



Article

Effects of Lewis Basicity and Acidity on σ -Hole Interactions in Carbon-Bearing Complexes: A Comparative Ab Initio Study

Mahmoud A. A. Ibrahim ^{1,2,*} , Mohammed N. I. Shehata ¹ , Al-shimaa S. M. Rady ¹ , Hassan A. A. Abuelliel ¹, Heba S. M. Abd Elhafez ¹, Ahmed M. Shawky ³ , Hesham Farouk Oraby ⁴, Tamer H. A. Hasanin ⁵, Mahmoud E. S. Soliman ⁶ and Nayra A. M. Moussa ¹

¹ Computational Chemistry Laboratory, Chemistry Department, Faculty of Science, Minia University, Minia 61519, Egypt

² School of Health Sciences, University of Kwa-Zulu-Natal, Westville, Durban 4000, South Africa

³ Science and Technology Unit (STU), Umm Al-Qura University, Makkah 21955, Saudi Arabia

⁴ Deanship of Scientific Research, Umm Al-Qura University, Makkah 21955, Saudi Arabia

⁵ Department of Chemistry, College of Science, Jouf University, Sakaka P.O. Box 2014, Saudi Arabia

⁶ Molecular Bio-Computation and Drug Design Research Laboratory, School of Health Sciences, University of Kwa-Zulu-Natal, Westville, Durban 4000, South Africa

* Correspondence: m.ibrahim@compchem.net



Citation: Ibrahim, M.A.A.; Shehata, M.N.I.; Rady, A.-s.S.M.; Abuelliel, H.A.A.; Abd Elhafez, H.S.M.; Shawky, A.M.; Oraby, H.F.; Hasanin, T.H.A.; Soliman, M.E.S.; Moussa, N.A.M. Effects of Lewis Basicity and Acidity on σ -Hole Interactions in Carbon-Bearing Complexes: A Comparative Ab Initio Study. *Int. J. Mol. Sci.* **2022**, *23*, 13023. <https://doi.org/10.3390/ijms232113023>

Academic Editors: Mihai V. Putz and Attila Bende

Received: 21 September 2022

Accepted: 19 October 2022

Published: 27 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: The effects of Lewis basicity and acidity on σ -hole interactions were investigated using two sets of carbon-containing complexes. In Set I, the effect of Lewis basicity was studied by substituting the X_3/X atom(s) of the $NC-C_6H_2-X_3$ and NCX Lewis bases (LB) with F, Cl, Br, or I. In Set II, the $W-C-F_3$ and $F-C-X_3$ (where X and W = F, Cl, Br, and I) molecules were utilized as Lewis acid (LA) centers. Concerning the Lewis basicity effect, higher negative interaction energies (E_{int}) were observed for the $F-C-F_3 \cdots NC-C_6H_2-X_3$ complexes compared with the $F-C-F_3 \cdots NCX$ analogs. Moreover, significant E_{int} was recorded for Set I complexes, along with decreasing the electron-withdrawing power of the X_3/X atom(s). Among Set I complexes, the highest negative E_{int} was ascribed to the $F-C-F_3 \cdots NC-C_6H_2-I_3$ complex with a value of -1.23 kcal/mol. For Set II complexes, E_{int} values of $F-C-X_3$ bearing complexes were noted within the -1.05 to -2.08 kcal/mol scope, while they ranged from -0.82 to -1.20 kcal/mol for the $W-C-F_3$ analogs. However, $V_{s,max}$ quantities exhibited higher values in the case of $W-C-F_3$ molecules compared with $F-C-X_3$; preferable negative E_{int} were ascribed to the $F-C-X_3$ bearing complexes. These findings were delineated as a consequence of the promoted contributions of the X_3 substituents. Dispersion forces (E_{disp}) were identified as the dominant forces for these interactions. The obtained results provide a foundation for fields such as crystal engineering and supramolecular chemistry studies that focus on understanding the characteristics of carbon-bearing complexes.

Keywords: σ -hole interactions; tetrel bonding interactions; Lewis basicity; Lewis acidity; ab initio calculations

1. Introduction

Noncovalent interactions are evoking resurgent interest owing to their ubiquitous contributions to several fields, including crystal materials [1,2], molecular recognition [3,4], chemical reactions [5,6], adsorption [7], and biological processes [8]. Accordingly, further understanding of the origin and nature of noncovalent interactions along with their impacts on controlling molecular systems is one of the metrics of progress in modern chemistry. σ -Hole interaction is a crucial point of concern in the scope of noncovalent interactions due to its significant roles in ligand-acceptor interactions [9,10], self-assembly [11], and anion recognition [12].

The concept of σ -hole [13–15], as proposed by Politzer et al., was initially introduced as an insight into the halogen bonding phenomenon [16]. Afterward, it was extended to a remarkable family of noncovalent interactions in which the elements of group IV–VII

tend to interact with a nucleophile (i.e., π -system [17,18], anion [19,20], or radical [21]). According to the literature, it was reported that the resulting attractive forces mainly depend on a local electron depletion region around the tetrel [22–24], pnictogen [25–27], chalcogen [28–30], and halogen [31–34] atoms. This region is usually directed along the extension of the σ -bond, and is hence labeled as a σ -hole. From this perspective, the σ -hole magnitude was principally associated with the electronegativity of the σ -hole donors and the covalently bonded atoms [35,36]. σ -hole interactions can also be strengthened by increasing the Lewis basicity of the nucleophile [37].

Among such σ -hole-based interactions, tetrel bonding interactions have gathered immense attention from experimental [10,38] and theoretical [23,39,40] viewpoints. Tetrel bonding plays significant roles in catalysis [41,42], supramolecular chemistry [43,44], and biological processes [6]. Preliminary studies uncovered the inability of the tetrel-bearing molecules to interact with Lewis bases (LB), NH_3 as an example, and form tetrel bonds [45,46]. Remarkably, the electrostatic potentiality of tetrel-bearing systems to participate in tetrel bonding interactions was investigated with the help of point-of-charge (PoC) [47], and these observations were then confirmed using real Lewis bases [48,49]. An up-to-date work addressed the occurrence of σ -hole interactions within tetrel-bearing molecule...Lewis acid (LA) dimers [50]. In addition, Lewis base...tetrel-bearing molecule...Lewis base trimers were precisely characterized [51]. Moreover, the favorable ability of tetrel-bearing molecules to engage in like...like and unlike interactions with other neutral [22,52] and anion [53] candidates was revealed. Further, the effect of tetrel atomic size and its substituents on the tetrel bonding interactions within $\text{W-T-X}_3\cdots\text{LB}$ complexes (where T and X/W were tetrrels and halogens, respectively) were studied [47,50]. It was reported that the interaction energy became more favorable with increasing: (i) the tetrel atomic size (i.e., $\text{C} < \text{Si} < \text{Ge} < \text{Sn}$), (ii) electronegativity of W atom, and (iii) the atomic size of the X_3 halogens. More recently, the impact of external electric field (EEF) on these interactions was precisely assessed [54]. The negatively-directed EEF was found to decrease the interaction energies unfavorably. In contrast, the positively-directed EEF showed preferential enhancement of these energies.

Indeed, tetrel bonding interactions are still an area of active research. In view of this, the presented study was designed to develop a comprehensive understanding of the effects of Lewis basicity and acidity on the interactions in carbon-bearing complexes (Figure 1). To pursue the aim of the current study, two sets of carbon-bearing complexes were investigated. In Set I complexes, the effect of Lewis basicity was thoroughly studied in $\text{F-C-F}_3\cdots\text{NC-C}_6\text{H}_2\text{-X}_3/\text{NCX}$ (where $\text{X} = \text{F, Cl, Br, and I}$). In Set II complexes, the W-C-F_3 and F-C-X_3 (where $\text{X and W} = \text{F, Cl, Br, and I}$) molecules were utilized as Lewis acid (LA) centres to interact with $\text{NC-C}_6\text{H}_2\text{-F}_3/\text{NCF}$ as Lewis bases (LB). Geometrical optimization, electrostatic potential (EP) analyses, and point-of-charge (PoC) calculations were carried out for $\text{NC-C}_6\text{H}_2\text{-X}_3$, NCX , W-C-F_3 , and F-C-X_3 molecules. Interaction energy, quantum theory of atoms in molecules (QTAIM), and noncovalent interaction (NCI) index calculations were performed to uncover the strength and nature of the considered interactions. Symmetry-adapted perturbation theory (SAPT) analysis was also utilized to investigate the dominant forces within the studied interactions of the modeled complexes. The obtained findings would be informative for various ongoing works relevant to the scope of crystal engineering and materials science.

