

Anion- π and Intramolecular Hydrogen Bond Interactions in the Various Complexes of 1,3,5-Triamino-2,4,6-trinitrobenzene with H^- , F^- , Cl^- and Br^- Anions

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The quantum chemical calculations were performed to investigate the interplay between the anion- π and intramolecular hydrogen bond (IMHB) interactions in the various complexes of 1,3,5-triamino-2,4,6-trinitrobenzene (ANB) with H^- , F^- , Cl^- and Br^- anions. For better understanding the cooperative effects, the parent molecules (ANB) and the corresponding complexes of 1,3,5-trinitrobenzene with the mentioned anions are also considered, as a set of the reference points. In this regard, the IMHB and anion- π interactions are comprehensively analyzed by energetic, geometrical, spectroscopic and topological descriptors. It was found that the coexistence of anion- π and IMHB increases the strength of both interactions. Furthermore, the influences of the anion- π and IMHB interactions on the significance of the π -electron delocalization (π -ED) of the resonance assisted hydrogen bond (RAHB) units and the aromaticity of the benzene ring are evaluated by the harmonic oscillator model of aromaticity (HOMA), as a geometry based index. According to the HOMA values, we concluded that the coexistence of the mentioned interactions decreases the aromaticity of benzene ring and increases the π -ED of RAHB units. Finally, the strength of the non-covalent interactions and the significance of π -ED and aromaticity strongly depend on type of the anion.

Keywords: Intramolecular hydrogen bond, Anion- π , Aromaticity and RAHB

INTRODUCTION

The anion- π interactions play an important role on recognition and sensing of anions in many chemical and biological systems [1-4]. Many theoretical and experimental studies have been focused on the interactions of anions and aromatic rings and revealed their energetic favorability [5-10]. Based on these research works, the presence of electron withdrawing groups can be turned the negative quadrupole value of ring into a positive one and consequently, the interaction of anions with benzene ring becomes feasible [11-13]. These interactions generally are controlled by the electrostatic and anion-induced polarization terms [14,15]. The nature of electrostatic component is illustrated *via* the positive permanent quadrupole moment of the aromatic ring. The anions

strongly interact with the aromatic rings which have large positive quadrupole moments and molecular polarizabilities. On the other hand, the anion- π interaction can be controlled by one of the electrostatic and polarization effects. For instance, the interaction of anions and the aromatic rings with the negligible negative quadrupole moments and large molecular polarizability are dominated by induction effects [16]. Additionally, the total interaction energy strongly depends on the properties of anion such as size, shape and polarizability [17-19].

Due to the presence of various non-covalent interactions in supramolecular and biological systems, the interplay between them has been frequently observed [20-22]. Hence, in the last years, many investigations have been devoted to study of the cooperative effects between the anion- π and the other non-covalent interactions such as hydrogen bond (HB) [23-28], cation- π [29-31], lone pair [32,33] and π - π stacking [34-36]. For example, the mutual interaction between

