Aerogen Bonds Formed between AeOF$_2$ (Ae = Kr, Xe) and Diazines: Comparisons between σ-Hole and π-Hole Complexes

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ABSTRACT

The interaction between KrOF$_2$ or XeOF$_2$ and the 1,2, 1,3, and 1,4 diazines is characterized chiefly by a Kr/Xe···N aerogen bond, as deduced from ab initio calculations. The most stable dimers take advantage of the σ-hole on the aerogen atom, wherein the two molecules lie in the same plane. The interaction is quite strong, as much as 18 kcal mol^{-1}. A second class of dimer geometry utilizes the π-hole above the aerogen atom in an approximate perpendicular arrangement of the two monomers; these structures are not as strongly bound: 6-8 kcal mol^{-1}. Both sorts of dimers contain auxiliary CH···F H-bonds which contribute to their stability, but even with their removal, the aerogen bond energy remains as high as 14 kcal mol^{-1}. The nature and strength of each specific interaction is confirmed and quantified by AIM, NCI, NBO, and electron density shift patterns. There is not a great deal of sensitivity to the identity of either the aerogen atom or the position of the two N atoms in the diazine.

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1. Introduction

Noncovalent interactions help shape many processes in chemistry and biology. [1-3] Improved understanding of the nature of these interactions allows progress in the fields of supramolecular chemistry (particularly host-guest complexes), [4-8] materials science, [9-11] and rational design of new drugs and biochemistry,[12-15] among many others. As yet, the hydrogen bond (HB) is the best understood type of noncovalent interaction including its properties and potential applications.[16-18] Examination of several other classes of bonds was accelerated following the work of Brinck et *al.* [19] concerning the role of the σ-hole in halogen-bonded complexes.[20-25] The σ-hole concept (expanded later by Politzer and co-workers)[26-32] defines a region of positive electrostatic potential [33] located along the extension of the covalent bond for atoms belonging to Groups 14-17 (tetrels, pnicogens, chalcogens and halogens) on the outermost portion of its surface. This region serves as an electrophilic site, the Lewis acid center, which can attract negative potentials on other molecules. The intensity of the σ-hole is governed primarily by the electronegativity and polarizability of the relevant atom, and any electron-withdrawing character of substituents on this atom.[34]

Some molecules also contain a π-hole,[35,36] situated above the plane of the molecule.[36-38] This idea was first suggested in the crystallographic works of Burgi and Dunitz regarding the π-hole of a C=O group. [39-41] Ensuing studies [20, 38, 42, 43] indicate that the π-hole owes its origin to much the same set of factors as those that lead to σ-hole development. The role and basic mechanisms of various π-π interactions were extensively inspected through the last decades in many examples as π-π porphyrine aggregations,[44] substituted sandwich benzene dimers[45] or aqueous-π interactions.[46] The π-hole bonded complexes involving SO_2 and SO_3 and O_2YBr (Y=N, P, As) have been also explored in recent works.[47,48]

The last few years have seen extension of these same ideas to Group 18 elements (noble gases or aerogens),[49] eponymously termed "aerogen bonding". Despite the low native reactivity of these atoms, ArO_3, KrO_3, XeO_3, XeF_2O have all been shown to form complexes with a variety of electron donors (NH_3, CH_3CN, Cl^-, Br^-) with interaction energies as large as -37.2 kcal mol^{-1}.[49] Comparison to other types of complexes, stabilized by halogen, chalcogen, pnicogen, and tetrel bonds, indicates that aerogen bonding follows the same energetic trends.[49] In addition to various σ-hole interactions, complexes with XeF_4 as π-hole donor have been also examined.[50] The authors found that complexes stabilized by this π-hole interaction had interaction energies

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comparable to those characterized by σ-holes.[50] Similar results were obtained for other π-hole bonded complexes involving XeOMe$_4$.[51] The interaction energies covered a wide range from -0.9 kcal mol^{-1} for electron donor CO up to -12.1 kcal mol^{-1} for chloride anion.[51] There are also reports wherein XeOF$_2$ engages in σ-hole bonded complexes with π-electron donors (ethyne, pyrrole, ethene, furan, benzene and thiophene) which were equivalent in strength to complexes stabilized by aerogen bonds with lone-pair donors.[52] Makarewicz *et al.* classified the F$_2$OXe···NCCH$_3$ complex as a short-contact weak interaction, rather than a covalent-dative or covalent-polarized bond, with electric polarization making the largest contribution to the total energy.[53] This sort of bonding continues to attract both computational [54,55] and experimental [56,57] attention, with additional implications for the field of supramolecular chemistry and molecular recognition [50,58] as well as rare gas chemistry in general.

