Aerogen Bonding

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Aerogen Bonding Interaction: A New Supramolecular Force?**

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Abstract: *We report evidence of the favorable noncovalent interaction between a covalently bonded atom of Group 18 (known as noble gases or aerogens) and a negative site, for example, a lone pair of a Lewis base or an anion. It involves a region of positive electrostatic potential (σ-hole), therefore it is a totally new and unexplored σ-hole-based interaction, namely aerogen bonding. We demonstrate for the first time the existence of σ-hole regions in aerogen derivatives by means of high-level ab initio calculations. In addition, several crystal structures retrieved from the Cambridge Structural Database (CSD) give reliability to the calculations. Energetically, aerogen bonds are comparable to hydrogen bonds and other σ-hole-based interactions but less directional. They are expected to be important in xenon chemistry.*

Noncovalent interactions are the main protagonists of supramolecular chemistry and biochemistry controlling the central parts of living systems. An appropriate comprehension of the different noncovalent forces is necessary for the rational design of new drugs and developing improved synthetic receptors capable to function in competitive media.[1] Among many interactions, the hydrogen bond is probably the most studied and analyzed noncovalent interaction.[2] However, σ-hole interactions involving tetrel, pnicogen, chalcogen, and halogen atoms have attracted substantial attention in recent years and they are recognized by the scientific community as powerful tools in supramolecular chemistry, crystal engineering, and biochemistry.[3] These interactions are moderately strong and directional basically due to the localization of a positive region on the extension of the covalent bonds (σ-hole) in the acceptor molecule. Usually, the name of the group (halogen, chalcogen, etc.) is used to specify the interactions and they are subgroups of a general definition of σ-hole bonding interactions given by Politzer and co-workers.[4] As far as our knowledge extends, the σ-hole interaction has not been described for Group 18 elements (noble gases or aerogens). This is likely due to the general assumption that these elements are monatomic gases with very low chemical reactivity. As a matter of fact, inertness of noble gases makes them suitable in applications in which reactions are not desired.

In this manuscript we propose the term "aerogen bonding" for describing the unprecedented σ-hole interaction between electron-rich entities (anions or lone pair possessing atoms) and elements belonging to Group 18. The energetic features and structural properties of aerogen bonding are discussed and two fascinating X-ray structures are selected to illustrate the existence of this interaction. Obviously, this rare type of bonding is not expected to be an effective and reliable instrument in crystal engineering or supramolecular chemistry; however, it is certainly important in terms of gaining knowledge in the molecular and supramolecular sciences.

The synthesis and crystal structure determination of xenon trioxide was reported in 1963 by Templeton et al.[5] The molecule XeO_3 is in the shape of a trigonal pyramid with dimensions similar to those of the isoelectronic iodate ion (Figure 1). The crystal packing shows that each xenon establishes three noncovalent Xe···O contacts with neighboring molecules at distances (from 2.8 to 2.9 Å) longer than the sum of the covalent radii of Xe and O (2.03 Å) and shorter than the sum of van der Waals radii (3.68 Å) that can be defined as σ-hole aerogen bonding interactions. In Figure 1 we show the molecular electrostatic potential surface (MEPS) computed at the MP2/aug-cc-pVTZ level of theory and a strong and extended σ-hole can be clearly observed. Unexpectedly a very positive potential is found at the position where the lone pair of the Xe^{VI} is located, which can be related to the inert pair effect.[6]

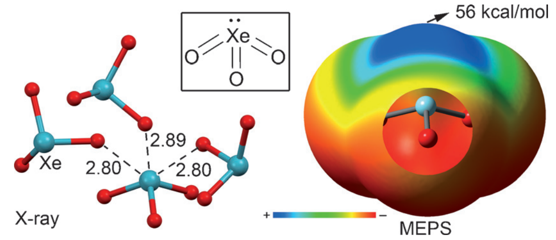

Figure 1. X-ray structure of XeO_3 (left) and MEPS of XeO_3 (right; distances in Å).