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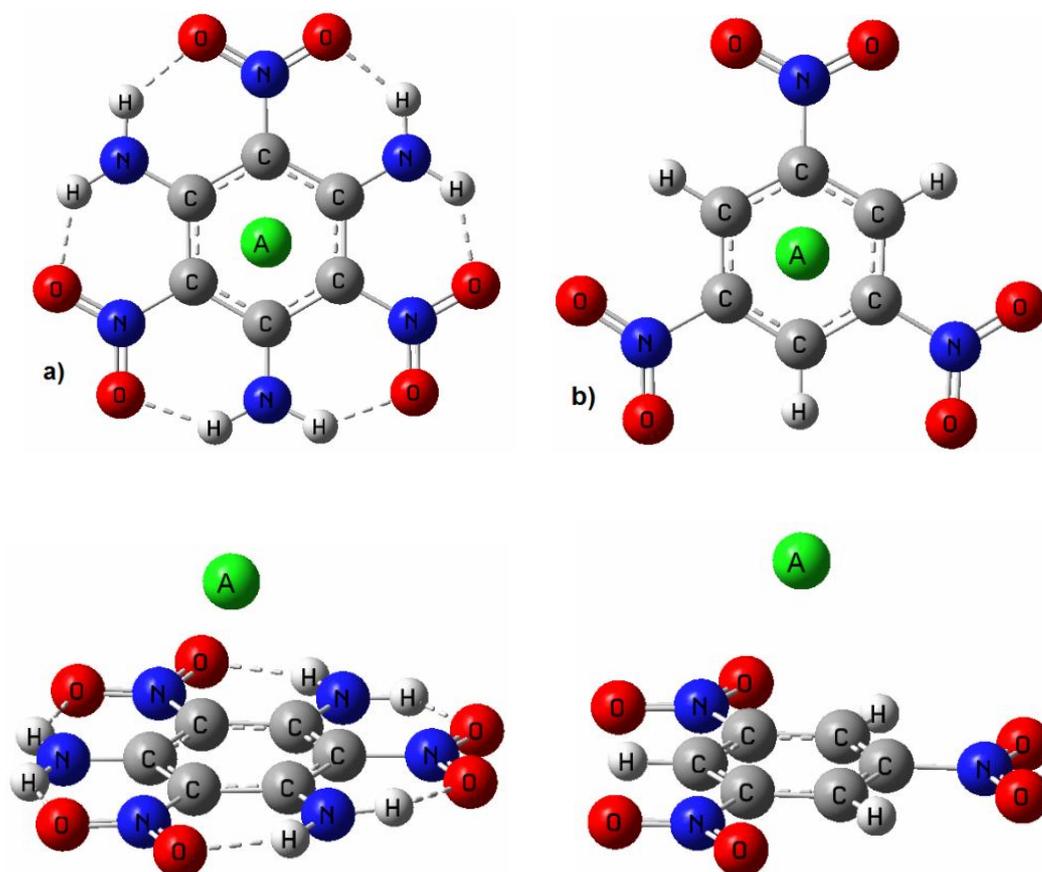


Fig. 1. Molecular structures of ANB...A (a) and TNB...A (b) complexes (A = H⁻, F⁻, Cl⁻ and Br⁻).

anion- π and *intermolecular* HB can lead to the interesting synergistic effects [37]. These effects also have been reported in complexes, where the distance between the HB donor-acceptor molecules and anions are approximately very large (11 Å) [24]. This interplay reinforces both of the interactions where the aromatic rings act as HB acceptors, while the reverse effect is observed where the aromatic ring is a HB donor.

The *intramolecular* hydrogen bond (IMHB) is an intriguing category of HB. In this type of interaction, the presence of proton donor and acceptor groups in the same molecule leads to the formation of a quasi-ring [38-40]. The intramolecular resonance assisted hydrogen bond (RAHB) is a specific case of this category [41-51], which has the significant influence on all of the molecular properties.

Unlike the *intermolecular* HB, the interplay between anion- π and IMHB interactions has not been investigated, so far. Hence, we decided to perform a comprehensive theoretical study to examine the mutual influences of the anion- π and intramolecular RAHB interactions in the various complexes of 1,3,5-triamino-2,4,6-trinitrobenzene (ANB) with H⁻, F⁻, Cl⁻ and Br⁻ anions (Fig. 1). Finally, the aims of the present work are as follows: (i) Estimation of the strengths of the anion- π and IMHB interactions by energetic, geometric, spectroscopic and topological parameters to investigate their cooperative effects, (ii) Evaluation of the significance of π -electron delocalization (π -ED) of RAHB unit and the aromaticity of benzene ring by harmonic oscillator model of aromaticity (HOMA) index [52] to investigate the mutual effects of IMHB and anion- π

Table 1. The Complexation and IMHB Energies (kcal mol⁻¹) at M062X/6-311++G(d,p) Level of Theory

Name	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE+DEFF}}$	E_{HB}
TNB \cdots Br ⁻	-23.12	-22.82	-22.36	-
TNB \cdots Cl ⁻	-25.50	-24.77	-24.19	-
TNB \cdots F ⁻	-36.47	-34.54	-33.61	-
TNB \cdots H ⁻	-28.10	-27.23	-26.23	-
ANB \cdots Br ⁻	-22.71	-22.32	-20.85	15.33
ANB \cdots Cl ⁻	-22.86	-22.12	-21.12	15.96
ANB \cdots F ⁻	-37.23	-35.03	-33.08	16.52
ANB \cdots H ⁻	-28.70	-27.76	-26.86	16.85
ANB	-	-	-20.85	15.19

interactions.

