

Quantum-Chemical Investigations on the Structural Variability of Anion- π Interactions

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Dedicated to Professor Dr. Jörg Fleischhauer on the occasion of his 75th birthday

The structural versatility of anion- π interactions was investigated computationally. Employing quantum-chemically optimized structures of a series of $C_6H_{6-n}F_n/Br^-$ complexes and the Coulomb law together with the London formula to calculate the electrostatic and the dispersion energy of the interaction between the anion and the π -system led to the result that up to the number of $n = 2$ due to a significantly repulsive electrostatic energy of interaction the dispersion energy is not sufficient to stabilize such structures in the gas phase where the anion is located above the plane defined by the aromatic ring. The energy surfaces resulting from the interaction of bromide anions with isolated arenes bearing varying numbers of fluorine atoms in different positions of the aromatic ring also show a pronounced dependency on the substitution pattern of the aromatic system. Depending on the nature of the electron withdrawing group and its position, the energy surface can have a sharply defined energetically low minimum, in which the anion is 'fixed'. Other substitution patterns result in very flat energy surfaces, and even a surface with more than two local minima within the scanned area was found. Thus, our study reveals the reason for the experimentally observed structural versatility depending on the substitution pattern in the solid state.

Key words: Anion- π Interactions; Ab Initio Calculations; Energy Surfaces; Fluorinated Aromatics.

1. Introduction

Anions are ubiquitous in biological as well as in artificial systems [1, 2]. Cystic fibrosis and an enhanced risk of heart attacks are only two examples where malfunctions of anion transport can lead to serious diseases [3, 4]. Additionally, the majority of enzymes and enzymatic cofactors are of anionic character [5]. Therefore, a lot of efforts have been made to find selective anion- π receptors [6–12]. Recently the interaction between anions and electron deficient aromatic rings came into the focus of intense investigations since the study of anion- π interaction seems to be a promising tool in the development of novel anion receptors [13–15].

Several computational studies [16, 17] as well as experimental structure determinations in the solid state [13–15] reveal the energetically favorable nature of such interactions. Since 2008, our group has been performing systematic studies of anion- π interactions in pentafluorophenyl ammonium and

phosphonium salts [18–20]. Many of these compounds could be subjected to X-ray structure determinations and the results of these studies revealed a high structural flexibility in the relative orientation of anions with respect to the more or less electron-deficient aromatic system [18]. Moreover, the position of the anion relative to the C_6RF_5 -unit (R = triethylammonium; dimethylphenylammonium; 1,4-bisazoniabicyclo[2.2.2] (DABCO); methylpyridinium; 2,6-dimethylpyridinium) was found to be a sensitive function of the distribution of the electron density in the six-membered ring which can be controlled by the substitution pattern of the aromatic system [19].

In our preceding experimental study on $N(C_2H_5)_3N^+-C_6H_{5-x}F_x$, we found that upon decreasing the number of fluorine atoms at the ring the anion is shifted away from its position above the center of the aromatic ring toward the periphery of the molecule. Our interpretation was that with an increasing number of fluorine atoms electron density is withdrawn from six-membered ring resulting in

an increasingly electron-deficient π -system and, therefore, in an increased electrostatic¹ interaction between the ring and the anion. Conversely, reducing the number of fluorine atoms at the ring weakens this attractive electrostatic attraction which is finally overwhelmed by the interaction between the anion and other parts of the fluoroarene (e.g. with the $\text{N}(\text{C}_2\text{H}_4)_3\text{N}^+$ -substituent). Consequently, the distance between an anion and the centre of the aromatic rings of the arenes is increased significantly [20]. However, the electrostatic energy of interaction is not the only component that varies with the number of fluorine substituents. The change in electron density upon variation of the substitution pattern also influences the molecular polarizabilities of the arenes as well as their ionization potentials. These quantities are involved in the dispersion (long range correlation) energy². Thus if the number of fluorine atoms decreases the stabilization by the Coulomb energy is diminished while the polarizability of the aromatic increases and the role of the dispersion energy relative to the electrostatic component will become more important.

Our experimental structural data come from X-ray structure determinations in the solid state. However, the results of a considerable number of quantum-chemical geometry optimizations in the gas phase starting from solid state structures lead us to the conclusion that in many cases the observed structure in the crystal is quite close to a local minimum obtained by quantum-chemical calculations for the free molecule in the gas phase. In order to explain the structural variability and to determine the borders of the attractive nature of anion- π interactions, we extend our previous research starting with a systematic computational gas phase study of the influence of the number of fluorine atoms at the aromatic ring on the contribution of the electrostatic and the dispersion to the energy of interaction with a bromide anion. Then we will evaluate the energy surfaces resulting from the interaction of bro-

mide anions with fluoroarenes of different substitution patterns.

