

Mutual Interplay Between π -Electron Interactions and Simultaneous σ -Hole Interactions: A Computational Study

M. Solimannejad* and A.R. Gholipour

Quantum Chemistry Group, Department of Chemistry, Faculty of Sciences, Arak University, Arak 38156-8-8349, Iran

(Received 29 August 2013, Accepted 4 November 2013)

In this study, the role of interaction of π -electrons on the strength of simultaneous σ -hole interactions (pnicogen, chalcogen and halogen bonds) is investigated using the quantum chemical calculations. X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes (X = CN, F, Cl, Br, CH₃, OH and NH₂, TAZ= s-triazine and Y₁,Y₂ and Y₃ denote PH₂F, HSF and ClF molecules) is introduced as a model. The results show that interaction of π -electrons of X-ben and TAZ rings in X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes are effective in enhancing the strength of simultaneous σ -hole interactions than that in the TAZ \cdots Y₁,Y₂,Y₃ complexes. We show that the effect of the substituents on the studied complexes strongly depends on the nature of the substituents on the X-ben ring. The electron-donor and electron-acceptor substituents increase and decrease the stability of complexes, respectively. The electronic properties of the complexes have been analyzed using molecular electrostatic potential (MEP), and the parameters were derived from the quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) methodologies.

Keywords: σ -Hole, Cooperativity, DFT, S-triazine

INTRODUCTION

Noncovalent interactions between molecules play a very important role in supramolecular chemistry, molecular biology, and materials science [1]. Although research has traditionally focused on the more common hydrogen-bond (HB) interactions, interest has recently grown in another type of intermolecular interactions, namely, σ -hole bonding.

A σ -hole is a region of positive electrostatic potential on the extension of a covalent bond [2-6]. The pnictogen, chalcogen and halogen bonds were united under the general heading σ -hole bonding in 2007 [6]. These interactions are electrostatically-driven noncovalent interaction between a covalently-bonded atom of groups V-VII and a negative site. The positive region on atoms corresponds to the electronically-depleted outer lobe of the half-filled p-type orbital atom of groups V-VII.

Recently, we have studied the simultaneous σ -hole

interactions in complexes of substituted s-triazine (TAZ) with PH₂F, HSF and ClF moieties using the quantum chemical calculations [7]. According to results of that study, the electron-withdrawing/donating substituents decrease/increase the magnitude of the stabilization energies compared to the unsubstituted complexes. We have concluded that the main reason for different behavior between electron withdrawing and donating substituents can be due to the decrease/increase of π -electron cloud, respectively.

In the present work, we wish to analyse the mutual interplay between the interaction of π electrons with simultaneous σ -hole interactions (pnictogen, chalcogen and halogen bonds) in X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes (X = CN, F, Cl, Br, CH₃, OH and NH₂, TAZ = s-triazine and Y₁,Y₂ and Y₃ denotes PH₂F, HSF and ClF molecules) by using the results of DFT calculations. Such simple models can be useful to design novel supramolecular systems and drugs. These interactions play pivotal roles in a wide range of chemical and biological processes.

*Corresponding author. E-mail: m-solimannejad@araku.ac.ir

Computational Methods

The geometries of the X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes as well as the respective monomers, and dimers were optimized by using the M06-2X density functional theory (DFT) functional [8,9] paired with the aug-cc-pVDZ basis sets. Harmonic vibrational frequencies were computed for all optimized structures to characterize the stationary points. In these cases, structures have no imaginary vibrational frequency.

The stabilization energies were computed as the difference between the energy of the complex and the energy sum of the isolate monomers optimized individually. They were corrected for basis set superposition error (BSSE) using the counterpoise procedure proposed by Boys and Bernardi [10].

The topological analysis was carried out with the AIM2000 program [11]. The most negative values of the MEP point ($V_{S,\min}$) for the lone-pair region of the nitrogen atoms in s-triazine and the most positive values ($V_{S,\max}$) surrounding PH₂F, HSF and ClF molecules have been calculated with the multiwfn package [12]. The NBO analysis was carried out at the M06-2X/aug-cc-pVDZ level of theory. All optimizations were carried out using the GAMESS program [13].

RESULTS AND DISCUSSIONS

Figure 1 shows the overall patterns of surface electrostatic potential maps for the s-triazine ring, PH₂F, HSF, ClF and two X-ben (X= CN and NH₂) molecules. The CN and NH₂ substituents are strong electron withdrawing and donating groups which leads to decrease and increase of electron density for the π -electron cloud than other substituents, respectively. The stability of the studied complexes correlated well with this substituent effects, as shown in Table 1. Table 1 lists the most positive surface electrostatic potentials ($V_{S,\max}$) in the PH₂F, HSF, ClF monomers, and the most negative values of the MEP point ($V_{S,\min}$) for the lone-pair region of the nitrogen atoms in s-triazine. Of primary interest are the locations of the most negative and the most positive V_S , the $V_{S,\min}$ and $V_{S,\max}$, that are relevant to the approach of electrophiles and nucleophiles, respectively. The positive region can interact with an electronegative atom/group, thereby giving rise to a

directional interaction.

