Computational and Theoretical Chemistry 1092 (2016) 12–18

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Exploring the role of substituents on cooperativity between N···HF and CH···F hydrogen bonds in ternary systems involving aromatic azine: Substituted complexes of s-triazine:HF:s-triazine as a working model

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A R T I C L E I N F O

Article history:
Received 10 June 2016
Received in revised form 2 July 2016
Accepted 4 July 2016
Available online 19 July 2016

Keywords:
Cooperativity
Substituent effects
s-triazine
Hammett constants
Ab initio

A B S T R A C T

In order to investigate the influence of substituents on cooperativity between N···HF and CH···F hydrogen bonds, a number of para- and meta-substituted s-triazine respectively in X′-s-triazine:HF:s-triazine and s-triazine:HF:s-triazine-X_2 complexes are chosen (X or X′ = H, F, Cl, Br, CN, NH_2, NO_2, CH_3 and N$(CH_3)_2$). Here, the cooperative effects on energetic, geometrical and topological properties are examined at the MP2/6-311++G(d,p) level. Unlike di-substituted complexes, the mono-substituted ones involving electron donating substituents are more stable and therefore preferable. A cooperativity is observed between N···HF and CH···F hydrogen bonds in the ternary complexes. In other words, these interactions in the ternary complexes work in concert with each other and enhance each other's strength. The favorable influences of N···HF and CH···F hydrogen bonds on each other are also confirmed by the results of natural bond orbital (NBO) and atoms in molecules (AIM) analyses. The results indicate that substituent effects on cooperativity between N···HF and CH···F hydrogen bonds can be expressed by Hammett constants.

1. Introduction

Cooperativity is a very important phenomenon in many areas of chemistry, particularly physical chemistry, biochemistry, and medicinal chemistry [1,2]. The idea of hydrogen bond (H-bond) cooperativity was first advanced by Frank and Wen, in 1957, who observed that the hydrogen atoms of the acceptor molecule in a dimer of water should become more positive as a result of the hydrogen bond and, consequently, as stronger Lewis acids, should form stronger successive hydrogen bonds [3]. The cooperativity between H-bonds has been investigated in different systems [4–9]. For example, Stokely et al. have investigated effect of H-bond cooperativity on the behavior of water. At first, they proposed four scenarios for the low-temperature phase behavior of liquid water, each predicting different thermodynamics. In following, they have shown that a microscopic cell model of water, by taking into account the cooperativity among H-bonds, is able to produce phase behaviors consistent with any of the proposed scenarios for water's phase diagram [7]. Pidko et al. have used density functional theory to rationalize the experimentally observed cooperative growth of C_3-symmetrical trialkylbenzene-1,3,5-tricarboxamide- (BTA-) based supramolecular polymers that self assemble into ordered one-dimensional supramolecular structures through H-bonding. They have indicated that the cooperative growth of these structures is caused by electrostatic interactions and nonadditive effects brought about by redistribution of the electron density with aggregate length [8]. A series of self-constituted multiple H-bonded complexes have theoretically been investigated by Chen et al. They indicated that stronger cooperative energy correlates well with larger interaction energy and thus more stable complex and vice versa [6].

The study of the intermolecular interactions of six-membered nitrogenated aromatic rings is of particular importance since they are known to constitute key building blocks of proteins, nucleotides, and many other important compounds [10]. For example, s-triazine (TAZ) is an intriguing heterocycle for high energy materials and exhibits a high degree of thermal stability [11,12]. Triazine rings have been studied for use in a number of applications such as chemicals, herbicides, synthesis, dyes, and polymers [13–17]. The H-bonding in systems involving aromatic azines was studied periodically by theoretical and experimental methods [18–22]. For instance, Da Silva et al. characterized H-bonded complexes between hydrogen fluoride as proton donor and aromatic azines (pyridine, pyrimidine, pyridazine, pyrazine, 1,3,5-triazine, and 1,2,4-triazine). They indicated that H-bond strength is dependent

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http://dx.doi.org/10.1016/j.comptc.2016.07.002
2210-271X/

on both the number of nitrogen atoms as well as the position of these atoms in aromatic ring [20]. Ebrahimi et al. theoretically examined the effects of electron-donating and electron-withdrawing substituents in para- and meta-positions on X-pyridine:HF H-bond. They also investigated the relationship between Hammett constants and H-bond formation energy [21].