The work presented here considers aerogen and other bonds that might be formed between AeOF$_2$ (Ae=Kr, Xe) and three different diazines, none of which have undergone study previously in this context. The KrOF$_2$ and XeOF$_2$ molecules were chosen as model aerogen bond donors, as they contain electron-withdrawing substituents. The latter atoms not only amplify the aerogen bond, but can also potentially serve as H-bond acceptors from the CH groups of the diazines, thus facilitating comparisons between these two sorts of interactions. Moreover, as will be shown below, the two Lewis acid molecules each contain both σ and π-holes, so it is possible to examine the competition between the two for the base. As background, the crystal structure of the XeOF$_2$ molecule was determined earlier by Brock *et al.*,[59] which can serve as an anchor for the computational data. The diazines (pyridazine, pyrimidine and pyrazine) were chosen as electron donors via the lone pair of their nitrogen atoms. They span the 1,2, 1,3, and 1,4 placements of the N atoms around the aromatic ring, so as to explore how the N placement affects the properties of the various dimers. Their prior participation in this same manner in previous study of their complexes with SF$_4$ adds another possible vehicle for detailed comparison of aerogen with chalcogen bonding.[60]

In the current work, the potential energy surface of the combination of AeOF$_2$ with each of the diazines has been examined so as to identify all possible heterodimer structures. The most stable of each combination, involving both σ-hole and π-hole interactions, are characterized, analyzed, and compared. The forces that hold together each dimer are elucidated and compared with one another via a number of different methods. AIM and NCI explore the topology of the

total electron density, while NBO elucidates the various interorbital charge transfers, which complements a visual examination of all density shifts that accompany dimer formation. The partitioning of the total interaction energy into its various components offers another window into the underlying nature of the bonding.

2. Computational methods

Full geometry optimizations, vibrational harmonic frequencies, and interaction energies were calculated for the complexes of $AeOF_2$ (Ae = Kr, Xe) with the diazines pyridazine, pyrimidine, and pyrazine at the MP2 level in conjunction with the aug-cc-pVDZ basis set.[61,62] For the Xe atom, the aug-cc-pVDZ-PP basis set was applied so as to incorporate relativistic effects.[63] This level of theory has demonstrated to be reliable for a range of noncovalent interactions.[64-71]

The interaction energies of the complexes were corrected for basis set superposition error (BSSE) by the standard counterpoise procedure.[72] All computations were carried out with the Gaussian 09 and MOLPRO 2012 programs.[73,74] The energy decomposition analysis (EDA) was performed at the BLYP/ZORA/TZ2P level using the ADF modeling suite.[75-77] The molecular electrostatic potentials (MEPs) of the isolated monomers were calculated on the electron density isosurface of 0.001 a.u. at the MP2/aug-cc-pVDZ level, and the extrema were computed using the WFA-SAS program.[78] NBO analysis was performed at the BLYP-D3/Def2TZVPP level of theory [79-81] using the NBO program.[82] MP2 electron densities were analyzed via AIM in order to characterize the intermolecular interactions.[83] The noncovalent interaction index (NCI) was calculated at the MP2/aug-cc-pVDZ level by means of the MultiWFN program.[84,85]

3. Results and Discussion

3.1. Electrostatic potentials of isolated molecules

Fig. 1 presents the molecular electrostatic potential (MEP) maps of the $KrOF_2$ and $XeOF_2$ isolated molecules where positive regions are designated by red, and blue areas indicate negative potential.

[Insert Fig. 1 about here]

Each molecule contains both a σ-hole opposite the O atom and a π-hole directly above the Ae (Kr or Xe) atom; the values of these maxima are collected in Table 1.

TABLE 1. Molecular electrostatic potential maxima ($V_{s,max}$) around the Kr and Xe atoms of the isolated $AeOF_2$ (Ae= Kr, Xe) molecules computed on the 0.001 a.u. surface of the electron density at the MP2/aug-cc-pVDZ and BLYP-D3/Def2TZVPP (in parentheses) levels of theory. All values in kcal mol^{-1}.

molecule	σ-hole	π-hole
$KrOF_2$	58.7 (53.6)	39.1 (37.2)
$XeOF_2$	63.4 (57.0)	36.2 (33.4)

The results obtained at two different levels of theory are similar suggesting little sensitivity to either basis set or method of calculation. The σ-holes opposite the O atom are more intense than their π counterparts by a factor of between 1.5 and 2. The σ-hole maximum is slightly larger for Xe than for Kr, but the reverse is true for the π-holes. The value of $V_{s,max}$ for the $XeOF_2$ molecule is consistent with previous studies [49,52] and is slightly higher than that measured for XeO_3 (55-56 kcal mol^{-1} at the MP2/aug-cc-pVTZ level).[49,50] The latter enhancement is likely due to the presence of two strongly electron-withdrawing F substituents in $XeOF_2$. The larger $V_{s,max}$ for $XeOF_2$ when compared to $KrOF_2$ can be understood in terms of the greater polarizability and lower electronegativity of the Xe atom. The π-hole maxima of 36-39 kcal mol^{-1} are close to those previously obtained for the π-hole of the XeF_4 molecule.[47,48] Although close in magnitude, $KrOF_2$ has a slightly more intense π-hole than does its Xe analogue. With respect to the diazines, their ability to act as electron donors was explored earlier.[60] The negative sites of these molecules are characterized by the absolute values of the $V_{s,min}$ on the nitrogen atom, in the following order: pyrazine (-29.6 kcal mol^{-1}) < pyrimidine (-30.5 kcal mol^{-1}) < pyridazine (-40.4 kcal mol^{-1}). Pyridazine with its two adjacent nitrogen atoms has the most negative $V_{s,min}$ and pyrazine the least.

3.2 σ-Bonded Dimers

3.2.1. Structures and interaction energies

The MP2 optimized structures of σ-hole bonded $KrOF_2$ and $XeOF_2$ complexes with each of the three diazines are illustrated in Fig. 2.

The interaction energies, corrected for the BSSE error, as well as selected intermolecular parameters are collected in Table 2.

