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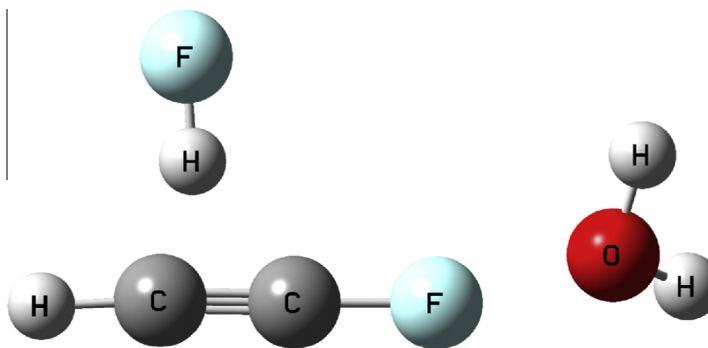
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saaCooperative effects in FH/Li...HCCX...OH₂ complexes (X = F, Cl, Br, H)Sean A.C. McDowell^{a,*}, A. David Buckingham^b^a Department of Biological and Chemical Sciences, The University of the West Indies, Cave Hill Campus, Barbados^b Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

HIGHLIGHTS

- A combination of H...π bonds and halogen bonds yield stable T-shaped trimers.
- Cooperative effects enhance trimer stability by 7–10%.
- Dimers of FH and C₂H₂ are T-shaped.
- Dimers of FLi and C₂H₂ have the monomers lying side by side.

GRAPHICAL ABSTRACT



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ABSTRACT

The dimers with general formula FH/FLi...HCCX and HCCX...OH₂, and the trimers FH...HCCX...OH₂ (X = F, Cl, Br, H), were optimized computationally to stable structures. These model systems derive their strength from a combination of H...π (or Li...π) electrostatic interactions in the T-shaped FH/FLi...HCCX dimers and halogen bonding between the X and the O atom of H₂O (or CH...O hydrogen-bonding in HCCH complexes). These cooperative interactions in the trimer clusters yield a non-additive energy which enhances the stability by between 7% and 10%. The variation in the interaction energies, as well as other selected properties, for different X is rationalized and discussed.

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Introduction

Hydrogen and halogen bonding are two types of noncovalent interactions which have been studied extensively [1–6]. Studies of hydrogen bonding have a long history, stretching back over more than a century, whereas work on halogen bonding is of more recent vintage. Halogen bonding has attracted much interest because its highly directional nature has opened up potential technological applications in a number of fields, including crystal engineering [6–8] and polymer chemistry [9]. Its importance for biological systems was pointed out in an early study by Auffinger et al. [10]. There have been several reviews of halogen bonding; two recent ones are in Refs. [6,11].

Both types of interaction may be represented as A–X...Y type interactions; for H-bonded complexes X = H, and for halogen-bonded species X = F, Cl, Br, I, with A being an atom or group of atoms with a greater electron affinity than X, and Y an atom or group of atoms with a region of high electron density (e.g. lone pairs localized on Y) [1–6]. The similarities between halogen and hydrogen bonding have been documented in the literature [6].

The hydrogen bond is mainly electrostatic in origin, resulting from the attraction between the positive H of A–H and the negative site on Y. The polarization of the A–H molecule by the electric field from Y (and of Y by A–H), as well as the dispersion force between the interacting monomers, may also make significant attractive contributions to the hydrogen bond [1]. By contrast, the halogen bond derives its strength from the interaction between the negative site on Y and a region of positive electrostatic potential along the extension of the A–X bond, called the σ-hole [6]. The halogen bond is thus also dominated by electrostatic interactions but is

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even more strongly oriented than the hydrogen bond and is almost always linear; the A–X···Y angle is close to 180°, with any significant deviations from linearity due mainly to secondary interactions [6].

Another interesting feature observed for hydrogen bonds is cooperativity, in which the strength of a hydrogen-bonded chain is enhanced as the chain length increases [1]. A recent example is the enhanced binding in trimers containing HBO and HCN relative to that of the hydrogen-bonded dimer species constituting the trimer [12]. Halogen bonds have also been shown to have a cooperative effect with other non-covalent interactions. For example, Solimannejad and Malekani found enhancements of both hydrogen and halogen bonding in HCCX/XCCH···NCH/CNH···NCH/CNH (X = Cl, Br) trimers relative to their constituent dimers [13]. They also noted that trimers with the HCCX in the middle of the chain (e.g. HCN···HCCX···NCH) showed a diminutive effect relative to the dimers – i.e. the non-covalent interactions were diminished when the HCCX acts as a double electron acceptor [13]. In a recent paper, Grabowski found that cooperativity in the T-shaped FH···HCCH···Cl[−], FH···HCCl···Cl[−] and FH···HCCl···F[−] trimers strengthened the hydrogen and halogen bonds present in the constituent dimers [14].

In the present study, we investigated the properties of the hydrogen-bonded FH···HCCX and lithium-bonded FLi···HCCX (X = F, Cl, Br, H) dimers, in which the H or Li atom interacts with the HCCX species via the π -electron cloud of the CC triple bond. We also studied the halogen-bonded HCCX···OH₂ (X = F, Cl, Br) and the hydrogen-bonded HCCH···OH₂ dimers. The combination and interplay of the non-covalent interactions arising from these two dimer systems were investigated in the FH/FLi···HCCX···OH₂ (X = F, Cl, Br, H) trimer systems. The cooperative effects in these trimer systems were also studied. The computational approach used is outlined in the next section.