Molecular models used in the present study as X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes are depicted in Fig. 2. It is actually the interaction of π -electrons on one system and the deficiency of π -electrons in the others along with σ -hole interactions. The presence of X-ben increases the π -electron cloud by pushing electron density forward the center of the s-triazine ring, so lone pairs of nitrogen atoms in s-triazine ring interact more with the P, S and Cl atoms, that means the π -cloud is transmitted from the X-ben ring to the π system of TAZ \cdots Y₁,Y₂,Y₃ complex.

The obtained results for X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes will be discussed first; then they are compared with TAZ \cdots Y₁,Y₂,Y₃ complexes. The total binding energies of X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes ($\Delta E = E_{X\text{-ben||TAZ}\cdots Y_1, Y_2, Y_3 \text{ complexes}} - \sum E_{\text{Monomer}}$), calculated at M06-2X/aug-cc-pVDZ level of theory and corrected with BSSE, are summarized in Table 2. The BSSE corrected binding energies increase from -26.77 to -30.92 kcal mol⁻¹. The inset of substituents in Table 2 is given in the order of electron donating strength NH₂ > OH > CH₃ > H > Br > Cl > F > CN in terms of the Hammett constants.

As can be seen in Table 2, the stabilization energies of X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes increase compared to ben||TAZ \cdots Y₁,Y₂,Y₃ complexes, and it is equal to -26.77 kcal mol⁻¹ for ben||TAZ \cdots Y₁,Y₂,Y₃ complexes. The highest and lowest stabilization energies correspond to NH₂-ben||TAZ \cdots Y₁,Y₂,Y₃ and CN-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes with -30.92 and -27.46 kcal mol⁻¹, respectively, among the substituted complexes. This can be interpreted according to MEP of CN-benzene and NH₂-benzene as depicted in Fig. 1. On the basis of the calculated binding energies, the trend in the strength of the intermolecular interactions in X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes is NH₂ > OH > CH₃ > Br > Cl > F > CN > H. All substituents, whether electron-donating or electron-withdrawing, increase the strength of stabilization energies compared to an unsubstituted case (X = H).

To clarify the substituent effect on these interactions, we considered the relationship between stabilization energies and Hammett constants. The Hammett constants σ_{para} or σ_{meta} may be useful parameters to describe intermolecular interactions in X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes. But it would be more realistic to use σ_{total} ($\sigma_{\text{total}} = \sigma_{\text{para}} + \sigma_{\text{meta}}$) as a

