Chemical Physics Letters 698 (2018) 1–6

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

A computational study on the strength and nature of bifurcated aerogen bonds

Mehdi D. Esrafili *, Asma Sadr-Mousavi

Laboratory of Theoretical Chemistry, Department of Chemistry, University of Maragheh, Maragheh, Iran

ARTICLE INFO

Article history:
Received 18 January 2018
In final form 27 February 2018

Keywords:
Electrostatic potential
Ab initio
QTAIM
NBO
Cooperativity

ABSTRACT

A quantum chemical study is performed to unveil the strength and bonding properties of bifurcated aerogen-bonding (BAB) interactions in complexes formed between ZO_3 molecules (Z = Ar, Kr and Xe) and 1,2-dihydroxybenzene derivatives. The interaction energies of the resulting complexes are between −7.70 and −15.59 kcal/mol. The nature of BAB interactions is identified by the molecular electrostatic potential, quantum theory of atoms in molecules, noncovalent interaction index and natural bond orbital analyses. The mutual influence between the BAB and a halogen, chalcogen, pnicogen or tetrel bonding interaction is also studied in systems where these interactions coexist.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Noncovalent interactions are very important in various fields of chemistry and biochemistry. Characterization of these interactions is critical for better understanding their decisive roles in the structure formation, dynamics, and chemical reactions [1,2]. In particular, noncovalent interactions involving groups 14–17 elements of the periodic table, acting as a Lewis acid center, have been recently attracted considerable attention, due to their key roles in many field of chemistry and biochemistry [3–5]. The term “σ-hole bonding“ has been coined for those attractive Lewis acid-Lewis base interactions, since their formation is usually described by an electron-deficient region (σ-hole) [6–8] developed on the outermost portion of an atomic surface. The halogen bond [9,10] is a well-known example of the σ-hole bond, where a halogen atom acts as the Lewis acid center. In the case of groups 14, 15 and 16 elements, such interactions can be similarly named as the tetrel [11–14], pnicogen [15–17] and chalcogen bonding [18–20], respectively,

The possibility that group 18 atoms (or aerogens) acting as an electron-acceptor center has been recognized for several years [21,22]. However, it was not until 2015 when, Bauzá and Frontera [23–25] were provided a theoretical evidence for the favorable attractive interaction between some rare gas containing molecules and negative regions over neutral or anionic molecules. The resulting interaction, called as “aerogen-bonding”, has drawn increasing attention recently due to its potential applications in crystal engineering, molecular recognition and in rare gases chemistry [26–28]. The aerogen-bonding shares fundamental characteristics with other σ-hole interactions. For example, in addition to the electrostatic effects, the formation of an aerogen bonding is partly related to the charge-transfer from the bonding orbital in the Lewis base to the antibonding orbital of the Lewis acid [23,25,28]. Furthermore, aerogen bonds exhibit cooperative effects with other intermolecular interactions [29]. The latter is related not only to the nature of aerogen atoms, but also to the strength of the interaction acting cooperatively with the aerogen-bonding.

Generally, the electron-donor moiety in the σ-hole bonding is a single negative site like a lone-pair or π-electron. However, it seems reasonable to expect three-centered or bifurcated σ-hole bonds, where a covalently-bonded atom of groups 14–18 interacts simultaneously with two electron-rich sites. Such interactions are commonly in the crystalline structures. For instance, the combined theoretical and experimental study [30] have indicated that the bifurcated halogen bonds may be more favorable than the monocoordinate halogen bonds in the solid phase. Our earlier study [31] has also showed the important substituent effects in the bifurcated pnicogen bonding. Although there is no any report on the occurrence of bifurcated aerogen bonds (BABs), however, Bauzá and Frontera [24] have provided the first theoretical evidence for the formation of four-centered or trifurcated aerogen bonds between the aromatic rings and XeO_3 or XeO_4 molecule. Britvin et al. [32] have recently reported an experimental study about the possibility of formation of trifurcated aerogen bonds in the layered perovskite $K_4Xe_3O_{12}$. According to their findings, the occurrence of such

---

* Corresponding author at: P.O. Box: 5513864596, Iran.
E-mail address: esrafili@maragheh.ac.ir (M.D. Esrafili).

https://doi.org/10.1016/j.cplett.2018.02.066

0009-2614/© 2018 Elsevier B.V. All rights reserved.

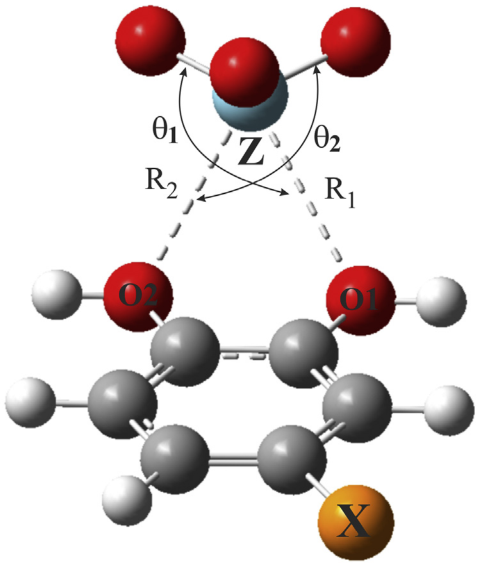
interactions may be a reason of explosive properties and high shock sensitivity of this material.

To expand our work in this area, we report herein a quantum mechanical study on the BAB interactions between ZO_3 molecules (Z = Ar, Kr and Xe) and 1,2-dihydroxybenzene (DHB) derivatives (Scheme 1). We show that it is also possible for an aerogen atom to form bifurcated interactions with two negative sites over the Lewis base. In addition, we consider the interplay and competition between the BAB and a halogen, chalcogen, pnicogen or tetrel bonding interactions in some model complexes, where these interactions coexist. To further understand the origin of the interactions, molecular electrostatic potential (MEP), quantum theory of atoms in molecules (QTAIM), noncovalent index (NCI) and natural bond orbital (NBO) analyses are also performed.