Computational methodology

The geometry and interaction energy (ΔE) for the complexes were computed at the MP2/6-311++G(d,p) level of theory with the Gaussian03 W suite of programs [15]; ΔE was corrected for the basis set superposition energy (BSSE) using the Boys-Bernardi counterpoise correction method [16]. The harmonic vibrational frequencies were determined by the analytic second derivatives procedure implemented in Gaussian03, which confirms that the optimized structures are minima on their respective potential energy surfaces.

Stable T-shaped FH···HCCX (X = F, Cl, Br, H) dimers, with the FH molecular axis perpendicular to the HCCX molecular axis and the H atom of FH pointing at the CC triple-bond, were obtained. Selected molecular parameters for these dimers are shown in Table 1. For the corresponding FLi···HCCX analogues, the only T-shaped dimer

obtained was for FLi···HCCBr. The other FLi···HCCX dimers adopt a geometry with the FLi and HCCX molecules lying nearly parallel to each other and with the F and Li atoms of FLi bonded respectively to the H and C atoms of the HCCX (see Fig. 1). The results for these dimers are in Table 2. The results for the optimized HCCX···OH₂ dimers are shown in Table 3; the C–X···O angle is close to linearity, with the HCCX and the O atoms in the same plane and the two H atoms of H₂O out of the plane containing the other atoms.

Stable T-shaped FH···HCCX···OH₂ (X = F, Cl, Br, H) and FLi···HCCBr···OH₂ trimers were obtained and their geometries are illustrated in Figs. 2 and 3, with selected results for these complexes displayed in Table 4. The pair interactions and pairwise non-additive contributions to the interaction energy ΔE in these trimers are shown in Table 5. The non-additive contribution was computed as $E_{\text{non-add}} = \Delta E - (\Delta E_{\text{ab}} + \Delta E_{\text{bc}} + \Delta E_{\text{ac}})$, with the pair interactions ΔE_{ab} , ΔE_{bc} and ΔE_{ac} being calculated for the geometry of each pair in the optimized trimer at the MP2/6-311++G(d,p) level of theory.

Discussion

Table 1 shows that the interaction energy $-\Delta E$ for the T-shaped FH···HC¹C²X dimers increases with decreasing electronegativity of

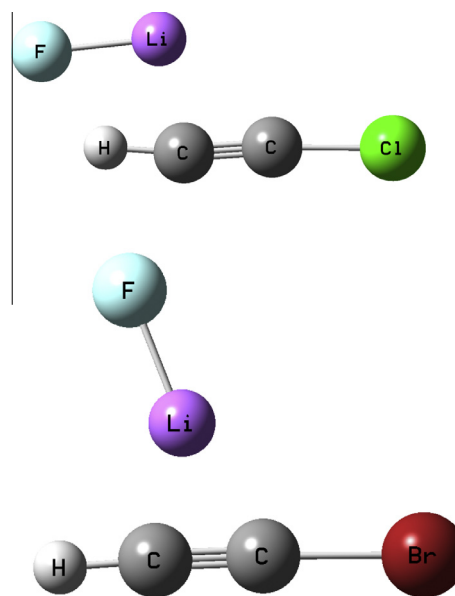


Fig. 1. MP2/6-311++G(d,p) optimized structures for the FLi···HCCCl and FLi···HCCBr dimers.

Table 2

Selected MP2/6-311++G(d,p) properties for the T-shaped FLi···HC¹C²Br complex and the FLi···HC¹C²X (X = F, Cl, H) complexes (with the FLi and HCCX lying parallel to each other). The properties shown are the interaction energy, relative to the isolated monomers, without (ΔE) and with counterpoise correction (ΔE_{CP}) in kJ/mol, bond distance (R) and bond length changes on complexation (ΔR) in Å, and the harmonic vibrational frequency shift on complexation ($\Delta\omega$) in cm^{−1}.

Property	FLi···HCCBr	FLi···HCCF	FLi···HCCCl	FLi···HCCH
ΔE	−40.6	−36.4	−41.4	−44.5
ΔE_{CP}	−27.6	−28.0	−30.5	−35.2
$\Delta R(\text{FLi})$	0.011	0.024	0.022	0.022
$\Delta R(\text{CX})$	−0.002	−0.002	0.001	0.002
$\Delta\omega(\text{FLi})$	−1.3	−48.7	−44.5	−44.4
$\Delta\omega(\text{CX})$	11.2	−0.8	−2.3	−38.4
$R(\text{Li} \cdots \text{C}^1)$	2.396 ^a	2.323	2.304	2.300
$R(\text{F} \cdots \text{H})$		2.267	2.423	2.573

^a $R(\text{Li} \cdots \text{C}^2) = 2.434 \text{ \AA}$.

Table 1

Selected MP2/6-311++G(d,p) properties for the T-shaped FH···HC¹C²X (X = F, Cl, Br, H) complexes. The properties shown are the interaction energy, relative to the isolated monomers, without (ΔE) and with counterpoise correction (ΔE_{CP}) in kJ/mol, bond distance (R) and bond length changes on complexation (ΔR) in Å, and the harmonic vibrational frequency shift on complexation ($\Delta\omega$) in cm^{−1}.

Property	FH···HCCF	FH···HCCCl	FH···HCCBr	FH···HCCH
ΔE	−13.8	−16.4	−16.8	−18.4
ΔE_{CP}	−8.9	−10.4	−10.8	−13.2
$\Delta R(\text{FH})$	0.005	0.006	0.006	0.006
$\Delta R(\text{CX})$	−0.005	−0.004	−0.002	0.001
$\Delta\omega(\text{FH})$	−130.7	−151.5	−147.4	−156.1
$\Delta\omega(\text{CX})$	8.2	3.9	−15.0	−13.5 ^{asym}
$R(\text{H} \cdots \text{C}^1)$	2.230	2.224	2.244	2.270
$R(\text{H} \cdots \text{C}^2)$	2.422	2.324	2.323	2.270

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