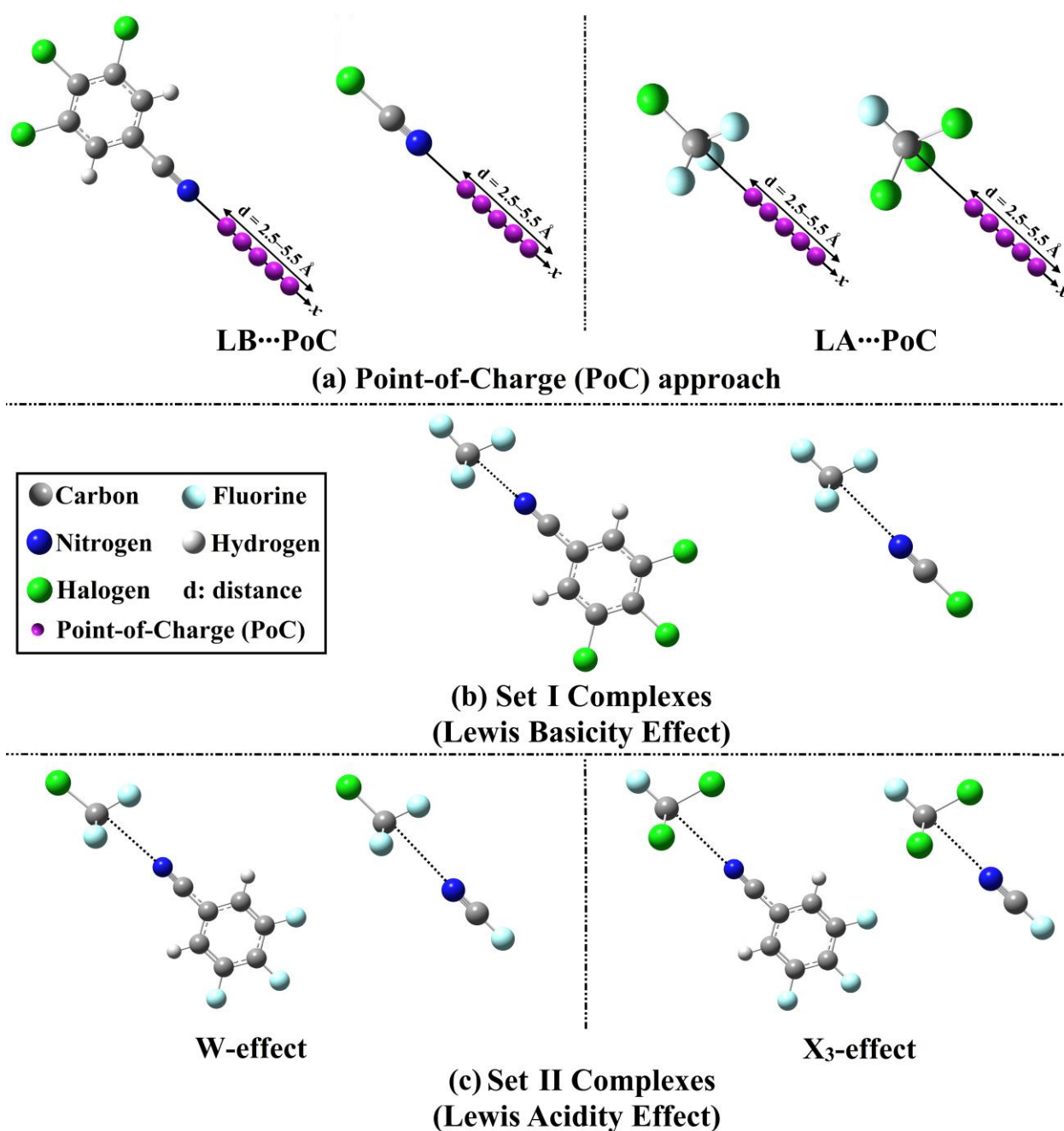


Figure 1. Illustrative representation for (a) the PoC calculations for Lewis base (LB)⋯ and Lewis acid (LA)⋯PoC systems, (b) Set I Complexes (F-C-F₃⋯NC-C₆H₂-X₃/⋯NCX), and (c) Set II Complexes (W-C-F₃⋯ and F-C-X₃⋯NC-C₆H₂-F₃/NCF).

2. Results and Discussion

2.1. Electrostatic Potential (EP) Analysis

EP analysis was applied as an informative tool that gives qualitative and quantitative insights into the nucleophilic and electrophilic nature of the chemical systems [55,56]. Figure 2 involves molecular electrostatic potential (MEP) maps for all the investigated systems along with the values of the $V_{s,min}$ (on NC-C₆H₂-X₃ and NCX Lewis bases), and $V_{s,max}$ (on W-C-F₃ and F-C-X₃ Lewis acids).

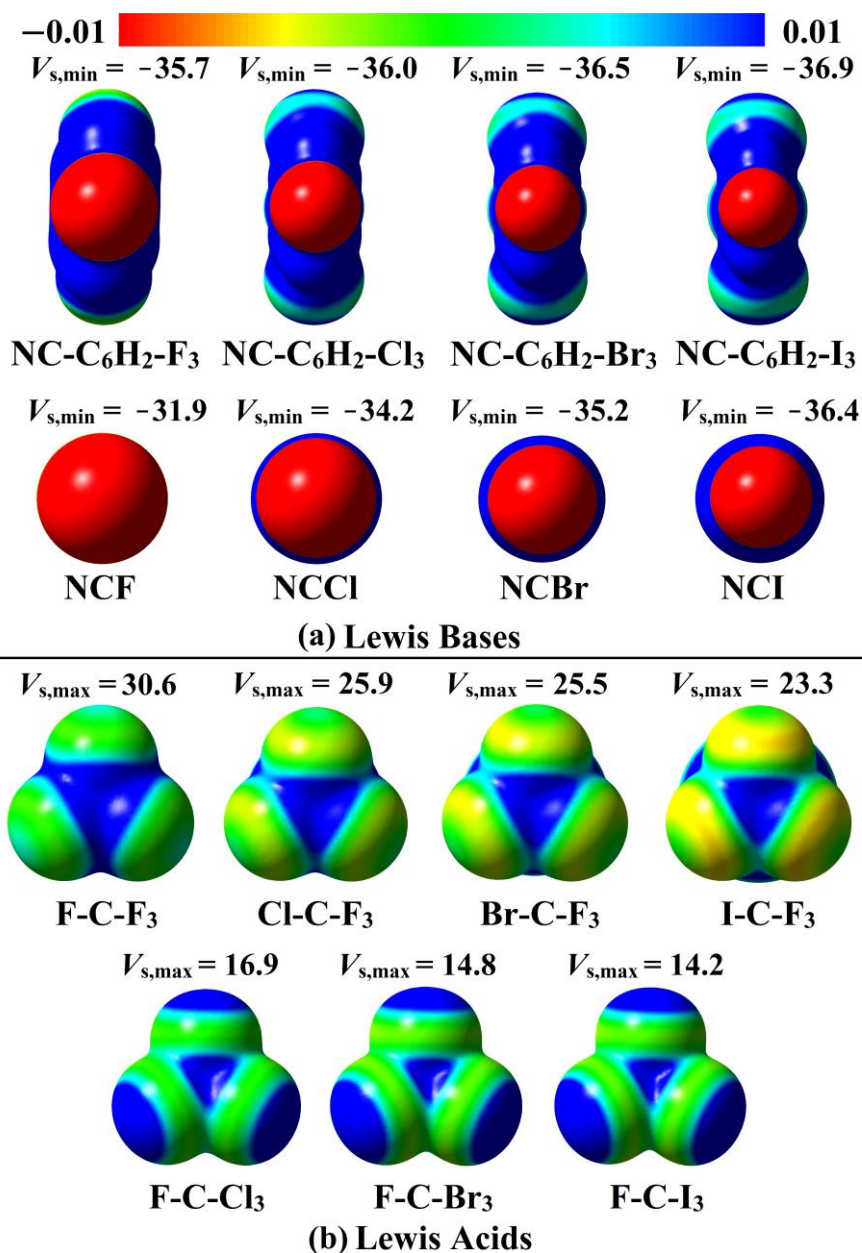


Figure 2. MEP maps of the utilized (a) NC-C₆H₂-X₃ and NCX Lewis bases (LB) and (b) W-C-F₃ and F-C-X₃ Lewis acids (LA) molecules. The EP in these maps aligned within the -0.01 and $+0.01$ au range (red to blue colors). The $V_{s,min}/V_{s,max}$ values are in kcal/mol.

From MEP maps shown in Figure 2, observable red (i.e., negative EP) regions were denoted over the N atom surfaces of the inspected LBs, spotting the favorable potentiality of the explored molecules to interact with LAs attractively. In addition, the $V_{s,min}$ values of the N atom (i.e., Lewis basicity) in the NC-C₆H₂-X₃ and NCX molecules were found to decrease with decreasing the atomic size of the X₃/X halogen(s) in the order of X = I > Br > Cl > F. For example, $V_{s,min}$ exhibited values of -36.4 , -35.2 , -34.2 , and -31.9 kcal/mol for the N atom of the NCI, NCBr, NCCl, and NCF molecules, respectively. It is also worth mentioning that the investigated NC-C₆H₂-X₃ molecules demonstrated more negative $V_{s,min}$ values than NCX analogs; for example, the $V_{s,min}$ values were -36.9 and -36.4 kcal/mol for NC-C₆H₂-I₃ and NCI, respectively.

Passing to the inspected LA centres, notable positive EP regions (i.e., σ -hole) with different sizes were perceived (Figure 2). Evidently, σ -holes with more prominent sizes

were observed within W-C-F₃ molecules compared with the F-C-X₃ counterparts, outlining the further ability of the former molecules to behave as carbon-bonding donors over the later ones. For instance, the $V_{s,max}$ values of the I-C-F₃ and F-C-I₃ molecules were 23.3 and 14.2 kcal/mol, respectively. As evident, the σ -hole size increased with raising the electron-withdrawing power of the W/X₃ halogen atom(s) that supported with appreciable $V_{s,max}$ values in the case of fluorine-bearing molecules. Illustratively, $V_{s,max}$ values were 23.3, 25.5, 25.9, and 30.6 kcal/mol for W-C-F₃ molecules, as W = I, Br, Cl, and F, respectively.

2.2. Point-of-Charge (PoC) Calculations

The PoC approach was recently reported as a trustworthy method to evaluate the σ -[17,57], π -[58,59], lp- [60], and R[•] [61]-hole interactions from an electrostatic perspective. PoC calculations were conducted to inspect the distance impact on NC-C₆H₂-X₃..., NCX..., W-C-F₃..., and F-C-X₃...PoC systems under the effect of PoC = ± 0.50 au. Molecular energy curves were calculated for the investigated systems (Figure 3). Table 1 summarizes molecular destabilization and stabilization energies ($E_{destabilization}$ and $E_{stabilization}$) of the LB... and LA...PoC systems under the effect of PoC = ± 0.50 au at N/C...PoC distance of 2.5 Å.

