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Cooperative and diminutive interplay between the hydrogen bonding and halogen bonding in ternary complexes of HCCX (X = Cl, Br) with HCN and HNC

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ABSTRACT

MP2 calculations with cc-pVTZ basis set were used to analyze intermolecular interactions in XCCH···Y···Y, HCCX···Y···Y, and Y···HCCX···Y triads (X = Cl, Br; Y = HCN, and HNC) which are connected via hydrogen and halogen bonds. To understand the properties of the systems better, the corresponding dyads are also studied. Molecular geometries, binding energies, and infrared spectra and NMR properties of monomers, dyads, and triads are investigated at the MP2/cc-pVTZ computational level. Particular attention is paid to parameters such as cooperative energies, and many-body interaction energies. Those complexes with simultaneous role of HCCX as hydrogen and halogen donor are diminutive being this energetic effect between 1.09 and 1.42 kJ mol^{-1}. Those complexes with the role of HCCX as hydrogen or halogen donor show cooperativity with energy values ranging between −1.00 and −2.81 kJ mol^{-1}. The electronic properties of the complexes are analyzed using parameters derived from the atoms in molecules (AIM) methodology.

1. Introduction

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

Halogen bonding describes a directional interaction between covalently bound halogen atoms (X) and Lewis bases (A). Several excellent reviews on halogen bonding are now available [2,3] together with a recent book [4].

When a half-filled p orbital participates in forming a covalent bond, its electron normally tends to be localized in the internuclear region, thereby diminishing the electronic density in the outer (noninvolved) lobe of that orbital. This electron-deficient outer lobe of a half-filled p orbital involved in a covalent bond is called a "σ-hole" [5]. Positive σ-holes have now been found computationally on the outer surfaces of group V, VI, and VII atoms in numerous molecules [6–9]. Halogen bonding is a subset of σ–hole bonding. It is increasingly recognized that σ-hole bonding, especially involving group VII, occurs widely in biological systems [6,7], and there is also considerable interest in applying this concept in crystal engineering [10].

Recently, a few articles concerning cooperativity between hydrogen and halogen bonding and σ-hole bonds have been published [11–17]. In the present work; we study some simple structures which include hydrogen bonding and halogen bonding. Thus, we have selected two halogenated acetylenes (HCCX, X = Cl and Br) due to their implications in atmosphere chemistry and green house effect [18], and the HCN/HNC isomers that are prototypes of linear hydrogen bond donor/acceptors. We have performed a theoretical study on the twelve XCCH···Y···Y, HCCX···Y···Y, and Y···HCCX···Y triads (X = Cl, Br; Y = HCN, and HNC) with the aim of investigating the effect of hydrogen bonding on a halogen bond and the cooperativity between them. Additionally, to understand this cooperativity effect, we have also performed a many-body interaction analysis of the title complexes.

2. Computational details

Structures of the monomers and the complexes have been optimized and characterized by frequency computations at the MP2/cc-pVTZ computational level. In a recent paper, Riley et al. pointed out that this method provides very good estimates of geometries and energies for noncovalent complexes [19]. The stabilization energy was calculated as the difference of the total energy of the complexes and the sum of the isolated monomers in their minima configuration. The full counterpoise (CP) method [20] was used to correct the stabilization energy from the inherent basis set superposition error (BSSE). NMR chemical shifts were computed by using the gauge-including atomic orbital (GIAO) approach [21] at

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the MP2 level. Calculations have been performed using the Gaussian 03 program package [22].

The atoms in molecules (AIM) methodology [23] was used to analyze the electron density of the systems considered at the MP2/cc-pVTZ computational level. The topological analysis was carried out with the AIMAll program [24].

3. Results and discussion

3.1. Geometries

The systems studied form stable triads with $C_{\infty v}$ symmetry (Scheme 1). The bond angle between halogen, hydrogen and nitrogen (carbon) atoms that are involved in the interactions are 180°. The intermolecular distances found for these systems are in the range of 3.03–3.29 Å for X···C(N) halogen bonds and 2.02–2.40 Å for hydrogen bonds (Table 1).

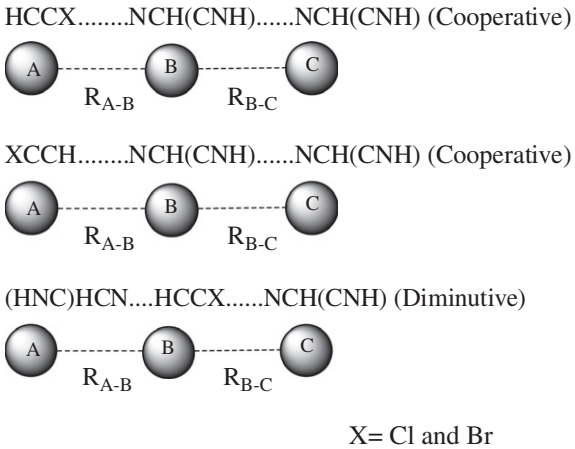
For the systems with XCCH···Y···Y and HCCX···Y···Y arrangements, the X···C(N) and H···C(N) distances in the triads are smaller than the corresponding values in the dyads, with differences in the range between 0.027–0.059 Å and 0.029–0.054 Å respectively. The values given are the differences in distances between trimers and dimers (Table 1). This trend can be interpreted as a cooperative effect of hydrogen bond and halogen bonds. For systems with Y···HCCX···Y arrangement, the X···C(N) and H···C(N) distances in the triads are larger than the corresponding values in the dyads, with differences in the range between 0.028–0.038 Å and 0.024–0.033 Å respectively (Table 1). This trend can be interpreted as a diminutive effect of hydrogen bond and halogen bonds that are reported here for the first time.