We have had two objectives with the current study: The first has been to investigate the influence of electron-donating and electron-withdrawing substituents on cooperativity between N···HF and CH···F H-bonds in the X′-TAZ:HF:TAZ and TAZ:HF:TAZ-X_2 complexes as a working model. Our second objective has been to investigate the performance of Hammett constants for prediction of cooperative effects between these interactions. Schematic representations of considered complexes are given in Schemes 1 and 2.

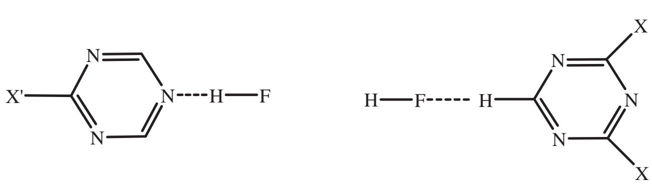
2. Computational methods

The geometry of all complexes was optimized at the second-order Møller–Plesset perturbation theory (MP2) with the 6-311++G(d,p) basis set using Gaussian 09 suite of programs [23]. Since the major objective of this work was to examine the cooperativity between N···HF and CH···F H-bonds in the presence of various substituents, the symmetrical constraints were imposed during geometry optimization. The basis set superposition error (BSSE) has been considered by the Boys-Bernardi counterpoise (CP) method [24] during the geometry optimization of complexes. In addition, the binding energies were also calculated at the MP2/6-311++G(d,p) level with correction for BSSE using the CP technique.

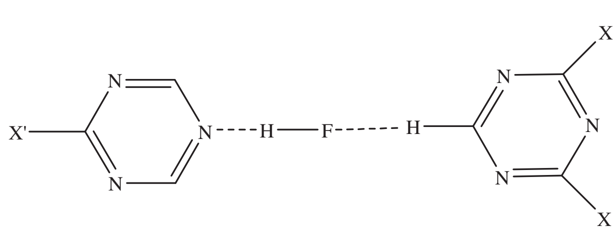
Frequency calculations were performed on the optimized structures at the same level.

The quantum theory of atoms in molecules (AIM) [25] of Bader was applied to characterize the analyzed interactions. The bond critical points (BCPs) of the H-bond interactions were found, and the features of them were analyzed since it is well-known that characteristics of BCPs, such as the electron density (ρ(r)), their Laplacians ($\nabla^2\rho(r)$), and that energy densities of BCPs (H(r)) allow us to categorize interactions and these topological parameters are also treated as measure of H-bonding strength. The AIM calculations were carried out using the AIM2000 program [26] on MP2/6-311++G(d,p) wave functions of complexes.

Moreover, the population analysis was performed by the natural bond orbital (NBO) method [27] at the HF/6-311++G(d,p) level on the optimized structures using GenNBO 5.0 program [28].



Scheme 1. Considered binary complexes. (X or X′ = H, F, Cl, Br, CN, NH_2, NO_2, CH_3 and $N(CH_3)_2$).



X=H X′= H, F, Cl, Br, CN, NH_2, NO_2, CH_3, $N(CH_3)_2$

X′=H X= H, F, Cl, Br, CN, NH_2, NO_2, CH_3, $N(CH_3)_2$

Scheme 2. Considered ternary complexes.

