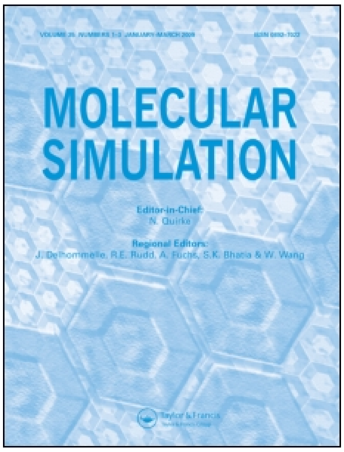

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Anion-π interactions: CP-corrected vs. standard optimisation, AIM and NBO analyses

Ali Ebrahimi[a]; Mostafa Habibi[a]; Omid Sayyad[a]
[a] Department of Chemistry, University of Sistan and Balouchestan, Zahedan, Iran

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Anion–π interactions: CP-corrected vs. standard optimisation, AIM and NBO analyses

Ali Ebrahimi*, Mostafa Habibi and Omid Sayyad

Department of Chemistry, University of Sistan and Balouchestan, Zahedan, Iran

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The anion–π interactions between Br^-, Cl^-, F^- and H^- anions and hexafluorobenzene (HFB), 1,2,4,5-tetracyanobenzene (TCB) and tetracyanopyrazine (TCP) have been studied by standard and counterpoise (CP) corrected methods at HF, B3LYP and MP2/6-31 + + G (d,p) levels of theory. The complexation energies were corrected for basis set superposition error (ΔE_{BSSE}) and zero point energy ($\Delta E_{\mathrm{BSSE+ZPE}}$). Also, the B3LYP results were corrected by single-point calculation at B3LYP/aug-cc-PVTZ level of theory. Although the CP-corrected method results in higher distances between anions and rings, the standard method gives lower complexation energies. $\mathrm{TCP}\cdots X^-$ series gives higher complexation energies in both CP-corrected and standard methods. Topological analysis of the charge density $\rho(r)$ has been performed by the means of atoms in molecules method on the wave functions obtained at MP2/6-31 + + G (d,p) level of theory. The number and the nature of critical points depend on aromatic ring and anion. Natural bond orbital analysis indicates that $n_X \rightarrow \pi^*_{CC}$ and $n_X \rightarrow \pi^*_{CN}$ interactions are the most important interactions for TCB (and HFB)$\cdots X^-$ and $\mathrm{TCP}\cdots X^-$ complexes, respectively.

Keywords: anion–π interaction; CP-corrected; HFB; TCP; TCB

1. Introduction

The substitution of hydrogen atoms of benzene by electron withdrawing groups changes the nature of charge cloud of ring (becomes positive) and noncovalent anion–π interactions become possible [1–18].

Most studies have investigated the nature and energetics of anion–π interactions [19–21] and it has been speculated that they can be used to construct receptors for the molecular recognition of anions [4–22]. Anion–π interactions have experimentally been observed in the solid state and solution [6,12,15,23].

Chloride and bromide complexes with one, two and three aromatic units (such as trifluoro-*s*-triazine and *s*-triazine) were optimised by Garau et al. [24]. Additivity of both the geometries and the binding energies of the anion–π interaction were confirmed by *ab initio* calculations. The maximum binding energies were calculated equal to -20.3, -38.2 and $-64.2\,\mathrm{kcal\,mol^{-1}}$ for complexes of one, two and three trifluoro-*s*-triazine with F^- at MP2/6-31 + + G(d,p) level of theory. They analysed the interaction using the atoms in molecules (AIM) theory and studied the charge-transfer using several methods for deriving atomic charges.

The complexation of 1,3,5-trifluorobenzene, *s*-triazine and 2,5-dichloropyrazine with F^- were studied at the MP2/6-31 + + G(d,p) level of theory (the binding energies were equal to -7.77, -9.70 and $-13.88\,\mathrm{kcal\,mol^{-1}}$, respectively) by Garau et al. [25]. They compared different aspects of the cation–π and anion–π interactions, including changes in the aromaticity of the ring upon complexation, charge-transfer effects using the Merz-Kollman and AIM charges, and the contribution of correlation and dispersion energies by comparing the complexation energies computed at different levels of theory.

Kim et al. [9] investigated the nature of the anion–π by carrying out *ab initio* calculations on the complexes of halide (F^-, Cl^- and Br^-), linear organic (CN^- and NC^-), and trigonal planar organic (NO_3^- and CO_3^{2-}) anions with different kinds of π systems, viz. olefinic (tetrafluoroethene), aromatic (hexafluorobenzene; HFB) and heteroaromatic (1,3,5-triazine). In contrast to cation–π interactions, anion–π interactions were marked by substantial contributions from dispersion energies. As in the case of cation–π interactions, the role of anions also has a marked influence on the nature and magnitude of the anion–π interaction with interactions involving halide anions being dominated by electrostatic and the induction energies. The calculated binding energies ranged from -5.20 to $-32.83\,\mathrm{kcal\,mol^{-1}}$ at MP2/6-31 + + G(d,p) level (the lowest and highest values correspond to $C_3N_3H_3\cdots Br$ and $C_6F_6\cdots CO_3^{2-}$, respectively). 1,3,5-triazine$\cdots NO_3^-$ interaction has also been studied theoretically by Casellas et al. [10], using a DFT method, with a different structure from that considered by Kim et al. [9]. In the latter study, the oxygen atoms were facing the electronegative nitrogen atoms instead of the electropositive carbon atoms of the aromatic ring.

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*Corresponding author. Email: ebrahimi@hamoon.usb.ac.ir

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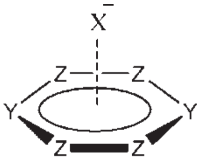
The binding energy was found to be higher in the latter model than in the former by about 0.5 kcal mol^{-1} (-3.23 and -2.67 kcal mol^{-1} for the latter and the former models, respectively).

