1,8-Chalcogen-bridged naphthalenes. Strong carbon bases in the gas phase†

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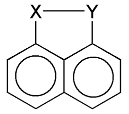
High-level density functional theory computations have been used to estimate the gas-phase proton affinities of the complete series of 1,8-chalcogen-bridged naphthalene derivatives. Our estimates show the 1,8-naphthalenediylbis(oxy) to be an oxygen base as strong as the so-called *proton sponges*. All the remaining chalcogen-bridged naphthalene derivatives are predicted to be among the strongest known carbon bases in the gas phase, the *para* carbon with respect to the most electronegative chalcogen atom being the most basic site. This enhanced basicity reflects the electron-donating ability of sulfur, selenium and tellurium, and the aromatization of the five-membered ring in the protonated form. Protonation at the heteroatoms is always disfavored with respect to ring protonation, but the energy gap between the carbon-protonated and chalcogen-protonated species decreases significantly on going from sulfur to tellurium derivatives. When the two chalcogen atoms involved are different the basicity of the system is controlled by the amount of charge transfer from the less electronegative chalcogen atom to the most electronegative one through the X–Y bond. This effect is maximum in **OTe**, which accordingly becomes the strongest base of the whole series.

A great deal of attention has been paid very recently to chalcogen derivatives, in particular those containing Se and Te, because they present interesting peculiarities from the structural and the reactivity points of view associated with their capacity to yield weak non-bonded interactions with atoms having lone pairs of electrons.[1–10] These stabilizing chalcogen-chalcogen interactions were characterized in a pioneering work by Minyaev and Minkin[3] for the particular case of unsaturated aldehydes, where the interaction involves X → Y (X = O, S; Y = Se, Te) dative bonds. These nonbonded interactions are not exclusive of chalcogen-chalcogen interactions, but have been also observed when the donor is either a nitrogen or a fluorine atom[2,5,9] and the acceptor is Se. Also importantly, we have recently showed[11] that these chalcogen-chalcogen interactions play a crucial role in the gas-phase reactivity of the system, because the change in the interaction strength upon going from the neutral toward the protonated or the unprotonated system modulates the intrinsic basicity and/or acidity of the molecule.

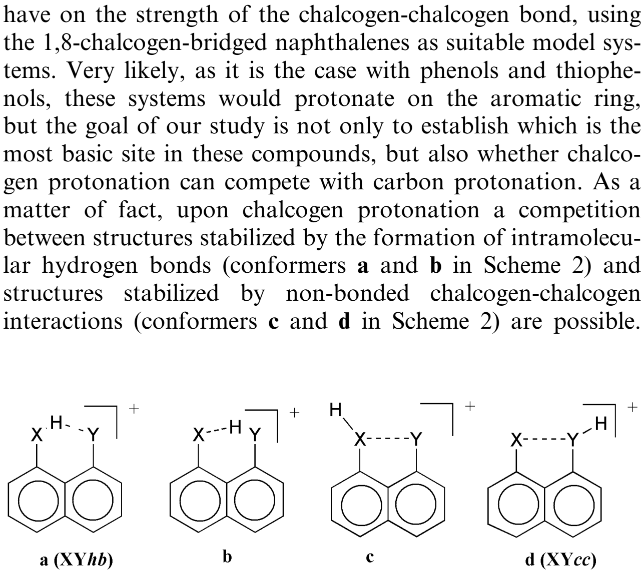
The extreme case, as far as the strength of the chalcogen-chalcogen interaction is concerned, is represented by some derivatives of naphthalene and tetracene, where a truly covalent chalcogen-chalcogen bond is formed. These chalcogen-bridged derivatives, in particular the 1,8-chalcogen-bridged naphthalenes (see Scheme 1), have attracted considerable attention[12–19] because they are good electron donors, good reactants in organic synthesis and because some of them exhibit interesting photochemical properties and antiviral activity,[20,21]among other things. In spite of this, very little is known on their reactivity. Indeed, to the best of our knowledge neither experimental nor theoretical values of their intrinsic basicities or acidities have been reported in the literature so far, and we are only aware of a theoretical study of the gas-phase basicity of the 1,8-naphthalenediol dianion.[22]



X = Y = O, S, Se, Te
X = O; Y = S
X = O, Y = Se
X = O, Y = Te
X = S, Y = Se
X = S, Y = Te
X = Se, Y = Te