COMPUTATIONAL METHODS

All of the computations were carried out at the M06-2X/6-311++G(d,p) level of theory. The geometry optimizations of all structures and the vibrational frequency calculations were performed by Gaussian 03 series of programs [43]. The binding energies are computed as the difference between the energy of the ANB \cdots A complex (A = anion) and the sum of the monomers' energies (ANB and A). These values were corrected for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise technique [54]. The atoms in molecules (AIM) analysis have been performed on the optimized structures by means of the AIM2000 package [55]. The π -ED of RAHB units and aromaticity of benzene ring were evaluated by the HOMA, as a geometry based index, and R_{opt} and α , for evaluation of HOMA index are calculated at the same level of theory (for CC, NO, and CN bonds: $R_{\text{opt, CC}} = 1.393$ Å, $R_{\text{opt, NO}} = 1.268$ Å, $R_{\text{opt, CN}} = 1.329$ Å, $\alpha_{\text{CC}} = 88.983$, $\alpha_{\text{NO}} = 66.508$, $\alpha_{\text{CN}} = 91.670$).

RESULTS AND DISCUSSION

In the present work, the various binary complexes of ANB with H⁻, F⁻, Cl⁻ and Br⁻ anions, were chosen as the benchmark systems to study the cooperative effects between the anion- π and IMHB interactions. For better understanding these effects, the parent molecule (ANB) and the corresponding complexes of 1,3,5-trinitrobenzene (TNB) with the mentioned anions (Fig. 1) are considered as a set of reference points. Also, the effects of these non-covalent interactions on the π -ED of RAHB units and the aromaticity of the benzene ring were studied.

Cooperative Effects

Energetic descriptors. The complexation energies, with and without the BSSE corrections (ΔE_{BSSE} and ΔE), are reported in Table 1. The results show that the ΔE values of both series are arranged in $\pi\cdots\text{F}^- > \pi\cdots\text{H}^- > \pi\cdots\text{Cl}^- > \pi\cdots\text{Br}^-$ order, which are different from the corresponding order of ΔE_{BSSE} values. In other words, the trend in the BSSE corrected complexation energies of the ANB \cdots A complexes is as follows; ANB \cdots F⁻ > ANB \cdots H⁻ > ANB \cdots Br⁻ >

Table 2. The Geometrical and Spectroscopic Descriptors (\AA , $^\circ$ and cm^{-1}) of Complexes

Name	$d_{\pi\cdots A}$	d_{N-H}	$d_{N\cdots O}$	$d_{H\cdots O}$	$\theta_{N-H\cdots O}$	$\nu_{\pi\cdots A}$	ν_{N-H}^{sym}	ν_{N-H}^{asym}
TNB \cdots Br $^-$	3.247	-	-	-	-	67.7	-	-
TNB \cdots Cl $^-$	3.054	-	-	-	-	151.1	-	-
TNB \cdots F $^-$	2.400	-	-	-	-	232.9	-	-
TNB \cdots H $^-$	2.603	-	-	-	-	523.3	-	-
ANB \cdots Br $^-$	3.168	1.010	2.497	1.714	131.3	98.9	3497.1	3612.0
ANB \cdots Cl $^-$	2.966	1.011	2.495	1.699	132.5	181.5	3473.8	3589.2
ANB \cdots F $^-$	2.252	1.012	2.492	1.691	132.8	284.2	3455.6	3570.6
ANB \cdots H $^-$	2.391	1.013	2.492	1.687	133.4	569.3	3440.4	3551.3
ANB	-	1.010	2.498	1.715	131.1	-	3500.0	3614.6

ANB \cdots Cl $^-$ that is slightly different from the corresponding order of TNB \cdots A ones. This difference could be related to the BSSE effect, which is a function of the number of electrons and their basis set. Also, the binding energies are simultaneously corrected by the BSSE and deformation energies, which is the difference between the full opt energy of the π systems (ANB and TNB) and the calculated energy using their geometries in complex by single-point energy calculations. The new results are in good agreement with uncorrected energies.

Comparison of the complexation energies of the ANB \cdots A and TNB \cdots A series shows that, for F $^-$ and H $^-$, the presence of the RAHB units increases the strength of anion- π interaction, while for Cl $^-$ and Br $^-$, the reverse behavior is observed. It seems that the high values of charge density of F $^-$ and H $^-$ causes that some of the electron density from the benzene ring to the RAHB units is transferred, which increase the strength the anion- π interaction. However, for Cl $^-$ and Br $^-$ with more ionic radii, the repulsion between the anions and negative heteroatoms of the RAHB units, probably reduce the strength of the anion- π .

