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Cooperativity between the hydrogen bonding and σ -hole interaction in linear $\text{NCX}\cdots(\text{NCH})_{n=2-5}$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_{n=2-5}$ complexes ($\text{X}=\text{Cl}, \text{Br}$; $\text{Z}=\text{Ar}, \text{Kr}$): A comparative study

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Abstract

Quantum chemical calculations are performed to investigate the cooperativity of hydrogen bonding with halogen or aerogen bonding interactions in linear $\text{NCX}\cdots(\text{NCH})_{n=2-5}$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_{n=2-5}$ clusters, where $\text{X}=\text{Cl}, \text{Br}$ and $\text{Z}=\text{Ar}, \text{Kr}$. To understand the cooperativity mechanism in these systems, the corresponding binary $\text{NCX}\cdots\text{NCH}$ and $\text{O}_3\text{Z}\cdots\text{NCH}$ complexes are also considered. The binding distances, interaction energies and bonding properties of the $\text{NCX}\cdots(\text{NCH})_{n=2-5}$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_{n=2-5}$ clusters are analyzed in detail. It is found that the cooperative effects in the hydrogen bonding tend to strengthen $\text{X}\cdots\text{N}$ and $\text{Z}\cdots\text{N}$ interactions. For both $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters, a small bond shrinkage is observed from $n=4$ to $n=5$, which suggests that the cooperativity effects are almost saturated in the larger clusters ($n > 5$). As the size of X or Z atom is increased, the magnitude of the cooperative energy in these systems is also increased, which is mainly ascribed to changes in electrostatic potentials and orbital interactions. Our results indicate that the cooperative effects lead to a substantial change in the ^{14}N nuclear quadrupole coupling constants of the NCH molecule.

Keyword: cooperativity; halogen bond; aerogen bond; electrostatic potential; NQR.

1. Introduction

In recent years, a proper characterization and intelligent utilization of noncovalent interactions have become one of the most active research fields¹⁻⁶. Noncovalent interactions play an increasingly important role in supramolecular chemistry, protein folding, drug design and material science⁷⁻⁸. Until now, many different types of noncovalent interactions have been characterized and investigated by various experiments and theoretical calculations, including hydrogen bonding⁹⁻¹⁰, π - π stacking¹¹⁻¹² and cation- π ¹³⁻¹⁴ interactions. Meanwhile, much attention has been recently devoted to halogen bonds¹⁵⁻²² owing to their diverse and potential applications in many fields including supramolecular chemistry, biochemistry and material science. A halogen bond is a directional interaction between a covalently-bonded halogen atom playing the role of the Lewis acid and an electron-rich site²³⁻²⁴. The formation of the halogen bond is mainly explained with the use of the σ -hole concept²⁵⁻³⁰, which is a low electron density region on the extension of the covalent bond to the halogen atom. The existence of this positive region lets the halogen atom acts as a Lewis acid center and it seems that the electrostatic attraction between the positive σ -hole on the halogen atom and the negative region associated with the Lewis base to be mainly responsible for the stability of the halogen-bonded complexes. However, Stone³¹ and Hill et al.³² demonstrated that the directivity of halogen-bonding is due to exchange-repulsion rather than electrostatic effects. It is worth mentioning that the σ -hole concept is not limited to the halogen atoms, and in recent years, σ -hole bonding involving other groups has been also identified. Such interactions are often named as the chalcogen-bonding^{21-22, 33-34}, pnictogen-bonding^{5-6, 17, 35-38} and tetrel-bonding³⁹⁻⁴² for the atoms of groups 16, 15 and 14, respectively. Even in the case of the group 18 atom (noble gases or aerogens), the σ -hole has been also observed and the corresponding interaction was named the “aerogen bonding”.

The aerogen bond is the newer member of the family of σ -hole bonds. The high-level ab initio calculations performed by Bauzá and Frontera⁴³ indicated that the aerogen atoms in compounds such as XeO₃ and XeOF₂ are able to interact with potential nitrogen bases, with strength comparable to hydrogen bonds. The formation of aerogen bonding interaction in these complexes is attributed to the existence of a positive electrostatic potential area (σ -hole) in the extension of the Xe-O bond, which is due to the depletion of the electron density in this region. The presence of the σ -hole indicates that aerogen bonding is mainly dominated by the electrostatic effects, although it may be also supplemented by other stabilizing energy terms, like

charge-transfer, polarization and dispersion effects⁴⁴⁻⁴⁶. Moreover, the formation of aerogen bonds can be due to the π -hole, a region of positive electrostatic potential that is perpendicular to a portion of a molecular framework. Recently, Bauzá and Frontera⁴⁴ have reported π -hole interactions involving Xe atoms to find a deeper understanding of the nature and physical properties of these particular interactions. Generally, the strength of aerogen bonding depends on the magnitude of the σ -hole on the aerogen atom, which is related to the size or polarizability of the aerogen atom, i.e. $\text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ ^{43, 47}. In addition, the strength of aerogen bonding can be increased by so-called cooperative effects⁴⁸⁻⁵⁰ with other types of intermolecular interactions, which can be evidenced by changes in the corresponding geometric and energetic parameters. It is worth mentioning that compared to other σ -hole interactions, the potential applications of aerogen bonding in the supramolecular chemistry and molecular recognition are very limited, most likely due to the low reactivity of the aerogen atoms. Nevertheless, the recent studies demonstrated that aerogen bonding can be very important in xenon and krypton chemistry^{24, 45, 51-52}.

Cooperativity is perhaps one of the most important characteristic shared by intermolecular interactions. In the crystalline structures or biomacromolecules, a great number of noncovalent interactions coexist and hence a cooperative effect may be found between them⁵³⁻⁵⁵. In addition, a complicated combination of these interactions is frequently identified as the driving force of many biological and chemical processes. So far, many studies have reported the cooperativity in systems where one of the interactions corresponds to the σ -hole bond⁴⁸⁻⁵⁰. For example, the cooperative enhancement between the hydrogen bonding and halogen bonding interactions has been studied by Li and co-workers⁵⁶. A recent research from this laboratory⁵⁰ indicated that a weak aerogen bond in the $\text{O}_3\text{Z}\cdots\text{NCM}\cdots\text{NCX}$ ($\text{Z}=\text{Ar}, \text{Kr}, \text{Xe}$; $\text{M}=\text{H}, \text{Li}$; $\text{X}=\text{H}, \text{F}$ and CH_3) complexes can be considerably strengthened in the presence of a hydrogen or lithium bonding. However, to the best of our knowledge, no previous study has considered the influence of cooperativity of hydrogen bonding on the strength and properties of a σ -hole interaction.