Scheme 1

The aim of this paper is to investigate, by means of high-level density functional theory calculations, the effect of the chalcogen-chalcogen bridge on the intrinsic basicity of the system, and, at the same time, the effects that protonation can have on the strength of the chalcogen-chalcogen bond, using the 1,8-chalcogen-bridged naphthalenes as suitable model systems. Very likely, as it is the case with phenols and thiophenols, these systems would protonate on the aromatic ring, but the goal of our study is not only to establish which is the most basic site in these compounds, but also whether chalcogen protonation can compete with carbon protonation. As a matter of fact, upon chalcogen protonation a competition between structures stabilized by the formation of intramolecular hydrogen bonds (conformers **a** and **b** in Scheme 2) and structures stabilized by non-bonded chalcogen-chalcogen interactions (conformers **c** and **d** in Scheme 2) are possible.



a (XY*hb*) **b** **c** **d (XY*cc*)**

Scheme 2

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† Electronic supplementary information (ESI) available: the optimized geometries (in Cartesian coordinates) of the neutral and protonated forms of 1,8-chalcogen-bridged naphthalenes with X, Y = O, S, Se and Te. See http://www.rsc.org/suppdata/nj/b2/b205601a/

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A study of the relative stability of these forms and how this stability depends on the nature of the chalcogen atom might provide further insight into the nature of the chalcogen-chalcogen interactions.

Computational details

The structures, harmonic vibrational frequencies and total energies of the different neutral and protonated forms of the compounds under investigation were evaluated through the use of the B3LYP approach. This method combines Becke's three-parameter nonlocal hybrid exchange potential[23] with the nonlocal correlation functional of Lee, Yang and Parr.[24] In general, geometries obtained using the aforementioned DFT method are in fairly good agreement with experimental values[25–32] and the harmonic vibrational frequencies are closer to experiment than those obtained by using other correlated methods such as the MP2 formalism.[33,34] Furthermore, we have shown previously[10] for other chalcogen derivatives that this approach yields results in good agreement with those obtained by means of G2(MP2) *ab initio* calculations, but at a much lower cost.

For oxygen and sulfur we have used a 6-31G(d) basis set expansion both for geometry optimizations and for the evaluation of the harmonic vibrational frequencies. The final energies were obtained using a much more extended 6-311+G(3df,2p) basis set. The corresponding basis sets for Se-containing compounds are those reported by Curtiss *et al.*[35]

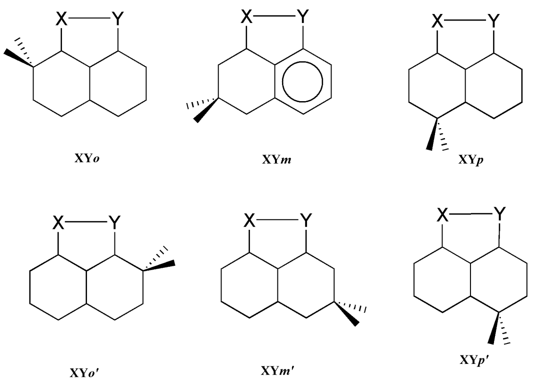
For Te we have used the SKBJ relativistic potential of Stevens *et al.*,[36], which accounts for the most important relativistic effects. For geometry optimizations and harmonic frequency calculations this effective core potential was used together with the [4,1] + d basis set described in ref. 10 for Te, together with a 6-31G(d) basis set for first-, second- and third-row atoms. Hereafter, for the sake of simplicity we will refer to this basis set as 6-31G(d). The corresponding final energies were evaluated using for Te the (6s,6p,3d,1f) basis set developed in a previous paper[10] and a 6-311+G(3df,2p) basis set expansion for the remaining atoms of the system. Again, for the sake of simplicity the (6s,6p,3d,1f) basis set for Te will be referred to hereafter as a 6-311+G(3df,2p) basis.