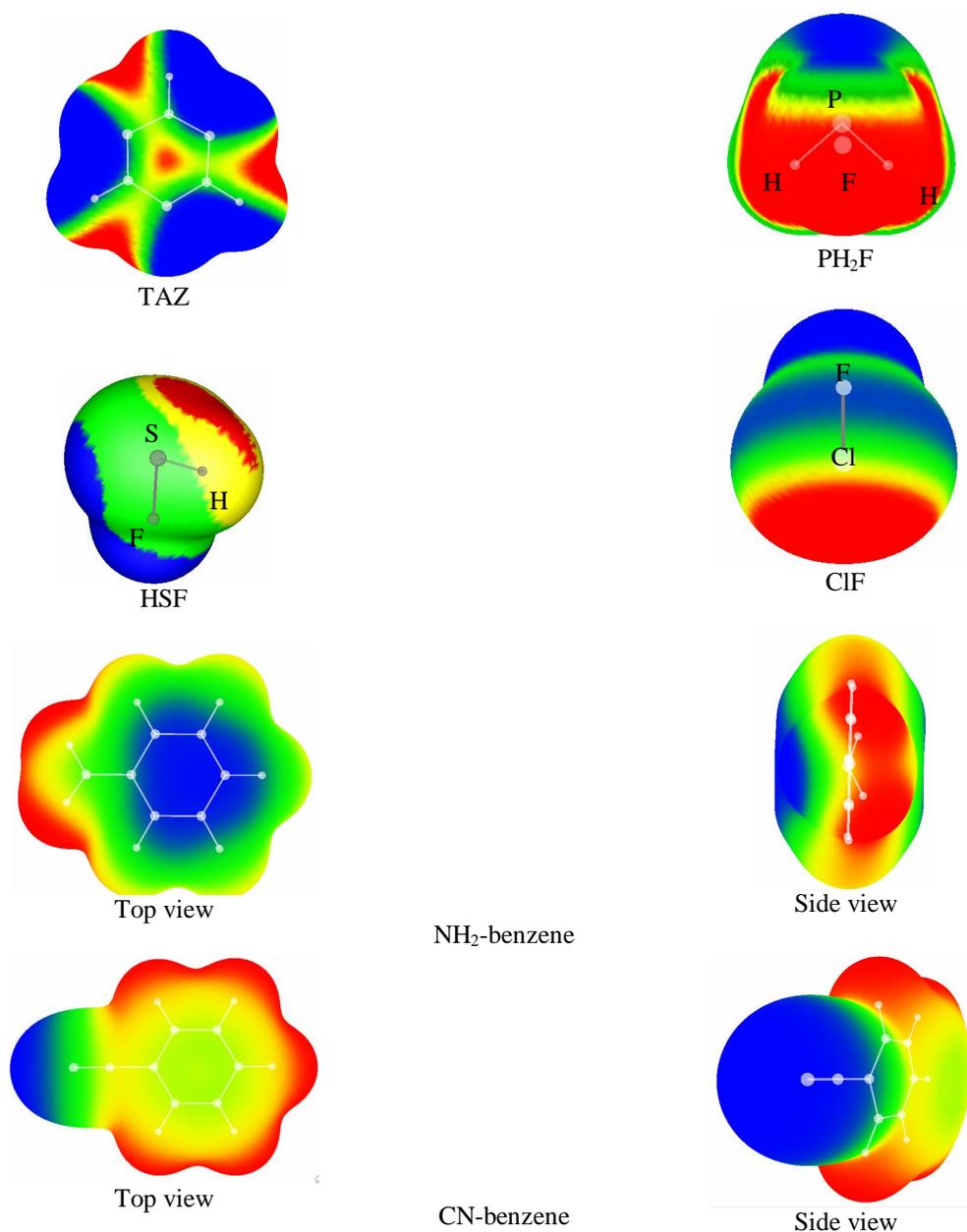
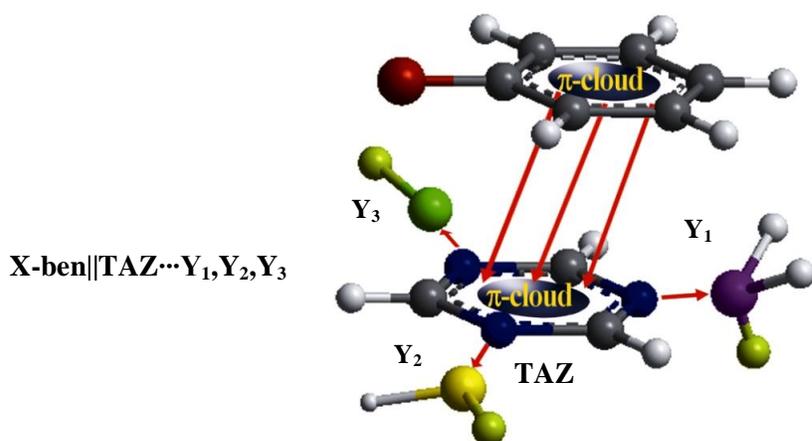


Fig. 1. The molecular electrostatic potential on the electron density isosurface of $0.001 \text{ electrons Bohr}^{-3}$ has been obtained and depicted using the surface analysis suite program. Among the electronic properties of these molecules, the molecular electrostatic potential (MEP) has been chosen to find those regions where electron rich moieties can interact. Molecular surface electrostatic potential of PH₂F, HSF, CIF, S-triazine, CN-ben and NH₂-ben computed on the 0.001 au contour of the electronic density. The σ -hole along the extension of the F-P, F-S and F-Cl bonds is shown in red. Note the negative and positive regions are blue and red, respectively.

Table 1. Maximum ($V_{S,max}$) and Minimum ($V_{S,min}$) Electrostatic Potentials (kcal mol^{-1}) on the 0.001 au Electron Density Isosurface of the Isolated Monomers at M06-2x/aug-cc-pVDZ

	CIF	HSF	PH ₂ F	s-triazine
$V_{S,max}$	38.968	40.469	37.2666	
$V_{S,min}$				-24.874

**Fig. 2.** Molecular models used in the present study. The results indicate the electron withdrawing and donating substituents increase the magnitude of the stabilization energies, compared to the unsubstituted ben||TAZ...Y₁,Y₂,Y₃ complex. (red spherical = CN, F, Cl, Br, CH₃, OH and NH₂ substituents and Y₁, Y₂ and Y₃ denotes PH₂F, HSF, and CIF molecules).**Table 2.** The Stabilization (ΔE) and Synergetic Energies (Kcal mol^{-1}) of Studied Complexes. The most Important Geometrical Parameters (in Å) Obtained for X-ben||TAZ...Y₁,Y₂,Y₃ Complexes at M06-2X/aug-cc-pVDZ Level of Theory