However, various models are developed to estimate the

IMHB energies of RAHB systems [56], however, due to the structural constraints, the potential energy density (PED) method of Espinosa *et al.*[57] is more appropriate;

$$E_{HB} = 1/2V(r_{cp}) \quad (1)$$

Hence, the IMHB energies of RAHB units were estimated by PED method, as presented in Table 1. Nevertheless, the IMHB energies obtained by this method are approximate and only can be used to interpret the variation of HB energies in the studied systems. The results show that the IMHB energies of the ANB \cdots A complexes are more than the corresponding value of the parent molecule (ANB), indicating that the presence of the anion- π interaction strengthens the IMHB. This phenomenon can be interpreted in terms of the repulsion effects between the anions and π -electrons of the benzene ring that increase the electron density within the RAHB units and their HB energies. Also, the increments of E_{HB} are obeyed the following order; ANB \cdots H $^-$ (1.66) > ANB \cdots F $^-$ (1.33) > ANB \cdots Cl $^-$ (0.77) > ANB \cdots Br $^-$ (0.14 kcal mol $^{-1}$), which is in line with the charge to the radius ratio of the anions.

Geometric descriptors. Undoubtedly, the distance

between the anion and center of the aromatic ring, $d_{\pi\cdots A}$, is the best geometrical descriptor of the anion- π strength. According to the previous studies, there is a reverse relationship between the $d_{\pi\cdots A}$ and strength of the anion- π interaction [7]. As can be observed in Table 2, the $d_{\pi\cdots A}$ values of the ANB \cdots A complexes are shorter than the TNB \cdots A ones. These results show that the coexistence of the anion- π and IMHB interactions leads to reinforcement of the interaction between the anion and the aromatic ring. On the other hand, the reductions of $d_{\pi\cdots A}$ values are also depending on the type of anions and obey the following order; $H^- (0.212) > F^- (0.148) > Cl^- (0.088) > Br^- (0.079 \text{ \AA})$, which is in agreement with their charge to the radius ratio.

Furthermore, the influences of the anion- π interaction on the nature of IMHB can be studied by the structural parameters of RAHB units. The consequences of strengthening of the X-H \cdots Y hydrogen bond on the geometrical parameters are as follows: (i) the elongation of the X-H bond length (ii) the shortening of the H \cdots Y and X \cdots Y distances (iii) the increment of the X-H \cdots Y angle. The values corresponding to these parameters are summarized in Table 2. These results clearly show that the ANB \cdots A complexes have longer N-H bond length (d_{N-H}), shorter the N \cdots O ($d_{N\cdots O}$) and H \cdots O ($d_{H\cdots O}$) distances and larger N-H \cdots O angle ($\theta_{N-H\cdots O}$) in comparison with the corresponding values of the parent molecule, ANB. These observations reflect the stronger IMHB in the presence of anion- π interaction. For example, the d_{N-H} values arrange as ANB $\cdots H^- (1.013) > ANB\cdots F^- (1.012) > ANB\cdots Cl^- (1.011) > ANB\cdots Br^- (1.010) \approx ANB (1.010 \text{ \AA})$, which is similar to the trend in E_{HB} values. This conclusion is also supported by other structural descriptors such as $d_{H\cdots O}$, $d_{N\cdots O}$ and $\theta_{N-H\cdots O}$.

Spectroscopic descriptors. Some of the vibrational normal modes of the benchmark systems can be employed to investigate the mutual influences between the anion- π and IMHB interactions. The $\pi\cdots A$ stretching vibration, $\nu_{\pi\cdots A}$, is directly related to the strength of the anion- π interaction. The wave numbers of $\nu_{\pi\cdots A}$ were approximately calculated and collected in Table 2. These values for TNB \cdots A and ANB \cdots A complexes are located in the range of 67.7-523.3 and 98.9-569.3 cm^{-1} , respectively. On the basis of these results, one can conclude that the presence of RAHB units increases the values of $\nu_{\pi\cdots A}$. The presence of amino groups causes to formation of a RAHB ring and consequently

enhancing the strength of anion- π and increasing the values of $\nu_{\pi\cdots A}$ frequencies. The augmented values can be as follows; $F^- (51.3) > H^- (46.0) > Br^- (31.2) > Cl^- (30.4 \text{ cm}^{-1})$, emphasising on the stronger anion- π interaction in the ANB \cdots A complexes with respect to the TNB \cdots A ones.