In the present study, our main objective is to compare the geometry, interaction energies and cooperativity effects in $\text{NCX}\cdots(\text{NCH})_{n=2-5}$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_{n=2-5}$ complexes, where $\text{X}=\text{Cl}, \text{Br}$ and $\text{Z}=\text{Ar}, \text{Kr}$. To this aim, molecular electrostatic potential (MEP), quantum theory of atoms in molecules (QTAIM), noncovalent interaction (NCI) index and natural bond orbital (NBO) analyses are performed. We hope that our theoretical study enrich the knowledge on

cooperativity in multiple noncovalent interactions and may be important for the extension of σ -hole interactions.

2. Computational details

All structures were fully optimized and subsequently characterized by frequency calculations at the MP2/aug-cc-pVTZ level using the Gaussian 09 package ⁵⁷. Interaction energies were computed as the differences between the total energies of the complexes and the energies of the isolated monomers and were corrected for basis set superposition error (BSSE) using the counterpoise method ⁵⁸. The MEP analysis was performed on the 0.001 electrons/Bohr³ contour of the electronic density using the Wave Function Analysis-Surface Analysis Suite (WFA-SAS) ⁵⁹. The NBO theory ⁶⁰ at the HF/aug-cc-pVTZ(-PP) level was applied to unveil the nature of the interactions, using the NBO 5.0 program ⁶¹. The QTAIM ⁶², NCI ⁶³ and electron density difference (EDD) analyses were carried out using the Multiwfn ⁶⁴. The ¹⁴N nuclear quadrupole coupling constants, $C_Q(^{14}\text{N})$, were calculated at the MP2/aug-cc-pVTZ level using the following equation ⁶⁵:

$$C_Q(^{14}\text{N}) = eQq_{zz}/h \quad (1)$$

where e , Q and h are the charge of electron, nuclear electric quadrupole moment (2.44 mb for ¹⁴N ⁶⁶) and Planck's constant, respectively. The q_{zz} is the largest component of the electric field gradient tensor at the site of ¹⁴N nuclei.

For each linear cluster, the cooperative energy (E_{coop}) was obtained using the model proposed by Parra et al. ⁶⁷:

$$E_{\text{coop}} = \frac{E_{\text{int}}(\text{NCX} \cdots (\text{NCH})_n) - [(n-1) \times E_{\text{int}}(\text{HCN} \cdots \text{HCN}) + E_{\text{int}}(\text{NCX}/\text{O}_3\text{Z} \cdots \text{NCH})]}{(n-2)+1} \quad (2)$$

where $E_{\text{int}}(\text{NCX}/\text{O}_3\text{Z} \cdots (\text{NCH})_n)$ is the interaction energy of the $\text{NCX} \cdots (\text{NCH})_n$ or $\text{O}_3\text{Z} \cdots (\text{NCH})_n$ cluster, $E_{\text{int}}(\text{NCH} \cdots \text{NCH})$ and $E_{\text{int}}(\text{NCX}/\text{O}_3\text{Z} \cdots \text{NCH})$ are the interaction energy of the isolated relaxed $\text{NCH} \cdots \text{NCH}$ and $\text{NCX} \cdots \text{NCH}$ or $\text{O}_3\text{Z} \cdots \text{NCH}$ dimers, respectively.

3. Results and discussion

3.1. Monomers. Initially, in order to describe the active Lewis acid/base sites, the overall electrostatic potential on the surface of the isolated NCX and ZO_3 molecules ($\text{X} = \text{Cl}, \text{Br}$ and $\text{Z} =$

Ar, Kr) has been analyzed. Figure 1 depicts the MEP maps on the 0.001 electrons/Bohr³ electron density isosurface of the isolated NCX and ZO₃ molecules. From Figure 1, one can see that there is a distinct positive region (σ -hole) in the extension of the C–X or Z–O bond(s) of these molecules, which are the interaction sites for the approach of a nucleophile to these molecules. The latter positive region is characterized by a maximum of electrostatic potential ($V_{S,max}$) value of 41.1, 47.8, 56.7 and 62.7 kcal/mol for NCCl, NCBBr, ArO₃ and KrO₃, respectively. Note that the value of the $V_{S,max}$ increases as the size of the halogen or aerogen atom increases, which is consistent with the usual trend that σ -hole become more positive in going to the heavier elements in a given group²⁹⁻³⁰. This finding is also supported by the ELF analysis of these molecules, as shown in Figure 1. The ELF isosurfaces clearly indicate an electron deficient region around the X or Z atom, in the extension of the C–X or Z–O bond(s), which confirm the strong tendency of these molecules to form σ -hole interaction with the potential negative sites.

3.2. Binary complexes. Figure 2 depicts the optimized structures of the binary NCX $\cdots$ NCH and O₃Z $\cdots$ NCH complexes, where X=Cl, Br and Z= Ar, Kr. The binding distances and interaction energies of these complexes are listed in Table 1. One can see that the binding distance of NCCl $\cdots$ NCH and NCBBr $\cdots$ NCH complexes is 2.960 and 2.920 Å, respectively. These are smaller than the sums of the van der Waals radii of the interacting atoms⁶⁸, which indicates an attractive interaction between the interacting molecules in these complexes. The calculated interaction energy of NCCl $\cdots$ NCH and NCBBr $\cdots$ NCH complexes is -3.49 and -4.44 kcal/mol, respectively. On the other hand, a shorter aerogen bond is obtained in the O₃Kr $\cdots$ NCH complex compared to the O₃Ar $\cdots$ NCH, which is consistent with the positive MEP on the σ -hole associated with the aerogen atom. This may indicate that electrostatic effects are responsible for the stability of these aerogen bonds. Table 1 also lists the calculated electron density, ρ_{BCP} , its Laplacian, $\nabla^2\rho_{BCP}$, and the total electron energy density, H_{BCP} , at the X $\cdots$ N and Z $\cdots$ N bond critical points (BCPs) of these binary complexes. The electron densities at these BCPs range from 0.0105 to 0.0162 au, and are within the range reported for other σ -hole bonds^{17, 38, 69-71}. One can see that the ρ_{BCP} values at the Z $\cdots$ N BCPs of O₃Z $\cdots$ NCH complexes are larger than the corresponding values at the X $\cdots$ N BCPs of NCX $\cdots$ NCH complexes, which confirms the stronger σ -hole interaction in the former complexes. The calculated Laplacian values of electron densities are all positive and hence, these interactions can be also classified as a closed-shell interaction.

In addition, the H_{BCP} values for these complexes are positive, indicating that these σ -hole bonds are electrostatic in nature.