TABLE 2. Interaction energies (ΔE, kcal mol^{-1}) corrected for BSSE and intermolecular parameters (distances in Å, angles in degrees) in σ-hole bonded AeOF$_2$ (Ae = Kr, Xe) complexes with diazines. R(N1···Ae) distance as percentage of the sum of the corresponding covalent radii (Σr_{cov}). Data obtained at the MP2/aug-cc-pVDZ level of theory.

System	ΔE	R(N1···Ae)	% of Σr_{cov}	∠O-Ae···N1	R(F1···H2)	∠C2-H2···F1	R(F2···H6)	∠C6-H6···F2	E_{Aer}[a]
pyrazine···KrOF$_2$	-17.68	2.451	131	180.0	2.145	120.3	2.145	120.3	-12.45
pyrimidine···KrOF$_2$	-17.12	2.465	132	179.8	2.137	121.1	2.178	120.6	-12.14
pyridazine···KrOF$_2$	-15.25	2.512	134	177.9	2.137	122.7	-	-	-13.30
pyrazine···XeOF$_2$	-17.94	2.569	122	180.0	2.255	120.9	2.255	120.9	-13.30
pyrimidine···XeOF$_2$	-17.46	2.583	122	179.6	2.239	122.0	2.302	121.2	-13.02
pyridazine···XeOF$_2$	-16.52	2.637	125	174.5	2.206	123.1	-	-	-14.35

[a]ΔE after removal of CH···F HB energies (see text)

All of these complexes are planar, or very nearly so. The intermolecular R(N···Kr) and R(N···Xe) distances are all considerably smaller than the sum of the corresponding van der Waals radii. This latter sum is equal to 3.57 (for Kr) and 3.71 Å (for Xe) if the Bondi vdW radii [86] are chosen, and 3.91 and 3.72 Å if the Alvarez values [87] are used instead, as compiled in Table S1. Rather than vdW radii, comparison may alternatively be drawn with the covalent radii instead.[88] These sums (Σr_{cov}) are of course much shorter, equal to 1.87 and 2.11 Å for Kr/N and Xe/N, respectively. Although the aerogen bonds under study are clearly not fully covalent in nature, R(N···Ae) nonetheless is only a little bit longer than Σr_{cov}. As may be observed in the third column of Table 2, the former exceeds the latter by only some 22-34%, and this percentage is slightly smaller for Xe than for Kr. In terms of the interaction energies, these quantities are all in the 15-18 kcal mol^{-1} range. There is little distinction between the Kr and Xe complexes,

although $V_{s,max}$ is some 8% larger for the σ-hole of the heavier Xe atom. As a second issue, the interaction energies diminish in the order pyrazine > pyrimidine > pyridazine, which is opposite to the pattern noted in the $V_{s,min}$ quantities. (The same sort of the opposite correlation between $V_{s,min}$ and ΔE was noted in our earlier work in the case of halogen bonded F_3CCl complexes with methylated ammonia derivatives.[89])

However, it must be understood that the interaction energy is not due solely to the aerogen bond. As may be seen in Fig. 2, there are CH groups on each diazine which are fairly close to F atoms of $AeOF_2$. These F⋯H distances are smaller than the sum of the corresponding van der Waals radii (2.66 Å). The presence of these putative CH⋯F H-bonds (HBs) was confirmed and quantified in a number of ways. To provide a direct energetic assessment of their influence, they were broken by a 90° rotation of the $AeOF_2$ molecule around the N⋯Ae axis. Such a rotation will break the HBs while maintaining the aerogen bond. The energy of this rotation (with geometry optimization of the rotated species) raised the energy of the pyrazine and pyrimidine complexes with $KrOF_2$ by 5.23 and 4.98 kcal mol^{-1}, respectively These quantities are only slightly smaller, by 0.59 and 0.54 kcal mol^{-1}, for the Xe counterparts. By its nature pyridazine can only form a single CH⋯F HB, as compared to the two such bonds for the other complexes. The rotation consequently required less energy, 1.95 and 2.17 kcal mol^{-1} respectively for the complexes with $KrOF_2$ and $XeOF_2$.

If one were to consider these energy rises due to rotation and consequent loss of HBs as a reasonable measure of the HB strength, then these quantities can be subtracted from the full interaction energies in Table 2 in order to estimate the true contribution from the aerogen bond itself, designated here as E_{Aer}, and displayed in the final column of Table 2. In other words, this quantity refers to the interaction energy of the complex with the stipulation that the two molecules are oriented by 90° with respect to one another. (This structure represents the transition state for this internal conversion between the two symmetrically equivalent minima.)

Doing so leads to some changes in the trends. In the first place, the aerogen bond strengths are in the 12-14 kcal mol^{-1} range, roughly 2-3 times stronger than the paradigmatic HB in the water dimer. As a second issue, once the secondary HBs are removed from consideration, it is pyridazine which forms the strongest aerogen bonds, followed by pyrazine and pyrimidine which are close to one another. This pattern closely fits the $V_{s,min}$ data. And finally, $XeOF_2$ engages in

a consistently stronger aerogen bond than does its Kr analogue, by 1 kcal mol^{-1}, also consistent with the MEP data in Table 1.

The another approach of estimation the secondary HBs strength in complexes studied was applied. In this approach the Ae, O, and one of the F atom were replaced by a H atom. The distance between the F and the H atoms was set as it is in the optimized isolated HF monomer. The interaction energies of these model dimers were computed to answer the question how strong the CH⋯F-H is. The values of the ΔE calculated for these model complexes range from -4.07 to -2.88 kcal mol^{-1}. Therefore, the strength of these interactions are in the same magnitude as estimated using previous approach.