Berryman et al. [26] studied the nature of the interactions between electron-deficient arenes and halide anions based on crystal structures containing alkali halide and tetracyanobenzene (TCB), and MP2/aug-cc-pVDZ calculations on F$^-$, Cl$^-$ and Br$^-$ complexes with TCB (-25.33 to -53.06), 1,3,5-tricyanobenzene (-20.29 to -44.10), triazine (-8.27 to -26.34) and HFB (-15.55 to -26.01). The data in the parentheses correspond to the ranges of binding energies in kcal mol^{-1}. Their results established that three distinctly different types of complexes are possible: strongly covalent σ-complexes, weakly covalent donor–π-acceptor complexes and non-covalent anion–π complexes.

Using finite basis sets leads to the well-known basis set superposition error (BSSE) in quantum mechanical calculations [27–29]. BSSE can be avoided by using sufficiently large basis sets. However, calculations with such basis sets for large systems are impracticable, and so, several approaches have been developed to correct this error [27–29]. The most popular one is the counterpoise (CP) correction of Boys and Bernardi [30]. Using the CP scheme, one has to recalculate the monomers in the basis of the whole supermolecule for every geometrical arrangement. In the case of single-point calculations, the situation is clear and the interaction energy is corrected for the BSSE. The CP correction approximately accounts for BSSE, but it often overestimates the actual correction [31].

The effect of BSSE on the surfaces of several H-bonded systems has been studied at different levels of theory [32,33]. The results show that as the interaction energy becomes weaker, the effect of CP correction on the geometrical parameters and the binding energies becomes larger [32,33].

Herein, the anion–π interaction has been considered in the complexes of HFB, TCB and tetracyanopyrazine (TCP) with a series of anions (Scheme 1) by the means of standard and CP-corrected methods. The effect of CP-correction on the structural parameters and energy data has been considered in this work. In addition, the natures and the strengths of interactions have been compared in three classes of complexes by using energy data and results of AIM [34,35] and natural bond orbital (NBO) [36] analysis.



X=H, F, Cl, Br
1) Y=N, Z=CCN
2) Y=CH, Z=CCN
3) Y=Z=CF

Scheme 1. The π···X$^-$ complexes.

2. Computational methods

Geometry optimisation and frequency calculation have been done using Gaussian 03 program package [37]. Firstly, the anions were positioned over the substituted benzene ring along the general axis. Then, the geometries of complexes were fully optimised at the HF, B3LYP [38] and MP2 [39] levels by the standard and CP-corrected [34,40] methods using 6-31++G(d,p) basis set. Although some complexes have previously been optimised by a standard method [15], we optimised in order to compare with CP-corrected results and the results of other complexes. For standard structures, the complexation energies were corrected for the BSSE and the zero point energy (ZPE). The values of BSSE were calculated by CP procedure. Single-point calculation has also been performed at B3LYP/aug-cc-PVTZ level of theory. Frequency calculations were performed at HF and B3LYP/6-31++G(d,p) levels of theory on the optimised structures at the same levels.

The AIM calculations were performed on wave functions obtained at MP2/6-31++G(d,p) level by AIM2000 program package [41]. The NBO analysis was carried out on these wave functions using the NBO package [42] included in the Gaussian 03 suite of programs. These analyses were performed to understand some contributing factors in the stability of complexes.

3. Results and discussion

3.1 *Geometrical parameters*

Some typical optimised structures of complexes are shown in Figure 1. The most important structural parameters and the complexation energies obtained at the HF, B3LYP and MP2 levels by the 6-31++G(d,p) basis set are reported in Table 1. R_{STD} and R_{CP} are the distances between anions and the centre of rings obtained by the standard and CP-corrected methods.

As can be seen in Table 1, in all cases, (a) the R values obtained at the MP2 level are shorter than the values obtained at HF and B3LYB levels. Interaction between monomers increases by electron correlation, (b) the R_{CP} values are longer than R_{STD} (with the exception of TCP···Cl$^-$ at the B3LYP level and TCP···H$^-$ and TCP···F$^-$ at the HF level). This is in agreement with the effect of CP-correction on hydrogen bonding and (c) the distance between anion and the centre of ring decreases by the increase in the ratio of charge to the radius of anion

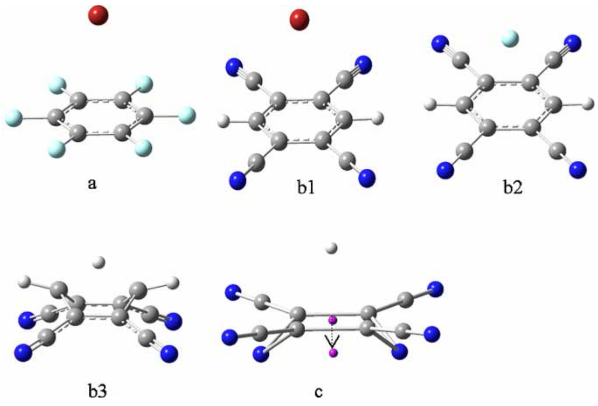


Figure 1. Some typical optimised structures for (a) HFB···X^- complexes, (b) TCB···X^- complexes where (1) X = F, Cl and Br (2) X = H with planar ring and (3) X = H with puckered ring and (c) TCP···X^- complexes.

(the distance between anion and ring centre in H^- is longer than F^-).

With the exception of TCB···H^-, six-membered ring has a planar structure in all HFB (and TCB)···X^- complexes. There are two structures for TCB···H^- complex; a structure with planar TCB ring and another with puckered ring (Figure 1(b3)). The puckered ring structure is more stable than planar one. The planar structure is not a stationary point at the MP2 and B3LYP levels.