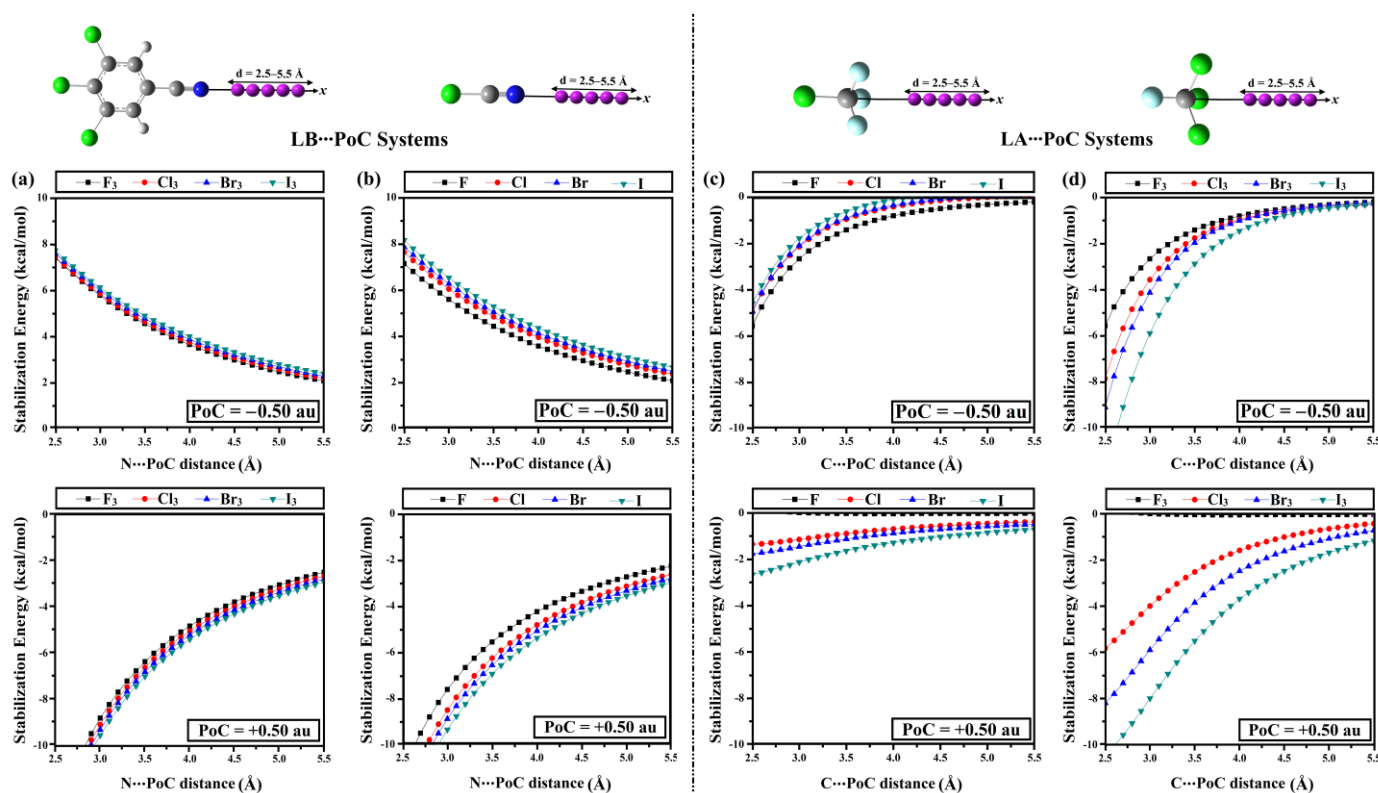


Figure 3. Stabilization/destabilization energy curve of the (a) NC-C₆H₂-X₃..., (b) NCX..., (c) W-C-F₃..., and (d) F-C-X₃...PoC systems (where X and W = F, Cl, Br, and I) under the effect of PoC = ± 0.50 au at N/C...PoC distance ranging from 2.5 to 5.5 Å.

Table 1. Molecular stabilization ($E_{\text{stabilization}}$) and destabilization ($E_{\text{destabilization}}$) energies of (a) NC-C₆H₂-X₃···, (b) NCX···, (c) W-C-F₃···, and (d) F-C-X₃···PoC systems (i.e., X and W = F, Cl, Br, and I) under the effect of PoC = ±0.50 au at N/C···PoC distance of 2.5 Å.

Molecular Energies (i.e., $E_{\text{destabilization}}$ and $E_{\text{stabilization}}$, in kcal/mol)				
Lewis base···PoC systems				
System	(a) NC-C ₆ H ₂ -X ₃ ···PoC		(b) NCX···PoC	
	−0.50 au	+0.50 au	−0.50 au	+0.50 au
F	7.41	−13.06	7.13	−11.20
Cl	7.44	−13.39	7.62	−11.40
Br	7.59	−13.64	7.85	−12.90
I	7.72	−13.92	8.15	−13.51
Lewis acid···PoC systems				
System	(c) W-C-F ₃ ···PoC		(d) F-C-X ₃ ···PoC	
	−0.50 au	+0.50 au	−0.50 au	+0.50 au
F	−5.58	0.30	−5.58	0.30
Cl	−4.98	−1.34	−7.88	−5.81
Br	−4.96	−1.75	−9.11	−8.18
I	−4.62	−2.66	−12.12	−10.41

As shown in Figure 3, energetic destabilization and stabilization were observed to decrease along with increasing the Lewis base···PoC intermolecular distance under the effect of negative and positive PoCs, respectively. Meanwhile, molecular stabilization energies were detected for all Lewis acid centres in the presence of negative and positive PoCs (Figure 3c,d). Generally, $E_{\text{stabilization}}$ enlarged along with decreasing the Lewis acid···PoC distance under the effect of negative and positive PoCs.

From Table 1, for all the NC-C₆H₂-X₃··· and NCX···PoC systems, $E_{\text{destabilization}}$ was found to increase as the $V_{s,\text{min}}$ values increase under the effect of negative PoC. For instance, $E_{\text{destabilization}}$ of NCF···, NCCl···, NCB···, and NCI···PoC systems were 7.13, 7.62, 7.85, and 8.15 kcal/mol along with $V_{s,\text{min}}$ values of −31.9, −34.2, −35.2, and −36.4 kcal/mol for NCF···, NCCl···, NCB···, and NCI···PoC systems, respectively. Contrarily, under the effect of positive PoC, an inverse correlation was stated between the $E_{\text{destabilization}}$ and the electron-withdrawing power of X₃ and X halogen atom(s) of the NC-C₆H₂-X₃ and NCX molecules, respectively. For instance, molecular stabilization energies ($E_{\text{stabilization}}$) were −13.06, −13.39, −13.64, and −13.92 kcal/mol for NC-C₆H₂-F₃···, NC-C₆H₂-Cl₃···, NC-C₆H₂-Br₃···, and NC-C₆H₂-I₃···PoC systems, respectively. Moreover, the NC-C₆H₂-X₃ molecules were characterized by more favorable $E_{\text{stabilization}}$ compared with the NCX ones that comply with $V_{s,\text{min}}$ values. As an example, $E_{\text{stabilization}}$ was −13.92 and −13.51 kcal/mol for NC-C₆H₂-I₃··· and NCI···PoC systems, accompanied by $V_{s,\text{min}}$ values of −35.7 and −31.9 kcal/mol for NC-C₆H₂-F₃ and NCF molecules, respectively. Turning to the W-C-F₃··· and F-C-X₃···PoC systems, the $E_{\text{stabilization}}$ was observed to decrease in the order F-C-X₃···PoC > F-C-X₃···PoC > W-C-F₃···PoC > W-C-F₃···PoC. PoC findings highlighted the further ability of the F-C-X₃ molecules to engage in tetrel bonding interactions compared with the W-C-F₃ ones, which verified a reversed pattern with $V_{s,\text{max}}$ values.

2.3. Interaction Energy

Set I and II complexes were utilized to study the effects of Lewis basicity and acidity on σ -hole interactions, respectively (see Figure 1). First, geometrical optimization for the investigated complexes was performed at MP2/aug-cc-pVTZ(PP) level of theory. The optimized structures of NC-C₆H₂-X₃ containing complexes, along with their intermolecular distances, are displayed in Figure 4. As well, the NCX-containing complexes are given in Figure S1. Interaction energies (E_{int}) were evaluated for Set I and II complexes at the same level of theory and are summarized in Table 2.

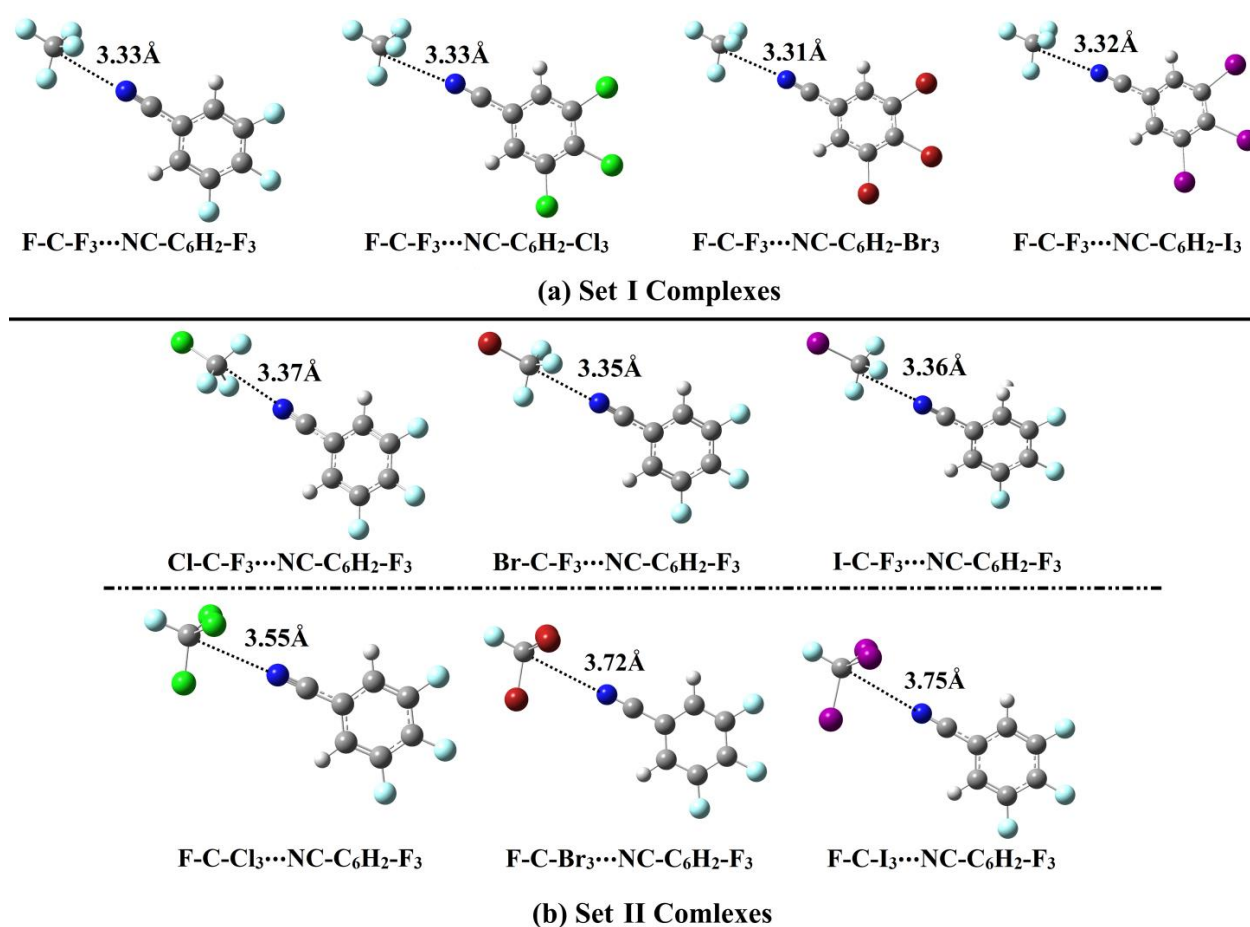


Figure 4. (a) Set I and (b) Set II complexes elucidating the Lewis basicity and acidity effects, respectively. The C...N distances are evaluated in Å.