Another powerful method to characterize the σ -hole interaction in these binary complexes is the NCI analysis. NCI analysis is based on the electron density (ρ) and its reduced density gradient ($\text{RDG} = |\nabla\rho|/2(3\pi^2)^{1/3}\rho^{4/3}$). While the QTAIM theory provides information on the so-called BCPs, NCI focuses on the points where the RDG is low, i.e., regions of space around these points. Plotting the RDG versus $\text{sign}(\lambda_2)\rho$, where λ_2 is the second eigenvalue of Hessian matrix, reveals the basic pattern of intermolecular interactions and the existence of one or more spikes in the low-density, low-gradient region, can be regarded as a signature of noncovalent interactions. Figure 3 indicates the plot of the RDG versus $\text{sign}(\lambda_2)\rho$ of the $\text{NCX}\cdots\text{NCH}$ and $\text{O}_3\text{Z}\cdots\text{NCH}$ complexes. As evident, all these complexes are characterized by a distinct spike in the low-density region, which verifies the formation of a σ -hole bond in these systems. Consistent with the earlier studies^{46-47, 72}, the corresponding spike of the $\text{X}\cdots\text{N}$ or $\text{Z}\cdots\text{N}$ interaction appears in the larger ρ (or more negative $\text{sign}(\lambda_2)\rho$) region, as the strength of the interaction increases. This is likely owing to the most remarkable contribution of the electrostatic effects in the latter complexes⁷³.

In order to study the role of orbital contribution in the stability of σ -hole bonds described above, we have performed NBO analysis focusing our attention on the second order perturbation analysis, since it is a useful tool to analyze donor-acceptor interactions. Table 2 lists the second-order perturbation stabilization energies $E^{(2)}$ and the amount of Wiberg bond index (WBI) associated with the σ -hole interactions. For all of the complexes under consideration, the NBO analysis indicates that the main stabilization element arises from the lone pair (Lp) donation by N atom of NCH to the $\sigma_{\text{C-X}}^*$ or $\sigma_{\text{Z-O}}^*$ acceptor orbital of the Lewis acid. An examination of the results reveals that the nature of X or Z itself influences the stabilization energy of these σ -hole interactions. For instance, the $\text{O}_3\text{Kr}\cdots\text{NCH}$ complex exhibit a larger $E^{(2)}$ value than the $\text{O}_3\text{Ar}\cdots\text{NCH}$ counterpart. Interestingly, the halogen-bonded complexes exhibits larger $E^{(2)}$ values than the aerogen-bonded ones. This may emphasize that the more important role of the charge-transfer interaction in the former complexes. Besides, Table 2 results indicates that the calculated WBI values are in the order of $\text{NCBr}\cdots\text{NCH} > \text{O}_3\text{Kr}\cdots\text{NCH} > \text{O}_3\text{Ar}\cdots\text{NCH} > \text{NCCl}\cdots\text{NCH}$, which is not correlated with the order of the interaction energies of these systems. From Table 2, it is also evident that the NBO atomic charges on the halogen or aerogen atoms in the binary

complexes are always larger than those of the isolated NCX or ZO₃ molecule. As seen, a greater change in the NBO atomic charge (Δq) is seen for the Kr and Br atoms, which indicates the large polarization of these atoms due to the X $\cdots$ N or Z $\cdots$ N interaction.

Table 3 lists the $C_Q(^{14}\text{N})$ values of the NCH moiety in the NCX $\cdots$ NCH and O₃Z $\cdots$ NCH complexes. The calculated $C_Q(^{14}\text{N})$ value of the isolated NCH molecule is 4.60 MHz, which is in good agreement with available experimental data (4.58 MHz)⁷⁴. From Table 3, it is seen that the formation of halogen or aerogen bond leads to a decrease in the $C_Q(^{14}\text{N})$ value, a finding already reported also for other related studies⁵³. The amount of shift in the $C_Q(^{14}\text{N})$ increases as O₃Kr $\cdots$ NCH > O₃Ar $\cdots$ NCH > NCB $\cdots$ NCH > NCCl $\cdots$ NCH, which is consistent with the calculated interaction energies of these systems. Moreover, a good linear correlation is found between the $C_Q(^{14}\text{N})$ and E_{int} values of these complexes (Figure S1 of Supporting Information), which reveals that the $C_Q(^{14}\text{N})$ parameter can be regarded as a useful tool for the characterization of strength of these σ -hole bonded complexes.

3.3. Cooperativity between halogen/aerogen and hydrogen bonding in NCX $\cdots$ (NCH)_{n=2-5} and O₃Z $\cdots$ (NCH)_{n=2-5} complexes

Figure S2 indicates the optimized structures of the linear NCX $\cdots$ (NCH)_{n=2-5} and O₃Z $\cdots$ (NCH)_{n=2-5} clusters. Table 4 lists the halogen and aerogen bond distances and their changes relative to the corresponding binary systems. One can see that the X $\cdots$ N and Z $\cdots$ N binding distances in the NCX $\cdots$ (NCH)_{n=2-5} and O₃Z $\cdots$ (NCH)_{n=2-5} are smaller than those in the corresponding dimers. For example, the calculated Cl $\cdots$ N binding distance in the NCCl $\cdots$ (NCH)₂ complex is 2.925 Å, which is 0.035 Å shorter than the corresponding interaction in NCCl $\cdots$ NCH complex. When a third HCN molecule is added as a proton acceptor, it contracts the Cl $\cdots$ N distance by 0.045 Å. A bigger contraction of 0.049 and 0.051 Å is found for the Cl $\cdots$ N distance when the fourth and fifth HCN molecules are added as an electron acceptor, respectively. For a given n, a larger halogen bond contraction is seen for the NCB $\cdots$ (NCH)_n complexes, which indicates the larger cooperative effects in these complexes compared to the NCCl $\cdots$ (NCH)_n ones. The calculated Ar $\cdots$ N binding distances in the O₃Ar $\cdots$ (NCH)_n complexes are 2.866, 2.863, 2.860 and 2.859 Å for n=2-5, respectively, which are 0.015, 0.018, 0.021 and 0.022 Å smaller than that of the binary O₃Ar $\cdots$ NCH system. As expected, a larger bond shortening is found in the O₃Kr $\cdots$ (NCH)_n complexes compared to the O₃Ar $\cdots$ (NCH)_n ones. Note

also that for a given $n=2-5$ cluster, the amount of bond contraction in the halogen bond is more important than that of the aerogen bond. Besides, for both $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters, a negligible bond shrinkage (less than 0.1 %) is found from the $n=4$ to $n=5$ cluster. This may suggest that the cooperativity effects are almost saturated in the larger clusters ($n > 5$).