Ring has a boat-shape structure in all TCP···X^- complexes, in which the N atoms are slightly out of the plane corresponding to four carbon atoms (Figure 1(c)). The departures from planar structure in MP2 and B3LYP methods are approximately identical in value, which are higher than the departures predicted by HF method. The departures of N atoms from the plane (indicated with an arrow in Figure 1(c)) are reported in Table 1. The trend in the deviation values is H > Br > F > Cl. This is in good agreement with natural charges (n.c.) on the N atoms of ring, which will be discussed in a following section.

3.2 *Energetics*

The calculated energy data at different levels are reported in Table 2. The ΔE_{STD}, ΔE_{BSSE}, $\Delta E_{\mathrm{BSSE+ZPE}}$ and ΔE_{CP} values are the complexation energies obtained for standard structures, corrected for BSSE and BSSE + ZPE, and the complexation energies acquired for CP-corrected structures, respectively.

The complexation energies at the MP2 level are more negative than the HF and B3LYP levels (Table 2). The complexation energy values are in agreement with geometrical parameters and increase with electron correlation. The difference between ΔE_{STD} values at the HF, B3LYP and MP2 levels are larger than the difference between ΔE_{CP} (ΔE_{BSSE} or $\Delta E_{\mathrm{BSSE+ZPE}}$) values at the mentioned levels. Thus the sensitivity of the energy values to the selected level (HF, B3LYP and MP2) decreases with BSSE correction. The result of single-point calculation at B3LYP/aug-cc-PVTZ level, on optimised structures at B3LYP/6-31+ +G(d,p) level, are reported in the parentheses in Table 2. As can be seen, with the exception of Br^- (~4–9 kcal/mol), the changes in the energy values are small (~0.1–1.4 kcal/mol). These values approach the BSSE corrected values with increasing basis set. Although the ΔE_{CP} values are more negative than the ΔE_{BSSE} values (calculated at MP2 level), the values of R_{CP} are longer than R_{STD}. On the other hand, the ΔE_{CP} values are approximately equal to the ΔE_{BSSE} values at the HF and B3LYP levels.

The complexation energy increases with the ratio of charge to the radius of anion. There is a good linear relationship ($R^2 \approx 0.9$–1.0, with the exception of HFB···H^-) between complexation energy and the ratio of charge to the radius of X^- anion.

Table 1. The distance between anion and the centre of the ring[a] in Å.

	HFB			TCB			TCP		
	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
Standard									
Br^-	3.478 (3.479)[b]	3.372	3.230 (3.214)[b]	3.343	3.252	3.121	3.187 (0.049)[c]	3.167 (0.110)[c]	3.043 (0.113)[c]
Cl^-	3.399 (3.404)	3.414	3.159 (3.155)	3.280	3.191	3.042	3.103 (0.038)	2.994 (0.090)	2.934 (0.090)
F^-	2.658 (2.669)	2.647	2.556	2.553	2.516	2.449	2.378 (0.052)	2.325 (0.105)	2.273 (0.098)
H^-	3.000 (3.034)	2.790	2.694 (2.706)	1.491[d]	1.482	1.479	2.374 (0.128)	2.105 (0.219)	1.851 (0.279)
CP-corrected									
Br^-	3.622	3.509	3.390	3.489	–	–	3.314 (0.035)	3.189 (0.092)	3.091 (0.081)
Cl^-	3.411	3.321	3.244	3.283	3.196	3.156	3.106 (0.037)	2.994 (0.090)	2.940 (0.080)
F^-	2.673	2.678	2.622	2.559	–	2.523	2.378 (0.051)	2.338 (0.104)	2.324 (0.093)
H^-	3.038	2.819	2.793	1.493[d]	1.485	1.505	2.371 (0.124)	2.113 (0.218)	1.915 (0.376)

[a] The values for nonplanar rings correspond to the distance between anion and the centre of rectangle, which is illustrated in Figure 1(c). [b] The data in the parentheses in these columns are taken from [15]. [c] The data in the parentheses in these columns correspond to the deviation of N atoms from the plane of four carbons (Figure 1(c)). [d] Corresponding value for planar ring structure equals 2.870 and 2.872 Å by standard and CP-corrected methods, respectively.

Table 2. The complexation energies[a] (in kcal mol^{-1}) obtained at different levels of theory.

	Br^-			Cl^-			F^-			H^-		
	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
HFB												
ΔE_{STD}	13.17 (13.2)[b]	13.75, *9.71*	19.99 (20.7)	10.99 (11.0)	11.14, *10.89*	17.84 (18.0)	18.73 (18.8)	18.94, *17.60*	21.64	11.12 (11.2)	15.30, *14.05*	17.39 (17.5)
ΔE_{CP}	9.39	9.64	12.68	10.77	10.97	13.00	18.09	17.48	18.83	10.97	14.81	14.39
ΔE_{BSSE}	9.22 (9.3)	9.46	12.31 (12.4)	10.77 (10.8)	10.88	12.87 (13.2)	18.09 (18.1)	17.54	18.71	10.97 (11.1)	14.82	14.31 (14.3)
$\Delta E_{BSSE+ZPE}$	10.08 (9.5)	10.42	13.17 (11.9)	10.60 (10.6)	10.84	12.70 (12.9)	17.87 (17.8)	17.55	18.48	10.11 (10.2)	14.85	13.44 (13.4)
ΔH		15.79			10.93			19.98			15.44	
ΔG		4.97			6.59			10.73			11.72	
TCB												
ΔE_{STD}	25.76	26.38, 19.40[c]	33.75	20.74	21.17, *21.93*	28.35	31.39	32.16, *32.35*	34.12	35.37, 21.39[d]	57.50, *56.68*	66.77
ΔE_{CP}	18.46	–	–	20.51	20.82	22.90	30.83	–	30.70	34.92, 21.17[d]	56.55	59.15
ΔE_{BSSE}	18.15	18.37	21.72	20.52	20.81	22.74	30.83	30.65	30.63	34.92, 21.17[d]	56.55	59.08
$\Delta E_{BSSE+ZPE}$	18.25	19.10	21.82	20.40	21.12	22.63	30.83	31.08	30.63	31.41, 20.33[d]	53.42	55.57
ΔH		27.79			22.36			33.51			55.88	
ΔG		19.69			13.60			25.31			48.99	
TCP												
ΔE_{STD}	32.27	34.18, *25.14*	42.00	26.86	27.77, *27.10*	35.96	41.86	42.18, *41.27*	44.98	31.25	46.28, *46.00*	51.39
ΔE_{CP}	23.79	24.95	28.70	26.60	27.45	29.72	41.21	40.53	41.01	31.04	45.55	46.52
ΔE_{BSSE}	23.46	24.58	28.01	26.61	27.45	29.50	41.21	40.52	40.91	31.04	45.55	46.42
$\Delta E_{BSSE+ZPE}$	23.69	25.52	28.24	26.36	27.85	29.25	40.88	40.83	40.58	30.38	45.28	45.75
ΔH		36.35			29.64			44.06			47.48	
ΔG		25.70			18.28			32.74			38.95	