Table 2. Interaction energies (E_{int} , in kcal/mol) for (a) Set I and (b) Set II complexes were evaluated at the MP2/aug-cc-pVTZ(PP) level of theory.

W/X	Complexation Parameters		Complexation Parameters	
	Distance (Å)	$E_{\text{MP2/aug-cc-pVTZ(PP)}}$ (kcal/mol)	Distance (Å)	$E_{\text{MP2/aug-cc-pVTZ(PP)}}$ (kcal/mol)
(a) Set I complexes				
	F-C-F ₃ ...NC-C ₆ H ₂ -X ₃		F-C-F ₃ ...NCX	
F	3.33	−1.20	3.35	−1.05
Cl	3.33	−1.21	3.34	−1.13
Br	3.31	−1.21	3.31	−1.13
I	3.32	−1.23	3.30	−1.16

Table 2. Cont.

W/X	Complexation Parameters		Complexation Parameters	
	Distance (Å)	$E_{\text{MP2/aug-cc-pVTZ(PP)}}^{\text{a}}$ (kcal/mol)	Distance (Å)	$E_{\text{MP2/aug-cc-pVTZ(PP)}}^{\text{a}}$ (kcal/mol)
(b) Set II complexes				
	W-C-F ₃ ...NC-C ₆ H ₂ -F ₃		W-C-F ₃ ...NCF	
F	3.33	−1.20	3.35	−1.05
Cl	3.37	−1.07	3.38	−0.91
Br	3.35	−1.07	3.37	−0.91
I	3.36	−0.97	3.38	−0.82
	F-C-X ₃ ...NC-C ₆ H ₂ -F ₃		F-C-X ₃ ...NCF	
F	3.33	−1.20	3.35	−1.05
Cl	3.55	−1.55	3.60	−1.25
Br	3.72 ^a	−1.66 ^a	3.57	−1.25
I	3.75 ^a	−2.08 ^a	3.58	−1.46

^a E_{int} was computed from the potential energy surface (PES) scan depicted in Figure S2.

As shown in Table 2a, a progressive interaction energy pattern was noticed for the investigated Set I complexes along with increasing the atomic size of the X₃/X halogen(s), as follows X = F < Cl < Br < I. This observation undoubtedly confirmed the contributions of the nucleophilic character of the Lewis bases (i.e., the effect of Lewis basicity) on σ -hole interactions within carbon-bearing complexes. For instance, the E_{int} were −1.16, −1.13, −1.13, and −1.05 kcal/mol for F-C-F₃...NCI, ...NCBr, ...NCCl, and ...NCF complexes along with $V_{\text{s,min}}$ values of −36.4, −35.2, −34.2, and −31.9 kcal/mol for the NCI, NCBr, NCCl, and NCF molecules, respectively.

Moreover, for Set I complexes, vast E_{int} were clearly seen in the case of F-C-F₃...NC-C₆H₂-X₃ complexes, i.e., more than in their F-C-F₃...NCX counterparts, which is in line with $V_{\text{s,min}}$ claims that showed higher negative EP regions for the former Lewis bases. For instance, E_{int} were −1.21 and −1.13 kcal/mol for the F-C-F₃...NC-C₆H₂-Br₃ and ...NCBr complexes alongside $V_{\text{s,min}}$ values of −36.5 and −5.2 kcal/mol for NC-C₆H₂-Br₃ and NCBr Lewis bases, respectively.

Interestingly, all Set II complexes showed negative E_{int} with different magnitudes, outlining the prominent impact of the Lewis acidity on the strength of carbon-bearing complexes. For Set II complexes, E_{int} of the W-C-F₃...Lewis base complexes were observed with lower negative values compared with the F-C-X₃...Lewis base analogs, in contrast with the results of the maximum positive EP regions (i.e., σ -hole). For example, from Table 2ii and Figure 2, E_{int} were −0.82 and −1.46 kcal/mol for the I-C-F₃... and F-C-I₃...NCF complexes and accompanied by 23.3 and 14.2 kcal/mol $V_{\text{s,max}}$ values for I-C-F₃ and F-C-I₃ molecules, respectively. This result was in agreement with the resurgent contributions of the X₃ substituents (i.e., X₃ = F₃ < Cl₃ < Br₃ < I₃) to the strength of the explored carbon-bearing complexes [50].

Comparatively, a linear correlation was found between E_{int} of W-C-F₃ containing complexes and the corresponding σ -hole size, ensuring the attractive electrostatic interactions between the negative clouds of Lewis base and the positive ones of σ -hole [50]. For instance, E_{int} were −0.82, −0.91, −0.91, and −1.05 kcal/mol for I-C-F₃..., Br-C-F₃..., Cl-C-F₃..., and F-C-F₃...NCF complexes versus $V_{\text{s,max}}$ values of 23.3, 25.5, 25.9, and 30.6 kcal/mol for I-C-F₃, Br-C-F₃, Cl-C-F₃, and F-C-F₃ molecules, respectively. Contrarily, the E_{int} of the F-C-X₃...Lewis base complexes was found to decrease with increasing the σ -hole size. For example, E_{int} of the F-C-X₃...NCF complexes were −1.05, −1.25, −1.25, and −1.46 kcal/mol versus $V_{\text{s,max}}$ values of 30.6, 16.9, 14.8, and 14.2 kcal/mol, when X₃ = F₃, Cl₃, Br₃, and I₃, respectively. Overall, the energetic features of Set II complexes were found to be consistent with PoC findings of W-C-F₃/F-C-X₃...PoC systems.

2.4. Quantum Theory of Atoms in Molecules (QTAIM) Analysis

QTAIM analysis was performed to elucidate the origin of the intermolecular interaction [62]. QTAIM diagrams of the $F-C-F_3 \cdots NC-C_6H_2-X_3$ and $W-C-F_3/F-C-X_3 \cdots NC-C_6H_2-F_3$ complexes are displayed in Figure 5. The corresponding diagrams for $F-C-F_3 \cdots NCX$ and $W-C-F_3/F-C-X_3 \cdots NCF$ complexes are represented in Figure S3. The computed ρ_b , $\nabla^2\rho_b$, and H_b values are listed in Table 3.

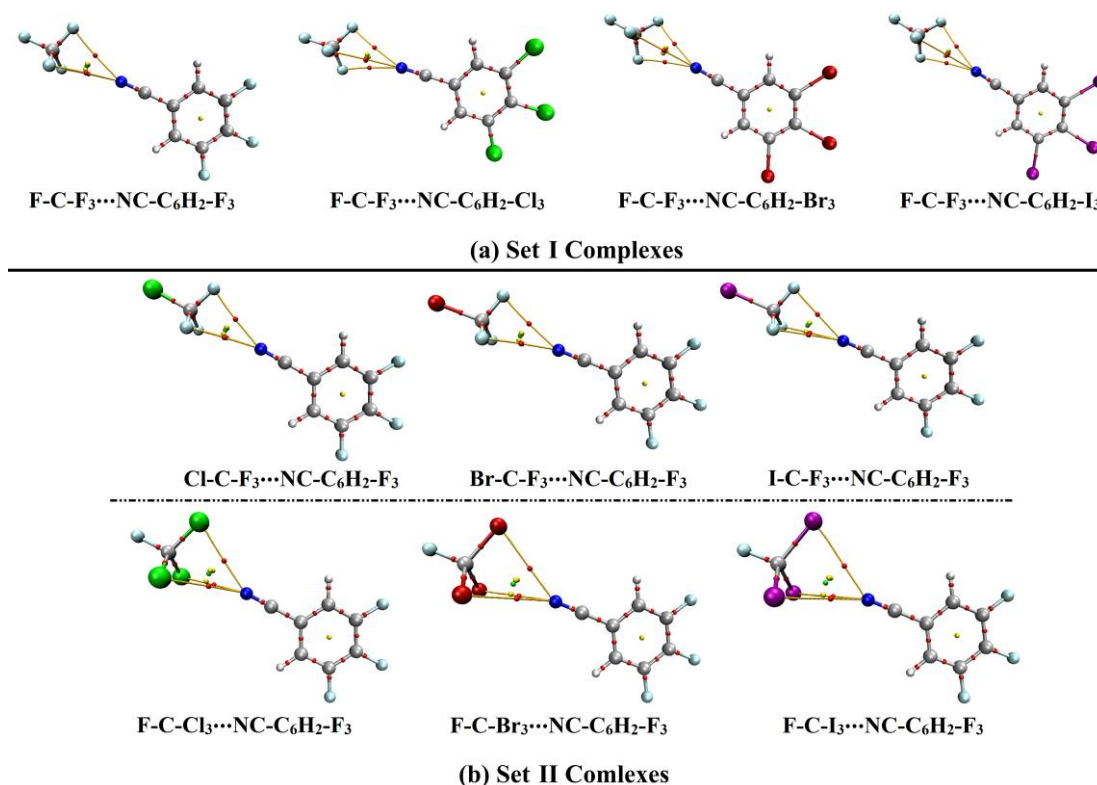


Figure 5. QTAIM diagrams of (a) Set I and (b) Set II complexes. Red dots point out the BCPs locations within the interacting species.

Table 3. Topological parameters, comprising ρ_b , $\nabla^2\rho_b$, and H_b (in au), for (a) Set I and (b) Set II complexes.