X	ΔE	E_{syn}	σ_{total}	$R_{P...N}$	$R_{S...N}$	$R_{Cl...N}$	$R_{cen...cen}$
NH ₂	-30.92	-3.10	-0.82	2.726	2.544	2.337	3.771
OH	-30.23	-3.02	-0.25	2.741	2.579	2.447	3.393
CH ₃	-29.02	-2.85	-0.20	2.742	2.569	2.416	3.820
H	-26.77	-2.05	0.00	2.747	2.592	2.431	3.881
Br	-28.88	-2.76	0.31	2.751	2.594	2.434	3.432
Cl	-28.55	-2.72	0.30	2.749	2.614	2.437	3.831
F	-27.98	-2.51	0.49	2.756	2.621	2.456	3.811
CN	-27.46	-2.50	1.26	2.760	2.634	2.462	3.510
TAZ...Y ₁ , Y ₂ , Y ₃	-19.42	2.31	-	2.775	2.640	2.484	-

new parameter to describe the interactions in these complexes [15-17] (see Table 2). As can be seen in Fig. 4, there is a reasonable correlation between ΔE and σ_{total} for X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes. The correlation ($R^2 = 0.87$) demonstrates that electrostatic effect of the substituents is prominent in these complexes.

As can be seen in Table 2, the X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes are more stabilized as the electron donating ability of the substituents increases, because of the increased amount of π -electron cloud in the s-triazine ring. The presence of electron donating substituents increases the π -electron cloud by pushing electron density forward the center of the s-triazine ring, so lone pairs of nitrogen atoms in s-triazine ring interact more with the P, S and Cl atoms. That means the π -cloud is transmitted from the X-ben ring to the π -system of TAZ \cdots Y₁,Y₂,Y₃ complex (see Fig. 2).

By replacing the electron-donating substituents with electron-withdrawing substituents, the interaction energy is decreased. The smallest interaction energy is found for the CN-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes (-27.46 kcal mol⁻¹). Electron-withdrawing substituents decrease the π -electron cloud by pulling electron density of the center of the X-ben ring, so the interaction of X-ben with TAZ \cdots Y₁,Y₂,Y₃ will be less able to transmit the electron density from the X-ben ring through the conjugated π -electron cloud to s-triazine ring, so lone pairs of nitrogen atoms in the TAZ \cdots Y₁,Y₂,Y₃ complex interact less with the P, S and Cl atoms.

All substituents, whether electron-donating or electron-withdrawing, increase the strength of stabilization energies relative to an unsubstituted case (X = H). Wheeler and Houk [18] indicated that the substituent effects in the sandwich configuration of the benzene dimers do not involve the π -system of the substituted benzene, but arise from direct electrostatic interactions between the substituents and the unsubstituted ring. They believed that additional dispersive interactions between the substituents and the other ring preferentially stabilize the most substituted dimers. Also, in a published communication [19], Ringer and Sherrill showed that the finding of Wheeler and Houk is true for the data presented in their work, but it is not true for π - π interactions in general. With respect to their results, the overall stability of the substituted complexes can be significantly affected by the differential dispersion effects.

We estimated the synergetic energy E_{syn} by using $E_{\text{syn}} = \Delta E_{\text{X-ben||TAZ}\cdots\text{Y}_1,\text{Y}_2,\text{Y}_3} - \Delta E_{\text{X-ben||TAZ}} - \Delta E_{\text{TAZ}\cdots\text{Y}_1} - \Delta E_{\text{TAZ}\cdots\text{Y}_2} - \Delta E_{\text{TAZ}\cdots\text{Y}_3}$. All the calculated terms are obtained from the optimized geometries. Synergetic energy (E_{syn}) is a practical parameter for estimating the interplay between different kinds of noncovalent interactions [20,21].

The values of E_{syn} range from -2.50 to -3.10 kcal mol⁻¹, and it is equal to -2.05 kcal mol⁻¹ for the unsubstituted case ben||TAZ \cdots Y₁,Y₂,Y₃ complex. The magnitude of E_{syn} for electron-donating substituents is more than that of the electron-withdrawing substituents. As can be seen in Fig. 5, a satisfactory linear relationship is observed between the synergetic energies and the stabilization energies ($R^2 = 0.97$). The values of E_{syn} were positive in X-TAZ \cdots Y₁,Y₂,Y₃ complexes [7], indicating diminutive effects in the complexes.

When s-triazine ring acts as an electron donor in the three simultaneous σ -hole bonds, diminutive effects occur in the TAZ \cdots Y₁,Y₂,Y₃ complex. On the contrary, where s-triazine ring takes part in interaction with X-ben and in the σ -hole bonds, cooperative effects are observed in the X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes. These results show that the addition of interaction with π -electrons is effective in enhancing the strength of simultaneous interactions of σ -hole (pnictogen, chalcogen and halogen) bonds.