The total BSSE-corrected total interaction energies of $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters are summarized in Table 4. One can see that for a given n , the interaction energies of the $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters are more negative than those of $\text{NCX}\cdots(\text{NCH})_n$ counterparts, which is consistent with the estimated $V_{\text{S,max}}$ value associated with the halogen and aerogen atoms in these complexes. Table 4 also lists the interaction energies of $\text{X}\cdots\text{N}$ and $\text{Z}\cdots\text{N}$ bonds in these systems. These are calculated as the total energy of the complexes minus the energy sum of the isolated units. For example, the halogen/aerogen bond interaction in the $n=5$ cluster (ABCDEF) is calculated as $E_{\text{int,X/Z}\cdots\text{N}} = E_{\text{ABCDEF}} - (E_{\text{A}} + E_{\text{BCDEF}}) - E'_{\text{int,AC}} - E'_{\text{int,AD}} - E'_{\text{int,AE}} - E'_{\text{int,AF}}$, in which E_{ABCDEF} means the total energy of the complex, E_{A} is the energy of the isolated optimized A monomer and E_{BCDEF} is the energy of the fully-relaxed BCDEF complex. The $E'_{\text{int,AC}}$, $E'_{\text{int,AD}}$, $E'_{\text{int,AE}}$ and $E'_{\text{int,AF}}$ terms are the interaction energy of $\text{A}\cdots\text{C}$, $\text{A}\cdots\text{D}$, $\text{A}\cdots\text{E}$ and $\text{A}\cdots\text{F}$ pairs in the geometry of the complex, respectively. All energies were corrected with BSSE. From Table 4, it is found that cooperative effects in both $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters tend to strengthen the $\text{X}\cdots\text{N}$ or $\text{Z}\cdots\text{N}$ interactions. For example, the cooperative enhancement increases the halogen bond energy in $\text{NCCl}\cdots(\text{NCH})_5$ and $\text{NCBr}\cdots(\text{NCH})_5$ clusters by -0.80 (23%) and -1.06 (24%) kcal/mol, respectively. Note that the larger cooperative enhancement in the Br complexes compared to the Cl counterparts confirms that the conclusion that the degree of cooperativity is dependent on the strength of the interaction. In both cases, we found almost a nice linear correlation between the halogen bond interaction energy and reciprocal of the number of HCN molecules in the clusters (Figure 4). For the $\text{O}_3\text{Z}\cdots(\text{NCH})_2$ through $\text{O}_3\text{Z}\cdots(\text{NCH})_5$, the interaction energy of the $\text{Z}\cdots\text{N}$ bond is also increased linearly with the cluster size (Figure 4). In particular, the interaction energy of $\text{Z}\cdots\text{N}$ bond increases by -0.95 (19%) and -1.24 (20%) kcal/mol compared to the binary $\text{O}_3\text{Z}\cdots\text{NCH}$ complex. Moreover, the small variation of aerogen bond energy from the $n=4$ to $n=5$ cluster, shown in Table 4, reaffirms our previous finding that the cooperativity effects are almost completely saturated in the larger clusters. Besides, it is evident from Figure 4 that the cooperative effects in larger $\text{NCX}\cdots(\text{NCH})_n$ or $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters increase further, approaching an asymptotic E_{int} value of -4.51, -5.79, -6.29 and -7.64

kcal/mol in the $\text{NCCl}\cdots(\text{NCH})_n$, $\text{NCBr}\cdots(\text{NCH})_n$, $\text{O}_3\text{Ar}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Kr}\cdots(\text{NCH})_n$ complexes, respectively, as $n \rightarrow \infty$.

Table 4 also lists the calculated cooperative energies (E_{coop}) of the title complexes, which are obtained from equation (2). As evident, all estimated E_{coop} values are negative, which indicate the stabilizing role of the cooperative effects in these clusters. The smallest E_{coop} value (-0.79 kcal/mol) is associated with $\text{NCCl}\cdots(\text{NCH})_2$ complex, while the largest one (-1.52 kcal/mol) is seen for $\text{O}_3\text{Kr}\cdots(\text{NCH})_5$. Note that the E_{coop} values obtained here is smaller than those of reported for the $(\text{LiCN})_n\cdots\text{HX}$ ($\text{X}=\text{F}, \text{Cl}$)⁷⁵ or $(\text{LiCN})_n\cdots\text{ClCF}_3/\text{SiF}_3\text{Cl}$ ⁷⁶ complexes. Moreover, for a given n , $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters exhibit larger E_{coop} values than $\text{NCX}\cdots(\text{NCH})_n$ counterparts. In fact, we found a good linear relationship between the E_{coop} values and the total interaction energies of the clusters in Figure 5.

To check whether the electron density and the corresponding Laplacian and energy density values at the $\text{X}\cdots\text{N}$ or $\text{Z}\cdots\text{N}$ BCPs are influenced by cooperative effects, the QTAIM analysis was performed on the linear clusters. The results are summarized in Table 5. As evident, the ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ values at the $\text{X}\cdots\text{N}$ or $\text{Z}\cdots\text{N}$ BCPs of these complexes are slightly larger than those in the isolated binary systems. This confirms that the strength of the halogen or aerogen bond in these clusters is increased in the presence of the hydrogen bond. On the other hand, the corresponding H_{BCP} values of the $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters are almost unchanged compared to the binary systems. This indicates that the covalency of halogen or aerogen bond in the larger clusters does not vary with the cluster size.

Table 5 summarizes the $E^{(2)}$ and WBI values of the $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters. It is seen that the calculated $E^{(2)}$ values of $\text{NCCl}\cdots(\text{NCH})_2$ and $\text{NCBr}\cdots(\text{NCH})_2$ complexes are 1.92 and 4.60 kcal/mol, respectively. The corresponding WBI values are 0.0090 and 0.0187, which indicates the small role of the orbital interaction in these systems. From Table 5, one can see that both $E^{(2)}$ and WBI values associated with the $\text{Cl}\cdots\text{N}$ and $\text{Br}\cdots\text{N}$ interactions are increased with the increase of cluster size. This can be understood as the cooperativity effects in these systems. For example, the $E^{(2)}$ values associated with the halogen bond interaction of $\text{NCCl}\cdots(\text{NCH})_5$ and $\text{NCBr}\cdots(\text{NCH})_5$ clusters are about 30% larger than those of corresponding binary complexes, respectively. On the other hand, a small increase in both $E^{(2)}$ and WBI values is evident in the $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ complexes, which may indicate the smaller role of orbital

interaction in the cooperativity between aerogen and hydrogen bond interactions in these systems.