3.2.2 AIM, NCI, NBO, EDA, and EDS Analyses

One means of assessing the importance of the various interactions is via AIM analysis of the topology of the electron density. The presence of a bond critical point (BCP) between a given pair of atoms indicates an attractive bonding interaction. Molecular graphs of these complexes in Fig. 3 designate each such bond critical point by a small green sphere.

[Insert Fig. 3 about here]

As anticipated, in addition to the N⋯Ae aerogen bonds, there are also indications of one or more CH⋯F HBs in each complex. More quantitative measures of the pertinent intermolecular interactions are reported in Table 3. Specifically listed here are the electron density (ρ) and Laplacian of electron density ($\nabla^2\rho$), as well as the total electron energy H, all at the bond critical point.

Perusal of the data offers several conclusions. The aerogen bonds are considerably stronger than the HBs, although the latter are far from negligible. The aerogen bond parameters obey the same pyrazine > pyrimidine > pyridazine order as was observed in ΔE. But the pyridazine quantities are only slightly smaller than for the other two. The larger difference in ΔE can thus be traced to the presence of only one stabilizing CH⋯F HB in the pyridazine complexes, compared to two for the others.

Another means of extracting the noncovalent bond types from the topology of the electron density derives from the noncovalent interaction (NCI) method.[90-93] NCI is based on the

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correlation between the electron density (ρ) and the reduced density gradient (RDG) generated from the density and its first derivatives.[84,85] Large ρ and a negative value of sign(λ_2)ρ indicates a strong attractive interaction, whereas a positive value of sign(λ_2)ρ suggests repulsive forces. Application of Multiwfn software[84,85] led to the plots of the reduced density gradient (RDG) versus sign(λ_2)ρ as well as the molecular diagrams illustrated in Fig. 4.

TABLE 3. AIM data for σ-hole bonded F_2OAe (Ae = Kr, Xe) complexes with diazines. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$ (both in atomic units) and total electron energy (H, kcal mol^{-1}). Calculations were performed at the MP2/aug-cc-pVDZ level.

System	interaction	ρ	$\nabla^2\rho$	H
pyrazine$\cdots$KrOF$_2$(σ)	Kr$\cdots$N1	0.049	0.125	-1.68
	F1$\cdots$H2	0.019	0.065	-0.10
	F2$\cdots$H6	0.019	0.065	-0.10
pyrimidine$\cdots$KrOF$_2$(σ)	Kr$\cdots$N1	0.047	0.123	-1.32
	F1$\cdots$H2	0.019	0.066	-0.15
	F2$\cdots$H6	0.017	0.062	0.00
pyridazine$\cdots$KrOF$_2$(σ)	Kr$\cdots$N1	0.043	0.118	-0.54
	F1$\cdots$H2	0.019	0.065	-0.15
pyrazine$\cdots$XeOF$_2$(σ)	Xe$\cdots$N1	0.047	0.103	-3.43
	F1$\cdots$H2	0.015	0.053	0.18
	F2$\cdots$H6	0.015	0.053	0.18
pyrimidine$\cdots$XeOF$_2$(σ)	Xe$\cdots$N1	0.046	0.102	-3.06
	F1$\cdots$H2	0.015	0.054	0.11
	F2$\cdots$H6	0.013	0.049	0.31
pyridazine$\cdots$XeOF$_2$(σ)	Xe$\cdots$N1	0.041	0.097	-2.11
	F1$\cdots$H2	0.016	0.057	0.04

The spikes in the plots, located on the negative side of the sign(λ_2)ρ axis represent attractive forces. All aerogen bonds are designated as rather strong (in the range of -0.040 to -0.045 au). The locations of the interactions are displayed in the molecular diagrams and their strengths indicated by color: red (repulsion) < brown (weak repulsion) < green (weak interactions, i.e. vdW interactions) < blue (strong interaction). All aerogen bond regions are blue, i.e. strongly attractive. The weaker auxiliary HBs appear as the green regions between the pertinent H and F atoms, and also as spikes in the plots located near zero on the negative side of the sign(λ_2)ρ axis (their values are about -0.015 and -0.005 au).

An alternate view of noncovalent interactions arises via NBO localized orbitals. It is widely accepted[60,94-99] that electron donation from a lone pair of the electron donor into the σ^*(R-X) antibonding orbital (where X can be hydrogen, halogen, chalcogen, etc) is one of the driving forces of these sorts of noncovalent bonding. The values of the second-order interaction energies (E^2) between the lone pair of the nitrogen atom [LP(N)] and the antibonding σ^*(Ae-O) orbital are listed in the first column of Table 4.

TABLE 4. Second-order NBO perturbation energies (E^2) for charge transfer between indicated orbitals in σ-hole bonded F_2OAe (Ae = Kr, Xe) complexes with diazines (kcal mol^{-1}). Results obtained at DFT level.