2. Computational Methods

In the first part of our study, we used a simple Coulomb term

$$E_{\text{els}} = \frac{1}{2} \sum_a \sum_{b \neq a} \frac{q(a)q(b)}{R_{ab}} \quad (1)$$

to calculate the electrostatic contribution to the energy of interaction between the anion and the aromatic ring. Two sets of atomic charges were used in these calculations, Mulliken charges and natural atomic charges. The London formula

$$E_{\text{dis}} = -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \sum_a \sum_{b \neq a} \alpha(a) \frac{\alpha(b)}{R_{ab}^6} \quad (2)$$

was used to calculate the dispersion energy. Two sets of polarizabilities were used in the London formula which are quantum-chemically calculated molecular polarizabilities and atomic polarizabilities from the literature [21]. The structures $\text{C}_6\text{H}_{6-n}\text{F}_n/\text{Br}^-$ complexes used in this initial part of our study were geometrically optimized at the MP2/6-31+G* level. The polarizabilities of the bromide anion and the fluoroarenes were then calculated with the aug-cc-pVTZ basis set without further structural optimization.

In our previous study [20], we confined our search to a single local minimum for each of the studied compounds. The choice of the starting geometry is, however, usually biased in that it is guided by certain expectations regarding the minimum which is often derived from the results of X-ray structure determinations. While this approach yields reasonable results in many cases, flexible systems like the anion- π complexes require special attentions since in such cases the position of the anion can be significantly influenced by lattice forces and, therefore, one cannot be sure that the experimentally observed position of the anion corresponds within the margin of the experimental error to the most stable structure of the free complex as well. Moreover, such calculations are just a single snapshot and do not provide any information regarding the shape of the corresponding energy surface surrounding the obtained minimum structure. Such problems can be treated by molecular dynamics. However, in the second part of our study, we used an alternative approach.

¹The term 'electrostatic' might be confusing since the potential energy part of the systems' Hamiltonians are entirely electrostatic. When we use the expression 'electrostatic' in this paper we refer to the Coulomb interaction between the charge of the anion with the atomic charges of the arene part as calculated by a quantum-chemical population analyses.

²The idea to use semiempirical expression for the calculation of the correlation energy goes probably back to Pitzer who used the formula by Slater and Kirkwood to calculate the correlation energy in paraffins [25].

In contrast to our previous investigations [20] and an earlier study by Estarellas et al. [22] (*vide infra*), we define a grid in a plane parallel to the aromatic ring and perform calculations for the position of the anion in this plane in more than 2200 points, a number which is sufficient to draw maps of the energy of interaction between the anion and the electron-deficient aromatics with a sufficient resolution. The plane is scanned automatically by a program that stepwise changes the position of the anion, saves each set of coordinates to a Gaussian input file and starts an *ab initio* single point calculation. As a test the minimized positions of the anions relative to fluorinated aromatics determined in our earlier study [20] were reproduced. Besides highly symmetric systems like hexafluorobenzene or 1,2,4,5-tetrafluorobenzene molecules of lower symmetry like 1,2,3,4-tetrafluorobenzene or 1,2,3-trifluorobenzene are included. The comparison of the results obtained for different substituents will provide an insight into the influence of the substitution pattern of the aromatic compound on the interaction with anions. The structures of the chosen fluorinated aromatics with different numbers of fluorine substituents were energetically optimized with the MP2 method and the 6-311++G** basis set as implemented in Gaussian09 [23]. Then the anion is moved along the *x*- and the *y*-axis within a plane parallel to the aromatic ring in steps of 0.1 Å, and the single point energy of each new position is calculated using MP2/6-311++G**. The plane (Fig. 1) is defined by the vertical distance between the anion and the plane of the aromatic ring in the fully optimized structure (r_{opt}). The boundaries of the area for the shift of the anion are defined by the atoms which are the furthest away from the anion in its starting position. In the case of hexafluorobenzene, these atoms are the fluoro atoms resulting in a rectangle of 23.85 \AA^2 (Fig. 1).

The chosen aromatic systems with different degrees of fluorination are presented in Figure 2.

The dependence of the position of the anion on the degree of fluorination of the aromatic ring was reported before [20] and served as a test for the program in this study (Fig. 3).

The study performed by Estarellas et al. [22] mentioned above considers only the most significant points parallel to the plane of hexafluorobenzene and trifluoro-*s*-triazine. Thus, for hexafluorobenzene four points on the *x*-axis and four points in the *y*-direction were calculated in [22].

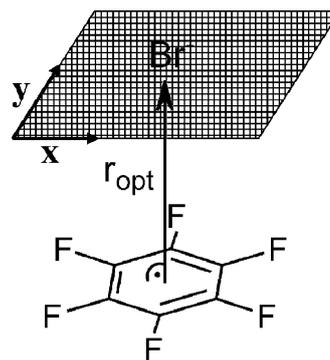


Fig. 1. The anion is moved in 0.1 Å steps in a plane parallel to the aromatic ring. r_{opt} is the distance between the anion in the fully optimized structure and the center of the aromatic ring.

