
20 (**11** + Li^+)	−2.1	11.5	−35.8	9.1	−0.7	0.1	−2.5	−20.5
21 (**11** + Na^+)	−3.4	8.9	−25.2	9.5	−0.6	0.1	0.8	−9.9
22 (**11** + F^-)	−9.7	15.9	−30.2	20.7	−8.0	2.8	0.1	−8.4
23 (**11** + Cl^-)	−7.4	12.1	−21.5	16.4	−7.9	2.4	−0.1	−6.0

creases the ability of the nitrogen lone pair of quinuclidine to form hydrogen bonds. On the other hand, for the interaction with cations, the ethynyl groups are able to compensate the diminution of the electrostatic term by increasing the ion-induced polarization, giving rise to interaction energies similar to those of benzene.

1,3,5-Trienethynyl Benzene As Charge Insulator. Because the ethynyl group has the unusual property of favoring the anion−π interaction with chloride and the cation−π interaction with sodium, aromatic hydrocarbons substituted with ethynyl groups are supposed to be well prepared to establish simultaneous interactions with cations and anions by combination of these two types of ion−π interactions. Systems with dual cation and anion regions have been described before, and more importantly, the simultaneous interaction of anions and cations on different faces of the same π-system has been studied.[54] In the mentioned complexes, the π-molecule can act as charge insulator or as intermediate in the transfer of “information” between the charged systems. In this section of the article, we compare the energetic and geometrical features of three ternary complexes. (See Figure 8.) The selected ions are chloride and sodium, and we have computed the binding energies of their ternary complexes with benzene (**24**), 1,3,5-triethynylbenzene (**25**), and 1,3,5-trifluorobenzene (**26**) as well as the charge transfer and AIM analyses. The results are gathered in Table 4.

The optimized complexes **24**−**26** are shown in Figure 9. The energetic and geometric results of Table 4 show that the ternary complex **25** is the most favorable. It presents the shortest equilibrium distances and the higher charge transfer from the anion to the cation, confirming the dual effect of the ethynyl group. The AIM results corroborate this finding. The distribution of CPs is similar to that observed for binary complexes. The values of ρ at the cage CPs of complex **25** are larger than those in complexes **24** and **26**. It is also interesting to compare the behavior of the three ternary complexes with respect to the binary complexes. It can be observed that both ion−π interactions in the ternary complexes **24**−**26** are stronger than the interactions in the related binary complexes (Table 2), as deduced by the shorter equilibrium distances and higher values of ρ. (See Δρ values of Table 4.) These results indicate that there are favorable cooperativity effects between both ion−π interactions in these complexes. That is, simultaneous interaction of the aromatic ring with anions and cations leads to a strengthening of both interactions. We have also studied the mutual influence between both interactions computing the genuine nonadditivity energies for complexes **24**−**26**, which are summarized in Table 4. The nonadditivity energy ($E - E_A$) is the difference between the binding energy of the ternary complex and the binding energy of the sum of all pair interaction energies (denoted as E_A). (See the Theoretical Methods for details.) It is worth mentioning that this term is large and negative in all complexes, which is in agreement with the geometric results and the AIM analysis and confirms the cooperativity effects of both interactions.

Symmetry-Adapted Perturbation Theory (SAPT) Results. To study the physical nature of the interaction from a rigorous methodology that does not use empirical parameters, we have carried out SAPT calculations. The SAPT interaction energy components of cation−π and anion−π complexes **12**−**23** are summarized in Table 5. The results show that electrostatic and induction terms are important for all cation and anion−π systems, and the dispersion term (E^2_{disp}) is important only in anion−π complexes. The partition energy scheme gives an explanation for the counterintuitive behavior of the 1,3,5-triethynylbenzene complexes, which agrees with previous energetic, geometric, and AIM results. The induction term (E^2_{ind}) is large in complexes **16**−**19** in comparison with benzene and trifluorobenzene complexes. This fact explains the duality of the ethynyl group. On one hand, it is able to favor the π-interaction with anions because it is an EWG and, consequently, it improves the electrostatic term compared with benzene. In addition, it increases the molecular polarizability of the aromatic ring improving the induction energy as well. On the other hand, for the interaction with cations, the ethynyl groups are able to compensate the diminution of the electrostatic term by increasing the induced polarization energy, giving rise to interaction energies that are more favorable than trifluorobenzene complexes.

Concluding Remarks

The results reported in this manuscript show that the ethynyl substituent is electron-withdrawing because it is able to favor the interaction of the aromatic ring with anions. An additional special feature of the ethynyl substituent is that it worsens the interaction of the aromatic ring with cations to a minor extent. The latter point has been confirmed by means of analyzing multiple results, such as energetic and geometric features of the complexes, charge transfer effects, and AIM analysis. The partitioning of the interaction energy allows us to give a plausible explanation. The ethynyl group has a dual effect. First, it is electron-withdrawing and favors the anion−π interaction by means of electrostatic effects. Second, it extends the π-system of the molecule and increments the molecular polarizability, improving the cation−π interaction by compensating the electrostatic term. Because trialkynyl benzenes are widely used as scaffolds for the construction of receptors, this special behavior should be taken into account. In the case of the ternary systems, favorable cooperative effects are observed for the three complexes studied. In addition, the ternary complex corresponding to the 1,3,5-triethynylbenzene is the most favorable in terms of interaction energy.

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Supporting Information Available: Cartesian coordinates of the SCS-RI-MP2(full)/aug-cc-pVTZ optimized structures **1**−**26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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