System	LP(N1)→σ^*AeO	LP(F1)^a→σ^*C2H2	LP(F2)^a →σ^*C6H6
pyrazine···KrOF$_2$(σ)	11.03	1.02	1.15
pyrimidine···KrOF$_2$(σ)	11.14	1.25	0.94
pyridazine···KrOF$_2$(σ)	8.59	1.86	-
pyrazine···XeOF$_2$(σ)	9.95	0.75	0.75
pyrimidine···XeOF$_2$(σ)	10.04	0.84	0.67
pyridazine···XeOF$_2$(σ)	7.41	1.38	-

^{a}sum of contributions from all three F lone pairs

These quantities are in the 7-11 kcal mol^{-1} range. They are highest for the pyrazine and pyrimidine complexes, with pyridazine somewhat lower. The values are also larger for Kr as compared to Xe. This pattern mimics closely the intermolecular R(N···Ae) distances in Table 2,

with the shortest distances corresponding to the larger NBO values. In agreement with the AIM analysis, NBO confirms the presence of the CH···F HBs, as evident in the last two columns of Table 4. Also consistent with the AIM data, NBO confirms that these HBs are considerably weaker than the aerogen bonds, with E^2 only on the order of 1-2 kcal mol^{-1}, as compared to 7-11 kcal mol^{-1} for the aerogen bonds.

As another means of understanding the forces involved in the aerogen bond from another perspective. It is known that the SAPT decomposition can fail for complexes with small intermolecular distances. That is the case of the σ-hole dimers investigated. Thus, in this work the total interaction energy was decomposed into its constituent parts, using variational EDA.
The data in Table 5 suggest the largest contributor to each interaction is the electrostatics.

TABLE 5. EDA/BLYP/ZORA/TZ2P decomposition of the total DFT-D interaction energy (ΔE) of σ-complexes into Pauli repulsion (E_{Pauli}), electrostatic (E_{elstat}) orbital interaction (E_{oi}) and dispersion (E_{disp}) terms. All energies in kcal mol^{-1}. The relative values in percent express the contribution to the sum of all attractive energy terms.

	ΔE	E_{Pauli}	E_{elec}	%	E_{oi}	%	E_{disp}	%
pyrazine···KrOF$_2$	-19.21	37.77	-30.93	54	-21.83	38	-4.22	7
pyrimidine···KrOF$_2$	-19.09	38.02	-31.21	55	-21.70	38	-4.20	7
pyridazine···KrOF$_2$	-18.31	31.77	-26.38	53	-19.92	40	-3.78	8
pyrazine···XeOF$_2$	-17.87	38.60	-32.09	57	-19.50	35	-4.88	9
pyrimidine···XeOF$_2$	-17.78	38.54	-32.18	57	-19.30	34	-4.84	9
pyridazine···XeOF$_2$	-17.25	30.44	-26.89	56	-16.54	35	-4.26	9

The orbital interactions (which encompass charge transfer and polarization effects) are a bit smaller, but quite appreciable as well, as high as 22 kcal mol^{-1}. The percentage contributions of each term as reported in the table indicate that electrostatics are responsible for somewhat more than half of the total attraction, followed by orbital interactions at 35-40%. Dispersion is not negligible but represents less than 10%. In terms of comparisons, the percentage contribution of E_{elec} is slightly larger for the Xe complexes than for Kr, and the reverse occurs for E_{oi}.

Further insights into the nature of noncovalent interactions arise when one considers the electron density shift (EDS) that arises as the two molecules engage with one another to from the complex. A three-dimensional map of these shifts can reveal both polarizations within each subunit and shifts from one molecule to the other. These shifts are illustrated in Fig. 5 where density accumulations are denoted by brown contours, while purple indicates loss.

[Insert Fig. 5 about here]

The 0.001 a.u. isodensity contour indicates quite a bit of density shift. The CH···F HBs are clearly visible via the density loss on the bridging proton, coupled with increase on the proton-accepting atom, a fingerprint of HBs in general. The aerogen bond manifests a fairly similar pattern, with purple density loss from the Kr/Xe atom and a concomitant increase in the lone pair region of the N. There are also patterns of polarization within each subunit, which is magnified on the right side of each diazine near the binding sites. Some density also appears to shift from the π system of the O atom, perpendicular to the Ae=O bond, into the σ-system, a trend which also appears around the 2 F atoms.

3.3. π-hole bonded complexes
3.3.1 Structures and interaction energies

The MP2 optimized structures of the π-hole bonded $KrOF_2$ and $XeOF_2$ complexes with the three diazines are illustrated in Fig. 6.

[Insert Fig. 6 about here]

Their interaction energies and selected intermolecular parameters are collected in Table 6. The intermolecular N···Ae distance is roughly 3 Å, considerably longer than in the σ-structures, but nonetheless remains smaller than the sum of the corresponding van der Waals radii. The two molecular planes are not quite perpendicular, with θ(N··AeO) between 73º and 80º. There appears once again to be a certain amount of CH··F H-bonding as there are numerous R(H··F) contacts that are well below 3 Å, even though the θ(CH··F) angle is well below its optimal value of 180º.

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The interaction energies fall into the 6-8 kcal mol^{-1} range, less than half the corresponding values for the σ complexes in Table 2. This reduction is consistent with the smaller values of $V_{s,max}$ for the π-holes listed in Table 1. On the other hand, there is little distinction between the interaction energies of the Kr and Xe complexes, even though $V_{s,max}$ is a bit larger for the Xe monomer. Like the σ systems where pyridazine was associated with the strongest aerogen bond, the same is found for the π systems.