The zero point energy (ZPE) corrections were scaled by the empirical factor 0.98, proposed by Scott and Radom.[37] The values of the nucleus-independent chemical shifts (NICS)[38,39] were obtained using the same basis set expansion as that employed to calculate the final energies. All these calculations have been carried out with the Gaussian-98 suite of programs.[40]

The bonding characteristics of the different tautomers were analyzed by using the atoms-in-molecules (AIM) theory of Bader,[41] which is based on a topological analysis of the electron charge density. Hence, we have located the different bond critical points because the charge density at these points is a good indication of the strength of the linkage. We have also located some relevant ring critical points. The net charges were calculated using the natural bond order (NBO) analysis of Weihnhold *et al.*[42] This method was also employed to estimate the intramolecular attractive orbital interactions that would be responsible for the stability of *c*- and *d*-type structures (Scheme 2).

Results and discussion

We have investigated all neutral and all possible protonated species. This amounts to a total of 106 different structures. In order to make the presentation of our results more systematic, the following nomenclature will be adopted. The different neutral compounds will be identified by the two chalcogen atoms involved, **XY**, where X will be systematically the more electronegative of the two. Although we have investigated protonation at all possible sites of the ring, in our discussion we shall concentrate our attention only on the most stable ones, which correspond to protonation at the *ortho*, *meta* and *para* positions with respect to the heteroatom. These forms will be identified by adding ***o***, ***m*** and ***p***, respectively, to the acronym of the corresponding neutral. When $X \neq Y$, there are two non-equivalent *ortho*, *meta* and *para* protonated forms, which will be distinguished by adding a prime when protonation takes place *ortho*, *meta* or *para* with respect to the less electronegative chalcogen atom (see Scheme 3).



Scheme 3

As mentioned above, protonation at the heteroatom can lead to conformers having an intramolecular hydrogen bond (**a** and **b** in Scheme 2). When $X \neq Y$ the most stable intramolecular hydrogen bond is formed when protonation takes place on the most electronegative chalcogen atom, so in what follows only those conformers (**a**-type) will be discussed and they will be identified by adding ***hb*** to the acronym of the neutral. Similarly, the most stable protonated form exhibiting a chalcogen-chalcogen interaction corresponds systematically to that protonated at the less electronegative chalcogen atom. Therefore, only those conformers (**d**-type) will be considered in our discussion and they will be named by adding ***cc*** to the acronym of the neutral (see Scheme 2).

Bonding and proton affinity of systems in which X = Y

The optimized geometries of the neutral and protonated forms of those compounds in which X = Y are given as electronic supplementary information (ESI). The corresponding total energies, ZPE, relative energies and proton affinities are summarized in Table 1.

Although a detailed discussion of the structure of the neutral compounds is not the aim of this paper, it should be pointed out that for all peri-bridged naphthalenes studied, with the only exception being the **OO** derivative, the system exhibits a tricyclic structure with a covalent X–X bond. For the oxygen-containing compound this tricyclic structure, with an O–O distance of 1.500 Å, was found to also be a local minimum of the potential energy surface (**OO′**), but it lies 64 kJ mol^{-1} above the diketone-like structure **OO**. Conversely, for the sulfur-containing compound, the diketone-like structure (**SS′**), which is also a local minimum of the potential energy surface with an S–S distance of 3.183 Å, was found to lie 54 kJ mol^{-1} above the tricyclic derivative **SS**. In what follows we shall refer exclusively to the most stable conformers **OO** and **SS**, respectively.

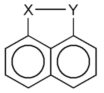
The first conspicuous result in Table 1 is that all the peri-bridged naphthalenes investigated, with the exception of the **OO** derivative, behave as carbon bases in the gas phase, the *para* carbon atom being systematically the most basic site of the system. Conversely, 1,8-naphthalenediylbis(oxy), **OO**,

Table 1 Total energy (E, hartrees), zero point energy (ZPE, hartrees), relative energy (ΔE, kJ mol^{-1}), and proton affinities (PA, kJ mol^{-1}) of chalcogen bridged naphthalene derivatives (X = Y)