The chemistry of Xe^{IV} has been recently reviewed[7] and most of the known compounds are salts in which purely electrostatic interactions dominate in their solid state structure. However, one neutral and interesting derivative of Xe^{IV} is the XeF_2O compound that was synthesized from the co-condensation of water and XeF_4.[8] Most interestingly, in the presence of CH_3CN, the isolation of $F_2OXe{\cdot}NCCH_3$ is achieved.[9] This structure is the first and unique example of a Xe^{IV}–N bond. Two further examples of Xe^{IV}–N donor–acceptor bonds have been reported,[10] but involve a positively charged Xe^{IV} moiety, i.e., $[C_6F_5XeF_2]^+$. A partial view of the $F_2OXe{\cdot}NCCH_3$ crystal structure is shown in Figure 2. It can be observed that the $XeOF_2$ moiety is planar showing a T-

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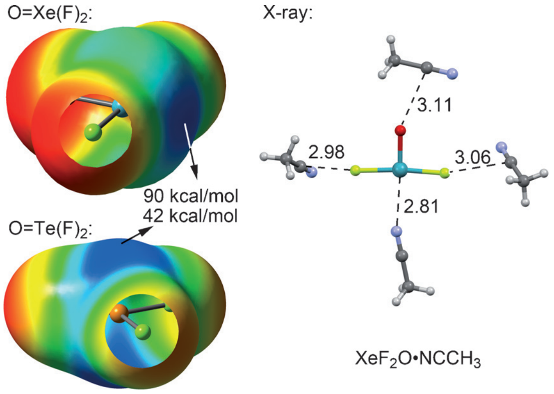

Figure 2. MEPS of XeF_2O and TeF_2O (left). X-ray structure of $XeF_2O{\cdot}CH_3CN$ (right; distances in Å).

shaped arrangement of two fluorine atoms and an oxygen double bond domain in the equatorial plane and two mutually *trans* valence electron lone pairs perpendicular to that plane. The nitrogen electron pair donor atom of CH_3CN interacts with the Xe atom opposite to the Xe=O bond and is coplanar with the $XeOF_2$ moiety. This has been defined as a coordination Xe^{IV}–N bond by the original authors.[9] We also show in Figure 2 the MEPS of $XeOF_2$ and $TeOF_2$ for comparison purposes. The MEP surface of the trigonal $TeOF_2$ molecule shows a clear π-hole above and below the Te atom. In contrast, the MEP surface of the T-shaped $XeOF_2$ molecule shows a strong σ-hole at the Xe atom in the prolongation of the Xe=O bond due to the existence of two valence lone pairs. Therefore the Xe^{IV}–N noncovalent contact observed in the solid state of $F_2OXe{\cdot}NCCH_3$ is a clear example of a σ-hole interaction (aerogen bonding). Interestingly, the $XeOF_2$ molecule in the solid state is surrounded by four CH_3CN molecules (Figure 2), one establishing the aerogen bonding interaction with the Xe and the rest forming O(F)···C noncovalent carbon bonding interactions.[3b–d]

We have optimized several complexes of XeO_3 and XeF_2O with two electron donor molecules (Figure 3) and compared their energetic and geometric features with complexes in which lighter aerogens (Ar and Kr, **1**–**4**) are used. The computational details are included in the Supporting Information (SI). Moreover, we also compare the interaction energies of the aerogen complexes to those using halogen, chalcogen, pnicogen, and tetrel atoms of the same row as σ-hole donors. These comparisons allow us, first, to investigate if the aerogen bonding follows the same energetic trend than the rest of σ-hole interactions. That is, the strength of the interaction augments as the bond donor atom is increasingly polarizable (heavier atoms). Secondly, to investigate whether the aerogen bonding is energetically similar to other well-known σ-hole interactions, using elements with similar polarizability values.