Table 5 also collects the NBO atomic charges ($q_{X/Z}$) on the X or Z atoms of the $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters. It is seen that the cooperativity effects between the halogen/aerogen bond and hydrogen bond interactions in the $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters can affect the charge density distribution around the halogen or aerogen atom. Again, the increase in NBO atomic charges of halogen atoms is larger than those of aerogen ones, which indicates the larger polarization of the halogen atoms in the $\text{NCX}\cdots(\text{NCH})_n$ clusters compared to the aerogen atoms in the $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ ones. To further consider the polarization of the halogen or aerogen atoms in the title clusters, we have provided the electron density different (EDD) isosurfaces of these systems. As Figure 6 indicates, the formation of hydrogen bond interactions in the $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters induces an electron loss region over the X or Z atom, which confirms the polarization of these atoms due to the cooperative effects. As evident, such polarization effects are more important in the halogen atoms than the aerogen ones, which is consistent with the obtained result from the NBO analysis. Also, for the clusters under consideration, a greater electron density rearrangement is seen for the $\text{H}\cdots\text{N}$ than the $\text{X/Z}\cdots\text{N}$, which is due to the weaker nature of the former interaction compared to the latter one.

Figure 7 shows the NCI analysis results of the $\text{NCX}\cdots(\text{NCH})_5$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_5$ clusters. It is seen that upon the formation of the $\text{H}\cdots\text{N}$ interactions, the spikes associated with the $\text{X}\cdots\text{N}$ or $\text{Z}\cdots\text{N}$ interactions in these clusters appear in the more negative $\text{sign}(\lambda_2)\rho$ region. This can be regarded as another signature for the cooperative enhancement of the $\text{X}\cdots\text{N}$ or $\text{Z}\cdots\text{N}$ interaction in these systems.

As discussed above, cooperative effects strengthen the $\text{X}\cdots\text{N}$ and $\text{Z}\cdots\text{N}$ interactions in the title clusters, and therefore they can lead to a considerable change in the $C_Q(^{14}\text{N})$ values of the $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters. From Table 6, it is evident that the calculated $C_Q(^{14}\text{N})$ values are in the range of 4.16-4.36 MHz. For each $\text{NCX}\cdots(\text{NCH})_n$ or $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ cluster considered, the formation of $\text{H}\cdots\text{N}$ interaction leads to a decrease in $C_Q(^{14}\text{N})$ value, which is in good agreement with the strengthening of $\text{X}\cdots\text{N}$ and $\text{Z}\cdots\text{N}$ interaction in these clusters. For a given n , the amount of change of $C_Q(^{14}\text{N})$ increases in the order $\text{O}_3\text{Kr}\cdots(\text{NCH})_n > \text{O}_3\text{Ar}\cdots(\text{NCH})_n > \text{NCBr}\cdots(\text{NCH})_n > \text{NCCl}\cdots(\text{NCH})_n$ which is consistent with the calculated interaction energies of the $\text{X}\cdots\text{N}$ and $\text{Z}\cdots\text{N}$ bonds in these systems. As Figure S3 indicates, we

found a good linear correlation between the $E_{\text{int},X/Z\cdots N}$ and $C_Q(^{14}\text{N})$ values, which suggests that the $C_Q(^{14}\text{N})$ can be regarded as a useful parameter to estimate the strength of σ -hole interactions in these systems.

4. Conclusion

Ab initio MP2/aug-cc-pVTZ calculations were carried out for a series of linear $\text{NCX}\cdots(\text{NCH})_{n=2-5}$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_{n=2-5}$ clusters. It was found that the $\text{X}\cdots\text{N}$ and $\text{Z}\cdots\text{N}$ binding distances in the $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters are smaller than those in the corresponding dimers. For a given $n=2-5$ complex, the amount of bond contraction in the halogen bond is more important than that of the aerogen bond. Besides, for both $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters, a negligible bond shrinkage (less than 0.1 %) was found from the $n=4$ to $n=5$ cluster. This indicates that the cooperativity effects are almost saturated in the larger clusters ($n > 5$). The cooperative effects in the hydrogen bonding in both $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters tend to strengthen the $\text{X}\cdots\text{N}$ or $\text{Z}\cdots\text{N}$ interactions. The mechanism of the cooperativity effects was studied by means of MEP, QTAIM, NBO and NCI analyses. Almost a good linear correlation was found between the interaction energies of the $\text{X}\cdots\text{N}$ and $\text{Z}\cdots\text{N}$ bonds and $C_Q(^{14}\text{N})$ values, which implies that the nuclear quadrupole coupling constants at the site of ^{14}N nuclei can be viewed as a useful parameter to predict the strength of σ -hole interactions in these clusters.