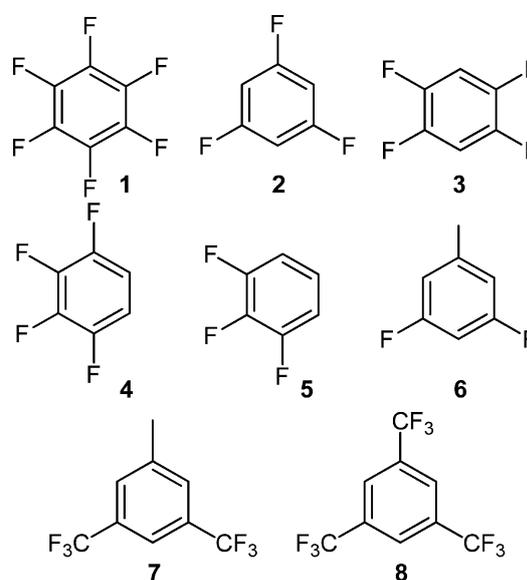


Fig. 2. Fluoroaromatics with different degrees of fluorination.

3. Results and Discussion

Our computational study began with an orienting survey of a series of aromatics where starting from benzene the hydrogen atoms were successively replaced by fluorine up to hexafluorobenzene. Calculations were performed for benzene, 1-fluoro-, 1,2-difluoro-, 1,2,3-trifluoro-, 1,2,3,4-tetrafluoro-, 1,2,3,4,5-pentafluoro-, and hexafluorobenzene. Table 1 contains the corresponding molecular polarizabilities (α_A , in Bohr³), the molecular (Koopmans) ionization potentials (I_A , in Hartree), and the *zz*-component of the

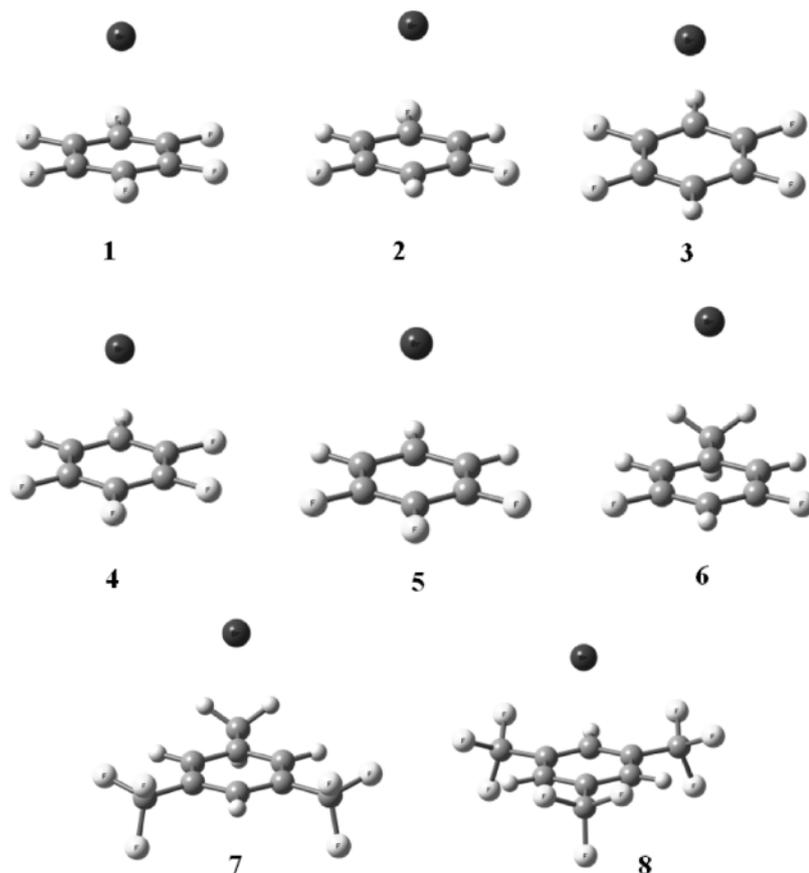


Fig. 3. Energetically optimized structures of aromatic/anion complexes with different degrees of fluorination (MP2/6-311++G**).

corresponding quadrupole tensor (Θ_{zz} , in Debye \cdot Å) calculated with the aug-cc-pVTZ basis set at the MP2/6-31+G*-optimized structures.

The London formula (2), derived from second-order perturbation theory, links the distance between the interacting centers (A, B)³ R_{AB} , their polarizabilities ($\alpha(A)$, $\alpha(B)$), as well as their ionization potentials (I_A , I_B)⁴ and produces the dispersion contribution to the energy of interaction (ΔE_{dis}). Although the number of electrons is increased by eight if a hydrogen atom is replaced by fluorine due to the high electronegativity of

³Capital letters are used to label molecular polarizabilities and ionization potentials, while lower case letters indicate atomic quantities.