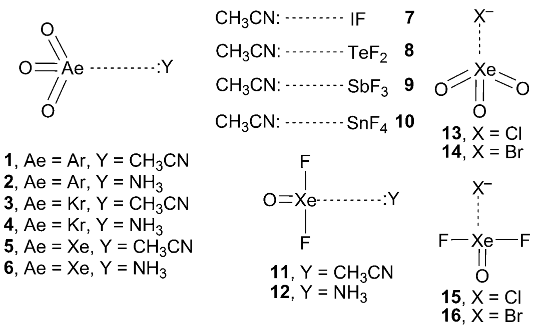

Figure 3. Complexes **1**–**16** studied in this work.

The energetic and geometric results of the ab initio optimized complexes **1**–**16** are gathered in Table 1 (see Figure S1 in the SI for a representation of the optimized geometries). From the inspection of the results, several interesting points arise. First, in the Ae^{VI} complexes **1**–**6**, the interaction energies follow the expected trend for a σ-hole-based interaction. That is, the largest interaction energies (in absolute value) are obtained for the heaviest aerogen atom (complexes **5** and **6**). Second, complexes **7**–**10**, in which elements of the same row are used as σ-hole donors present interaction energies that are larger in absolute value than the one obtained for complex **5** ($O_3Xe{\cdots}NCCH_3$) apart from the pnicogen-bonded complex **9**. The most favorable one is the tetrel complex (**10**) that correspond to the strongest σ-hole donor molecule (Figure 4) followed by the halogen-bonded complex **7** also in agreement with the MEP analysis. The strength of chalcogen and pnicogen complexes is comparable to the aerogen bonding complex **5**. Third, the interaction energies of Xe^{IV} complexes **11**–**12** are larger in absolute value than those computed for the equivalent Xe^{VI} complexes **5**–**6**, in agreement with the electrostatic potential values at the σ-holes (Figures 1 and 2). Finally, we have also included several complexes with anions (**13**–**16**) and the interaction energies

Table 1: Interaction energies without and with the basis set superposition error (ΔE and ΔE_{CP}, respectively), and equilibrium distances (R_e) for complexes **1**–**16** at the RI-MP2/aug-cc-pVTZ level of theory. The point group (PG) and imaginary frequencies (NImag) are also indicated.

Complex	ΔE [kcal mol^{-1}]	ΔE_{CP} [kcal mol^{-1}]	R_e [Å]	PG (NImag)
1	−6.6	−6.4	2.934	C_1 (0)
1a	−6.7	−5.9	2.909	C_{3v} (3)
2	−7.1	−6.5	2.853	C_s (0)
2a	−6.4	−5.1	2.978	C_{3v} (2)
3	−8.1	−7.2	2.980	C_s (0)
3a	−7.4	−6.8	3.053	C_{3v} (3)
4	−9.0	−8.3	2.843	C_s (0)
4a	−6.9	−6.5	3.127	C_{3v} (2)
5	−11.6	−9.5	3.142	C_s (0)
5a	−9.2	−8.0	2.960	C_{3v} (3)
6	−10.4	−9.0	2.779	C_s (0)
6a	−8.3	−7.4	3.221	C_{3v} (2)
7	−15.0	−12.2	2.450	C_s (0)
8	−13.1	−10.3	2.535	C_s (0)
9	−10.4	−8.1	2.722	C_s (0)
10	−21.6	−16.6	2.273	C_s (0)
11	−12.1	−10.1	2.798	C_s (0)
12	−14.6	−12.6	2.690	C_1 (0)
13	−39.0	−37.2	2.784	C_s (0)
14	−34.2	−32.6	2.983	C_s (0)
15	−41.9	−40.0	2.697	C_s (0)
16	−37.2	−35.4	2.874	C_s (0)