	E	ZPE	ΔE	PA
X = O				
OO[a]	−535.22230	0.13103	0	
OO′	−535.20031	0.13336	64	
OO*o*	−535.53726	0.14203	207	804
OO*m*	−535.49341	0.14015	318	694
OO*p*	−535.53869	0.14250	205	807
OO*hb*	−535.61951	0.14521	0	1012
OO*cc*	−535.60376	0.14468	40	972
X = S				
SS[b]	−1181.25592	0.12889	0	
SS′	−1181.16957	0.12858	54	
SS*o*	−1181.60320	0.14082	11	886
SS*m*	−1181.56582	0.13896	104	793
SS*p*	−1181.60738	0.14079	0	897
SS*hb*	−1181.54909	0.13701	143	754
SS*cc*	−1181.55187	0.13808	139	759
X = Se				
SeSe	−5187.92806	0.12825	–	
SeSe*o*	−5188.27302	0.13960	12	882
SeSe*m*	−5188.23968	0.13817	97	798
SeSe*p*	−5188.27807	0.13976	0	895
SeSe*hb*	−5188.20914	0.13336	164	730
SeSe*cc*	−5188.24863	0.13736	71	824
X = Te				
TeTe	−399.75890	0.12590		
TeTe*o*	−400.10636	0.13711	17	889
TeTe*m*	−400.07576	0.13592	94	811
TeTe*p*	−400.11291	0.13718	0	906
TeTe*hb*[c]	–	–	–	–
TeTe*cc*	−400.10044	0.13333	23	883

[a] **OO** is the global minimum and corresponds to a diketone-like structure, whereas **OO′** designates the corresponding tricyclic structure. [b] **SS** is the global minimum and corresponds to a tricyclic species, whereas **SS′** designates the corresponding diketone-like structure. [c] This conformer does not exist as it collapses without activation barrier to the **TeTe*cc*** form.

Table 2 X–Y bond distances (R, Å) and charge density at the bond critical point (ρ, e au^{-3}) for HX–YH compounds and chalcogen-bridged naphthalenes

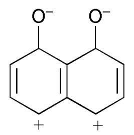
	HX–YH			
Bond	R	ρ	R	ρ
S–S	2.098	0.134	2.133	0.127
Se–Se	2.343	0.102	2.371	0.099
Te–Te	2.963	0.051	2.927	0.057
O–S	1.695	0.180	1.736	0.169
O–Se	1.828	0.144	1.866	0.134
O–Te	2.065	0.049	2.079	0.048

behaves as an oxygen base. This can be understood if one takes into account that in contrast with the S-, Se- and Te-containing analogs, this neutral system has a diketone-like structure, so that the six-membered rings are not strictly aromatic. In fact, the C–O distances in the neutral system (1.239 Å) correspond to typical C=O bonds, rather than to C–O linkages, and no bond critical point is found between both oxygen atoms. Conversely, for X = S, Se, Te, the C–X distances (1.779, 1.911, 2.227 Å, respectively) correspond typically to single carbon–chalcogen bonds and there is a bond critical point between both chalcogen atoms. The formation of the corresponding five-membered ring is also confirmed by the existence of a ring critical point. It is also worth mentioning that both the X–X distance and the charge density at the corresponding bond critical points in these compounds are rather close to those calculated, at the same level of theory, for the corresponding X_2H_2 dihydride derivatives (see Table 2), ratifying the existence of a normal X–X covalent linkage. It is interesting to note that only for the **TeTe** derivative is the X–X bond length shorter in the peri-bridged naphthalene derivative than in the corresponding HTe–TeH dihydride. The reason is that while for S and Se derivatives the C1–C8 distance (≈2.5 Å) is longer than a typical X–X bond, for the Te derivatives is the other way around, and this constrains the Te–Te bond to be shorter.

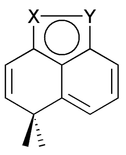
It is also important to note that **OO** behaves as a quite strong oxygen base in the gas phase. Indeed, the intrinsic basicity of this compound (1012 kJ mol^{-1}) is much higher than other strong carbonyl bases such as cyclohexanone (857 kJ mol^{-1})[43] or $[(CH_3)_2N]_2C{=}O$ (925 kJ mol^{-1})[43] and identical to the experimental value reported for the so-called proton sponge (*N*,*N*,*N′N′*-tetramethyl-1,8-naphthalenediamine).[43] The enhanced basicity of **OO** is due to two concomitant effects: on the one hand, zwitterionic forms such as those shown in Scheme 4 contribute significantly to the stability of this diketone-like compound and secondly, the protonated species is significantly stabilized through the formation of an intramolecular hydrogen bond (form **a** in Scheme 2). The former effect is consistent with the rather low intrinsic basicity of the *para* carbon atom (see Table 1), and with the fact that the C2–C3 and C6–C7 bonds are significantly shorter than the other C–C bonds of the rings. Also consistently the *para* carbon atom has the smallest charge density. The second effect is mirrored in the much lower stability of the ***cc*** conformer where the intramolecular hydrogen bond is replaced by an oxygen lone pair interaction (see Table 1).