[a] All data multiplied by −1. [b] The data in the parentheses are taken from [15], in which ZPE correction performed at HF/6-311 + + G(d,p) level of theory. [c] The italicised data correspond to single-point calculation at B3LYP/aug-cc-PVTZ level of theory. [d] Corresponds to the structure with planar ring.

The ZPE values were obtained by the frequency calculation at the HF and B3LYP/6-31 + + G (d,p) levels on the obtained structures at the same levels. HF results were applied to ZPE correction of MP2 results. With the exception of ring···Br^- complexes, the ZPE correction decreases the complexation energy. Enthalpy and Gibbs free energy of complexation are reported in Table 2. The trends in ΔH and ΔG are the same as ΔE. The entropy of complexation is negative in all cases.

The trends in ΔE_{BSSE} and ΔE_{CP} at B3LYP and MP2/6-31 + + G(d,p) levels are similar in all cases. The trend is $F^- > H^- > Cl^- > Br^-$ in HFB series and $H^- > F^- > Cl^- > Br^-$ in TCB and TCP series. ZPE correction did not change the order with the exception of HFB series at MP2/6-31 + + G(d,p) level, in which the correction performed by frequency calculation data at HF level of theory. The trend in ΔE_{STD} is different with the exchange of Br^- and Cl^- in position.

As can be seen from Table 2, complexation energies depend strongly on the nature of *substituents*. The $\Delta E_{BSSE+ZPE}$ values calculated at MP2 level of theory range in -13 to -19, -22 to -56 and -28 to $-46\,\mathrm{kcal\,mol^{-1}}$ in HFB···X^-, TCB···X^- and TCP···X^- complexes, respectively. With the exception of TCB···H^-, in which the nature of interaction is different from other complexes, the trend in interaction energy is TCP > TCB > HFB with each anion. The differences of $\Delta E_{BSSE+ZPE}$ values between HFB and TCB series range in 8–12 $\mathrm{kcal\,mol^{-1}}$ and the corresponding differences between TCB and TCP series range in 7–10 $\mathrm{kcal\,mol^{-1}}$. The highest complexation energies correspond to TCP···X^- and the lowest values correspond to HFB···X^-.

The most stable complexes are HFB···F^-, TCB···H^- and TCP···H^- in HFB, TCB and TCP series, respectively. On the other hand, the shortest R value corresponds to these complexes, too. TCB···H^- with the puckered ring is more stable than planar ring at all levels of theory.

3.3 AIM analysis

The AIM analyses on the obtained wave functions at MP2/6-31 + + G(d,p) level show a series of the critical points (CP) between anions and ring. A sample molecular graph of HFB···X^- is shown in Figure 2(a). As previously indicated [15], there are six bond CP (BCP), six ring CP (RCP) and 1 cage CP (CCP) in HFB···X^- complexes. The bond and RCP are symmetrically distributed. The BCP connect the anions to the carbon atoms; the RCP connect the anions to the middle of the C—C bonds and the CCP connects the anion to the centre of the ring. Finally, the interaction is further described by the CCP located over the ring along the general axis.

Three sample molecular graphs of TCB···X^- complexes obtained from AIM analyses are shown in Figure 2(b). The number and the nature of CPs are not equal for different complexes in TCB···X^- series. Six BCPs, six RCPs and one CCP are observed in the molecular graph of TCB···Br^- that are distributed similar to HFB complexes. Two BCPs and two RCPs are observed in other complexes. The BCPs connect the anion to unsubstituted carbon atoms and the RCPs connect the anion to the middle of CN-substituted C—C bonds. The CCP is not observed in the puckered structure of TCB···H^- complex.

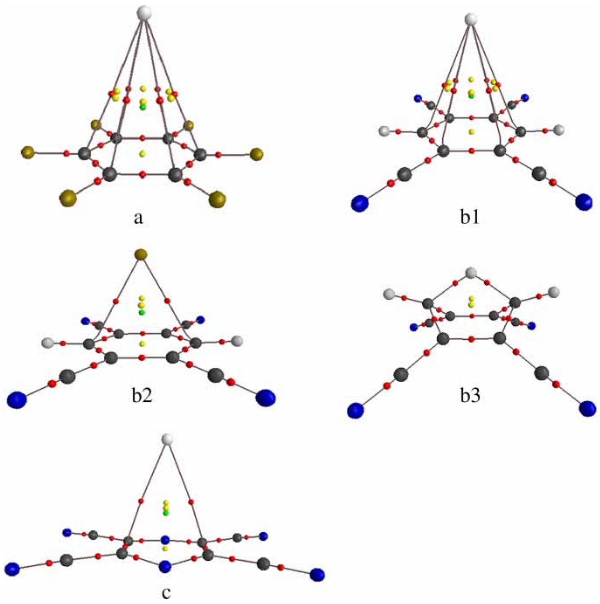


Figure 2. Some typical molecular graphs for (a) HFB···X^-, (b1) TCB···Br^-, (b2) TCB···X^- in which X = Cl, F, H, (b3) puckered ring structure of TCB···H^- and (c) TCP···X^- complexes obtained from AIM analysis. Small red, yellow and green spheres and lines represent BCPs, RCPs and bond paths, respectively.