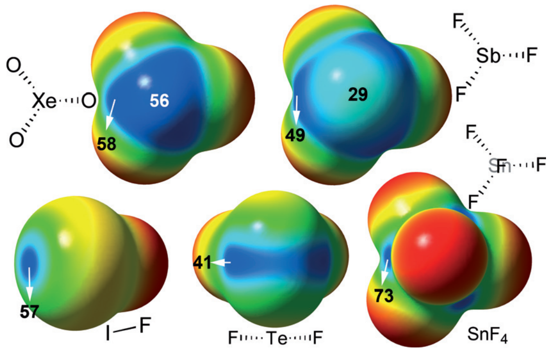

Figure 4. MEP surfaces computed for several σ-hole donor molecules at the MP2/aug-cc-pVTZ level of theory. Some MEP energy values in kcal mol^{-1} are indicated.

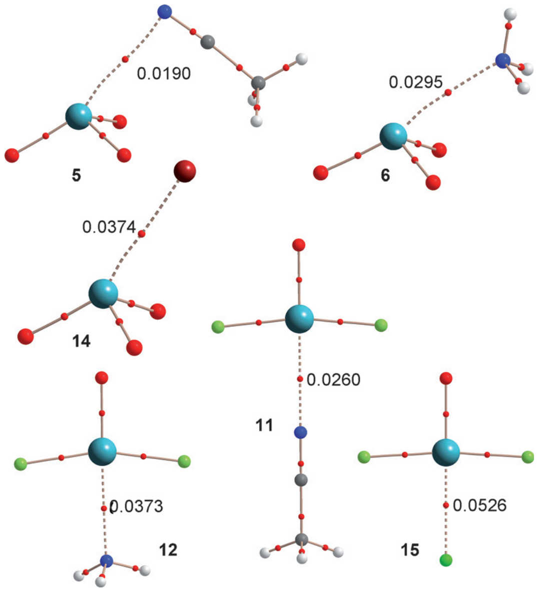

Figure 5. AIM distribution of critical points (red spheres correspond to bond critical points) at the MP2/aug-cc-pVTZ level of theory. The $\rho(r)$ values at the bond critical points are indicated in atomic units (a.u.).

Table 2: Donor and acceptor NBOs with indication of the second-order interaction energy $E^{(2)}$ and type of interaction for aerogen neutral complexes.

Complex	Donor[a]	Acceptor	$E^{(2)}$ [kcal mol^{-1}]	Type
1	BD(3) N-C	BD(1)* Ar-O	0.49	π→σ*
2	LP N	BD(1)* Ar-O	0.77	n→σ*
3	BD(3) N-C	BD(1)* Kr-O	0.99	π→σ*
4	LP N	BD(1)* Kr-O	2.22	n→σ*
5	BD(3) N-C	BD(1)* Xe-O	2.23	π→σ*
6	LP N	BD(1)* Xe-O	6.76	n→σ*
11	LP N	BD(1)* Xe-O	4.49	n→σ*
	LP Xe	BD(1)* N-C	2.06	n→σ*
12	LP N	BD(1)* Xe-O	12.32	n→σ*

[a] BD, BD*, and LP stand for bonding, anti-bonding, and lone pair orbital, respectively.

are very large, in line with reported anionic complexes between halides and traditional σ-hole donor atoms.[11]