W/X	ρ_b (au)	$\nabla^2\rho_b$ (au)	H_b (au)	ρ_b (au)	$\nabla^2\rho_b$ (au)	H_b (au)
(a) Set I complexes						
	$F-C-F_3 \cdots NC-C_6H_2-X_3$			$F-C-F_3 \cdots NCX$		
F	0.005043	0.020899	0.001060	0.004768	0.019982	0.001032
Cl	0.005062	0.020980	0.001064	0.004907	0.020402	0.001041
Br	0.005260	0.021898	0.001106	0.005265	0.021980	0.001110
I	0.005130	0.021289	0.001078	0.005317	0.022116	0.001111
(b) Set II complexes						
	$W-C-F_3 \cdots NC-C_6H_2-F_3$			$W-C-F_3 \cdots NCF$		
F	0.005033	0.020836	0.001056	0.004768	0.019982	0.001032
Cl	0.004860	0.019906	0.001005	0.004558	0.018900	0.000974
Br	0.004977	0.020428	0.001028	0.004660	0.019332	0.000993
I	0.005258	0.022034	0.000912	0.004624	0.019122	0.000981
	$F-C-X_3 \cdots NC-C_6H_2-F_3$			$F-C-X_3 \cdots NCF$		
F	0.005033	0.020836	0.001056	0.004768	0.019982	0.001032
Cl	0.005739	0.017131	0.000847	0.005088	0.018951	0.001156
Br	0.005030 ^a	0.016791 ^a	0.000928 ^a	0.006197	0.021593	0.001184
I	0.005591 ^a	0.020600 ^a	0.001220 ^a	0.006986	0.021434	0.001017

^a The QTAIM parameters were recorded at the most favorable parameters based on the PES scan depicted in Figure S2.

From QTAIM diagrams demonstrated in Figure 5, three BPs and BCPs were denoted within the Set I and II complexes, highlighting the eminent contributions of the three coplanar halogens within the considered interactions that were in great agreement with previous studies [63]. The same observations were found for the F-C-F₃...NCX and W-C-F₃/F-C-X₃...NCF complexes (Figure S3). As listed in Table 3, positive values of $\nabla^2\rho_b$ and H_b accompanied by low values of ρ_b were obtained for all the studied complexes, asserting the closed-shell nature of the deemed interactions. For both the Set I and II complexes, the topological properties were remarked to be consistent with the interaction energy pattern.

Obviously, for Set I complexes, larger ρ_b , $\nabla^2\rho_b$, and H_b values were generally found for F-C-F₃...NC-C₆H₂-X₃ complexes than their ...NCX counterparts (Table 3). For example, $\nabla^2\rho_b$ were 0.020980 and 0.020402 au for the F-C-F₃...NC-C₆H₂-Cl₃ and ...NCCl complexes, respectively. In general, ρ_b , $\nabla^2\rho_b$, and H_b values of the F-C-F₃...NC-C₆H₂-X₃ and ...NCX complexes were revealed to increase with decreasing the nucleophilicity of the interacted Lewis bases according to the following order X = I > Br > Cl > F. For instance, H_b of NCF, NCCl, NCBBr, and NCI molecules were found with values of 0.001032, 0.001041, 0.001110, and 0.001111 au for F-C-F₃...NCF, ...NCCl, ...NCBr, and ...NCI complexes, against $V_{s,min}$ values of −31.9, −34.2, −35.2, and −36.4 kcal/mol, respectively.

Generally, for Set II complexes, the F-C-X₃...Lewis base complexes were characterized by higher ρ_b , $\nabla^2\rho_b$, and H_b values over the W-C-F₃...Lewis base counterparts, which coincided with the corresponding MP2 energetic features (Table 2). For example, H_b of I-C-F₃... and F-C-I₃...NCF complexes were 0.000981 and 0.001017 au, along with E_{int} of −0.82 and −1.46 kcal/mol, respectively.

2.5. Noncovalent Interaction (NCI) Analysis

Following the announcement of Johnson et al. of the NCI index, the occurrence of inter- and intra-molecular interactions could be three-dimensionally recognized [64]. Subsequently, 2D and 3D NCI plots were generated with a 0.50 au reduced density gradient value. The color scale was in the range starting from blue (−0.035) to red (0.020) au. 3D NCI plots of F-C-F₃...NC-C₆H₂-X₃ and W-C-F₃/F-C-X₃...NC-C₆H₂-F₃ complexes along with the F-C-F₃...NCX and W-C-F₃/F-C-X₃...NCF analogs are illustrated in Figure 6 and Figure S4, respectively. Similarly, for the same pattern of complexes, 2D NCI-RDG plots were generated and are depicted in Figures S5 and S6.

As shown in Figure 6, the green surfaces between the interacting species outlined the weak attractive interactions within the Set I and II complexes. Further, the strength enhancement of the studied complexes was obviously noted by increasing the size of the obtained green regions (Figure 6 and Figure S4). Notably, the prominent role of the coplanar halogens was observed, ensuring the QTAIM findings. As can be seen from Figures S5 and S6, all the spikes were found with negative values of $\text{sign}(\lambda_2)\rho$, affirming the occurrence of weak attractive interactions between the two interacting species.

2.6. Symmetry-Adapted Perturbation Theory (SAPT) Calculations

SAPT analysis was previously applied for its efficiency in analyzing the physical energetic components of noncovalent interactions [65]. Figure 7 represents the attractive forces versus the repulsive ones that were obtained from Total SAPT2+(3)dMP2 energies, revealing the most dominant energetic aspect within the interactions of Set I and II complexes. Table S1 lists the corresponding energetic values of such attractive and repulsive forces.

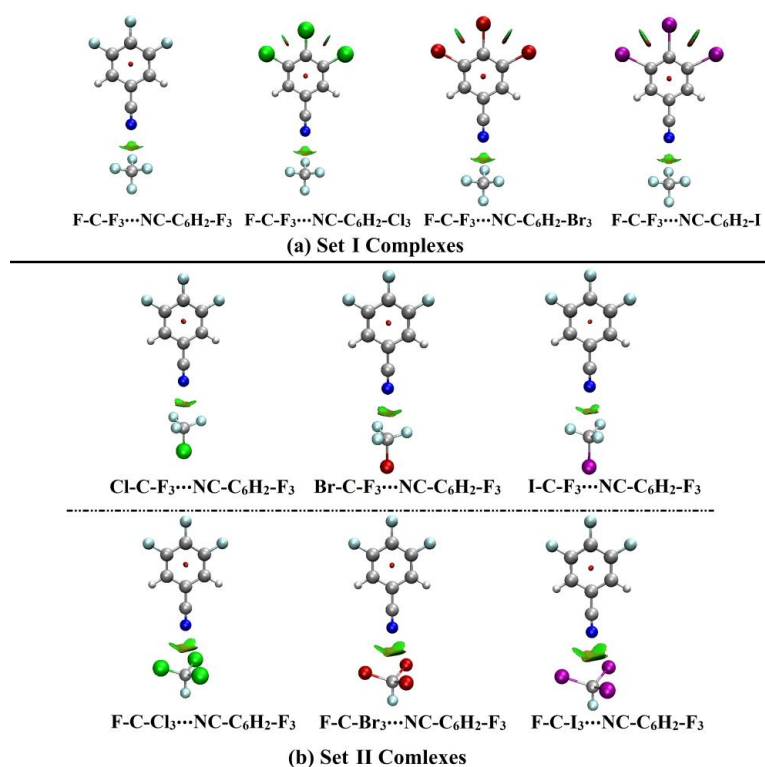


Figure 6. 3D NCI plots of the (a) Set I and (b) Set II complexes. The color range extended based on the $\text{sign}(\lambda_2)\rho$ from -0.035 to 0.020 au (blue to red).

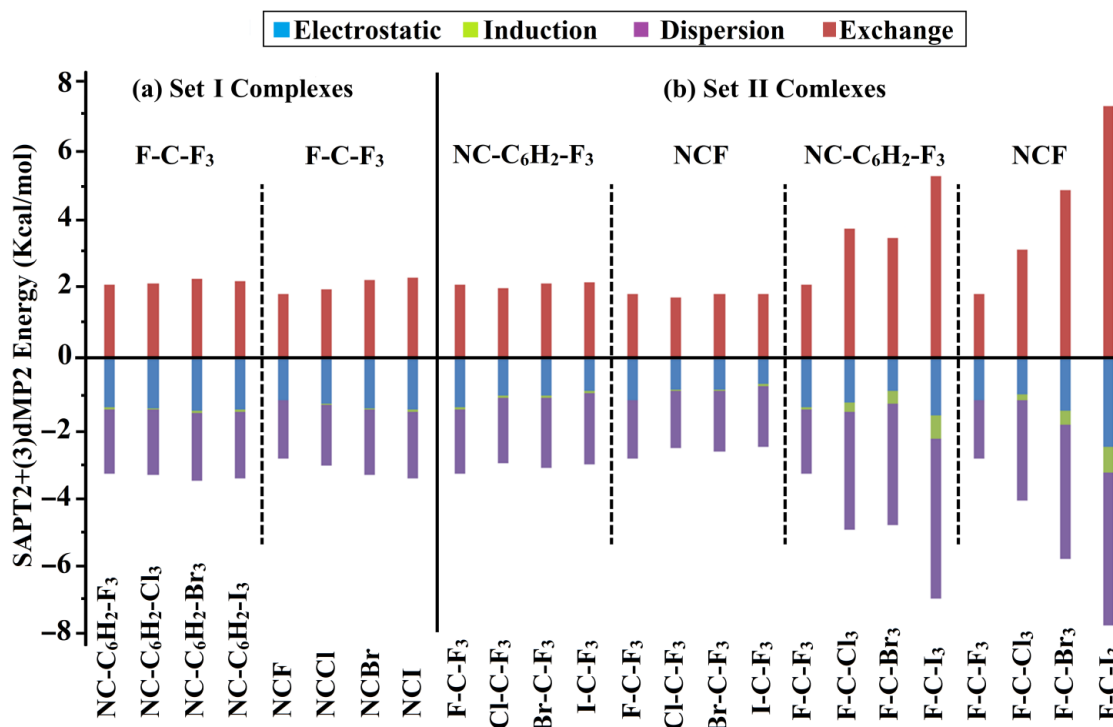


Figure 7. Bar chart illustrating the attractive forces against the repulsive ones of total SAPT2+(3)dMP2 energy for (a) Set I and (b) II complexes.

As can be seen from Figure 7, negative energetic values were denoted for the electrostatic (E_{elst}), induction (E_{ind}), and dispersion energy (E_{disp}) forces, outlining their contri-

butions in stabilizing all the Set I and II complexes. Apparently, the E_{disp} was the most dominant force within such attractive forces. On the other hand, unfavorable contributions for the exchange energy (E_{exch}) with positive values were also admitted. Illustratively, E_{elst} , E_{ind} , E_{disp} , and E_{exch} values were -2.66 , -0.78 , -5.24 , and 7.53 kcal/mol for F-C-I₃...NC-C₆H₂-F₃ complex (Table S1).