⁴A better agreement between experimental and calculated dispersion energies is obtained when about twice the ionization potentials are used. However, since we do not aim at numerical precision but are rather interested in a general trend, the factor 2 was omitted in our back-on-the-envelope calculations [26, 27].

the halogen the molecular polarizabilities of the arenes decrease with an increasing number of fluorine substituents continuously from a value of about 46 for benzene ($n = 0$) to approximately 41 Bohr³ for hexafluorobenzene ($n = 6$, Tab. 1). Using the calculated polarizability of the bromide anion (39.720 Bohr³) the contribution of the polarizabilities ($\alpha(A) \cdot \alpha(B)$) to the dispersion energy therefore decreases from ca. 1817 for benzene to 1629 Bohr⁶ for hexafluorobenzene (Tab. 2). Using Koopmans' ionization potentials from our ab initio calculations we obtain an increase from 0.33615 for benzene to 0.39463 Hartree for hexafluorobenzene (Tab. 1). Together with a value of 0.13934 Hartree for the bromide anion the contribution of the ionization potentials ($I_A \cdot I_B / (I_A + I_B)$) remains almost constant in that it only slightly increases from 0.09851 for $n = 0$ to 0.10298 Hartree for $n = 6$ (Tab. 2). The third quantity to be considered is the distance between the interacting systems. The unequivocal choice is to use the dis-

Table 1. Molecular polarizabilities α_A (in Bohr³), molecular (Koopmans) ionization potentials I_A (in Hartree), and the zz -component of the quadrupole tensor Θ_{zz} (in Debye · Å) of fluoroarenes C₆H_{6-n}F_nHF/aug-cc-pVTZ//MP2/6-31+G*.

N	α_A^a	I_A^a	Θ_{zz}
0	45.735	0.33615	-41.1
1	44.342	0.34246	-44.2
2	43.430	0.35177	-47.4
3	42.653	0.36665	-50.6
4	41.903	0.37189	-53.8
5	41.312	0.38099	-57.1
6	41.012	0.39463	-60.4

^a The polarizability and the (Koopmans) ionization potential of the Br⁻ anion are $\alpha_B = 39.720$ Bohr³ and $I_B = 0.13934$ eV, respectively (MP2/aug-cc-pVTZ).

Table 2. Contributions of the molecular polarizabilities $\alpha(A) \cdot \alpha(B)$ (in Bohr⁶) and the molecular (Koopmans) ionization potentials $I_A \cdot I_B / (I_A + I_B)$ (in Hartree) for the fluoroarene/Br⁻ complexes C₆H_{6-n}F_n/Br⁻. R_{AB} is the distance between the position of the anion and the arene's center of core charge (in Å).

n	$\alpha(A) \cdot \alpha(B)^a$	$I_A \cdot I_B / (I_A + I_B)^a$	R_{AB}
0	1816.6	0.09851	3.792
1	1761.3	0.09904	3.585
2	1725.0	0.09981	5.398 ^b
3	1694.2	0.10097	3.353
4	1664.4	0.10136	3.292
5	1640.9	0.10203	3.243
6	1629.0	0.10298	3.197

^a For the polarizability and the ionization potential of the bromide anion see the footnote to Table 1. ^b The anion lies not above the aromatic ring but in the plane defined by the 1,2-difluorobenzene unit.

tances between the anion and the single atoms of the arenes (R_{ab}) and to sum up the atom-atom contributions as indicated in (1). Taking the atomic polarizabilities given by Ketelaar [21] ($\alpha(\text{F}) = 2.565$, $\alpha(\text{H}) = 2.834$, $\alpha(\text{Br}^-) = 28.615$ Bohr³)⁵, assuming a value for the carbon atoms of $\alpha(\text{C}) = 6.749$ Bohr³, and using the ionization potentials in Table 1, we obtained the dispersion energies ($\Delta E_{\text{dis,atm}}$) in the fifth column of Table 3. In a second approach, we used the same ionization potentials together with the molecular polarizabilities from Table 1. Here we chose the distance between the position of the anion and the center of the core charge of the arene (R_{AB}) for the distance between the interacting centers. The resulting values of $\Delta E_{\text{dis,mol}}$ are given

⁵Converted from the original values in [21] using 1 Bohr = 0.5291673 Å.

in the fourth column of Table 3. The dispersion energies obtained with both methods agree fairly well as long as the Br⁻ is located somewhere above the aromatic ring and does not lie outside this area in the plane defined by the arene. For those arene/Br⁻ complexes where the anion lies above the ring the stabilizing character of the dispersion energy slightly increases from -1.31 kcal/mol for benzene to -3.03 kcal/mol in the case of hexafluorobenzene when interatomic distances and atomic polarizabilities are used. A similar trend is obtained when molecular polarizabilities and the distance of the anion to the arene's center of positive charge are used (-1.24 to -3.24 kcal/mol). This increasingly stabilizing contribution of ΔE_{dis} with an increasing number of fluorine atoms is due to the decreasing values of R_{ab} and R_{AB} in the same direction.