At this point, it is worth emphasizing the difference observed in the MEP surfaces of XeO_3 and SbF_3 (Figure 3, top). Both molecules have a lone pair located in the molecular C_{3v} axis and both present positive potential values at the location of the lone pair. However, the MEPS of SbF_3 shows three well-defined σ-holes located at the extensions of the Sb–F bonds with a MEP value that is 20 kcal mol^{-1} more positive than that at the location of the inert lone pair (Figure 4). In contrast, the MEP surface of XeO_3 shows a negligible difference between the MEP values measured at the σ-hole and lone pair locations. Similar result is observed in the MEP surfaces of ArO_3 and KrO_3 molecules (Figure S2). Therefore the aerogen bonding is less directional than the rest of the σ-hole bonding interactions. As a matter of fact, we have also optimized complexes **1**–**6** imposing C_{3v} symmetry (lone pair directed to the inert lone pair,[6] complexes denoted as **1a**–**6a** in Table 1) and the interaction energies are comparable. The geometries of some representative complexes and their corresponding distribution of critical points[12] (see SI for details) are given in Figure 5. It can be observed that the electron-rich atom of the Lewis acid (or anion) is positioned at the σ-hole location (extension of the Xe=O covalent bond). All complexes are characterized by the presence of a bond critical point (small red sphere) connecting the Xe atom to the electron-rich atom thus confirming the interaction. The values of the charge density $\rho(r)$ at the bond critical point in the aerogen bonding complexes shown in Figure 5 (values in italics) are similar to those reported for σ-hole interactions of groups 14–17.[3]

To study if orbital contributions are important to explain the aerogen interactions described above, we have performed natural bond orbital (NBO) calculations focusing our attention on the second order perturbation analysis,[13] because it is very useful to study donor–acceptor interactions.[13] The results are summarized in Table 2. For Ae^{VI} complexes, the orbital contribution is small (≈10 % of the total interaction energy) for the lighter aerogens and the contribution is important in xenon complexes, especially in complex **6**, in which the orbital contribution dominates the interaction, in agreement with the short Xe···N distance (2.779 Å). A very remarkable finding derived from the NBO analysis is that in the AeO_3 complexes with CH_3CN (**1**, **3**, and **5**), the electron donor orbital does not correspond to the lone pair of the N atom; instead it is the π-system of the CN triple bond. This result likely explains the unexpected similar interaction energies obtained for NH_3 and CH_3CN complexes with AeO_3 σ-hole donor molecules. That is, the CH_3CN is a weak Lewis base (sp-hybridized lone pair) and therefore it is expected to have smaller complexation energies than the stronger NH_3 Lewis base (sp^3-hybridized lone pair). The geometry of the optimized complexes (Figure 5) clearly agrees with the fact that the electron-rich part of the molecule that interacts with the σ-hole is the π-system of the triple bond. For the Xe^{IV} complexes **11** and **12**, the orbital contribution is very large, especially in complex **12** in which the concomitant stabilization energy due to the electron donation from the lone pair of N to the antibonding Xe–O orbital ($n\rightarrow\sigma^*$) is approximately equal to the interaction energy reported in Table 1, thus representing a major factor in the stabilization. More interestingly, complex **11** (the one observed experimentally) presents two types of donor–acceptor orbital interactions. One corresponds to the expected $n \rightarrow \sigma^*$ donation with a $E^{(2)} = 4.49$ kcal mol^{-1}, which is considerably smaller than the value obtained for complex **12** due to the larger N–Xe distance in complex **11** and low basicity of the sp-hybridized lone pair. The other one corresponds to a back-bonding donation from one lone pair of Xenon to the N–C antibonding orbital. This surprising back-bonding orbital donation is not negligible, because it has a concomitant stabilization energy of $E^{(2)} = 2.06$ kcal mol^{-1} that is approximately 20% of the total interaction energy.

In conclusion, in this manuscript we report unprecedented σ-hole interactions involving noble gases. We propose the use of aerogen bonding to refer to the noncovalent interaction between atoms of Group 18 acting as Lewis acids and any entity with the ability to act as an electron donor (lone pair, anion, etc.). Aerogen bonds have, at least, comparable strength to hydrogen bonds and other σ-hole-based interactions, though are less directional. Due to the increasing interest and research on xenon derivatives, this interaction is expected to play an important role in their solid-state chemistry. Moreover, from a pedagogic point of view, this newly defined interaction is certainly of interest, being the ultimate subclass of σ-hole noncovalent bonding interactions.

Keywords: ab initio calculations · aerogens · noncovalent interactions · supramolecular chemistry · xenon

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