3. Results and discussion

3.1. Binary complexes

X′-TAZ:HF and X_2-TAZ:FH dyads are model systems considered to depict the N···HF and CH···F H-bonds, respectively (see Scheme 1). Here, derivatives of TAZ and HF in X′-TAZ:HF complexes act as proton acceptors and proton donor, respectively. This behavior is reversed for X_2-TAZ:FH complexes. The binary complexes have C_{2V} symmetry except for CH_3-TAZ:HF which has C_S symmetry. Binding energy is a most convincing measure of the strength of an intermolecular interaction. The binding energy of N···HF and CH···F H-bonds in mono- and di-substituted dyads was respectively calculated as:

$$\Delta E_{N\cdots H} = E_{X'\text{-TAZ:HF}} - (E_{X'-TAZ} + E_{HF}) \quad (1)$$

$$\Delta E_{H\cdots F} = E_{X2\text{-TAZ:FH}} - (E_{X2\text{-TAZ}} + E_{HF}) \quad (2)$$

where $E_{X'\text{-TAZ:HF}}$, $E_{X2\text{-TAZ:FH}}$ correspond to the total energy of the binary complexes and $E_{X'\text{-TAZ}}$, $E_{X2\text{-TAZ}}$, E_{HF} are of the total energies of optimized monomers. As evident from Table 1, the $\Delta E_{H\cdots F}$ and $\Delta E_{N\cdots H}$ tend to more negative values as the strength of H-bond increases. The absolute values of binding energy in mono-substituted complexes ($|\Delta E_{N\cdots H}|$) are much greater than those in di-substituted ones ($|\Delta E_{H\cdots F}|$). The results in Table 1 indicate that X′-TAZ:HF complex is destabilized by electron-withdrawing substituent and is stabilized by electron-donating substituent. An opposite order is found for X_2-TAZ:FH complexes. The acidity and thus donation ability of the H-bond donor may be a good test for description of interaction preferences driven by the character of the substituent. On the other hand, the basicity and thus the ability of being an acceptor for H-bonds may be used in a similar way. The substituent effect on the ring is related to both the inductive and the resonance effects. These effects are highly correlated to Ham-

Table 1
Hammett constants, geometrical parameters (Å), change of H—F and C—H stretching frequency upon formation complex (cm^{-1}), $E_{EML,HB}$ and $\Delta E_{N\cdots H}/\Delta E_{F\cdots H}$ values (kcal/mol) in X′-TAZ:HF/X_2-TAZ:FH calculated at MP2/6-311++G(d,p) level of theory.

X′	σ_P	$\Delta E_{N\cdots H}$	$E_{EML,HB}$	d_{HB}	$\Delta d_{H-F} \times 10^2$	$\Delta\nu_{H-F}$
X′-TAZ:HF						
H	0	−8.11	−9.82	1.815	1.919	−454.4
F	0.06	−7.52	−9.37	1.827	1.788	−424.6
Cl	0.23	−7.58	−9.43	1.825	1.813	−430.2
Br	0.23	−7.52	−9.35	1.828	1.794	−426.4
CN	0.66	−6.71	−8.58	1.851	1.588	−381.6
NO_2	0.78	−6.41	−8.45	1.854	1.541	−370.4
NH_2	−0.66	−9.84	−11.44	1.773	2.384	−550.9
CH_3	−0.17	−8.62	−10.22	1.804	2.044	−481.9
$N(CH_3)_2$	−0.83	−10.54	−12.02	1.759	2.563	−596.1
X	σ_m	$\Delta E_{F\cdots H}$	$E_{EML,HB}$	d_{HB}	$\Delta d_{C-H} \times 10^2$	$\Delta\nu_{C-H}$
X_2–TAZ:FH						
H	0	−0.961	−1.302	2.467	−0.071	16.7
F	0.34	−1.589	−1.578	2.374	−0.062	19.0
Cl	0.37	−1.44	−1.524	2.39	−0.053	18.3
Br	0.39	−1.452	−1.537	2.387	−0.068	19.7
CN	0.56	−2.073	−1.74	2.329	−0.067	20.5
NO_2	0.71	−2.342	−1.85	2.298	−0.059	19.4
NH_2	−0.16	−0.292	−0.982	2.595	−0.056	15.8
CH_3	−0.07	−0.695	−1.181	2.512	−0.069	18.4
$N(CH_3)_2$	−0.21	−0.059	−0.814	2.677	−0.064	15.6