A sample molecular graph of TCP···X^- complex obtained from AIM analyses are shown in Figure 2(c). As can be seen, two BCPs, two RCPs and one CCP are observed for these complexes, in which the BCPs connect anion to the middle of CN-substituted C—C bonds and the RCPs connect the anion to the nitrogen atoms of the ring.

The values of electron density $\rho(r)$, Laplacian of electron density $\nabla^2\rho(r)$ and energy density $H(r)$ at CPs describe the type and the intensity of the interactions.

The values of $\rho(r)$ and $\nabla^2\rho(r)$ at BCPs of HFB···X^- complexes are reported in Table 3. The values of $\rho(r) \times 10^2$ and $\nabla^2\rho(r) \times 10^2$ in the atomic units are in the ranges of 0.802–1.165 and 1.856–4.950 at BCPs, 0.798–1.157 and 1.873–4.990 at RCPs, and 0.590–0.778 and 2.626–4.733 at CCP, respectively. The value of $H(r)$, which is negative for all cases, confirms nonbonding behavior of anion–π interaction.

In this series, $\nabla^2\rho(r)$ values at the BCPs are positive, which indicates a depletion of the electron density as is common in closed-shell interactions.

Table 3. The type and the number of the CPs and the $\rho(r)$, $\nabla^2\rho(r)$ and H values at those points (in atomic unit).

	Br^-			Cl^-			F^-			H^-		
	BCP	RCP	CCP	BCP	RCP	CCP	BCP	RCP	CCP	BCP	RCP	CCP
HFB												
n	6	6	1	6	6	1	6	6	1	6	6	1
$10^2\rho$	0.866 (0.618)[a]	0.861 (0.616)	0.626 (0.480)	0.802 (0.572)	0.798 (0.571)	0.590 (0.450)	1.165 (1.001)	1.157 (0.996)	0.778 (0.702)	0.845 (0.578)	0.843 (0.576)	0.649 (0.426)
$10^2\nabla^2\rho$	2.454 (1.612)	2.465 (1.613)	2.739 (1.887)	2.491 (1.637)	2.496 (1.637)	2.630 (1.820)	4.950 (4.200)	4.990 (4.226)	4.733 (4.106)	1.856 (1.135)	1.873 (1.139)	2.626 (1.611)
10^2H	−0.085	−0.089	−0.102	−0.102	−0.106	−0.105	−0.176	−0.192	−0.248	−0.039	−0.042	−0.086
TCB												
n	6	6	1	2	2	1	2	2	1	2	2	1
$10^2\rho$	1.007	0.993	0.725	0.931	0.900	0.675	1.342	1.307	0.895	12.260	3.992	–
$10^2\nabla^2\rho$	2.922	2.966	3.188	2.926	2.931	3.027	5.653	5.673	5.421	−12.625	25.601	–
10^2H	−0.099	−0.103	−0.115	−0.117	−0.119	−0.119	−0.173	−0.191	−0.267	6.628	−0.610	–
TCP												
n	2	2	1	2	2	1	2	2	1	2	2	1
$10^2\rho$	1.397	1.129	0.945	1.323	1.102	0.911	1.911	1.555	1.201	2.905	2.004	1.842
$10^2\nabla^2\rho$	4.135	3.923	4.333	4.373	4.088	4.348	8.193	7.604	7.565	5.513	7.731	9.192
10^2H	−0.155	−0.126	−0.146	−0.184	−0.150	−0.160	−0.208	−0.258	−0.317	0.017	−0.195	−0.299

[a] The data in the parentheses are taken from [15] which calculated at HF/6-31 + + G(d,p) level of theory.

The trend in $\rho(r)$ values is

$$(3,-1): \quad F^- > Br^- > H^- > Cl^-,$$

$$(3,+1): \quad F^- > Br^- > H^- > Cl^-,$$

$$(3,+3): \quad F^- > H^- > Br^- > Cl^-,$$

in these complexes. On the other hand, the trend in $\Delta E_{\mathrm{BSSE+ZPE}}$ values is

$$F^- > H^- > Br^- > Cl^-.$$

This is similar to the trend in $\rho(r)$ values at CCP. The correlation between complexation energies and $\rho(r)$ values at CCPs is better than other CPs.

The $\rho(r)$ and $\nabla^2\rho(r)$ values at CP of HFB···F$^-$ complex, which is the most stable one in this series, is higher than other HFB···X$^-$ complexes.

For TCB···X$^-$ series, the values of $\rho(r) \times 10^2$ and $\nabla^2\rho(r) \times 10^2$ at BCPs are in the ranges of 0.931–1.342 and 2.926–5.653 in the atomic units, respectively, for F$^-$, Cl$^-$ and Br$^-$ anions. These are higher than the values obtained for the HFB···X$^-$ complexes; thus, the interactions are expected to be stronger in the comparison with HFB···X$^-$ complexes. This point is in a good agreement with complexation energies. The corresponding values in the atomic units are in the ranges of 0.900–1.307 and 2.931–5.673 at RCPs and 0.675–0.895 and 3.063–5.465 at CCP, respectively. These are high in comparison with the corresponding values for HFB···X$^-$ complexes. This result is also in a good agreement with complexation energies.