Using a simple Coulomb term (1), we also calculated the electrostatic contribution to the energy of interaction between the arenes and the bromide anion ($\Delta E_{\text{els,Mul}}$ and $\Delta E_{\text{els,ANO}}$). The atomic charges used in these calculations were

- (i) those from a Mulliken population analysis and
- (ii) natural atomic (ANO) charges.

We first consider the values obtained for those complexes where the anion is located above the ring. Not all of these structures are local minima, however our calculations were performed in the gas phase, and it is reasonable to assume that such structures like those for $n = 0-3$ could be stabilized by intermolecular interactions in the solid state. The trend of the values in column two of Table 3 concurs with our interpretation outlined in the Introduction in that the stabilizing character of the electrostatic (Coulomb) contribution to the energy of interaction increases with an increasing number of fluorine substituents. Thus with both sets of charges the electrostatic energy is repulsive for $n = 1$ and 2. With Mulliken charges it is neutral for $n = 3$ and stabilizing when ANO charges are used. Its stabilizing character further increases in steps of up to 9 kcal/mol from tetrafluoro- to hexafluorobenzene. Moreover, the numbers in Table 3 also show that such positions of the anion in the plane defined by the aromatic ring where its charge can effectively interact with the arene's dipole moment are electrostatically strongly favored (Tab. 3, numbers in italics).

Now that we arrived at a semi-quantitative explanation of our previously more vivid interpretation of the experimental data, we use more sophisticated meth-

Table 3. Electrostatic energies calculated using Mulliken ($\Delta E_{\text{els,Mul}}$) and ANO charges ($\Delta E_{\text{els,ANO}}$) of the studied $\text{C}_6\text{H}_{6-n}\text{F}_n/\text{Br}^-$ complexes. Dispersion energies were calculated with molecular ($\Delta E_{\text{dis,mol}}$) and atomic ($\Delta E_{\text{dis,atm}}$) polarizabilities. All values in kcal/mol.

n	$\Delta E_{\text{els,Mul}}$	$\Delta E_{\text{els,ANO}}$	$\Delta E_{\text{dis,mol}}$	$\Delta E_{\text{dis,atm}}$
0	9.62	11.05	-1.24	-1.31
1	11.13	9.51	-1.70	-1.77
	<i>-24.69^{a,d}</i>	<i>-14.53</i>	<i>-0.30</i>	<i>-2.17</i>
2 ^b	<i>-31.37^c</i>	<i>-18.12</i>	<i>-0.14</i>	<i>-2.22</i>
3	-0.08	-7.44	-2.48	-2.34
	<i>-21.31^c</i>	<i>-24.61</i>	<i>-0.11</i>	<i>-2.16</i>
	<i>-40.97^d</i>	<i>-26.35</i>	<i>-0.16</i>	<i>-2.47</i>
4	-6.05	-15.60	-2.74	-2.58
	<i>-48.51^d</i>	<i>-30.35</i>	<i>-0.18</i>	<i>-2.71</i>
5	-13.19	-25.62	-2.97	-2.80
	<i>-25.12^c</i>	<i>-21.47</i>	<i>-0.17</i>	<i>-2.72</i>
6 ^e	-19.86	-34.79	-3.24	-3.03

^aThe numbers in italics refer to minima where the anion lies not above the aromatic ring but in the plane of the molecule. We did not perform a systematic study of such structures. ^bNo stationary point with the anion above the plane defined by the ring could be located. ^c Br^- on the twofold axis. ^d Br^- chelated by two hydrogen atoms. ^eNo stationary point with the anion in the plane defined by the aromatic ring could be located.

Table 4. X and Y coordinate of the position relative to the original position of the anion in the fully optimized structures in Å (MP2/6-311++G**).

Structure	Position (1.0 kcal/mol)	Position (1.5 kcal/mol)	Position (2.0 kcal/mol)
1	+0.0, +1.1	± 0.3 , +1.3	+0.0, +1.5
2	+0.0, -1.7	± 1.7 , +1.0	-1.9, +1.1
3	± 1.3 , -0.3	+1.5, -0.5	± 1.8 , +0.0
4	+0.3, +1.2	+0.5, +1.4	+0.4, +1.6
5	+0.0, +1.4	± 0.4 , +1.6	± 0.4 , +1.8
6	± 1.0 , -1.0	-1.3, -0.9	-1.4, -1.0
7	+0.0, -1.1	+0.0, -1.3	+0.0, -1.6
8	+0.0, +0.9	+0.0, +1.1	+0.0, +1.3

ods to explore the energy surfaces of the arene/ Br^- complexes. The previously reported optimized distances between the center of the aromatic rings and the anion are 3.268 Å for **1**, 3.457 Å for **2**, 3.385 Å for **3**, 3.380 Å for **5**, 3.372 Å for **6**, 3.268 Å for **7**, and 3.315 Å for **8** (Fig. 2 and Fig. 3)⁶. These numbers clearly show that this distance increases with decreasing number of fluorine atoms at the aromatic ring (v. s.) or if the symmetry of the substitution pattern is reduced while the number of fluorine atoms is retained. Scanning the planes above the aromatics resulted in the energy surfaces presented in Figure 4.