The $R_{\text{cen}\cdots\text{cen}}$, $R_{\text{P}\cdots\text{N}}$, $R_{\text{S}\cdots\text{N}}$ and $R_{\text{Cl}\cdots\text{N}}$ geometry parameters are used to indicate the strength of interactions; $R_{\text{cen}\cdots\text{cen}}$ is the distance between the center of X-ben and TAZ rings and $R_{\text{P}\cdots\text{N}}$, $R_{\text{S}\cdots\text{N}}$ and $R_{\text{Cl}\cdots\text{N}}$ are intermolecular distance of P \cdots N, S \cdots N and Cl \cdots N interactions in these complexes, respectively. Full geometry optimizations were performed for X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes at M06-2X/aug-cc-pVDZ level of theory. The $R_{\text{P}\cdots\text{N}}$, $R_{\text{S}\cdots\text{N}}$ and $R_{\text{Cl}\cdots\text{N}}$ of X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes decrease with increasing electron-donating character of substituents. As the electron-donating character of substituents in X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes increases, the pnictogen, chalcogen and halogen bond lengths decrease. A reverse behavior is observed for electron-withdrawing substituents, so that the decrease of π -electron cloud inside the ring causes the increase in the $R_{\text{P}\cdots\text{N}}$, $R_{\text{S}\cdots\text{N}}$ and $R_{\text{Cl}\cdots\text{N}}$. It is the smallest/largest in NH₂-ben||TAZ \cdots Y₁,Y₂,Y₃/CN-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes, respectively.

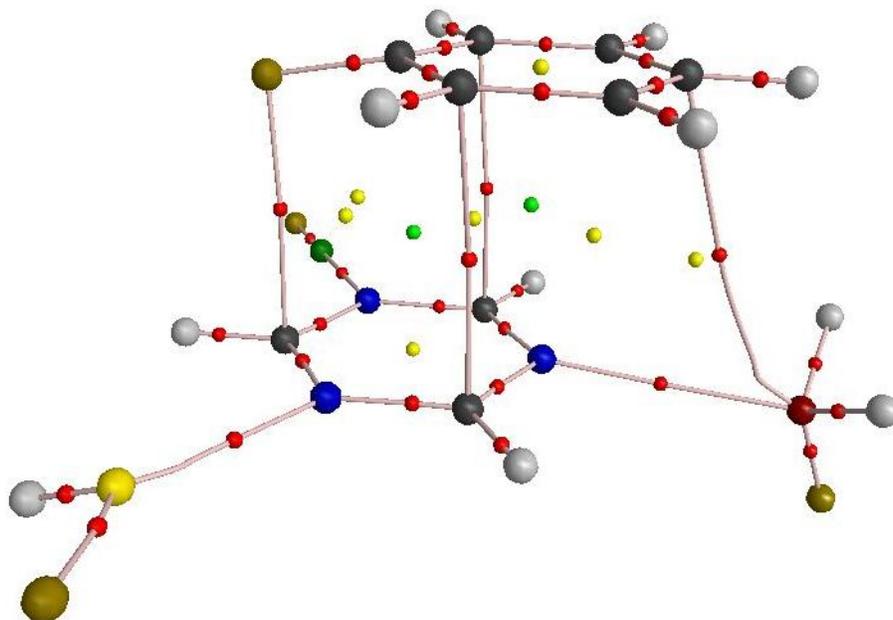


Fig. 3. Typical molecular graphs for X-ben||TAZ...Y₁, Y₂, Y₃ complexes. The small red, yellow, and green spheres correspond to BCP, RCP and CCP, respectively. Y₁, Y₂ and Y₃ denote PH₂F, HSF, and ClF molecules.

Table 3. Electron Densities ρ (in Electrons Bohr⁻³) at P...N, S...N and Cl...N BCPs in X-ben||TAZ...Y₁, Y₂, Y₃ Complexes Calculated at M06-2X/aug-cc-pVDZ level of Theory

X	P...N	S...N	Cl...N			
	ρ_{BCP}	ρ_{BCP}	ρ_{BCP}	ρ_{CCP}	ρ_{CCP}	$\Sigma\rho_{\text{CCP}}$
NH ₂	2.75	3.03	4.78	5.29	4.47	9.76
OH	2.19	2.80	3.64	5.43	4.30	9.73
CH ₃	2.30	2.85	3.92	5.30	4.40	9.70
H	2.15	2.71	3.70	4.74	4.38	9.12
Br	1.95	2.61	3.75	4.84	4.49	9.34
Cl	2.02	2.59	3.62	4.98	4.57	9.55
F	1.93	2.51	3.53	5.40	4.10	9.50
CN	1.93	2.51	3.50	5.22	4.23	9.45
TAZ...Y ₁ , Y ₂ , Y ₃	1.90	2.50	3.34	-	-	-