As far as S, Se and Te derivatives are concerned our results indicate that the intrinsic basicity of the system follows the opposite trend to the electronegativity of the heteroatom. Hence, the tellurium derivative is the most basic one, whereas sulfur- and selenium-containing compounds have rather similar basicities. Indeed, our calculations show that Te transfers more electronic charge than S or Se to the aromatic ring, increasing its electron donor capacity. Also interestingly, the gap between *para* and *ortho* proton affinities increases as the electronegativity of the heteroatom decreases. In all cases, as expected, protonation at the *meta* position is the least favorable process.

Our results predict all these compounds to be quite strong carbon bases in the gas phase. As a matter of fact, the naphthalene ring of these peri-bridged compounds exhibits a basicity that is 72–92 kJ mol^{-1} higher than that of the unsubstituted parent compound (PA = 815 kJ mol^{-1})[43] and 61–70 kJ mol^{-1} higher than that of its monomethyl derivative (PA = 837 kJ mol^{-1}).[43] Indeed, all of them are predicted to be among the strongest known carbon bases, being much stronger than acenaphthene (PA = 851 kJ mol^{-1})[43] or hexamethylbenzene (PA = 867 kJ mol^{-1}),[43] and as strong as carbenes such as 1,5,5-trimethylenecylcohexene (PA = 904 kJ mol^{-1}).[43]



Scheme 4



Scheme 5

This enhanced basicity reflects the ability of these chalcogen atoms to transfer electronic charge to the aromatic ring, which becomes an electron-rich system. In fact, an NBO analysis shows that this charge transfer is already significant for sulfur (0.24 electrons per ring), and quite large for tellurium. (0.47 electrons per ring). There is a second factor, associated with the aromatization of the five-membered ring, that also contributes to stabilize the protonated forms. Indeed, protonation at the *para* position leads systematically to a significant shortening of both the C–X and the X–X bonds (about 0.07 and 0.04 Å, respectively). This seems to indicate that protonation on the *para* carbon atom induces a certain aromatization of the five-membered ring through the contribution of mesomeric forms such as those showed in Scheme 5.

This effect is nicely reflected in an increase of the charge density at the corresponding ring critical point (see Table 3). Furthermore, the nucleus-independent chemical shift (NICS) evaluated at this ring critical point is in all cases larger than that estimated for benzene at the same level of theory, ratifying the significant aromatic character of the five-membered ring in the protonated species. Also the X–X stretching frequency (507 cm^{-1} for S, 295 cm^{-1} for Se and 195 cm^{-1} for Te) appears blue-shifted in the protonated species with regards to the neutral form. This shift is of 2% for S, 3% for Se and 4% for Te. The C–X stretching frequencies (911 and 995 cm^{-1} for S, 876 and 979 cm^{-1} for Se, 841 and 958 cm^{-1} for Te) appear as symmetric and asymmetric combinations, and are also slightly shifted to higher frequencies.

It can be also observed that protonation at the heteroatom is always disfavored with respect to ring protonation, and that the relative stability of the **XX*cc*** conformer increases, in relative terms, on going from S to Te. Indeed, for the sulfur derivative the **XX*hb*** form is predicted to be only slightly less stable than the **XX*cc*** one, while it does not exist for the Te-containing compound. The most important consequence is that the energy gap between **XX*p*** and **XX*cc*** forms drastically decreases down the group (see Table 1). Actually, while for the sulfur-containing compound this gap is 139 kJ mol^{-1}, for the Te derivative it is only 23 kJ mol^{-1}. Concomitantly, a reinforcement of the X–X bond is observed, which is maximum for the Te derivative. This seems to indicate that a non-bonded chalcogen-chalcogen interaction similar to those described for β-chalcogenovinylaldehydes[10] and other chalcogen derivatives[3,17] is taking place in the protonated forms. Indeed, the formation of the new X–H linkage favors a dative interaction from the lone pairs of the unprotonated chalcogen atom towards the σ^*_{XH} antibonding molecular orbital, which reinforces the X–X bond. Similarly to what was found for other chalcogen derivatives,[3,10,11] these kinds of non-bonded interactions are maximum when the acceptor is a Te–H group. In fact, a second-order NBO analysis indicates that for **TeTe*p*** the corresponding orbital interaction energy amounts to 88 kJ mol^{-1}, while for **SS*p*** and **SeSe*p*** it is three to five times smaller.