In TCB···H$^-$, $\rho(r) \times 10^2$ and $\nabla^2\rho(r) \times 10^2$ values are equal to 12.260 and -12.625 at BCPs and 3.992 and 25.601 at RCPs, respectively, in the atomic units. A negative $\nabla^2\rho(r)$ value at BCP is in agreement with a bonding interaction. Against other anions, the H value in the BCPs is positive in TCB···H$^-$ which is in agreement with a bonding interaction. This is in agreement with higher stability of ring puckered structure of TCB···H$^-$ complex.

As can be seen from the optimised structures and the results of AIM calculation, the interaction between anion and unsubstituted carbon atoms is stronger than the substituted carbon atoms. The strength of interaction increases by the ratio of charge to the radius of the anion. The weakest interaction corresponds to the Br$^-$ anion. Although the values of $\rho(r)$ at BCPs in TCB···Br$^-$ are lower than other TCB···X$^-$ complexes, the number of BCPs is higher in this complex (6 vs. 2). This interaction in TCB···H$^-$ complex is so strong that could be considered as a bonding contact.

The $\rho(r)$ values at all CPs of this series of complexes can be viewed in the following order

$$H^- > F^- > Br^- > Cl^-.$$

The $\Delta E_{\mathrm{BSSE+ZPE}}$ values can be viewed in the following order in these complexes

$$H^- > F^- > Cl^- > Br^-.$$

This is similar to the order of H values in all CPs.

For TCP···X$^-$ series, the values of $\rho(r) \times 10^2$ and $\nabla^2\rho(r) \times 10^2$ (Table 3) are in the ranges of 1.323–2.905 and 4.135–8.193 at BCPs, 1.102–2.004 and 3.923–7.604 at RCPs, and 0.911–1.842 and 4.348–9.192 at CCP, respectively, in the atomic units. The values of energy density, which is negative for all cases (with the exception of TCP···H$^-$ complex that is positive), confirms nonbonding behaviour of anion···ring interaction.

The following order is observed in this series of complexes for $\rho(r)$ values

$$H^- > F^- > Br^- > Cl^-.$$

The ΔE_{CP} (ΔE_{BSSE} or $\Delta E_{\mathrm{BSSE+ZPE}}$) values at mentioned levels can be viewed in the following order

$$H^- > F^- > Cl^- > Br^-.$$

This is similar to trend in H values (with the exception of TCP···H$^-$, in which the nature of interaction is different).

3.4 NBO analysis

Some results of NBO analysis are reported in Table 4. The most important donor–acceptor interaction is from a lone pair orbital of X$^-$ to an antibonding orbital (0% of s character and 100% of p character) of C—C bonds ($n_X \rightarrow \pi^*_{CC}$) in TCB and HFB series. Corresponding interaction energies $E^{(2)}$ in HFB is lower than TCB series. The $n_X \rightarrow \pi^*_{CN}$ (an antibonding orbital with 0% s character and 100% p character, which corresponds to the CN bonds of the ring, not to CN *substituents*) in TCP series is the most important donor–acceptor interaction and is stronger than $n_X \rightarrow \pi^*_{CC}$. Its interaction energy is equal to 31.58, 1.28, 1.24 and 1.72 kcal mol^{-1} in H$^-$, F$^-$, Cl$^-$ and Br$^-$, respectively. Higher $n_X \rightarrow \pi^*_{CN}$ interaction in TCP in comparison with $n_X \rightarrow \pi^*_{CC}$ interaction in TCB and HFB series is in good agreement with the complexation energy values. The occupancies of n_X and π^*, which enter in mentioned donor–acceptor interactions are given in Table 4. The changes in the occupancies of these orbitals are negligible in agreement with $E^{(2)}$ values, in TCB and HFB series. The changes are higher in TCP series. Also, the n.c. calculated

Table 4. The $n_X \rightarrow \pi^*_{CC(CN)}$ interaction energy (in kcal mol^{-1}) and the occupancy of n_X calculated at MP2/6-31 + + G(d,p) level of theory.

	$n_X \rightarrow \pi^{*a}$	$n_X{}^a$	π^{*a}	n.c.^{b}	n.c.^{c}
HFB					
H	–	1.988	0.402	0.374	–
F	0.13	1.999	0.401	0.379	–
Cl	0.09	1.999	0.403	0.372	–
Br	0.09	1.999	0.403	0.371	–
TCB					
H	–	–	–	−0.151	−0.451
F	0.14	1.998	0.361	−0.105	−0.009
Cl	0.09	1.999	0.364	−0.112	−0.021
Br	0.10	1.998	0.390	−0.113	−0.025
TCP					
H	<0.05 (31.58)	1.482	0.332 (0.522)	0.147	−0.524
F	1.03 (1.28)	1.996 (1.978)	0.350 (0.358)	0.174	−0.347
Cl	0.65 (1.24)	1.997 (1.972)	0.354 (0.362)	0.162	−0.348
Br	0.80 (1.72)	1.995 (1.960)	0.354 (0.368)	0.160	−0.355

[a] The data in the parentheses correspond to $n_X \rightarrow \pi^*_{CN}$ interaction. [b] The n.c. calculated on the CN-substituted carbon atoms. [c] The n.c. calculated on the carbon (without CN *substituent*) or nitrogen atoms of ring.

on carbon and nitrogen atoms of ring are reported in Table 4. The n.c. values are positive on carbon atoms of ring in HFB. The n.c. values are small and negative on the CN-substituted C atoms and negligible on unsubstituted C atoms in TCB series. On the other hand, the BCPs are observed between anion and unsubstituted C atoms in AIM analysis. The n.c. values are positive on carbon atoms and are negative on nitrogen atoms of ring.