$\rho \times 10^2$

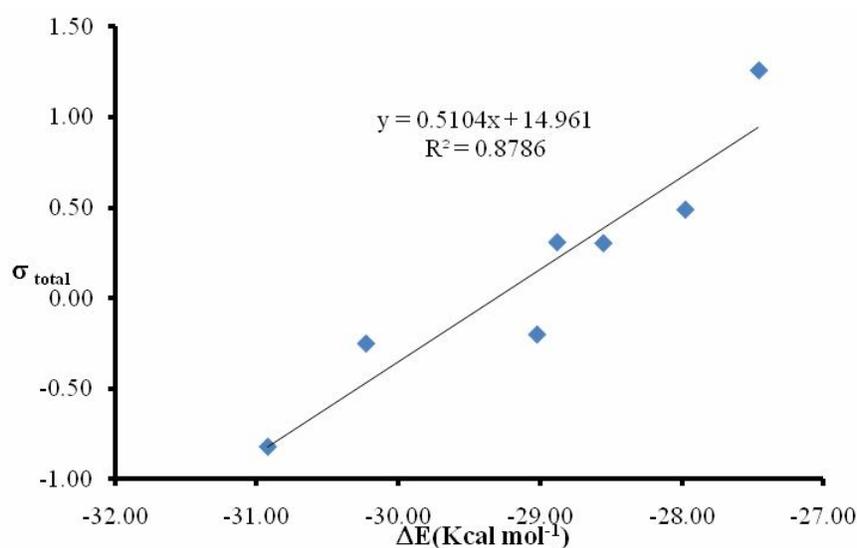


Fig. 4. Correlation between the stabilization energies (ΔE) and the Hammett constants (σ_{total}) for X-ben||TAZ...Y₁, Y₂, Y₃ complexes.

Table 4. The Results of $E^{(2)}$ from NBO Analysis in X-ben||TAZ...Y₁, Y₂, Y₃ Complexes, Corresponds to $n_N \rightarrow \sigma_{P-F}^*$, $n_N \rightarrow \sigma_{S-F}^*$ and $n_N \rightarrow \sigma_{Cl-F}^*$ Interactions

X	$n_N \rightarrow \sigma_{P-F}^*$	$n_N \rightarrow \sigma_{S-F}^*$	$n_N \rightarrow \sigma_{Cl-F}^*$
NH ₂	13.69	15.46	22.21
OH	10.89	13.79	18.91
CH ₃	11.79	14.2	21.20
H	11.00	13.70	20.50
Br	10.07	13.40	19.80
Cl	10.93	13.31	20.51
F	10.91	13.21	19.40
CN	9.99	12.31	18.42
TAZ...Y ₁ , Y ₂ , Y ₃	9.65	12.25	18.32

The equilibrium distance of the pnictogen, chalcogen and halogen bonds ($R_{P...N}$, $R_{S...N}$ and $R_{Cl...N}$) in the X-ben||TAZ...Y₁, Y₂, Y₃ complexes is shorter compared to that in TAZ...Y₁, Y₂, Y₃ complex. These results indicate that the presence of additional interaction with π -electrons strengthens the simultaneous σ -hole bonds (see Table 2). The difference between the P...N, S...N and Cl...N bond

lengths in TAZ...Y₁, Y₂, Y₃ and X-ben||TAZ...Y₁, Y₂, Y₃ complexes reflects the influence of π -electron interaction on the pnictogen, chalcogen and halogen bond interactions (in a cooperative fashion).

Table 2 shows that the substituted complexes have shorter $R_{\text{cen-cen}}$ in comparison with unsubstituted ones, in agreement with higher interactions in substituted

complexes. The longest and shortest $R_{\text{cen-cen}}$ correspond to $\text{NH}_2\text{-ben||TAZ}\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ and $\text{CN-ben||TAZ}\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes (without considering unsubstituted case), respectively.

Detailed information about the strength and nature of interactions in the present study can be obtained from topological analysis of their electron densities. Applying the QTAIM to all the complexes discussed gives us the opportunity to find bond critical points, BCP, and analyze their electron density properties. It has previously shown that the properties of cage critical points (CCPs) correlate with interaction of π -electrons [22]. Two CCPs describe interactions of X-ben and TAZ rings in the X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes (see Fig. 3).

The topological properties of ρ calculated at the CCPs of the π -stacking may be treated as a measure of the π -stacking strength [22]. All substituents, whether electron-donating or electron -withdrawing, increase electron density relative to an unsubstituted case ($X = \text{H}$). Thus, increasing ρ_{CCPs} reveals that the π -stacking involved in X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes is enhanced by all substituents. The comparison of the strength of interactions is difficult by evaluation of individual CCPs. We added the values of ρ calculated at intermolecular CCPs, $\Sigma\rho_{\text{ccp}}$ to obtain a measure for comparing π -stacking interactions.

It is worthwhile to mention that the values of the electron density calculated at the BCPs of P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ interactions are lower for electron-withdrawing substituents than those for other substituents. The electron-withdrawing substituents in X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes pull the lone pair of nitrogen atoms of s-triazine inside the ring and decrease electron density of P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ interactions. On the other hand, complexes containing electron-donating substituents exhibit higher ρ BCPs values than other substituents (see Table 3). The maximum/minimum values of electron density for the σ -hole bonds have been observed in $\text{NH}_2\text{-ben||TAZ}\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ / $\text{CN-ben||TAZ}\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes compared to other complexes.