Inspection of Fig.6 suggests that the π-complexes, like their σ analogues, contain auxiliary CH··F HBs that add to the stability of these dimers, a supposition which is confirmed by the analyses described below. In an effort to quantify the energetic consequences of these auxiliary interactions, they were removed as follows. An optimization was performed in which the θ(Ae-N1-X4) angle (where X4= C4 or N4) was held to linearity and the φ(C2-N1-Ae-O) dihedral angle was set to 450. While these restrictions do not completely eliminate any attractive forces between the CH groups and the atoms surrounding the aerogen, they should be severely diminished.

TABLE 6. Intermolecular parameters (distances in Å, angles in degrees) in π-hole bonded $AeOF_2$ (Ae = Kr, Xe) complexes with diazines. Calculations performed at the MP2/aug-cc-pVDZ level of theory.

System	ΔE	R(N1···Ae)	∠O-Ae···N1	R(F1···H2)	∠C2-H2···F1	R(O···H2)	∠C2-H2···O
pyrazine···KrOF$_2$(π)	-6.19	2.953	79.2	2.467	127.1	3.588	87.6
pyrimidine···KrOF$_2$(π)	-6.17	2.963	79.7	2.442	127.8	3.516	76.8
pyridazine···KrOF$_2$(π)[a]	-7.14	2.929	79.7	2.454	122.2	3.486	91.2
pyrazine···XeOF$_2$(π)	-6.05	3.090	73.1	2.651	112.9	2.721	107.9
pyrimidine···XeOF$_2$(π)	-6.24	3.093	73.7	2.758	108.1	2.616	113.1
pyridazine···XeOF$_2$(π)	-8.17	2.977	73.6	3.794	83.8	2.583	117.0

The ensuing calculations indicated that these auxiliary HBs contribute less than 1 kcal mol^{-1}. The weakness of these HBs was confirmed by AIM analysis of the associated electron densities (see below). It can thus be concluded that the values of ΔE in Table 7 represent a fair assessment of the aerogen bond energy of each complex, with only minimal contamination from HBs.

3.3.2 **AIM, NCI, NBO, EDA, and EDS Analyses**

AIM diagrams verify the presence of CH··F HBs, as well as CH··O in the Xe cases, as is clear from the molecular diagrams in Fig. S1. The quantitative data in Table 7 place these HBs at roughly a third to a half the strength of the aerogen bond. These same HBs are also confirmed by NBO analysis, as reported in Table S2.

Comparison of these data with those obtained for the σ complexes in Tables 3 and 4 indicates weaker bonding, both aerogen and HB, consistent with the energetics. Note also that the orientation of the two molecules does not perfectly align the N lone pair of the diazine with the σ*(AeO) antibonding orbital. One therefore does not see charge transfer into the latter orbital in these systems. Rather, the bulk of the N lone pair density is acquired by the σ*(AeF2) orbital which is somewhat better oriented to interact with the lone pair. But even so, E2 for this transfer remains only some 20% of the corresponding quantity in the σ structures. It is in part due to the poor orbital alignments that the π complexes are weaker than their σ counterparts.

TABLE 7. AIM data for π-hole bonded F_2OAe (Ae = Kr, Xe) complexes with diazines. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$ (both in atomic units) and total electron energy (H, kcal mol^{-1}). Calculations were performed at the MP2/aug-cc-pVDZ level.

System	interaction	ρ	$\nabla^2\rho$	H
pyrazine···KrOF$_2$(π)	Kr···N1	0.018	0.059	1.07
	F1···H2	0.009	0.035	0.53
pyrimidine···KrOF$_2$(π)	Kr···N1	0.017	0.057	1.06
	F1···H2	0.009	0.036	0.48
pyridazine···KrOF$_2$(π)	Kr···N1	0.019	0.064	0.93
	F1···H2	0.009	0.034	0.85
pyrazine···XeOF$_2$(π)	Xe···N1	0.017	0.050	0.57
	F1···H2	0.006	0.030	0.87
	O···H2	0.007	0.030	0.78
pyrimidine···XeOF$_2$(π)	Xe···N1	0.017	0.050	0.59
	F1···H2	0.005	0.027	0.96
	O···H2	0.009	0.032	0.60
pyridazine···XeOF$_2$(π)	Xe···N1	0.022	0.064	0.57
	O···H2	0.008	0.032	0.60

There is one anomalous observation for the pyridazine···XeOF$_2$ complex. Whereas AIM suggests this to be a fairly strong aerogen bond, the NBO charge transfer energy would indicate this to be much weaker, with E^2 only some 20% of its value in the other π complexes. The relative weakness of the π as compared to the σ structures is also supported by NCI analyses in Fig. S2. Comparison with Fig.4 shows much less extensive green attractive regions, and the blue areas designating strong interactions are gone entirely.

Energy decomposition data for the π complexes confirm the central idea that the π complexes are systematically weaker than their σ cousins. All of the components are smaller in Table S3 as compared to Table 5. The electrostatic terms are reduced by a factor of 2-3, but there is a larger drop in the orbital interaction energy that is in the 3-7 range. On the other hand, dispersion suffers only a marginal decrease on going from σ to π complexes. Consequently, the dispersion makes a nearly equal contribution to the binding as do orbital interactions, both roughly half that of electrostatics.

The electron density shifts illustrated in Fig. S3 are less intense than in the corresponding σ-complexes, in line with the weaker binding in the π-dimers. Nonetheless, the main feature in either case is the (purple) density loss from the Ae atom and the nearly matching (brown) increase in the lone pair region of the N atom. There is also evidence of the purported CH···F HBs via the purple regions surrounding the bridging protons.