On the other hand, the symmetrical and asymmetrical N-H stretching (ν_{N-H}^{sym} and ν_{N-H}^{asym}) of RAHB units have been also used to estimate the strength of the IMHB at the presence of the anion- π interactions. It is evident that with strengthening of the IMHB, ν_{N-H} shifts to the lower values. In the studied systems, the interaction of the anions with the aromatic ring reduces the values of ν_{N-H}^{sym} (2.9-60.0) and ν_{N-H}^{asym} (2.6-63.3 cm^{-1}). These changes intensely reflect the presence of stronger IMHB interactions in the benchmark complexes, with respect to the parent molecule (ANB). Furthermore, on the basis of Table 2, the trend in these values is ANB $>$ ANB $\cdots Br^- >$ ANB $\cdots Cl^- >$ ANB $\cdots F^- >$ ANB $\cdots H^-$, which is in good agreement with the E_{HB} and d_{N-H} .

Topological descriptors. According to the AIM theory, the mutual effects between the anion- π and IMHB interactions can be investigated by topological properties of the bond critical points of the interactions. In the AIM analysis of the studied complexes three bond critical points (BCPs) between anion and benzene ring (with the exception of TNB $\cdots H$) are appeared, which connect the anion to the NO_2 -substituted carbons (Fig. 2). The selected topological parameters of the mentioned BCPs are calculated and gathered in Table 3. It has been clarified that the electron density values, $\rho(r)_{\pi\cdots A}$, at the BCPs of anion- π strongly correlate with their strength [8,15,58,59]. As the results indicate, the $\rho(r)_{\pi\cdots A}$ of the ANB \cdots A complexes are larger than the corresponding values of TNB \cdots A ones that reveal the cooperative effects of the IMHB and the anion- π interactions. Also, the effect of the RAHB units on the $\rho(r)_{\pi\cdots A}$ values depends on the anion type and obey the complexation energies order; $F^- (0.295 \times 10^{-2}) > H^- (0.256 \times 10^{-2}) > Cl^- (0.196 \times 10^{-2}) > Br^- (0.113 \times 10^{-2} \text{ a.u.})$.

Based on the topological characteristic of HB critical point, especially the charge density ($\rho(r)_{H\cdots O}$), the following order is obtained; ANB $\cdots H^- (5.040 \times 10^{-2}) >$ ANB $\cdots F^- (4.959 \times 10^{-2}) >$ ANB $\cdots Cl^- (4.824 \times 10^{-2}) >$ ANB $\cdots Br^- (4.682 \times 10^{-2}) >$ ANB ($4.642 \times 10^{-2} \text{ a.u.}$). This order is similar to the trends in the E_{HB} , d_{N-H} and ν_{N-H} descriptors that