3.2. Energies

The stabilization energy in the dyads can be regarded as the energy difference between the complex and the monomers: $Ei(AB) = E_{AB} - (E_A + E_B)$ and the corresponding value in the triads (Ei(ABC)) is calculated in a similar way. Ei(AB,T) and Ei(BC,T) are the interaction energies of AB and BC dyads while they are in the geometry of triads. In Table 2, the stabilization energy of the twelve studied triads and respective dyads are presented. All results were corrected for BSSE using the counterpoise method. As shown in Table 2, the binding energy of the title complexes ranges from −16.24 to −46.13 kJ mol^{-1}.

An energetic cooperativity parameter has been calculated using Eq. (1) [25–27].

$$E_{Coop} = Ei(ABC) - Ei(AB) - Ei(BC) - Ei(AC) \quad (1)$$



Scheme 1. Disposition of the monomers within the complexes.

Table 1
Intermolecular distances R in the investigated triads (T), and dyads. ΔR indicates the changes relative to the respective dyads.

Triads(A···B···C)	R(AB,T)	R(AB)	ΔR_{AB}	R(BC,T)	R(BC)	ΔR_{BC}
BrCCH–CNH–CNH	2.397	2.452	−0.054	2.021	2.051	−0.029
BrCCH–NCH–NCH	2.272	2.316	−0.044	2.166	2.197	−0.030
ClCCH–CNH–CNH	2.402	2.456	−0.054	2.022	2.051	−0.029
ClCCH–NCH–NCH	2.277	2.315	−0.038	2.166	2.197	−0.031
HCCBr–CNH–CNH	3.113	3.172	−0.059	2.023	2.051	−0.028
HCCBr–NCH–NCH	3.036	3.071	−0.035	2.171	2.197	−0.026
HCCCl–CNH–CNH	3.206	3.252	−0.046	2.034	2.051	−0.016
HCCCl–NCH–NCH	3.074	3.101	−0.027	2.177	2.197	−0.019
HCN–BrCCH–NCH	3.099	3.071	0.028	2.340	2.316	0.024
HNC–BrCCH–CNH	3.209	3.172	0.037	2.488	2.452	0.037
HCN–ClCCH–NCH	3.132	3.101	0.031	2.343	2.315	0.028
HNC–ClCCH–CNH	3.290	3.252	0.038	2.489	2.456	0.033

Table 2
Stabilization energies (kJ mol^{-1}) of hydrogen and halogen bonding in the studied dyads (D) and triads (T) at MP2/cc–pVTZ level.

Triads(A···B···C)	Ei(ABC)	Ei(AB)	Ei(BC)	Ei(AB,T)	Ei(BC,T)	E_{COOP}[a]
BrCCH–CNH–CNH	−46.13	−11.37	−31.40	−10.35	−31.22	−2.81
BrCCH–NCH–NCH	−32.16	−11.07	−18.75	−10.80	−18.63	−1.75
ClCCH–CNH–CNH	−46.04	−11.31	−31.40	−10.30	−31.23	−2.78
ClCCH–NCH–NCH	−32.10	−11.01	−18.75	−10.76	−18.62	−1.74
HCCBr–CNH–CNH	−44.86	−10.62	−31.40	−9.55	−31.24	−2.51
HCCBr–NCH–NCH	−31.11	−10.40	−18.75	−10.16	−18.65	−1.53
HCCCl–CNH–CNH	−40.17	−6.99	−31.40	−6.16	−31.32	−1.62
HCCCl–NCH–NCH	−27.28	−7.27	−18.75	−7.11	−18.68	−1.00
HCN–BrCCH–NCH	−19.45	−10.4	−11.07	−10.42	−11.09	1.29
HNC–BrCCH–CNH	−19.71	−10.62	−11.37	−10.62	−11.39	1.42
HCN–ClCCH–NCH	−16.43	−7.27	−11.01	−7.25	−11.05	1.09
HNC–ClCCH–CNH	−16.24	−6.99	−11.31	−6.95	−11.34	1.18

[a] E_{COOP} is calculated using the Eq. (1) in the text.

where Ei(ABC) is the stabilization energy of the trimer, Ei(AB) and Ei(BC) are the stabilization energy of the isolated dimers within their corresponding minima configuration and Ei(AC) is the interaction energy of the molecules A and C in the geometry they have in the trimer.

In XCCH···Y···Y, and HCCX···Y···Y studied complexes, a favorable cooperativity is observed with values that range between −1.00 and −2.81 kJ mol^{-1}. In the same way, diminutive effects are observed for those complexes with Y···HCCX···Y arrangement in the ranges between 1.09 and 1.42 kJ mol^{-1}. The present results are consistent with the expectation that negative cooperativity results when the central molecule acts as double electron acceptor. When central molecule acts as electron donor and proton donor at the same time, then cooperativity is obtained.

Now let us to compare results of the present study with that of its older cousin, the H-bond. The properties of hydrogen bonding of molecular complexes are directly connected to the cooperativity effect. For example, in the A–H···B–H···C arrangement of the hydrogen-bonded system, if the proton-acceptor group, B–H, accepts a proton from the proton-donating group A–H and donates its proton to C at the same time, the hydrogen bonding between the A–H···B and B–H···C becomes stronger. Therefore, the hydrogen bonding in this molecular cluster makes a positive contribution to the cooperativity; as a result, the total interaction energy becomes larger than the sum of the molecular pair interaction energies [28]. However, sometimes, the hydrogen bonding in the molecular clusters makes a negative contribution to the cooperativity, and it is called the anticooperativity effect. For example, in the hydrogen-bonded molecular cluster, such as the A–H···C···H–B arrangement, if the proton-acceptor group C accepts two protons from the two proton-donating groups A–H and B–H at the same time, the total interaction energy becomes less than the sum of