With respect to Set I complexes, the total attractive forces also affirmed the favorability of F-C-F₃...NC-C₆H₂-X₃ complexes, with highly energetic features, over the F-C-F₃...NCX analogs. For Set II complexes, significant total attractive forces in the case of the F-C-X₃ bearing complexes compared to W-C-F₃ bearing complexes, which might be interpreted as a result of the resurgent contributions of X₃ substituents. Generally, the total attractive forces (i.e., E_{elst} , E_{ind} , and E_{disp}) were found to be consistent with the energetic features with some exceptions. Such exceptions might be interpreted by considering the E_{exch} contributions. Illustratively, the $E_{\text{elst}}/E_{\text{ind}}/E_{\text{disp}}/E_{\text{exch}}$ values of the F-C-F₃...NCF and F-C-Cl₃...NCF complexes were $-1.26/-0.03/-1.73/1.91$ and $-1.09/-0.20/-3.00/3.32$ kcal/mol, respectively.

3. Methods and Materials

In the current study, Set I and II complexes were used to investigating the effects of Lewis basicity and acidity on σ -hole interactions, respectively (see Figure 1). In that spirit, the F-C-F₃...NC-C₆H₂-X₃/NCX and W-C-F₃/F-C-X₃...NC-C₆H₂-F₃/NCF complexes (where X and W = F, Cl, Br, and I) were well-characterized using various ab initio calculations. Geometrical optimization was first carried out for the investigated monomers at the MP2/aug-cc-pVTZ level of theory [66–68] for all atoms, except Br and I atoms. The aug-cc-pVTZ-PP basis set was utilized for the excepted atoms [66,67]. To envisage the electrophilic and nucleophilic regions over the molecular surfaces of the optimized molecules, the electrostatic potential (EP) analysis was carried out. In this perspective, molecular electrostatic potential (MEP) maps were built and then generated using 0.002 electron density envelopes according to the literature [69]. Further quantitative assessment was established by the evaluation of the surface electrostatic potential extrema in terms of $V_{\text{s,min}}$ and $V_{\text{s,max}}$ values, with the help of the Multiwfn 3.7 software [70], along the molecular surface of the inspected LB and LA, respectively.

The PoC approach was utilized to investigate the Lewis basicity and acidity roles on the tetrel-based interactions from an electrostatic perspective [18,47,50,71]. Using PoC approach, the effect of N... and C...PoC distances were examined for the considered the NC-C₆H₂-X₃/NCX (LB)... and W-C-F₃.../F-C-X₃ (LA)...PoC systems under the effect of PoC = ± 0.50 au in distance range of 2.5–5.5 Å along the x -axis with a 0.1 Å step size. The molecular stabilization energies ($E_{\text{stabilization}}$) were then evaluated and given from Equation (1) [63,72,73]:

$$E_{\text{stabilization}} = E_{\text{molecule...PoC}} - E_{\text{molecule}} \quad (1)$$

In order to thoroughly investigate the effect of Lewis basicity on interactions concerned with the carbon-bearing complexes, the NC-C₆H₂-X₃ and NCX models were devoted to interacting with F-C-F₃. Alternatively, the W-C-F₃ and F-C-X₃ molecules were adopted for interactions with NC-C₆H₂-F₃ and NCF to outline the effect of Lewis acidity on tetrel bonding interactions. Geometrical optimization was performed for the designed Set I and II complexes. Using the optimized complexes, the interaction energies were evaluated using Equation (2). Principally, the Boys-Bernardi procedure was utilized to give a proper correction for the resulted interaction energies from the basis set superposition error (BSSE) [74].

$$E_{\text{int}} = E_{\text{Set I and Set II complexes}} - (E_{\text{LA in complex}} + E_{\text{LB in complex}}) + E_{\text{BSSE}} \quad (2)$$

where $E_{\text{Set-I and Set-II complexes}}$, $E_{\text{LA in complex}}$, and $E_{\text{LB in complex}}$ represent energies of the complex, the deformed structures of LA, and LB, respectively. Energies of deformed monomers were considered based on their respective coordinates in the optimized Set I and II complexes.

To give qualitative and quantitative descriptions of the nature of the intermolecular interactions, quantum theory of atoms in molecules (QTAIM) [75] and noncovalent interaction (NCI) [64] analyses were carried out via Multiwfn 3.7 package [70]. The QTAIM diagrams and 2D/3D NCI plots were generated with the help of Visual Molecular Dynamics (VMD) software [76]. Gaussian 09 software was utilized for performing the executed calculations [77].

To investigate the physical behavior of the interactions embraced in the present study, symmetry-adapted perturbation theory (SAPT) analysis was performed at the SAPT2+(3)dMP2 level of truncation [78] using PSI4 code [79–81]. In the vein of SAPT, total SAPT2+(3)dMP2 energy was obtained as the sum of its physical nominees, including electrostatic (E_{elst}), induction (E_{ind}), dispersion (E_{disp}), and exchange (E_{exch}) terms, based on per Equations (3)–(7) [82].

$$E_{\text{int}}^{\text{SAPT2+(3)dMP2}} = E_{\text{elst}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{disp}} \quad (3)$$

$$E_{\text{elst}} = E_{\text{elst}}^{(10)} + E_{\text{elst}}^{(12)} + E_{\text{elst}}^{(13)} \quad (4)$$

$$E_{\text{exch}} = E_{\text{exch}}^{(10)} + E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)} \quad (5)$$

$$E_{\text{ind}} = E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + E_{\text{ind}}^{(22)} + E_{\text{exch-ind}}^{(22)} + \delta E_{\text{HF}}^{(2)} + \delta E_{\text{MP2}}^{(2)} \quad (6)$$

$$E_{\text{disp}} = E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)} (\text{SDQ}) + E_{\text{disp}}^{(22)} \text{T} + E_{\text{disp}}^{(30)} \quad (7)$$

4. Conclusions

Ab initio calculations were performed to investigate the effects of Lewis basicity and acidity on the tetrel bonding interactions using F-C-F₃...NC-C₆H₂-X₃/NCX and W-C-F₃/F-C-X₃...NC-C₆H₂-F₃/NCF complexes (i.e., Set I and II complexes), respectively. Regarding the Lewis basicity effect, the MP2 energetic quantities of Set I complexes further confirmed the favorability of the F-C-F₃...NC-C₆H₂-X₃ complexes with favorable E_{int} (i.e., more negative) over their F-C-F₃...NCX counterparts. Additionally, E_{int} of Set I complexes increased along with decreasing the electron-withdrawing power of the X₃/X halogen(s) in the following order F < Cl < Br < I. Regarding the Lewis acidity effects, $V_{\text{s,max}}$ quantities exhibited higher values in the case of W-C-F₃ molecules compared with F-C-X₃. Nevertheless, higher negative E_{int} were ascribed to the F-C-X₃ bearing complexes compared with the W-C-F₃ bearing ones. QTAIM diagrams and NCI plots validated the prominent contributions of the X₃ halogen substituents. Moreover, SAPT observations identified E_{disp} as the most dominant energetic aspect that contributed to the total strength of all the studied complexes. These observations provide informative characteristics of carbon-bearing complexes that may be fundamental in future studies related to crystal engineering and materials science.

Supplementary Materials: The supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ijms232113023/s1>.