2. Computational details

All quantum chemical calculations were carried out within the Gaussian 09 electronic structure package [33]. The geometries of all monomers and complexes studied in this work were optimized with the M06-2X density functional. Earlier studies have indicated the reliability of M06-2X density functional to predict the geometry and strength of the σ-hole bonded complexes [34,35]. For all atoms, a large def2-TZVPPD triple-ζ basis set [36] equipped with two sets of polarization and diffusion functions was used. In the case of the Xe atom, the corresponding effective core potential was also employed to account relativistic effects in this atom. Harmonic frequencies were computed to ensure that the optimized structures are true minima. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise method [37].

The MEP analysis was performed on the 0.001 au electrons/Bohr^3 contour of the electronic density with the wave function analysis-surface analysis suite (WFA-SAS). The QTAIM analysis [38] was performed using the AIM2000 program. The NBO [39] theory at the M06-2X/def2-TZVPPD level was applied to unveil the atomic charges and charge-transfer values, using the NBO 5.0 program [40]. The NCI index [41] and electron density difference (EDD) analyses were carried out using the Multiwfn [42].



1. Z=Ar, X=H
2. Z=Ar, X=NH_2
3. Z=Ar, X=OH
4. Z=Ar, X=F
5. Z=Ar, X=CN
6. Z=Kr, X=H
7. Z=Kr, X=NH_2
8. Z=Kr, X=OH
9. Z=Kr, X=F
10. Z=Kr, X=CN
11. Z=Xe, X=H
12. Z=Xe, X=NH_2
13. Z=Xe, X=OH
14. Z=Xe, X=F
15. Z=Xe, X=CN

Scheme 1. Schematic representation of BAB bonded complexes.

3. Results and discussion

Scheme 1 indicates the sketch map of the binary complexes paired by ZO_3 and DHB derivatives. As seen, the aerogen atom of ZO_3 molecule interacts with two oxygen atoms of DHB molecule, hence forming a BAB interaction. All these complexes are characterized by two Z···O binding distances (R_1 and R_2) as well as two O–Z···O angles (θ_1 and θ_2). The formation of these complexes is easily understood by the MEP analysis of the isolated monomers (Fig. 1). As shown, a negative electrostatic potential region is found between the oxygen atoms of the DHB, which represents the propensity of this molecule to form a bifurcated interaction with a potential electron-acceptor center. The MEP value associated with this region ($V_{S,min}$) is between −29.4 kcal/mol for X = CN and −42.4 kcal/mol for X = NH_2 (Fig. 1). As expected, the substitution of an electron-withdrawing group in the DHB molecule decreases the absolute value of the $V_{S,min}$, while a reverse trend is obtained for an electron-donating group. On the other hand, ZO_3 molecules are characterized by three isoenergetic positive regions (σ-holes) developed on the extension of the Z–O covalent bonds. These σ-holes become more positive as the polarizability of the Z atom increases (Z = Ar < Kr < Xe). Thus, according to the MEP analysis, ZO_3 molecules can participate in a bifurcated σ-hole interaction with the DHB derivatives.

The optimized structures of the complexes paired by ZO_3 and DHB derivatives are collected in Fig. S1 of Supporting Information. The corresponding binding distances and binding angles are summarized in Table 1. For the all complexes considered, the interaction between the Z and O atoms is found to be asymmetric ($R_1 \neq R_2$), which is consistent with other bifurcated σ-hole bonds in the literature [31,43]. In fact, a symmetric arrangement for these complexes is characterized as a first-order saddle point on the potential energy surface. The R_1 and R_2 distances are in a range of 2.741–3.058 and 2.781–3.054 Å, respectively, which are smaller than the sum of the van der Waals radii of the Z and O atoms [44]. We note that the bifurcated Xe···O bonds in the XeO_3 complexes (2.741–2.798 Å) are shorter than the corresponding trifurcated bonds between the XeO_3 and C_6H_6 (2.904 Å) or C_6F_6 (3.061) [24]. On the other hand, they are longer than the Xe···O bond distances (2.475 Å) in the crystalline structure of $K_4Xe_3O_{12}$ [32], indicating the weak nature of Xe···O interactions in the former systems. For a given X substitution on the aromatic ring, XeO_3 always forms the shortest R_1 distances, followed by KrO_3. Generally, the nature of the X moiety has a different influence on the R_1 and R_2 binding distances. In many cases, the substitution of an electron-donor group (OH and NH_2) tends to decrease the R_1 distances, while a reverse trend is evident for the R_2 distances. It is also interesting to note the variation of the θ_1 angles, which increases upon going from the Ar to Xe complexes.

The interaction energies of the BAB bonded complexes are between −7.70 and −15.59 kcal/mol, which are comparable with those of bifurcated σ-hole bonded complexes [31,43,45]. As seen, the interaction energies of the XeO_3 complexes are obviously more favorable than those computed for the KrO_3 and ArO_3 complexes, most likely due to the larger positive MEP value associated with the Xe atom (Table 1). Besides, the interaction energies of the X = OH and NH_2 substituted complexes are considerably more negative than the X = F and CN ones, which is in line with the $V_{S,min}$ values associated with the DHB derivatives given in Fig. 1. In fact, we found a linear relationship between the $V_{S,min}$

Download English Version:

https://daneshyari.com/en/article/7837786

Download Persian Version:

https://daneshyari.com/article/7837786

Daneshyari.com