⁶The numbers given here for compounds **1**, **4**, **5**, and **6** differ from those for R_{AB} in Table 2 because another basis set was used and another reference point on the aromatic ring was chosen.

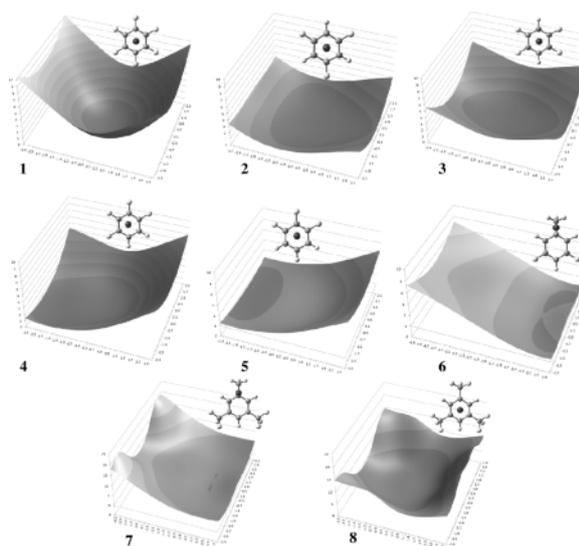


Fig. 4. Cut through the energy surface of structure **5** along the y -axis at $x = \pm 0$ (MP2/6-311++G**).

In most cases the energy difference between the fully optimized structure and any other point on the corresponding energy surface is lower than 10.0 kcal/mol. Exceptions are the compounds **7** and **8** where the increase of the energy upon shifting the anion rises up to 14.5 and 20.2 kcal/mol. This is due to repulsive interactions between Br^- and the CF_3 groups of these molecules upon approach of the anion which outnumber the attractive forces.

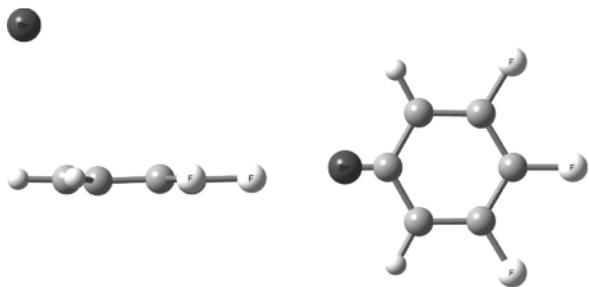


Fig. 5. Local minimum of compound **5** (MP2/6-311++G**).

To further compare the effect of moving the anion away from their optimized positions in differently substituted structures (**1–8**), the shifts of the anion causing increases of the energy of 1.0 kcal/mol, 1.5 kcal/mol, and 2.0 kcal/mol are listed in Table 4. These values show that the curvature of the energy surface in the vicinity of the local minimum is flat if the anion receptor has a symmetric structure like in the case of **1**, **2**, **3** or **8**. Such relatively low energy bar-

riers can easily be surmounted by forces in the crystal lattice, and this finding explains the high flexibility in the relative orientation of the anions with respect to the electron-deficient arenes found in the solid state [18–20].

If the aromatic ring is not fluorinated centrosymmetrically, like for example in **5** (Fig. 5), not only the distance between the center of the aromatic ring and the anion is larger but also the shape of the energy surface is different. Thus the energy surface of **5** has two local minima. The minimum corresponding to the fully optimized structure is very shallow and is separated from the second one at a shift of 2.4 Å which is 0.35 kcal/mol lower in energy by a barrier as low as 0.02 kcal/mol (Fig. 6). The existence of two local minima could be reproduced by the numerical analysis of the optimized structures of **6** and **7**. The two minima are separated by saddle points which were identified by normal mode analyses. Both **6** and **7** have one single imaginary frequency in the spectra of their normal modes (14.2 cm^{-1} for **6** and 7.78 cm^{-1} for **7**).