Author Contributions: Conceptualization, M.A.A.I.; Data curation, M.N.I.S., A.-s.S.M.R., H.A.A.A., H.S.M.A.E. and N.A.M.M.; Visualization, M.N.I.S.; Methodology, M.A.A.I.; Software, M.A.A.I. and M.E.S.S.; Formal analysis, M.N.I.S. and N.A.M.M.; Investigation, M.N.I.S. and N.A.M.M.; Resources, M.A.A.I., A.M.S., and T.H.A.H.; Supervision, M.A.A.I.; Project administration, M.A.A.I.; Writing—original draft, M.N.I.S.; Writing—review and editing, M.A.A.I., A.M.S., H.F.O., T.H.A.H., M.E.S.S. and N.A.M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: Ahmed M. Shawky would like to thank the Scientific Research at Umm Al-Qura University for supporting this work with grant No. 22UQU4331174DSR22. The computational work was completed with resources provided by the Science and Technology Development Fund (STDF), Egypt, grants No. 5480 and 7972 (Granted to Mahmoud A. A. Ibrahim).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Gimeno, N.; Ros, M.B.; Serrano, J.L.; De la Fuente, M.R. Noncovalent interactions as a tool to design new bent-core liquid-crystal materials. *Chem. Mater.* **2008**, *20*, 1262–1271. [\[CrossRef\]](#)
- Munarriz, J.; Rabuffetti, F.A.; Contreras-Garcia, J. Building Fluorinated Hybrid Crystals: Understanding the Role of Noncovalent Interactions. *Cryst. Growth Des.* **2018**, *18*, 6901–6910. [\[CrossRef\]](#)
- Ariga, K.; Ito, H.; Hill, J.P.; Tsukube, H. Molecular recognition: From solution science to nano/materials technology. *Chem. Soc. Rev.* **2012**, *41*, 5800–5835. [\[CrossRef\]](#) [\[PubMed\]](#)
- Mazik, M. Molecular recognition of carbohydrates by acyclic receptors employing noncovalent interactions. *Chem. Soc. Rev.* **2009**, *38*, 935–956. [\[CrossRef\]](#) [\[PubMed\]](#)
- Riel, A.M.S.; Rowe, R.K.; Ho, E.N.; Carlsson, A.C.; Rappe, A.K.; Berryman, O.B.; Ho, P.S. Hydrogen Bond Enhanced Halogen Bonds: A Synergistic Interaction in Chemistry and Biochemistry. *Acc. Chem. Res.* **2019**, *52*, 2870–2880. [\[CrossRef\]](#)
- Choudhuri, K.; Pramanik, M.; Mal, P. Noncovalent Interactions in C-S Bond Formation Reactions. *J. Org. Chem.* **2020**, *85*, 11997–12011. [\[CrossRef\]](#) [\[PubMed\]](#)
- Malhotra, D.; Cantu, D.C.; Koech, P.K.; Heldebrant, D.J.; Karkamkar, A.; Zheng, F.; Bearden, M.D.; Rousseau, R.; Glezakou, V.A. Directed Hydrogen Bond Placement: Low Viscosity Amine Solvents for CO₂ Capture. *ACS Sustain. Chem. Eng.* **2019**, *7*, 7535–7542. [\[CrossRef\]](#)
- Stasyuk, O.A.; Jakubec, D.; Vondrasek, J.; Hobza, P. Noncovalent Interactions in Specific Recognition Motifs of Protein-DNA Complexes. *J. Chem. Theory Comput.* **2017**, *13*, 877–885. [\[CrossRef\]](#)
- Mani, D.; Arunan, E. The X-C...pi (X = F, Cl, Br, CN) carbon bond. *J. Phys. Chem. A* **2014**, *118*, 10081–10089. [\[CrossRef\]](#)
- Mahmoudi, G.; Bauza, A.; Amini, M.; Molins, E.; Mague, J.T.; Frontera, A. On the importance of tetrel bonding interactions in lead(ii) complexes with (iso)nicotinohydrazide based ligands and several anions. *Dalton Trans.* **2016**, *45*, 10708–10716. [\[CrossRef\]](#)
- Zeng, R.; Gong, Z.; Chen, L.; Yan, Q. Solution Self-Assembly of Chalcogen-Bonding Polymer Partners. *ACS Macro Lett.* **2020**, *9*, 1102–1107. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lim, J.Y.C.; Beer, P.D. Sigma-Hole Interactions in Anion Recognition. *Chem* **2018**, *4*, 731–783. [\[CrossRef\]](#)
- Murray, J.S.; Lane, P.; Clark, T.; Riley, K.E.; Politzer, P. Sigma-holes, pi-holes and electrostatically-driven interactions. *J. Mol. Model.* **2012**, *18*, 541–548. [\[CrossRef\]](#) [\[PubMed\]](#)
- Politzer, P.; Murray, J.S.; Concha, M.C. Sigma-hole bonding between like atoms; a fallacy of atomic charges. *J. Mol. Model.* **2008**, *14*, 659–665. [\[CrossRef\]](#)
- Murray, J.S.; Lane, P.; Clark, T.; Politzer, P. Sigma-hole bonding: Molecules containing group VI atoms. *J. Mol. Model.* **2007**, *13*, 1033–1038. [\[CrossRef\]](#) [\[PubMed\]](#)
- Clark, T.; Hennemann, M.; Murray, J.S.; Politzer, P. Halogen bonding: The sigma-hole. Proceedings of “Modeling interactions in biomolecules II”, Prague, September 5th–9th, 2005. *J. Mol. Model.* **2007**, *13*, 291–296. [\[CrossRef\]](#) [\[PubMed\]](#)
- Ibrahim, M.A.A.; Ahmed, O.A.M.; El-Taher, S.; Al-Fahemi, J.H.; Moussa, N.A.M.; Moustafa, H. Cospacial sigma-Hole and Lone Pair Interactions of Square-Pyramidal Pentavalent Halogen Compounds with pi-Systems: A Quantum Mechanical Study. *ACS Omega* **2021**, *6*, 3319–3329. [\[CrossRef\]](#)
- Ibrahim, M.A.A.; Ahmed, O.A.M.; Moussa, N.A.M.; El-Taher, S.; Moustafa, H. Comparative investigation of interactions of hydrogen, halogen and tetrel bond donors with electron-rich and electron-deficient π -systems. *RSC Adv.* **2019**, *9*, 32811–32820. [\[CrossRef\]](#)
- McDowell, S.A.; Joseph, J.A. The effect of atomic ions on model sigma-hole bonded complexes of AH₃Y (A = C, Si, Ge; Y = F, Cl, Br). *Phys. Chem. Chem. Phys.* **2014**, *16*, 10854–10860. [\[CrossRef\]](#)
- Clark, T.; Hesselmann, A. The coulombic sigma-hole model describes bonding in CX₃IY(−) complexes completely. *Phys. Chem. Chem. Phys.* **2018**, *20*, 22849–22855. [\[CrossRef\]](#)
- Li, Q.; Guo, X.; Yang, X.; Li, W.; Cheng, J.; Li, H.B. A sigma-hole interaction with radical species as electron donors: Does single-electron tetrel bonding exist? *Phys. Chem. Chem. Phys.* **2014**, *16*, 11617–11625. [\[CrossRef\]](#)
- Scheiner, S. The ditetrel bond: Noncovalent bond between neutral tetrel atoms. *Phys. Chem. Chem. Phys.* **2020**, *22*, 16606–16614. [\[CrossRef\]](#) [\[PubMed\]](#)
- Scheiner, S. Competition between a Tetrel and Halogen Bond to a Common Lewis Acid. *J. Phys. Chem. A* **2021**, *125*, 308–316. [\[CrossRef\]](#) [\[PubMed\]](#)
- Scheiner, S. Origins and properties of the tetrel bond. *Phys. Chem. Chem. Phys.* **2021**, *23*, 5702–5717. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhuo, H.; Li, Q.; Li, W.; Cheng, J. The dual role of pnictogen as Lewis acid and base and the unexpected interplay between the pnictogen bond and coordination interaction in H₃N ··· FH₂X ··· MCN (X = P and As; M = Cu, Ag, and Au). *New J. Chem.* **2015**, *39*, 2067–2074. [\[CrossRef\]](#)

26. Bauza, A.; Quinonero, D.; Deya, P.M.; Frontera, A. Pnictogen-pi complexes: Theoretical study and biological implications. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14061–14066. [CrossRef] [PubMed]
27. Alkorta, I.; Elguero, J.; Solimannejad, M. Single electron pnictogen bonded complexes. *J. Phys. Chem. A* **2014**, *118*, 947–953. [CrossRef] [PubMed]
28. Guo, X.; An, X.; Li, Q. Se...N chalcogen bond and Se...X halogen bond involving F₂C horizontal line Se: Influence of hybridization, substitution, and cooperativity. *J. Phys. Chem. A* **2015**, *119*, 3518–3527. [CrossRef]
29. Varadwaj, P.R.; Varadwaj, A.; Marques, H.M.; MacDougall, P.J. The chalcogen bond: Can it be formed by oxygen? *Phys. Chem. Chem. Phys.* **2019**, *21*, 19969–19986. [CrossRef] [PubMed]
30. Wang, W.; Ji, B.; Zhang, Y. Chalcogen bond: A sister noncovalent bond to halogen bond. *J. Phys. Chem. A* **2009**, *113*, 8132–8135. [CrossRef] [PubMed]
31. Riley, K.E.; Murray, J.S.; Fanfrlik, J.; Rezac, J.; Sola, R.J.; Concha, M.C.; Ramos, F.M.; Politzer, P. Halogen bond tunability I: The effects of aromatic fluorine substitution on the strengths of halogen-bonding interactions involving chlorine, bromine, and iodine. *J. Mol. Model.* **2011**, *17*, 3309–3318. [CrossRef] [PubMed]
32. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The halogen bond. *Chem. Rev.* **2016**, *116*, 2478–2601. [CrossRef] [PubMed]
33. Hauchecorne, D.; van der Veken, B.J.; Moiana, A.; Herrebout, W.A. The C–Cl...N halogen bond, the weaker relative of the C–I and C–Br...N halogen bonds, finally characterized in solution. *Chem. Phys.* **2010**, *374*, 30–36. [CrossRef]
34. Ibrahim, M.A.A.; Saeed, R.R.A.; Shehata, M.N.I.; Ahmed, M.N.; Shawky, A.M.; Khowdiary, M.M.; Elkaeed, E.B.; Soliman, M.E.S.; Moussa, N.A.M. Type I-IV Halogen...Halogen Interactions: A Comparative Theoretical Study in Halobenzene...Halobenzene Homodimers. *Int. J. Mol. Sci.* **2022**, *23*, 3114. [CrossRef] [PubMed]
35. Hennemann, M.; Murray, J.S.; Politzer, P.; Riley, K.E.; Clark, T. Polarization-induced sigma-holes and hydrogen bonding. *J. Mol. Model.* **2012**, *18*, 2461–2469. [CrossRef] [PubMed]
36. Politzer, P.; Murray, J.S. σ -Hole Interactions: Perspectives and Misconceptions. *Crystals* **2017**, *7*, 212. [CrossRef]
37. Politzer, P.; Murray, J.S. Halogen bonding: An interim discussion. *ChemPhysChem* **2013**, *14*, 278–294. [CrossRef]
38. Bauza, A.; Mooibroek, T.J.; Frontera, A. Tetrel Bonding Interactions. *Chem. Rev.* **2016**, *16*, 473–487. [CrossRef] [PubMed]
39. Murray, J.S.; Lane, P.; Politzer, P. Expansion of the sigma-hole concept. *J. Mol. Model.* **2009**, *15*, 723–729. [CrossRef] [PubMed]
40. Bauza, A.; Frontera, A. Competition between Halogen Bonding and pi-Hole Interactions Involving Various Donors: The Role of Dispersion Effects. *ChemPhysChem* **2015**, *16*, 3108–3113. [CrossRef] [PubMed]
41. Frontera, A. Tetrel bonding interactions involving carbon at work: Recent advances in crystal engineering and catalysis. *C.-J. Carbon Res.* **2020**, *6*, 60. [CrossRef]
42. Karim, A.; Schulz, N.; Andersson, H.; Nekoueishahraki, B.; Carlsson, A.C.; Sarabi, D.; Valkonen, A.; Rissanen, K.; Grafenstein, J.; Keller, S.; et al. Carbon's three-center, four-electron tetrel bond, treated experimentally. *J. Am. Chem. Soc.* **2018**, *140*, 17571–17579. [CrossRef] [PubMed]
43. Afkhami, F.A.; Mahmoudi, G.; Qu, F.R.; Gupta, A.; Kose, M.; Zangrando, E.; Zubkov, F.I.; Alkorta, I.; Safin, D.A. Supramolecular lead (II) architectures engineered by tetrel bonds. *CrystEngComm* **2020**, *22*, 2389–2396. [CrossRef]
44. Bauza, A.; Mooibroek, T.J.; Frontera, A. Tetrel-bonding interaction: Rediscovered supramolecular force? *Angew. Chem. Int. Ed.* **2013**, *52*, 12317–12321. [CrossRef] [PubMed]
45. Grabowski, S. Lewis Acid Properties of Tetrel Tetrafluorides—The Coincidence of the σ -Hole Concept with the QTAIM Approach. *Crystals* **2017**, *7*, 43–56. [CrossRef]
46. Scheiner, S. Systematic elucidation of factors that influence the strength of tetrel bonds. *J. Phys. Chem. A* **2017**, *121*, 5561–5568. [CrossRef] [PubMed]
47. Ibrahim, M.A.A.; Moussa, N.A.M.; Safy, M.E.A. Quantum-mechanical investigation of tetrel bond characteristics based on the point-of-charge (PoC) approach. *J. Mol. Model.* **2018**, *24*, 219. [CrossRef]
48. Hou, M.C.; Yang, S.B.; Li, Q.Z.; Cheng, J.B.; Li, H.B.; Liu, S.F. Tetrel Bond between 6-OTX(3)-Fulvene and NH(3): Substituents and Aromaticity. *Molecules* **2018**, *24*, 10. [CrossRef]
49. Karpfen, A. On the interaction of propynal with HNO, HF, HCl, H₂O, CH₃OH, and NH₃: Red- and blue-shifting hydrogen bonds and tetrel bonds. *Comput. Theor. Chem.* **2019**, *1160*, 1–13. [CrossRef]
50. Ibrahim, M.A.A.; Mahmoud, A.H.M.; Moussa, N.A.M. Comparative investigation of $\pm\sigma$ -hole interactions of carbon-containing molecules with Lewis bases, acids and di-halogens. *Chem. Pap.* **2020**, *74*, 3569–3580. [CrossRef]
51. Michalczyk, M.; Zierkiewicz, W.; Wysokinski, R.; Scheiner, S. Hexacoordinated Tetrel-Bonded Complexes between TF₄ (T = Si, Ge, Sn, Pb) and NCH: Competition between sigma- and pi-Holes. *ChemPhysChem* **2019**, *20*, 959–966. [CrossRef]
52. Ibrahim, M.A.A.; Moussa, N.A.M.; Kamel, A.A.K.; Shehata, M.N.I.; Ahmed, M.N.; Taha, F.; Abourehab, M.A.S.; Shawky, A.M.; Elkaeed, E.B.; Soliman, M.E.S. External Electric Field Effect on the Strength of sigma-Hole Interactions: A Theoretical Perspective in Likeddots, three dots, centeredLike Carbon-Containing Complexes. *Molecules* **2022**, *27*, 2963. [CrossRef] [PubMed]
53. Grabar, A.; Michalczyk, M.; Zierkiewicz, W.; Scheiner, S. Noncovalent bonds between tetrel atoms. *ChemPhysChem* **2020**, *21*, 1934–1944. [CrossRef]
54. Ibrahim, M.A.A.; Mohamed, Y.A.M.; Abuelliel, H.A.A.; Rady, A.-S.S.M.; Soliman, M.E.S.; Ahmed, M.N.; Mohamed, L.A.; Moussa, N.A.M. σ -Hole Interactions of Tetrahedral Group IV–VIII Lewis Acid Centers with Lewis Bases: A Comparative Study. *ChemistrySelect* **2021**, *6*, 11856–11864. [CrossRef]