Table 3 Charge density (ρ, e au^{-3}) at the ring critical point of the five-membered ring of chalcogen-bridged naphthalenes and the NICS[a] (ppm) evaluated at that point

	ρ		NICS[b]
Compound	Neutral	Protonated	Protonated
SS	0.0248	0.0272	9.9
SeSe	0.0206	0.0224	10.1
TeTe	0.0149	0.0161	10.4

[a] Evaluated at the B3LYP/6-311+G(3df,2p) level of theory. [b] For benzene, at the same level of accuracy, the calculated NIST is 7.9 ppm.

Bonding and proton affinity of systems in which $X \neq Y$

The optimized geometries of the neutral and protonated forms of those compounds in which $X \neq Y$ are given as ESI. Total energies, relative energies and proton affinities of the 1-,8-chalcogen bridged naphthalenes in which $X \neq Y$ are summarized in Table 4.

It is important to realize that, in contrast with the **OO** compound, neither the **OS** nor **OSe** or **OTe** derivatives behave as oxygen bases. Therefore, all these compounds, without any exception, behave as carbon bases in the gas phase. This is so because as soon as one of the oxygen atoms in **OO** is replaced by another chalcogen atom a new O–X (X = S, Se or Te) bond is formed. The existence of a bond critical point associated with the O–Y linkage confirms the formation of this oxygen–chalcogen linkage (see Table 2). Furthermore, the charge density at this bond critical point and the bond length are rather similar to those predicted, at the same level of theory, for the HO–YH dihydrides (see Table 2). Hence, in no case does the oxygen form a ketone structure, the C–O bond length (≈1.37 Å) being typical of a single bond. The main consequence is that the aromatic ring becomes activated and protonation takes place preferentially on the carbon atom that is *para* with respect to the most electronegative chalcogen atom (see Table 4). It can be also observed that for oxygen-containing compounds the intrinsic basicity of the system increases as the electronegativity of the second chalcogen atoms decreases. Therefore, **OTe** is the most basic compound of the whole series. Consistently, among the sulfur derivatives **STe** is more basic than **SSe**. Concomitantly, the energy gap between **XY*p*** and **XY*p*′** protonated species increases as the electronegativity of Y decreases.

All these findings have a common origin. Let us consider as suitable model systems the oxygen derivatives, **OY**. In all these compounds oxygen is bound to a less electronegative atom, so that the $\mathrm{O}^{-\delta} - \mathrm{Y}^{+\delta}$ polarity of the OY bond is always sizably large. The obvious consequence is that oxygen becomes an excessive-electron atom that significantly activates the aromatic ring to which it is attached. In fact, it must be remembered that in the extreme situation we would have an O^{-}, which is the most activating substituent, combining a large electron-donating inductive effect with a conjugation effect. When the partner in the OY bond is tellurium we are close to this limiting situation, the estimated NBO charge at the oxygen being −0.83, and therefore the basicity of the aromatic ring is also at a maximum. Consistently, the Te atom becomes electron-poor, and therefore its electron-donating capacity is drastically reduced, explaining that protonation at the corresponding *para* position is 25 kJ mol^{-1} less favorable. As a consequence of this effect, for Se and Te derivatives the stability of structures **OY*o*** and **OY*p*′** appears reversed. Actually, with the sole exceptions of the **OSe** and **OTe** derivatives, the relative stability of the protonated forms follows the sequence **XY*p*** > **XY*p*′** > **XY*o***. Similar effects, but quantitatively smaller, are observed for S-containing derivatives.

Also, when $X \neq Y$ aromatization of the five-membered ring triggered by protonation contributes to enhance the basicity of these compounds. As it was found for those derivatives in which X = Y, there is a clear increase of the charge density at the ring critical point on going from the neutral to the protonated species, and also protonation at the heteroatoms is clearly disfavored.