As can be seen from the optimised structures in TCP$\cdots$X$^-$ complexes, an electrostatic repulsion force is expected between the negative charged anions and the nitrogen atoms of the ring. The interaction between anion and ring increases by anion charge density. On the other hand, the electrostatic repulsion force between anion and the nitrogen atom of the ring increases, too. These two different interactions result in the ring puckering and increase by anion charge density. There is a good linear relationship between calculated n.c. on the nitrogen atoms of ring and the deviation of N atoms from the plane of four carbon atoms of ring (Figure 2(c)), which its correlation coefficient is equal to 0.995.

4. Conclusions

Theoretical study of interaction between H$^-$, F$^-$, Cl$^-$ and Br$^-$ anions and HFB, TCB and TCP rings at different levels indicates that both complexation energy and the nature of interaction change with changing anion and aromatic ring.

The distances between anions and the centre of rings obtained by CP-corrected optimisation are longer than standard method. Despite this, the complexation energies obtained by CP-corrected method (ΔE_{CP}) are more negative than the values obtained from standard method (ΔE_{BSSE}). With the exception of ring$\cdots$H$^-$, complexation energy increase with increasing the ratio of charge to the radius of anion, and obey TCP > TCB > HFB order.

The results of single-point calculation at B3LYP/aug-cc-PVTZ level indicate that with the exception of Br$^-$ (~4–9 kcal/mol), the ΔE values change slowly (~0.1–1.4 kcal/mol) with basis set. The values of ΔE approach the BSSE corrected values with increasing basis set. The ZPE correction decreases the complexation energy. The trend in ΔH and ΔG values is the same as ΔE. The entropy of complexation is negative in all cases.

The AIM analysis indicates that the nature of interaction changes with changing anion and aromatic ring. Although six BCPs are detected between anions and the carbon atoms of ring in HFB$\cdots$X$^-$ complexes, two BCPs are observed between anions and C—C bonds of ring in TCP$\cdots$X$^-$ complexes. In TCB$\cdots$X$^-$ complexes, the nature of BCPs depends on the anion. In TCB$\cdots$Br$^-$, six BCPs are observed between Br$^-$ and carbon atoms of TCB. In other TCB$\cdots$X$^-$ complexes, two BCPs are shown between anion and two carbon atoms. With the exception of ring$\cdots$H$^-$, the trend in $\rho(r)$, $\nabla^2\rho(r)$ and $H(r)$ is TCP > TCB > HFB for all anions.

The most important donor–acceptor interactions obtained from NBO analysis are $n_X \rightarrow \pi^*_{CC}$ for TCB$\cdots$X$^-$ and HFB$\cdots$X$^-$ and $n_X \rightarrow \pi^*_{CN}$ for TCP$\cdots$X$^-$ complexes. $n_X \rightarrow \pi^*_{CN}$ interaction in TCP$\cdots$X$^-$ is stronger than $n_X \rightarrow \pi^*_{CC}$ interaction in TCB$\cdots$X$^-$ and HFB$\cdots$X$^-$ complexes. In contrast to TCP, the changes of occupancies of n_X and π^* orbitals are negligible in HFB and TCB series. There is a very good linear relationship between negative n.c. on N atoms of ring and the departure of these atoms from the plane of four C atoms.

References

[1] M. Luhmer, K. Bartik, A. Dejaegere, J. Reisse, and P. Bouvy, *The importance of quadrupolar interactions in molecular recognition processes involving a phenyl group*, J. Bull. Soc. Chim. Fr. 131 (1994), pp. 603–606.

[2] J.H. Williams, J.K. Cockcroft, and A.N. Fitch, *Structure of the lowest temperature phase of the solid benzene–hexafluorobenzene adduct*, Angew. Chem. Int. Ed. Engl. 31 (1992), pp. 1655–1657.

[3] J.H. Williams, *The molecular electric quadrupole moment and solid-state architecture*, Acc. Chem. Res. 26 (1993), pp. 593–598.

[4] M. Mascal, A. Armstrong, and M. Bartberger, *Anion-aromatic bonding: A case for anion recognition by pi-acidic rings*, J. Am. Chem. Soc. 124 (2002), pp. 6274–6276.

[5] I. Alkorta, I. Rozas, and J. Elguero, *Interaction of anions with perfluoro aromatic compounds*, J. Am. Chem. Soc. 124 (2002), pp. 8593–8598.

[6] D. Quinonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa, and P.M. Deya, *Anion–π interactions: Do they exist?* Angew. Chem. Int. Ed. 41 (2002), pp. 3389–3392.

[7] C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa, and P.M. Deya, *A topological analysis of the electron density in anion–π interactions*, Chem. Phys. Chem. 4 (2003), pp. 1344–1348.

[8] ———, s-*Tetrazine as a new binding unit in molecular recognition of anions*, Chem. Phys. Lett. 370 (2003), pp. 7–13.

[9] D. Kim, P. Tarakenshwar, and K.S. Kim, *Theoretical investigations of anion–π interactions: The role of anionsand the nature of π systems*, J. Chem. Phys. A 108 (2004), pp. 1250–1258.

[10] H. Casellas, C. Massera, F. Buda, P. Gamez, and J. Reedijk, *Crystallographic evidence of theoretically novel anion–p interactions*, New. J. Chem. 30 (2006), pp. 1561–1566.

[11] C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa, and P.M. Deya, *Anion–π interactions in five-membered rings: A combined crystallographic and* ab initio *study*, Chem. Phys. Lett. 382 (2003), pp. 534–540.

[12] S. Demeshko, S. Dechert, and F. Meyer, *Anion–π interactions in a carousel copper(II)-triazine complex*, J. Am. Chem. Soc. 126 (2004), pp. 4508–4509.

[13] C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa, and P. M. Deya, *Anion–π interactions: Must the aromatic ring be electron deficient?* New. J. Chem. 27 (2003), pp. 211–214.