55. Weiner, P.K.; Langridge, R.; Blaney, J.M.; Schaefer, R.; Kollman, P.A. Electrostatic potential molecular surfaces. *Proc. Natl. Acad. Sci. USA* **1982**, *79*, 3754–3758. [[CrossRef](#)] [[PubMed](#)]
56. Murray, J.S.; Politzer, P. The electrostatic potential: An overview. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 153–163. [[CrossRef](#)]
57. Ibrahim, M.A.A.; Shehata, M.N.I.; Soliman, M.E.S.; Moustafa, M.F.; El-Mageed, H.R.A.; Moussa, N.A.M. Unusual chalcogen...chalcogen interactions in like...like and unlike $Y=C=Y\cdots Y=C=Y$ complexes ($Y = O, S$, and Se). *Phys. Chem. Chem. Phys.* **2021**, *24*, 3386–3399. [[CrossRef](#)] [[PubMed](#)]
58. Ibrahim, M.A.A.; Rady, A.-S.S.M.; Al-Fahemi, J.H.; Telb, E.M.Z.; Ahmed, S.A.; Shawky, A.M.; Moussa, N.A.M. $\pm\pi$ -Hole Interactions: A Comparative Investigation Based on Boron-Containing Molecules. *ChemistrySelect* **2020**, *5*, 13223–13231. [[CrossRef](#)]
59. Ibrahim, M.A.A.; Saeed, R.R.A.; Shehata, M.N.I.; Mohamed, E.E.B.; Soliman, M.E.S.; Al-Fahemi, J.H.; El-Mageed, H.R.A.; Ahmed, M.N.; Shawky, A.M.; Moussa, N.A.M. Unexplored σ -hole and π -hole interactions in $(X_2CY)_2$ complexes ($X = F, Cl$; $Y = O, S$). *J. Mol. Struct.* **2022**, *1265*, 133232. [[CrossRef](#)]
60. Ibrahim, M.A.A.; Saad, S.M.A.; Al-Fahemi, J.H.; Mekhemer, G.A.H.; Ahmed, S.A.; Shawky, A.M.; Moussa, N.A.M. External electric field effects on the σ -hole and lone-pair hole interactions of group V elements: A comparative investigation. *RSC Adv.* **2021**, *11*, 4022–4034. [[CrossRef](#)]
61. Ibrahim, M.A.A.; Mohamed, Y.A.M.; Abd Elhafez, H.S.M.; Shehata, M.N.I.; Soliman, M.E.S.; Ahmed, M.N.; El-Mageed, A.H.R.; Moussa, N.A.M. $R\bullet$ -hole interactions of group IV–VII radical-containing molecules: A comparative study. *J. Mol. Graph. Model.* **2022**, *111*. [[CrossRef](#)] [[PubMed](#)]
62. Cukrowski, I.; de Lange, J.H.; Adeyinka, A.S.; Mangondo, P. Evaluating common QTAIM and NCI interpretations of the electron density concentration through IQA interaction energies and 1D cross-sections of the electron and deformation density distributions. *Comput. Theor. Chem.* **2015**, *1053*, 60–76. [[CrossRef](#)]
63. Ibrahim, M.A.A.; Kamel, A.A.K.; Soliman, M.E.S.; Moustafa, M.F.; El-Mageed, H.R.A.; Taha, F.; Mohamed, L.A.; Moussa, N.A.M. Effect of external electric field on tetrel bonding interactions in $(FTF_3\cdots FH)$ complexes ($T = C, Si, Ge$, and Sn). *ACS Omega* **2021**, *6*, 25476–25485. [[CrossRef](#)] [[PubMed](#)]
64. Johnson, E.R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A.J.; Yang, W. Revealing noncovalent interactions. *J. Am. Chem. Soc.* **2010**, *132*, 6498–6506. [[CrossRef](#)]
65. Jeziorski, B.; Moszynski, R.; Szalewicz, K. Perturbation-theory approach to intermolecular potential-energy surfaces of van der Waals complexes. *Chem. Rev.* **1994**, *94*, 1887–1930. [[CrossRef](#)]
66. Woon, D.E.; Dunning, T.H. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. *J. Chem. Phys.* **1993**, *98*, 1358–1371. [[CrossRef](#)]
67. Woon, D.E.; Dunning, T.H. Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties. *J. Chem. Phys.* **1994**, *100*, 2975–2988. [[CrossRef](#)]
68. Møller, C.; Plesset, M.S. Note on an approximation treatment for many-electron systems. *Phys. Rev.* **1934**, *46*, 618–622. [[CrossRef](#)]
69. Ibrahim, M.A.A. Molecular mechanical perspective on halogen bonding. *J. Mol. Model.* **2012**, *18*, 4625–4638. [[CrossRef](#)] [[PubMed](#)]
70. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592. [[CrossRef](#)]
71. Ibrahim, M.A.A.; Moussa, N.A.M.; Soliman, M.E.S.; Moustafa, M.F.; Al-Fahemi, J.H.; El-Mageed, H.R.A. On the potentiality of $X-T-X_3$ compounds ($T = C, Si$, and Ge , and $X = F, Cl$, and Br) as tetrel- and halogen-bond donors. *ACS Omega* **2021**, *6*, 19330–19341. [[CrossRef](#)] [[PubMed](#)]
72. Ibrahim, M.A.A.; Rady, A.S.S.M.; Soliman, M.E.S.; Moustafa, M.F.; El-Mageed, H.R.A.; Moussa, N.A.M. π -hole interactions of group III–VI elements with π -systems and Lewis bases: A comparative study. *Struct. Chem.* **2022**, *33*, 9–21. [[CrossRef](#)]
73. Ibrahim, M.A.A.; Moussa, N.A.M. Unconventional Type III Halogen...Halogen Interactions: A Quantum Mechanical Elucidation of sigma-Hole...sigma-Hole and Di-sigma-Hole Interactions. *ACS Omega* **2020**, *5*, 21824–21835. [[CrossRef](#)] [[PubMed](#)]
74. Boys, S.F.; Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol. Phys.* **1970**, *19*, 553–566. [[CrossRef](#)]
75. Bader, R.F.W. Atoms in molecules. *Acc. Chem. Res.* **1985**, *18*, 9–15. [[CrossRef](#)]
76. Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graph.* **1996**, *14*, 33–38. [[CrossRef](#)]
77. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09*; Revision E01; Gaussian Inc.: Wallingford, CT, USA, 2009.
78. Hohenstein, E.G.; Sherrill, C.D. Efficient evaluation of triple excitations in symmetry-adapted perturbation theory via second-order Moller-Plesset perturbation theory natural orbitals. *J. Chem. Phys.* **2010**, *133*, 104107. [[CrossRef](#)]
79. Turney, J.M.; Simmonett, A.C.; Parrish, R.M.; Hohenstein, E.G.; Evangelista, F.A.; Fermann, J.T.; Mintz, B.J.; Burns, L.A.; Wilke, J.J.; Abrams, M.L.; et al. PSI4: An open-source ab initio electronic structure program. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 556–565. [[CrossRef](#)]
80. Hohenstein, E.G.; Sherrill, C.D. Wavefunction methods for noncovalent interactions. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 304–326. [[CrossRef](#)]

-
81. Hohenstein, E.G.; Sherrill, C.D. Density fitting and Cholesky decomposition approximations in symmetry-adapted perturbation theory: Implementation and application to probe the nature of pi-pi interactions in linear acenes. *J. Chem. Phys.* **2010**, *132*, 184111–184120. [[CrossRef](#)]
 82. Parker, T.M.; Burns, L.A.; Parrish, R.M.; Ryno, A.G.; Sherrill, C.D. Levels of symmetry adapted perturbation theory (SAPT). I. Efficiency and performance for interaction energies. *J. Chem. Phys.* **2014**, *140*, 094106. [[CrossRef](#)] [[PubMed](#)]