References

1. Gao, S.; Wu, W.; Mo, Y., *J. Phys. Chem. A* **2009**, *113*, 8108.
2. Baker, R. J.; Colavita, P. E.; Murphy, D. M.; Platts, J. A.; Wallis, J. D., *J. Phys. Chem. A* **2011**, *116*, 1435.
3. Metrangolo, P.; Murray, J. S.; Pilati, T.; Politzer, P.; Resnati, G.; Terraneo, G., *CrystEngComm* **2011**, *13*, 6593.
4. Zahn, S.; Frank, R.; Hey-Hawkins, E.; Kirchner, B., *Chem. Eur. J.* **2011**, *17*, 6034.
5. Alkorta, I.; Elguero, J.; Solimannejad, M., *J. Phys. Chem. A* **2014**, *118*, 947.
6. Del Bene, J. E.; Alkorta, I.; Elguero, J., *J. Phys. Chem. A* **2014**, *118*, 3386.
7. Müller-Dethlefs, K.; Hobza, P., *Chem. Rev.* **2000**, *100*, 143.
8. Strekowski, L.; Wilson, B., *Mutat. Res. Fund. Mol. Mech. Mut.* **2007**, *623*, 3.
9. Scheiner, S. *Hydrogen bonding. A theoretical perspective*. Oxford University Press: New York, 1997.
10. Rozas, I.; Alkorta, I.; Elguero, J., *J. Am. Chem. Soc.* **2000**, *122*, 11154.
11. Ye, X.; Li, Z.-H.; Wang, W.; Fan, K.; Xu, W.; Hua, Z., *Chem. Phys. Lett.* **2004**, *397*, 56.
12. Grimme, S., *Angewandte Chemie International Edition in English* **2008**, *47*, 3430.
13. Tsuzuki, S.; Yoshida, M.; Uchimaru, T.; Mikami, M., *J. Phys. Chem. A* **2001**, *105*, 769.
14. Mahadevi, A. S.; Sastry, G. N., *Chem. Rev.* **2012**, *113*, 2100.
15. Murray, J. S.; Lane, P.; Clark, T.; Politzer, P., *J. Mol. Model.* **2007**, *13*, 1033.
16. Murray, J. S.; Lane, P.; Politzer, P., *J. Mol. Model.* **2009**, *15*, 723.
17. Alkorta, I.; Elguero, J.; Del Bene, J. E., *J. Phys. Chem. A* **2013**, *117*, 10497.
18. Politzer, P.; Murray, J. S.; Janjić, G. V.; Zarić, S. D., *Crystals* **2014**, *4*, 12.
19. Del Bene, J. E.; Alkorta, I.; Elguero, J., *J. Phys. Chem. A* **2015**, *119*, 5853.
20. Esrafil, M. D.; Mohammadian-Sabet, F., *Chem. Phys. Lett.* **2015**, *638*, 122.
21. Esrafil, M. D.; Mohammadian-Sabet, F., *Chem. Phys. Lett.* **2015**, *628*, 71.
22. Esrafil, M. D.; Mohammadian-Sabet, F., *J. Mol. Model.* **2015**, *21*, 65.
23. Wang, H.; Wang, W.; Jin, W. J., *Chem. Rev.* **2016**, *116*, 5072.
24. Bauzá, A.; Mooibroek, T. J.; Frontera, A., *ChemPhysChem* **2015**, *16*, 2496.
25. Metrangolo, P.; Murray, J. S.; Pilati, T.; Politzer, P.; Resnati, G.; Terraneo, G., *Cryst. Growth Des.* **2011**, *11*, 4238.
26. Murray, J. S.; Politzer, P., *WIREs Comput. Mol. Sci.* **2011**, *1*, 153.
27. Hennemann, M.; Murray, J. S.; Politzer, P.; Riley, K. E.; Clark, T., *J. Mol. Model.* **2012**, *18* (6), 2461.
28. Murray, J. S.; Lane, P.; Clark, T.; Riley, K. E.; Politzer, P., *J. Mol. Model.* **2012**, *18*, 541.
29. Politzer, P.; Murray, J. S.; Clark, T., *Phys. Chem. Chem. Phys.* **2013**, *15*, 11178.
30. Murray, J. S.; Macaveiu, L.; Politzer, P., *J. Comput. Sci.* **2014**, *5*, 590.
31. Stone, A. J., *J. Am. Chem. Soc.* **2013**, *135*, 7005.
32. Hill, J. G.; Legon, A. C., *Phys. Chem. Chem. Phys.* **2015**, *17*, 858.
33. Wang, W.; Ji, B.; Zhang, Y., *J. Phys. Chem. A* **2009**, *113*, 8132.
34. Esrafil, M. D.; Mohammadian-Sabet, F., *Chem. Phys. Lett.* **2015**, *634*, 210.
35. Solimannejad, M.; Gharabaghi, M.; Scheiner, S., *J. Chem. Phys.* **2011**, *134*, 024312.
36. Del Bene, J. E.; Alkorta, I.; Sanchez-Sanz, G.; Elguero, J., *J. Phys. Chem. A* **2011**, *115*, 13724.
37. Alkorta, I.; Elguero, J.; Del Bene, J. E., *J. Phys. Chem. A* **2013**, *117*, 4981.
38. Alkorta, I.; Elguero, J.; Grabowski, S. J., *Phys. Chem. Chem. Phys.* **2015**, *17*, 3261.
39. Grabowski, S. J., *Phys. Chem. Chem. Phys.* **2014**, *16*, 1824.

40. Li, Q.; Guo, X.; Yang, X.; Li, W.; Cheng, J.; Li, H.-B., *Phys. Chem. Chem. Phys.* **2014**, *16*, 11617.
41. Esrafil, M. D.; Mohammadirad, N.; Solimannejad, M., *Chem. Phys. Lett.* **2015**, *628*, 16.
42. Esrafil, M. D.; Mohammadian-Sabet, F., *J. Mol. Model.* **2015**, *21*, 60.
43. Bauzá, A.; Frontera, A., *Angew. Chem. Int. Ed.* **2015**, *54*, 7340.
44. Bauzá, A.; Frontera, A., *Phys. Chem. Chem. Phys.* **2015**, *17*, 24748.
45. Bauzá, A.; Frontera, A., *ChemPhysChem* **2015**, *16*, 3625.
46. Gao, M.; Cheng, J.; Li, W.; Xiao, B.; Li, Q., *Chem. Phys. Lett.* **2016**, *651*, 50.
47. Esrafil, M. D.; Mohammadian-Sabet, F., *Chem. Phys. Lett.* **2016**, *654*, 23.
48. Miao, J.; Song, B.; Gao, Y., *Chem. Asian J.* **2016**, *22*, 2586.
49. Esrafil, M. D.; Asadollahi, S., *Mol. Phys.* **2016**, *114*, 2177.
50. Esrafil, M. D.; Vessally, E., *Mol. Phys.* **2016**, *114*, 3265.
51. Haner, J.; Schrobilgen, G. J., *Chem. Rev.* **2015**, *115*, 1255.
52. Miao, J.; Song, B.; Gao, Y., *Chem. Eur. J.* **2015**, *10*, 2615.
53. Esrafil, M. D.; Hadipour, N. L., *Mol. Phys.* **2011**, *109*, 2451.
54. Li, Q.; Hu, T.; An, X.; Li, W.; Cheng, J.; Gong, B.; Sun, J., *ChemPhysChem* **2009**, *10*, 3310.
55. Li, Q.; Li, R.; Liu, Z.; Li, W.; Cheng, J., *J. Comput. Chem.* **2011**, *32*, 3296.
56. Li, Q.; Lin, Q.; Li, W.; Cheng, J.; Gong, B.; Sun, J., *ChemPhysChem* **2008**, *9*, 2265.
57. 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.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.
58. Boys, S. F.; Bernardi, F., *Mol. Phys.* **1970**, *19*, 553.
59. Bulat, F.; Toro-Labbé, A.; Brinck, T.; Murray, J.; Politzer, P., *J. Mol. Model.* **2010**, *16*, 1679.
60. Reed, A. E.; Curtiss, L. A.; Weinhold, F., *Chem. Rev.* **1988**, *88*, 899.
61. Glendenning, E.; Badenhoop, J.; Reed, A.; Carpenter, J.; Bohmann, J.; Morales, C.; Weinhold, F., *Theoretical Chemistry Institute, University of Wisconsin, Madison* **2001**.
62. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*. Oxford University Press: New York, 1990.
63. Johnson, E. R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A. J.; Yang, W., *J. Am. Chem. Soc.* **2010**, *132*, 6498.
64. Lu, T.; Chen, F., *J. Comput. Chem.* **2012**, *33*, 580.
65. Lucken, E., *Nuclear Quadrupole Coupling Constants*. Academic Press: New York, 1969.
66. Pyykkö, P., *Mol. Phys.* **2001**, *99*, 1617.
67. Parra, R. D.; Bulusu, S.; Zeng, X. C., *J. Chem. Phys.* **2003**, *118*, 3499.
68. Bondi, A., *J. Phys. Chem.* **1964**, *68*, 441.
69. Alkorta, I.; Sánchez-Sanz, G.; Elguero, J.; Del Bene, J. E., *J. Phys. Chem. A* **2012**, *117*, 183.