As can be seen in Fig. 6, there are correlations between bonds length and electron density at BCPs of P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ interactions. It is observed that the magnitude of slope in established linear correlations, for complexes with S $\cdots\text{N}$ interaction is higher than those of with P $\cdots\text{N}$ and

Cl $\cdots\text{N}$ interactions (Fig. 6). It means that electron density at BCPs of chalcogen interaction is more dependent on the nature of substituent compared with halogen, and pnictogen interactions. Comparing the results of the present study with the previous one [7] about X-TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes reveals that electron density at BCPs of pnictogen and chalcogen interaction is more dependent on the nature of substituent in X-TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ and X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$, respectively.

As shown in Table 3, for all substituents the ρ_{BCP} values calculated at P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ BCPs in X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes are much larger than those of TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complex. We realized that an important cooperative effect tends to increase the stabilization of pnictogen, chalcogen and halogen bonds. These values give information about the effect of π electron interaction on P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ interactions in X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes.

For a better understanding of substituents effect on the σ -hole bonds in X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes, NBO analysis has been carried out at M06-2X/aug-cc-pVDZ level of theory. Herein, the $n_{\text{N}} \rightarrow \sigma_{\text{P-F}}^*$, $n_{\text{N}} \rightarrow \sigma_{\text{S-F}}^*$ and $n_{\text{N}} \rightarrow \sigma_{\text{Cl-F}}^*$ interaction energies can be considered as measure of the strength of pnictogen, chalcogen and halogen bonds, respectively. These interactions are due to a large degree of charge transfer from the N lone pairs into the sigma anti-bonding orbital of the P-F, S-F and Cl-F bonds.

The $E^{(2)}$ values of these interactions can be used as an index to predict the strength and play an important role in the stabilization of the P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ interactions in X-ben||TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes. Table 4 shows that the electron-donating substituents increase the electron density on the nitrogen atoms of s-triazine ring and increase its inclination in polarization of P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ interactions by increasing the $E^{(2)}$ values of $n_{\text{N}} \rightarrow \sigma_{\text{P-F}}^*$, $n_{\text{N}} \rightarrow \sigma_{\text{S-F}}^*$ and $n_{\text{N}} \rightarrow \sigma_{\text{Cl-F}}^*$ interactions. For the pnictogen, chalcogen and halogen bonds the maximum/minimum values of $E^{(2)}$ have been observed for $\text{NH}_2\text{-ben||TAZ}\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ / $\text{CN-ben||TAZ}\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complexes in line with stability of them.

For all substituents the $E^{(2)}$ values of $n_{\text{N}} \rightarrow \sigma_{\text{P-F}}^*$, $n_{\text{N}} \rightarrow \sigma_{\text{S-F}}^*$ and $n_{\text{N}} \rightarrow \sigma_{\text{Cl-F}}^*$ value is much larger than the those of TAZ $\cdots\text{Y}_1, \text{Y}_2, \text{Y}_3$ complex, this means that orbital interactions of P $\cdots\text{N}$, S $\cdots\text{N}$ and Cl $\cdots\text{N}$ interactions in X-

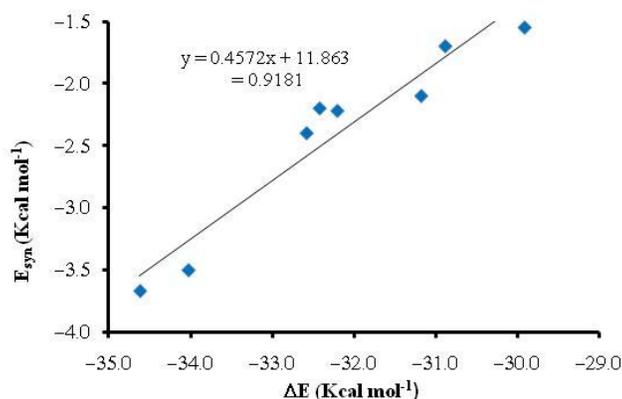


Fig. 5. Correlation between the stabilization energies (ΔE) and synergetic energies (E_{syn}) for X-ben||TAZ... Y_1, Y_2, Y_3 complexes.

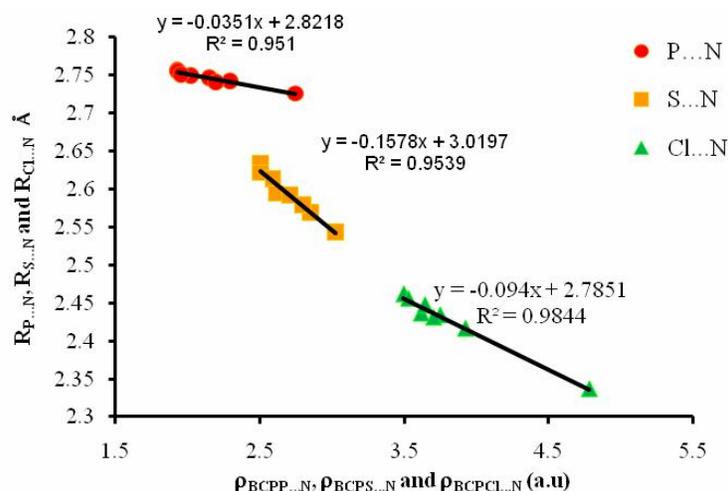


Fig. 6. The electron density at the bond critical points of the simultaneous σ -hole (pnictogen, chalcogen and halogen) bonds vs. bond lengths in X-ben||TAZ... Y_1, Y_2, Y_3 complexes.