As charge is transferred into the Ae=O antibonding orbital, one would expect the bond to weaken and therefore to lengthen as well. Table 8 shows that this lengthening does indeed occur for the σ complexes.

TABLE 8. Changes in bond lengths (Å) caused by formation of complex at MP2/aug-cc-pVDZ level of theory.

complex	σ			π		
	Ae=O	Ae-F$_1$	Ae-F$_2$	Ae=O	Ae-F$_1$	Ae-F$_2$
pyrazine···KrOF$_2$	+0.006	+0.099	+0.099	-0.004	+0.012	+0.007
pyrimidine···KrOF$_2$	+0.006	+0.094	+0.090	-0.004	+0.013	+0.005
pyridazine···KrOF$_2$	+0.003	+0.074	+0.046	-0.004	+0.015	+0.004
pyrazine···XeOF$_2$	+0.008	+0.062	+0.062	0.000	+0.003	+0.003
pyrimidine···XeOF$_2$	+0.009	+0.063	+0.056	+0.001	+0.002	+0.002

pyridazine$\cdots$XeOF$_2$	+0.007	+0.059	+0.024	+0.002	-0.001	+0.005

The stretch is some 0.006 Å for the Kr complexes, and slightly longer for Xe. As indicated in Table S2, the π complexes are more weakly bound and do not transfer significant charge directly into the σ*(AeO) bond. There are consequently smaller changes in the r(AeO) bond length in the π complexes, which tend to be contractions for Kr and small elongations for Xe. The behavior of the Ae-F bonds can be traced to formation of CH$\cdots$F HBs. These bonds elongate in the σ complexes by a fair amount, about 0.06 Å for the Xe σ complexes, and even more for the Kr analogues. These same HBs are considerably weaker in the π complexes, and the bond stretches are accordingly diminished to 0.01 Å, and even less for Xe.

The near equal interaction energies of the complexes involving KrOF$_2$ and XeOF$_2$ is interesting from another perspective as well. The dipole moment of the latter molecule is more than twice that of the former (2.46 vs 0.96 D). One would have anticipated that from an electrostatic perspective this difference would have been reflected in a considerably greater interaction energy. Yet not only are these quantities very similar for the two aerogens, but even the electrostatic energies themselves are insensitive to the nature of the aerogen atom.

Finally, in order to insure that the energetics are not distorted by any particular level of theory, the interaction energies were recomputed by expanding the basis set from aug-cc-pVDZ to Def2TZVPP, and changing the level from MP2 to BLYP-D3. Comparison of the first two columns of Table 9 shows that these dual modifications had a negligible effect on these quantities. Switching to the application of the CCSD(T) treatment of electron correlation, while maintaining the same basis set, reduces the σ binding energies by some 4-5 kcal mol^{-1}; a much smaller change of less than 1 kcal mol^{-1} occurs for the π structures. Most importantly, there is no substantive change in any of the trends.

There are a number of studies in the literature with which our data may be compared and placed in perspective. First with respect to σ-complexes, Bauza and Frontera [49] examined the similar complexes of XeOF$_2$ with simpler N-bases NCCH$_3$ and NH$_3$. At the MP2/aug-cc-pVTZ level, they found interactions energies of -10.1 and -12.6 kcal mol^{-1}, respectively, smaller than our results with the diazines. A very similar value of -10.0 kcal mol^{-1} was obtained by Makarewicz *et al.* for NCCH$_3$.[53] Change to the oxygen base furan reduces this quantity to -7.8

kcal mol^{-1},[100] only about half those calculated for the σ-hole bonded complexes discussed in the current work.

Some of this reduction may be attributed to the weaker nature of the O base, as characterized in part by the lesser $V_{s,min}$ in this oxygen base.[100] Smaller values of -11.7 and -4.6, were also obtained for the KrO$_3$ Lewis acid when combined with NCLi and NCCN, respectively;[54,101] enlarging the aerogen atom to Xe raises these interaction energies somewhat, to -15.72 and -5.47 kcal mol^{-1}. KrO$_3$ and XeO$_3$ were also the acids used in complexes with a number of other nitrogen bases as well.[54,101] Esrafili and Vessally found that the calculated MP2/aug-cc-pVTZ R(N···Kr) distances range from 2.68 to 2.94 Å for the O$_3$Ae···NH$_2$CH$_3$ and O$_3$Ae···NH$_2$CN complexes, respectively. This range is longer than the intermolecular distances in our σ complexes, but a bit shorter than in our π dimers.

Table 9. Interaction energies (ΔE, kcal mol^{-1}) corrected for BSSE of AeOF$_2$ (Ae = Kr, Xe) complexes with diazines calculated at the MP2/aug-cc-pVDZ (I), BLYP-D3/Def2TZVPP (II), and CCSD(T)/aug-cc-pVDZ (III) levels of theory.