70. Lv, H.; Zhuo, H.-Y.; Li, Q.-Z.; Yang, X.; Li, W.-Z.; Cheng, J.-B., *Mol. Phys.* **2014**, *112*, 3024.
71. Li, Q.-Z.; Zhuo, H.-Y.; Li, H.-B.; Liu, Z.-B.; Li, W.-Z.; Cheng, J.-B., *J. Phys. Chem. A* **2015**, *119*, 2217.
72. Esrafil, M. D.; Mohammadian-Sabet, F.; Solimannejad, M., *Chem. Phys. Lett.* **2016**, 667, 337.
73. Li, Q.; Zhu, H.; Zhuo, H.; Yang, X.; Li, W.; Cheng, J., *Spectrochim. Acta Mol. Biomol. Spectrosc.* **2014**, *132*, 271.
74. Simmons, J. W.; Anderson, W. E.; Gordy, W., *Phys. Rev.* **1950**, *77*, 77.
75. Solimannejad, M.; Orojloo, M.; Amani, S., *J. Mol. Model.* **2015**, *21*, 183.
76. Solimannejad, M.; Orojloo, M.; Amani, S., *Struct. Chem.* **2015**, *26*, 793.

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Figure 1. Calculated MEP (above) and ELF (below) isosurfaces of the NCX and ZO₃ monomers. The color code for MEP plots, in kcal/mol, is: red > 20; 20 > yellow > 5; 5 > green > -10 and blue < -10. The locations of the σ -holes at the halogen or aerogen atoms associated with the C–X or Z–O bond are indicated with black circles, and their values are given in kcal/mol. The isosurface values of the MEP and ELF maps are 0.001 and 0.75 au, respectively.

Figure 2. Optimized structure of $\text{NCX}\cdots\text{NCH}$ and $\text{O}_3\text{Z}\cdots\text{NCH}$ complexes

Figure 3. NCI isosurface (green disk; isovalue=0.5 au) and plot of the reduced density gradient (RDG) versus $\text{sign}(\lambda_2)\rho$ of $\text{NCX}\cdots\text{NCH}$ and $\text{O}_3\text{Z}\cdots\text{NCH}$ complexes

Figure 4. Linear correlation between the halogen or aerogen bond interaction energies and reciprocal of the number of HCN molecules in the clusters

Figure 5. Relationship between the cooperative energy and total interaction energy of the linear $\text{NCX}\cdots(\text{NCH})_{2-5}$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_{2-5}$ clusters

Figure 6. Electron density difference plots (± 0.004 au) of the $\text{NCX}\cdots(\text{NCH})_5$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_5$ complexes. The cyan and olive regions indicate regions of decreased and increased electron densities, respectively.

Figure 7. NCI isosurface (green disk; isovalue=0.5 au) and plot of the reduced density gradient (RDG) versus $\text{sign}(\lambda_2)\rho$ of $\text{NCX}\cdots(\text{NCH})_5$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_5$ complexes

Table 1. Binding distances (R , Å), interactions energies (E_{int} , kcal/mol), electron density (ρ_{BCP} , au), its Laplacian ($\nabla^2\rho_{\text{BCP}}$, au) and total electron energy density (H_{BCP} , au) at $X\cdots N$ and $Z\cdots N$ BCPs of $\text{NCX}\cdots\text{NCH}$ and $\text{O}_3\text{Z}\cdots\text{NCH}$ complexes

complex	R	E_{int}	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	H_{BCP}
$\text{NCCl}\cdots\text{NCH}$	2.960	-3.49	0.0105	0.0521	0.0029
$\text{NCBr}\cdots\text{NCH}$	2.920	-4.44	0.0138	0.0614	0.0027
$\text{O}_3\text{Ar}\cdots\text{NCH}$	2.881	-5.10	0.0139	0.0660	0.0031
$\text{O}_3\text{Kr}\cdots\text{NCH}$	2.903	-6.09	0.0162	0.0685	0.0025

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Table 2. NBO charge-transfer energy ($E^{(2)}$, kcal/mol), Wiberg bond index (WBI), NBO atomic charges on the X or Z ($q_{X/Z}$, e) and complexation-induced change of these atomic charges ($\Delta q_{X/Z}$, e) in the $NCX \cdots NCH$ and $O_3Z \cdots NCH$ complexes

complex	$E^{(2)}$	WBI	$q_{X/Z}$	$\Delta q_{X/Z}$
$NCCl \cdots NCH$	1.61	0.0077	0.166	0.019
$NBr \cdots NCH$	3.86	0.0158	0.262	0.022
$O_3Ar \cdots NCH$	0.21	0.0094	2.051	0.021
$O_3Kr \cdots NCH$	0.67	0.0126	2.524	0.031

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Table 3. ^{14}N nuclear quadrupole coupling constant ($C_Q(^{14}\text{N})$, MHz) of NCH molecule and its change ($\Delta C_Q(^{14}\text{N})$, MHz) due to the complex formation in the $\text{NCX}\cdots\text{NCH}$ and $\text{O}_3\text{Z}\cdots\text{NCH}$ complexes

complex	$C_Q(^{14}\text{N})$	$\Delta C_Q(^{14}\text{N})$
$\text{NCCl}\cdots\text{NCH}$	5.32	-0.20
$\text{NCBr}\cdots\text{NCH}$	5.24	-0.28
$\text{O}_3\text{Ar}\cdots\text{NCH}$	5.22	-0.30
$\text{O}_3\text{Kr}\cdots\text{NCH}$	5.13	-0.39