[14] I. Alkorta and J. Elguero, *Aromatic systems as charge insulators: Their simultaneous interaction with anions and cations*, J. Phys. Chem. A 107 (2003), pp. 9428–9433.

[15] Y.S. Rosokha, S.V. Lindeman, S.V. Rosokha, and J.K. Kochi, *Anion–π interactions: Molecular complexes of Cl^-, Br^-, and I^- with olefinic and aromatic receptors*, Angew. Int. Ed. 116 (2004), pp. 4750–4752.

[16] P.D. Beer and P.A. Gale, *Anion recognition and sensing: The state of the art and future perspectives*, Angew. Chem. Int. Ed. 40 (2001), pp. 486–516.

[17] A. Bianchi, K. Bowman-James, and E. Garcia-Espana, *Supermolecular Chemistry of Anion*, Wiley-VCH, New York, 1997.

[18] C. Garau, D. Quiñonero, A. Frontera, D. Escudero, P. Ballester, A. Costa, and P.M. Deya, *MP2 study of anion–p complexes of trifluoro-*s*-triazine with tetrahedral and octahedral anions*, Chem. Phys. Lett. 438 (2007), pp. 104–108.

[19] H.-J. Schneider and A. Yatsimirski, *Principles and Methods in Supramolecular Chemistry*, Wiley, New York, 2000.

[20] H.-J. Schneider, F. Werner, and T. Blatter, *Attractive interactions between negative charges and polarizable aryl parts of host–guest systems*, J. Phys. Org. Chem. 6 (1993), pp. 590–594.

[21] H.-J. Schneider, T. Blatter, B. Palm, U. Pfingstag, V. Rudiger, and J. Theis, *Complexation of nucleosides, nucleotides, and analogs in an azoniacyclophane. Van der Waals and electrostatic binding increments and NMR shielding effects*, J. Am. Chem. Soc. 114 (1992), pp. 7704–7708.

[22] D. Quinonero, C. Garau, A. Frontera, P. Ballester, A. Costa, and P.M. Deya, *Counterintuitive interaction of anions with benzene derivatives*, Chem. Phys. Lett. 359 (2002), pp. 486–492.

[23] H. Maeda, A. Osuka, and H. Furuta, *Anion binding properties of N-confused porphyrins at the peripheral nitrogen*, J. Incl. Phenom. Macro. Chem. 49 (2004), pp. 33–36.

[24] C. Garau, D. Quinonero, A. Frontera, P. Ballester, A. Costa, and P.M. Deya, *Approximate additivity of anion-interactions: An* ab initio *study on anion-, anion-2 and anion-3 complexes*, J. Phys. Chem. A 109 (2005), pp. 9341–9345.

[25] C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa, and P.M. Deya, *Cation- versus anion-interactions: Energetic, charge transfer, and aromatic aspects*, J. Phys. Chem. A 108 (2004), pp. 9423–9427.

[26] O.B. Berryman, V.S. Bryantsev, D.P. Stay, D.W. Johnson, and B.P. Hay, *Structural criteria for the design of anion receptors: The interaction of halides with electron-deficient arene*, J. Am. Chem. Soc. 129 (2007), pp. 48–58.

[27] F. Jensen, *Introduction to Computational Chemistry*, John Wiley & Sons, Chichester, 1999.

[28] E. Lewars, *Computational Chemistry*, Kluwer Academic Publishers, Boston, 2004.

[29] E. Gianinetti, M. Raimondi, and E. Tornaghi, *Theoretical and computational developments modification of the Roothaan equations to exclude BSSE from molecular interaction calculations*, Int. J. Quant. Chem. 60 (1996), pp. 157–166.

[30] S.F. Boys and F. Bernardi, *The calculations of small molecular interaction by the difference of separate total energies – some procedures with reduced error*, Mol. Phys. 19 (1970), pp. 553–566.

[31] P. Hobza, O. Bludsky, and S. Suhai, *Reliable theoretical treatment of molecular clusters: Counterpoise-corrected potential energy surface and anharmonic vibrational frequencies of the water dimer*, Phys. Chem. Chem. Phys. 1 (1999), pp. 3073–3078.

[32] P. Hobza and Z. Havlas, *Counterpoise-corrected potential energy surfaces of simple H-bonded systems*, Theor. Chem. Acc. 99 (1998), pp. 372–377.

[33] S. Simon, J. Bertran, and M. Sodupe, *Effect of counterpoise correction on the geometries and vibrational frequencies of hydrogen bonded systems*, J. Phys. Chem. A 105 (2001), pp. 4359–4364.

[34] R.F.E. Bader, *A quantum theory of molecular structure and its applications*, Chem. Rev. 91 (1991), pp. 893–928.

[35] ———, *Atoms in molecules*, *A Quantum Theory*, Clarendon, Oxford, 1990.

[36] A.E. Reed, L.A. Curtiss, and F. Weinhold, *Intermolecular interactions from a natural bond orbital, donor–acceptor viewpoint*, Chem. Rev. 88 (1988), pp. 899–926.

[37] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant et al. Gaussian 03. Revision B.03, Gaussian, Inc., Pittsburgh, PA (2003)

[38] A.D.J. Becke, *Density-functional thermochemistry. III. The role of exact exchange*, J. Chem. Phys. 98 (1993), pp. 5648–5652.

[39] C. Moller and M.S. Plessent, *Note on an approximation treatment for many-electron systems*, Phys. Rev. 46 (1934), pp. 618–622.

[40] S. Simon, M. Duran, and J.J. Danneberg, *How does basis set superposition error change the potential surfaces for hydrogen-bonded dimers?* J. Chem. Phys. 105 (1996), pp. 11024–11031.

[41] F. Biegler-König, J. Schönbohm, and D.J. Bayles, *AIM2000, a program to analyze and visualize atoms in molecules*, Comput. Chem. 22 (2001), p. 545.

[42] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold. NBO Version 3.1.