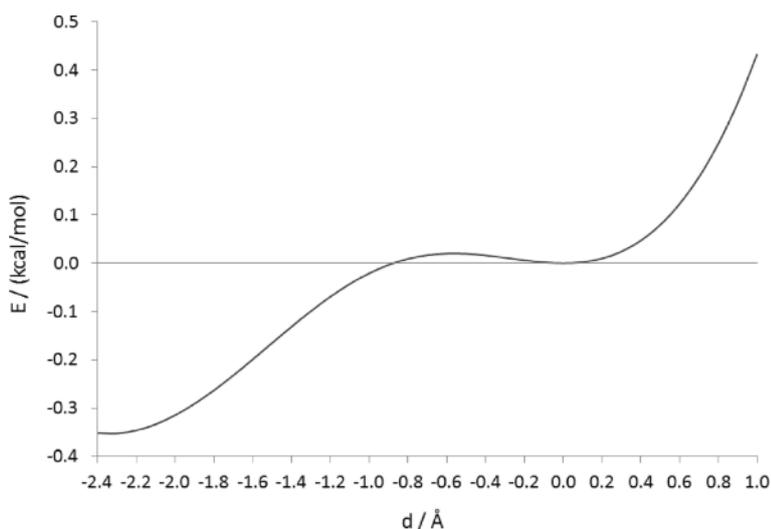


Fig. 6. Energy surfaces of **1–8** obtained by shifting the Br^- anion in the plane above the aromatic at a constant distance from the plane defined by the six-membered ring as described in the text. The numbers at the x - and y -axis are the displacements of the bromide anion from the position in the fully optimized structure. The numbers on the z -axis are the energies relative to the energy of the local minimum (in kcal/mol, MP2/6-311++G**).

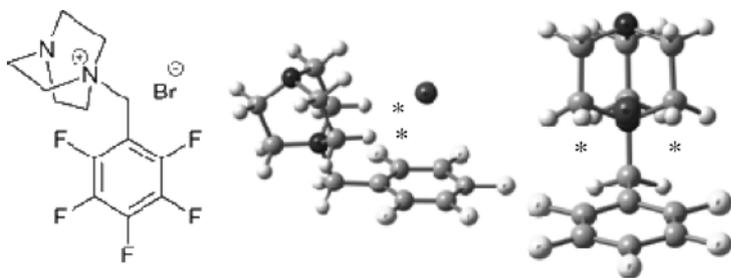


Fig. 7. Energetically optimized structure of the DABCO derivate **9** (MP2/6-311++G**).