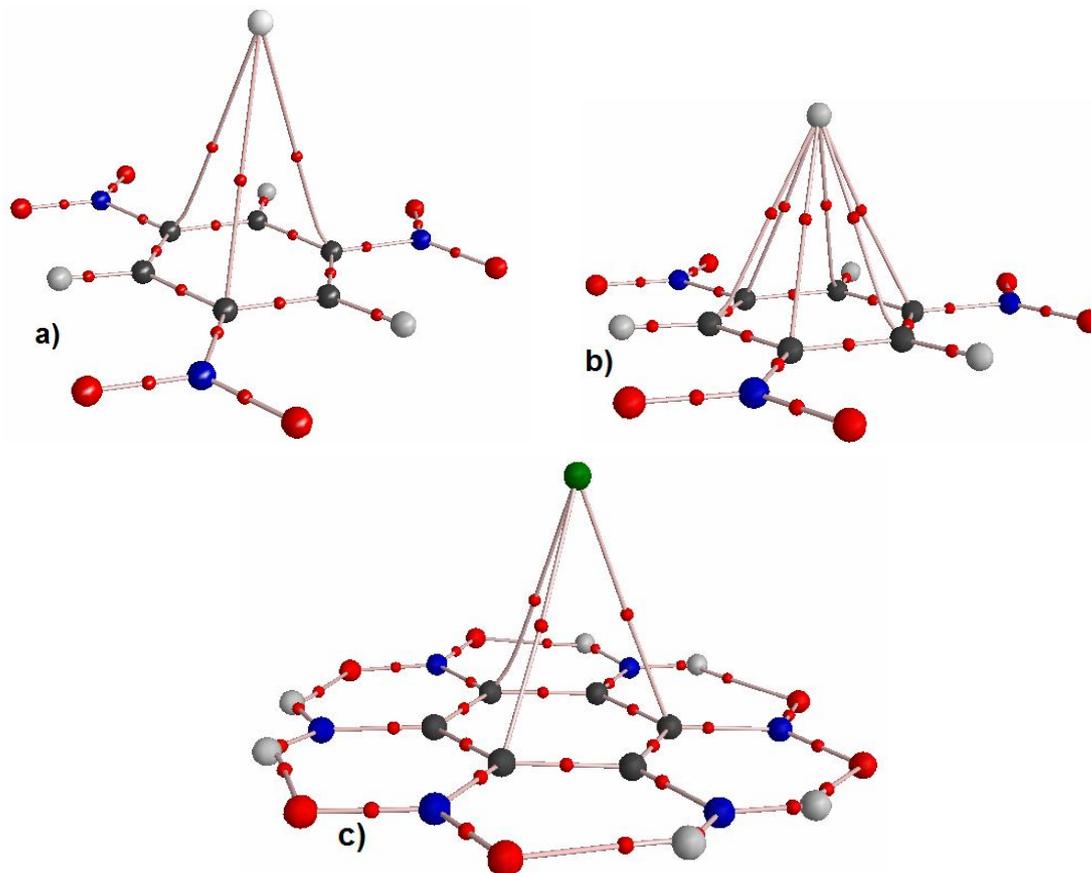


Fig. 2. Some typical molecular graphs obtained from AIM analysis for TNB...A (a and b) and ANB...A (c) complexes (A = H⁻, F⁻, Cl⁻ and Br⁻). Small red spheres represent bond critical points (BCPs).

demonstrate the strengthening of IMHBs of the parent molecule (ANB) in the presence of the anion- π interactions.

Additionally, the nature of non-covalent interactions has been explored by the negative ratio of the Hamiltonian components ($-G/V$). This value is equal to 0.5 for the covalent and ≥ 1 for the electrostatic interactions, while the partial covalent interactions have the $-G/V$ value between 0.5 and 1. As can be seen in Table 3, the $-G/V_{\pi \cdots A}$ values are more than 1 that reveals their electrostatic nature. However, the $-G/V_{H \cdots O}$ values of the IMHB interactions indicate its partial covalent character. Additionally, these values clearly show that the simultaneous presence of anion- π and IMHB interactions increases the covalent nature of both of the interactions.

The Effects of Non-covalent Interactions on the Aromaticity and π -ED

It is obvious that the π -ED of RAHB units and aromaticity of the benzene ring can be under the influence of the anion- π and IMHB interactions. In the RAHB unit, the presence of six delocalized π -electrons leads to the formation of a quasi-aromatic ring [60], which its π -ED can be approximately evaluated by some aromaticity indices. On the basis of the previous works [61-63], the HOMA geometry based index is considered for evaluation of the π -ED and the aromaticity (Table 4). This index is calculated according to formula proposed by Kruszewski and Krygowski [52]:

Table 3. The Selected Topological Properties of Electron Density (a.u. $\times 10^2$ Except -G/V) Obtained by AIM Analysis

Name	n	π -A Interaction					HB Interaction				
		$\rho(r)$	$\nabla^2\rho(r)$	H(r)	V(r)	-G/V	$\rho(r)$	$\nabla^2\rho(r)$	H(r)	V(r)	-G/V
TNB \cdots Br $^-$	3	0.876	2.552	-0.107	-0.423	1.254	-	-	-	-	-
TNB \cdots Cl $^-$	3	0.933	2.967	-0.134	-0.474	1.282	-	-	-	-	-
TNB \cdots F $^-$	3	1.555	6.327	-0.161	-1.261	1.127	-	-	-	-	-
TNB \cdots H $^-$	6	0.963	2.199	-0.064	-0.422	1.151	-	-	-	-	-
ANB \cdots Br $^-$	3	0.989	2.798	-0.111	-0.478	1.232	4.682	18.454	0.136	-4.886	0.972
ANB \cdots Cl $^-$	3	1.129	3.413	-0.133	-0.588	1.226	4.824	18.712	0.205	-5.088	0.960
ANB \cdots F $^-$	3	1.850	7.342	-0.149	-1.536	1.097	4.959	18.778	0.285	-5.264	0.946
ANB \cdots H $^-$	3	1.219	2.657	-0.068	-0.528	1.130	5.040	18.813	0.333	-5.370	0.938
ANB	-	-	-	-	-	-	4.642	18.481	0.110	-4.840	0.977