ben||TAZ... Y_1, Y_2, Y_3 complexes are stronger than TAZ... Y_1, Y_2, Y_3 complex. These results show that the addition of π -interaction is effective in enhancing the strength of $E^{(2)}$ values of σ -hole bonds in X-ben||TAZ... Y_1, Y_2, Y_3 complexes.

CONCLUSIONS

The X-ben||TAZ... Y_1, Y_2, Y_3 complexes are investigated

to find ways to enhance the strength of simultaneous σ -hole (pnictogen, chalcogen and halogen) bonds in the ben||TAZ... Y_1, Y_2, Y_3 complexes.

The interaction strength has been estimated mainly in terms of the stabilization energies and the binding distances. All substituents increase the magnitude of the binding energies compared to the unsubstituted ben||TAZ... Y_1, Y_2, Y_3 complexes. The strength of interactions is correlated with nature of substituents. The binding energies in the electron-

donating substituents are more negative than the electron-withdrawing substituents. The maximum/minimum values of stabilization energies in the complexes are -30.92 and -27.46 kcal mol⁻¹ for NH₂ and CN, respectively.

Good correlations are observed among energetic, geometries data and the other parameters obtained from AIM, and σ_{total} values the in X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes. The negative values of E_{syn} indicate cooperative effects in the X-ben||TAZ \cdots Y₁,Y₂,Y₃ complexes.

REFERENCES

- [1] K. Muller-Dethlefs, P. Hobza, *Chem. Rev.* 100 (2000) 143.
- [2] P. Politzer, J.S. Murray, T. Clark, *Phys. Chem. Chem. Phys.* 15 (2013) 11178 and references therein.
- [3] T. Clark, *WIREs Comput. Mol. Sci.* 3 (2013) 13.
- [4] P. Politzer, J.S. Murray, T. Clark, *Phys. Chem. Chem. Phys.* 12 (2010) 7748.
- [5] J.S. Murray, A.K.E. Riley, P. Politzer, T. Clark, *Aust. J. Chem.* 63 (2010) 1598.
- [6] T. Clark, M. Hennemann, J.S. Murray, P. Politzer, *J. Mol. Model.* 2 (2007) 291.
- [7] M. Solimannejad, A.R. Gholipour, *Struct. Chem.* 24 (2013) 1705.
- [8] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [9] Y. Zhao, N.E. Schultz, D.G. Truhlar, *J. Chem. Theory. Comput.* 2 (2006) 364.
- [10] S.B. Boys, F. Bernardi, *Mol. Phys.* 19 (1970) 553.
- [11] K.F. Biegler, W.J. Schonbohm, D. Bayles, J. Comput. Chem. 22 (2001) 545, AIM2000.
- [12] T. Lu, F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.* 33 (2012) 580.
- [13] M.W. Schmidt, K.K. Baldrige, J.A. Boat, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347.
- [14] F.A. Bulat, A. Toro-Labbe, T. Brinck, J.S. Murray, P. Politzer (2010) *J. Mol. Model.* 16 (2010) 1679.
- [15] A. Ebrahimi, M. Habibi, R.S. Neyband, A.R. Gholipour, *Phys. Chem. Chem. Phys.* 11 (2009) 11424.
- [16] A.R. Gholipour, H. Saydi, M.S. Neiband, R.S. Neyband, *Struct. Chem.* 23 (2012) 367.
- [17] W. Zhu, X. Tan, J. Shen, X. Luo, F. Cheng, P.C. Mok, R. Ji, K. Chen, H. Jiang, *J. Phys. Chem. A* 107 (2003) 2296.
- [18] S.E. Wheeler, K.N. Houk, *J. Am. Chem. Soc.* 130 (2008) 10854.
- [19] A.L. Ringer, C.D. Sherrill, *J. Am. Chem. Soc.* 131 (2009) 4574.
- [20] X. Lucas, C. Estarellas, D. Escudero, A. Frontera, D. Quinonero, P.M. Deya, *Chem. Phys. Chem.* 10 (2009) 2256.
- [21] D. Escudero, A. Frontera, D. Quinonero, P.M. Deya, *J. Comput. Chem.* 30 (2009) 75.
- [22] O.A. Zhikol, O.V. Shishkin, K.A. Lyssenko, J. Leszczynski, *J. Chem. Phys.* 122 (2005) 144104.