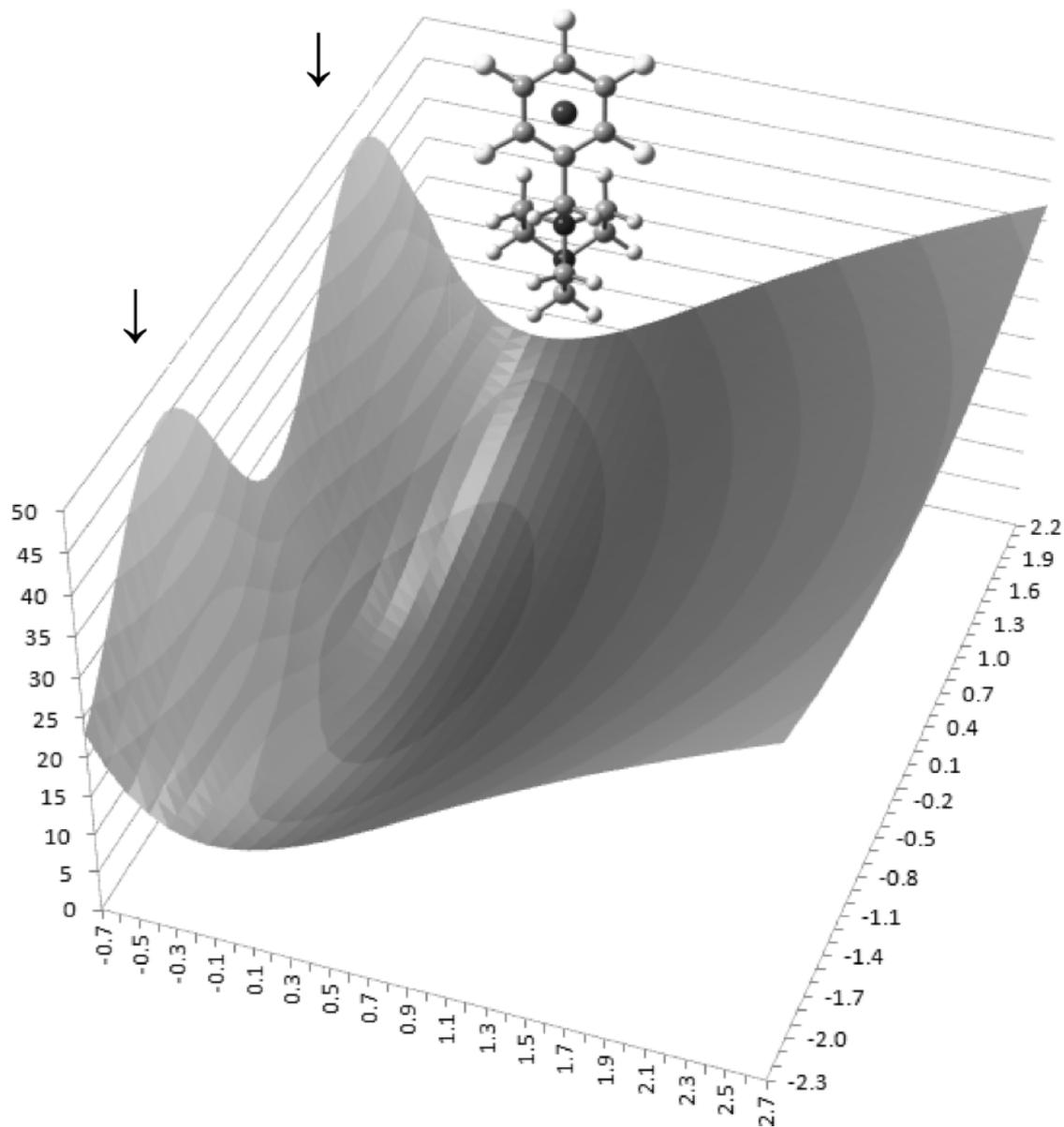


Fig. 8. Energy surfaces obtained by shifting the Br^- anion in the plane above the aromatic **9** at a constant distance from the plane defined by the six-membered ring as described in the text. The numbers at the x - and y -axis are the displacements of the bromide anion from the position in the fully optimized structure. The numbers on the z -axis are the energies relative to the energy of the local minimum (in kcal/mol, MP2/6-311++G**).

The minima are very shallow and the anion- π interactions in these cases are presumably very weak and other effects like CH-anion interactions can be dominant. Thus the study of compounds **6** and **7** revealed

a stronger interaction between the anion and the side chain than between the anion and the π -system.

The distance between the anion and the plane of the aromatic ring in the optimized structure of molecule **9**

(Fig. 7) with a 1,4-diazabicyclo[2.2.2]octane (DABCO) substituent is 3.359 Å. This compound differs significantly from complexes **1–8** and carries no net charge. It was also studied previously on the ab initio level, and its structure in the solid state was elucidated by X-ray structure analysis [20]. Here, we extend the study of **9** by analysing the energy surface resulting from the shift of the anion in the plane parallel to the aromatic ring (cf. Fig. 8). The shape of the energy surface of structure **9** differs significantly from those of **1–8**. The highest energy in the scanned area is about 45.7 kcal/mol above the minimum, which is twice as much as the highest increase in energy obtained by shifting the anion in compound **8**. The energy rises steeply when the bromide anion approaches one of those two hydrogen atoms which are indicated by stars in Figure 7 resulting in the two ‘horns’ labelled by arrows in Figure 8. We located a stationary point where the anion is trapped symmetrically in a position between the hydrogen atoms with H–Br distances of 2.486 Å. This is below the sum of the van der Waals radii of hydrogen (1.20 Å) and bromine (1.85 Å) [24] probably indicating weak hydrogen bonds. A normal mode analysis of this structure results in one imaginary frequency of 19.56 cm⁻¹ indicating that this stationary point corresponds to a saddle point connecting the minimum of the fully optimized structure with another minimum outside the scanned area.

4. Conclusions

Orienting calculations on model systems led us to the conclusion that in the gas phase the C₆H_{6-*n*}F_{*n*}/Br⁻ complexes with $n \leq 2$ and the anion above the aromatic ring are not local minima and that structures of

such complexes are energetically preferred where the anion lies in the plane defined by the arene. The analyses of the energy surfaces resulting from the interaction of bromide anions with different aromatic systems following our initial orienting calculations proved to be a valuable tool to investigate the influence of the symmetry of the substitution pattern and of hydrogen bonds (like in the DABCO system). Our analyses show that the hexafluorobenzene/bromide system has only one clearly defined minimum within the scanned area, which is surrounded by an energy barrier. If the number of fluorine atoms is reduced, the attractive interaction between the anion and the π -system is reduced and larger shifts of the anion away from its minimum position are required to cause an increase in energy of 1 kcal/mol than in the case of **1**. These energy barriers always reflect the structure of the aromatic ring: a fluorinated C-atom leads to an energy barrier closer to the position of the anion in the optimized structure, and a CH-group leads to a ‘shift’ of the energy barrier towards the outer parts of the aromatic system leaving more space for the position of the anion.

Introduction of CF₃ groups cause a major change of the aromatic system. In this case, the system still has to be symmetric to result in a well-defined minimum for the anion/arene complex. If hydrogen bonds are involved (like observed with the DABCO substituent) the energy barrier tends to increase and the position of the anion seems to be well ‘fixed’. Experimental studies could not underline these theoretical findings as diverse substitution effects take place. Nevertheless, our theoretical analysis explains the great variability of the structures in which anion- π interactions are possible.

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