Table 4 Total energy (E, hartrees), zero point energy (ZPE, hartrees), relative energy (ΔE, kJ mol^{-1}), and proton affinities (PA, kJ mol^{-1}) of chalcogen-bridged naphthalene derivatives ($X \neq Y$)

	E	ZPE	ΔE	PA
X = O, Y = S				
OS	−858.25208	0.13115		
OS*o*	−858.59866	0.14331	10	884
OS*o′*	−858.59612	0.14326	16	877
OS*m*	−858.56165	0.14127	102	792
OS*m′*	−858.56130	0.14131	103	791
OS*p*	−858.60247	0.14336	0	894
OS*p′*	−858.60018	0.14320	6	888
OS*hb*	−858.59101	0.14266	28	866
OS*cc*	−858.57937	0.14021	52	841
X = O, Y = Se				
OSe	−2861.58909	0.13100		
OSe*o*	−2861.93814	0.14292	10	891
OSe*o′*	−2861.93117	0.14263	27	873
OSe*m*	−2861.90101	0.14106	103	798
OSe*m′*	−2861.90103	0.14107	103	798
OSe*p*	−2861.94211	0.14307	0	901
OSe*p′*	−2861.93532	0.14273	17	884
OSe*hb*	−2861.92453	0.14226	44	857
OSe*cc*	−2861.91080	0.13904	72	829
X = O, Y = Te				
OTe	−467.52187	0.12954		
OTe*o*	−467.87777	0.14150	10	909
OTe*o′*	−467.86759	0.14127	36	883
OTe*m*	−467.84000	0.13968	104	814
OTe*m′*	−467.83993	0.13982	105	814
OTe*p*	−467.88177	0.14167	0	919
OTe*p′*	−467.87184	0.14121	25	894
OTe*hb*	−467.83912	0.14099	110	809
OTe*cc*	−467.85085	0.13686	69	850
X = S, Y = Se				
SSe	−3184.59166	0.12856		
SSe*o*	−3184.93894	0.14034	12	887
SSe*o′*	−3184.93654	0.14003	17	881
SSe*m*	−3184.90237	0.13857	103	795
SSe*m′*	−3184.90269	0.13853	102	796
SSe*p*	−3184.94347	0.14038	0	898
SSe*p′*	−3184.94119	0.14015	5	893
SSe*hb*	−3184.88263	0.13639	149	749
SSe*cc*	−3184.90878	0.13782	84	814
X = S, Y = Te				
STe	−790.51025	0.12737		
STe*o*	−790.86113	0.13901	12	897
STe*o′*	−790.85631	0.13890	25	884
STe*m*	−790.82496	0.13741	103	806
STe*m′*	−790.82522	0.13748	103	806
STe*p*	−790.86596	0.13909	0	909
STe*p′*	−790.86171	0.13890	11	898
STe*hb*	−790.84032	0.13706	62	847
STe*cc*	−790.84563	0.13488	42	867
X = Se, Y = Te				
SeTe	−2793.84591	0.12697		
SeTe*o*	−2794.19403	0.13823	14	890
SeTe*o′*	−2794.19147	0.13837	21	883
SeTe*m*	−2794.16074	0.13694	98	806
SeTe*m′*	−2794.16081	0.13705	98	806
SeTe*p*	−2794.19942	0.13844	0	904
SeTe*p′*	−2794.19745	0.13844	5	899
SeTe*hb*	−2794.17374	0.13567	60	844
SeTe*cc*	−2794.18332	0.13444	32	872

Conclusions

We have shown that chalcogen-bridged naphthalene derivatives are quite strong bases in the gas phase. The 1,8-naphthalenediylbis(oxy) is predicted to be an oxygen base as strong as the so-called *proton sponges*. The remaining peri-bridged chalcogen derivatives are systematically carbon bases, the *para* carbon with respect to the most electronegative chalcogen atom being the most basic site. Protonation at the heteroatoms is always disfavored with respect to ring protonation, but the energy gap between the corresponding protonated species decreases significantly on going from sulfur to tellurium derivatives, because for Te there is a significant reinforcement of the chalcogen-chalcogen bond upon Te-protonation.

All chalcogen-bridged naphthalene derivatives are predicted to be among the strongest known carbon bases in the gas phase. Two reasons are responsible for their enhanced basicity, the electron-donating ability of sulfur, selenium and tellurium, and the aromatization of the five-membered ring in the protonated form.

When the two chalcogen atoms involved are different the basicity of the system is controlled by the amount of charge transfer from the less electronegative atom to the most electronegative one through the X–Y bond. This effect is at a maximum in **OTe**, which accordingly becomes the strongest base of the whole series.

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