	(I)	(II)	(III)
σ			
pyrazine···KrOF$_2$	-17.68	-18.24	-12.65
pyrimidine···KrOF$_2$	-17.12	-18.23	-12.91
pyridazine···KrOF$_2$	-15.25	-17.08	-10.65
pyrazine···XeOF$_2$	-17.94	-17.29	-13.63
pyrimidine···XeOF$_2$	-17.46	-17.34	-13.90
pyridazine···XeOF$_2$	-16.52	-16.52	-12.90
π			
pyrazine···KrOF$_2$	-6.19	-6.18	-5.62
pyrimidine···KrOF$_2$	-6.17	-6.38	-5.86
pyridazine···KrOF$_2$	-7.14	-7.97	-6.44
pyrazine···XeOF$_2$	-6.05	-6.47	-5.51
pyrimidine···XeOF$_2$	-6.24	-6.75	-5.90
pyridazine···XeOF$_2$	-8.17	-8.22	-7.23

AIM analysis has been widely used in the literature for aerogen, as well as related sorts of bonds. The value of the density at the aerogen bond critical point in the complexes studied in this work varies from 0.041 to 0.049 au. Prior values for other systems are smaller, denoting weaker bonds. ρ_{BCP} fell in the range of 0.026 to 0.037 au for complexes of $XeOF_2$ with CH_3CN and NH_3,[49] and 0.028 au for its dimer with furan.[100] A very similar value of 0.029 au was noted in the $O_3Xe\cdots NCLi$ complex,[54] and 0.016 - 0.022 au when O_3Ae (Ae=Kr, Xe) is combined with NCH and NCLi. There are also NBO quantities in the literature for related aerogen bonds. E^2 was computed to be only 0.67 to 3.72 kcal mol^{-1} [54] for the LP(N)→σ*(AeO) transfers involving KrO_3 and XeO_3 complexes with various nitrogen bases, much smaller than these same quantities which are as large as 11.1 kcal mol^{-1} for the systems examined here. With respect to energy decomposition, Gao *et al.* [100] observed that orbital overlap accounted for some 43% of the attractive force in $XeOF_2\cdots$furan, quite similar to the percentage observed here for other aerogen bonds. A different sort of decomposition, SAPT, suggested [53] a nearly equal contribution from induction in the $XeOF_2\cdots NCCH_3$ complex.

Turning to parallel dimer geometries, there are fewer such aerogen bonds, but comparisons may be useful nonetheless. The MP2 interaction energy calculated for the parallel $F_2OXe\cdots NCCH_3$ complex is -6.5 kcal mol^{-1},[53] in the same range as found here for the diazines. The interactions are a bit weaker, less than 4 kcal mol^{-1}, for the π-hole bonded complexes of XeF_4 with a range of electron donors, ranging from N_2 to HCN.[51] These binding energies are even smaller when XeF_4 is replaced by $Xe(OMe)_4$. Lewis acids XeO_3 and XeF_4 engage in a stronger π complex of 12 and 9 kcal mol^{-1}, respectively [50] with aromatic benzene.

One can also draw comparisons of these aerogen bonds to related sorts of noncovalent bonds. SF_4, for example, engages in a chalcogen bond with the same set of diazines as studied here.[60] The binding energies of these σ-complexes lie in the 7.4-8.6 kcal mol^{-1} range, more weakly bound than the aerogen bonded structures considered here. Consistent with the results described above, pyridazine engages in the strongest interaction of the three diazines.

4. Conclusions

In summary, the calculations reported here document a particularly strong aerogen bond that connects $KrOF_2$ and $XeOF_2$ with each of a set of diazines. The aerogen bond energies for the σ-structures are in the 12-14 kcal mol^{-1} range. When the weak CH··F HBs are added, the

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total complexation energy rises up near 18 kcal mol^{-1}. Since the AeOF$_2$ molecule contains a positively charged region directly above the molecular plane, there are another set of π-minima wherein the N lone pair of the diazine approaches from the perpendicular direction. Although these interactions are considerably weaker, in the 6-8 kcal mol^{-1} range, they nonetheless constitute a fairly strong bond, greater than many typical HBs. Electrostatic attractions account for a bit more than half of the total attractive force in either σ or π dimer types. Orbital interactions make a major contribution, only slightly smaller than ES, to the σ-complexes. Dispersion is more important for the π-dimers, making a contribution on a par with orbital interactions.

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Fig. captions

Fig. 1 Molecular electrostatic potential surfaces (MEPs) of the isolated $KrOF_2$ and $XeOF_2$ molecules on the 0.001 a.u.isodensity contour of the electron density computed at the MP2/aug-cc-pVDZ level. Color ranges, in kcal mol^{-1}, are: red greater than 40, yellow between 20 and 40, green between 0 and 20, blue less than 0 (negative). Selected surface critical points $V_{s,max}$ (σ- and π-holes) are indicated as black dots.

Fig. 2 MP2-optimized structures of σ-hole bonded $AeOF_2$ (Ae = Kr, Xe) complexes with diazines.

Fig. 3 Molecular graphs of σ-hole bonded F_2OAe (Ae = Kr, Xe) complexes with diazines. Small green dots represent critical points. Results obtained at the MP2/aug-cc-pVDZ level.

Fig. 4 Plots of the RDG versus sign $(\lambda_2)\rho$ and noncovalent interaction regions (bonding isosurfaces are illustrated as green and blue disks while red parts represent repulsive forces) for the σ-hole bonded $AeOF_2$ (Ae=Kr, Xe) complexes with diazines.

Fig. 5 Electron density shift in σ-hole bonded $AeOF_2$ (Ae = Kr, Xe) complexes with diazines. The brown isosurface represents the regions in which electron density is increased as a result of complex formation (+0.001 a.u.), while the purple contour denotes decrease (-0.001 a.u.). Results obtained at the MP2/aug-cc-pVDZ level.

Fig. 6   MP2 optimized structures of π-hole bonded AeOF$_2$ (Ae = Kr, Xe) complexes with diazines.