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Table 4. Halogen or aerogen bond distances (R , Å) and their changes (ΔR , Å), total interaction energies (E_{int} , kcal/mol), $X/Z \cdots N$ interaction energies ($E_{\text{int},X/Z \cdots N}$, kcal/mol) and their changes ($\Delta E_{\text{int},X/Z \cdots N}$, kcal/mol) with respect to the binary complexes, and cooperative energies (E_{coop} , kcal/mol) of the linear $\text{NCX} \cdots (\text{NCH})_n$ and $\text{O}_3\text{Z} \cdots (\text{NCH})_n$ clusters

complex	R	ΔR	$E_{\text{int},\text{total}}$	$E_{\text{int},X/Z \cdots N}$	$\Delta E_{\text{int},X/Z \cdots N}$	E_{coop}
$\text{NCCl} \cdots (\text{NCH})_2$	2.925	-0.035	-9.00	-3.97	-0.48	-0.79
$\text{NCCl} \cdots (\text{NCH})_3$	2.915	-0.045	-15.12	-4.16	-0.67	-1.10
$\text{NCCl} \cdots (\text{NCH})_4$	2.911	-0.049	-21.47	-4.24	-0.75	-1.27
$\text{NCCl} \cdots (\text{NCH})_5$	2.909	-0.051	-27.92	-4.29	-0.80	-1.39
$\text{NCBr} \cdots (\text{NCH})_2$	2.881	-0.039	-10.16	-5.08	-0.64	-1.00
$\text{NCBr} \cdots (\text{NCH})_3$	2.870	-0.050	-16.35	-5.33	-0.89	-1.24
$\text{NCBr} \cdots (\text{NCH})_4$	2.865	-0.055	-22.73	-5.44	-1.00	-1.38
$\text{NCBr} \cdots (\text{NCH})_5$	2.863	-0.057	-29.20	-5.50	-1.06	-1.47
$\text{O}_3\text{Ar} \cdots (\text{NCH})_2$	2.866	-0.015	-10.74	-5.71	-0.61	-0.92
$\text{O}_3\text{Ar} \cdots (\text{NCH})_3$	2.863	-0.018	-16.88	-5.92	-0.82	-1.17
$\text{O}_3\text{Ar} \cdots (\text{NCH})_4$	2.860	-0.021	-23.23	-6.01	-0.91	-1.32
$\text{O}_3\text{Ar} \cdots (\text{NCH})_5$	2.859	-0.022	-29.68	-6.05	-0.95	-1.43
$\text{O}_3\text{Kr} \cdots (\text{NCH})_2$	2.878	-0.025	-11.97	-6.90	-0.81	-1.16
$\text{O}_3\text{Kr} \cdots (\text{NCH})_3$	2.874	-0.029	-18.18	-7.17	-1.08	-1.33
$\text{O}_3\text{Kr} \cdots (\text{NCH})_4$	2.872	-0.031	-24.56	-7.28	-1.19	-1.44
$\text{O}_3\text{Kr} \cdots (\text{NCH})_5$	2.871	-0.032	-31.03	-7.33	-1.24	-1.52

Table 5. QTAIM and NBO analyses of the halogen or aerogen bond in the linear $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters

complex	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	H_{BCP}	$E^{(2)}$	WBI	$q_{\text{X/Z}}$	$\Delta q_{\text{X/Z}}$
$\text{NCCl}\cdots(\text{NCH})_2$	0.0115	0.0560	0.0030	1.92	0.0090	0.172	0.006
$\text{NCCl}\cdots(\text{NCH})_3$	0.0118	0.0574	0.0030	2.02	0.0094	0.174	0.008
$\text{NCCl}\cdots(\text{NCH})_4$	0.0119	0.0579	0.0030	2.06	0.0096	0.175	0.009
$\text{NCCl}\cdots(\text{NCH})_5$	0.0120	0.0581	0.0030	2.08	0.0096	0.175	0.009
$\text{NCBr}\cdots(\text{NCH})_2$	0.0152	0.0663	0.0026	4.60	0.0187	0.267	0.005
$\text{NCBr}\cdots(\text{NCH})_3$	0.0156	0.0678	0.0026	4.84	0.0196	0.270	0.008
$\text{NCBr}\cdots(\text{NCH})_4$	0.0158	0.0683	0.0026	4.94	0.0200	0.271	0.009
$\text{NCBr}\cdots(\text{NCH})_5$	0.0159	0.0686	0.0026	4.99	0.0201	0.271	0.009
$\text{O}_3\text{Ar}\cdots(\text{NCH})_2$	0.0148	0.0693	0.0031	0.32	0.0096	2.054	0.003
$\text{O}_3\text{Ar}\cdots(\text{NCH})_3$	0.0150	0.0700	0.0031	0.37	0.0096	2.055	0.004
$\text{O}_3\text{Ar}\cdots(\text{NCH})_4$	0.0151	0.0704	0.0031	0.40	0.0096	2.056	0.005
$\text{O}_3\text{Ar}\cdots(\text{NCH})_5$	0.0151	0.0705	0.0031	0.41	0.0096	2.056	0.005
$\text{O}_3\text{Kr}\cdots(\text{NCH})_2$	0.0176	0.0731	0.0025	0.77	0.0134	2.529	0.005
$\text{O}_3\text{Kr}\cdots(\text{NCH})_3$	0.0179	0.0743	0.0024	0.82	0.0135	2.530	0.006
$\text{O}_3\text{Kr}\cdots(\text{NCH})_4$	0.0180	0.0747	0.0024	0.85	0.0136	2.531	0.007
$\text{O}_3\text{Kr}\cdots(\text{NCH})_5$	0.0181	0.0748	0.0024	0.87	0.0136	2.531	0.007

Table 6. ^{14}N nuclear quadrupole coupling constants (C_Q , MHz) of the linear $\text{NCX}\cdots(\text{NCH})_n$ and $\text{O}_3\text{Z}\cdots(\text{NCH})_n$ clusters and their changes (ΔC_Q , MHz) relative to the corresponding binary complexes ^a

complex	C_Q	ΔC_Q
$\text{NCCl}\cdots(\text{NCH})_2$	4.36	-0.06
$\text{NCCl}\cdots(\text{NCH})_3$	4.34	-0.08
$\text{NCCl}\cdots(\text{NCH})_4$	4.33	-0.09
$\text{NCCl}\cdots(\text{NCH})_5$	4.32	-0.10
$\text{NCBr}\cdots(\text{NCH})_2$	4.28	-0.07
$\text{NCBr}\cdots(\text{NCH})_3$	4.26	-0.09
$\text{NCBr}\cdots(\text{NCH})_4$	4.24	-0.11
$\text{NCBr}\cdots(\text{NCH})_5$	4.24	-0.11
$\text{O}_3\text{Ar}\cdots(\text{NCH})_2$	4.28	-0.05
$\text{O}_3\text{Ar}\cdots(\text{NCH})_3$	4.25	-0.08
$\text{O}_3\text{Ar}\cdots(\text{NCH})_4$	4.24	-0.09
$\text{O}_3\text{Ar}\cdots(\text{NCH})_5$	4.24	-0.09
$\text{O}_3\text{Kr}\cdots(\text{NCH})_2$	4.20	-0.06
$\text{O}_3\text{Kr}\cdots(\text{NCH})_3$	4.17	-0.09
$\text{O}_3\text{Kr}\cdots(\text{NCH})_4$	4.16	-0.10
$\text{O}_3\text{Kr}\cdots(\text{NCH})_5$	4.16	-0.10

^a For each complex, the calculated C_Q values refers to the NCH fragment which interacts with the NCX or O_3Z molecule.