$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{opt} - R_i)^2 \quad (2)$$

where n is the number of bonds, R_{opt} and R_i are the optimal values of bond lengths for ideally and studied aromatic systems and α is constant. This geometrical index is directly related to the bond equalization and lies in the range 0-1. In other words, the aromatic rings with full delocalization have maxima (1) and full localization leads to minima (zero) values of HOMA.

Table 4 shows that the HOMA values of benzene ring for the ANB \cdots A complexes are considerably lower than those of the TNB \cdots A ones. According to these values, the aromaticity of benzene ring decreases in the presence of IMHB interactions. This conclusion is in agreement with the results obtained by Palusiak *et al.* [64]. The maximum reduction of HOMA is related to the $\pi\cdots\text{H}^-$ system (0.219) that is followed by $\pi\cdots\text{F}^-$ (0.213), $\pi\cdots\text{Br}^-$ (0.201) and $\pi\cdots\text{Cl}^-$

(0.192) systems. Also, the HOMA values of RAHB units arranged in the following order; ANB $\cdots\text{F}^-$ (0.800) > ANB $\cdots\text{H}^-$ (0.796) > ANB $\cdots\text{Cl}^-$ (0.748) > ANB $\cdots\text{Br}^-$ (0.744) > ANB (0.649). This order is in the fair agreement with the corresponding complexation energies and points that the π -ED of the RAHB units increase with strengthening the anion- π interaction. It seems that due to the repulsion effects between the negative charge of anions with π -electrons of the aromatic ring and also the electron affinity of the RAHB units some of the electron density of the benzene ring is transferred to the RAHB units. This phenomenon reduces the aromaticity of benzene ring and increases the π -ED of RAHB units and consequently strengthening both of the anion- π and IMHB interactions.

CONCLUSIONS

In the present study, the cooperative effects between the

Table 4. The HOMA Values of Investigated Complexes

Name	Benzene ring	RAHB unit
TNB...Br ⁻	0.990	-
TNB...Cl ⁻	0.990	-
TNB...F ⁻	0.988	-
TNB...H ⁻	0.991	-
TNB	0.994	-
ANB...Br ⁻	0.789	0.744
ANB...Cl ⁻	0.798	0.748
ANB...F ⁻	0.775	0.800
ANB...H ⁻	0.772	0.796
ANB	0.789	0.649

anion- π and IMHB interactions in the complexes of ANB with H⁻, F⁻, Cl⁻ and Br⁻ anions, at M06-2X/6-311++G(d,p) level of theory, were investigated. In this regard, various descriptors such as energetic, geometrical, spectroscopic and topological are employed to estimate the strength of the non-covalent interactions and compared with the corresponding values of the parent molecule (ANB) and TNB-A complexes, as a set of reference points. Finally, the influences of the simultaneous presence of the anion- π and IMHB on the significance of the π -ED of the RAHB units and aromaticity of the benzene ring are analyzed by the HOMA indicator.

Based on the complexation energies, for F⁻ and H⁻ anions, the strength of anion- π interactions increases at the presence of RAHB units, while for the Cl⁻ and Br⁻ anions, the reverse behavior is observed. It seems that the repulsion between the negative charge of the anion and the lone-pairs of N atoms, which are oriented toward the anion, reduce the attractive interactions of the anions and the benzene ring. However, the other results show that the coexistence of the anion- π and IMHB interactions increase the strength of the anion- π .

Additionally, the results obtained for all of the HB descriptors indicate that the interactions of the anions and the aromatic ring strengthen the IMHB interaction, which obey the following order; ANB...H⁻ > ANB...F⁻ > ANB...Cl⁻ > ANB...Br⁻ > ANB.

Furthermore, it was found that the simultaneous presence of the anion- π and IMHB interactions decreases the aromaticity of the benzene ring and increases the π -ED of the RAHB units.

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